INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.
SYNTHESIS AND POLYMERIZATION OF SIMPLE IMINE MONOMERS

by

Dallas Don Parker

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF CHEMISTRY

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1995
THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Dallas Don Parker entitled Synthesis and Polymerization of Simple Imine Monomers and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy/Chemistry

Dr. Hank Hall

Dr. Gene Mash

Dr. David O'Brien

Dr. Mark Smith

Dr. Mike Barfield

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

H. K. Hull Jr.
Dissertation Director
STATEMENT BY AUTHOR

This dissertation has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Dallas D. Parker
ACKNOWLEDGMENTS

The author wishes to gratefully acknowledge Dr. H.K. Hall, Jr. for his understanding and guidance throughout the project. The author also wishes to thank Dr. Anne Padias for her advice and assistance. Best wishes and thanks to the members of the Hall group whose support was greatly appreciated. Special thanks to Ben Bonner who worked on the conjugated imine systems in our group and to Dr. A.B. Kim who previously worked on the polymerization of the simple imines. The author is also greatly indebted to the U.S. Army for financial support of this research project.
Dedicated to my parents whose faith in me sometimes outweighed my own.
# TABLE OF CONTENTS

LIST OF TABLES.......................................................................................................................... 10

LIST OF SCHEMES....................................................................................................................... 11

ABBREVIATIONS USED IN THIS DISSERTATION........................................................................... 12

ABSTRACT......................................................................................................................................... 13

CHAPTER 1  INTRODUCTION......................................................................................................... 15

CHAPTER 2  BACKGROUND............................................................................................................. 17
  2.1. Stability of C=N Compounds............................................................................................. 17
  2.2. Polymerization of Imines.................................................................................................... 19
      2.2.1 Polymerization of conjugated imine systems............................................................. 19
      2.2.2 Polymerization of simple imine systems..................................................................... 24

CHAPTER 3  RESULTS.................................................................................................................... 27
  3.1. Synthesis of Azaethylenecarbonitrile Monomers.............................................................. 27
  3.2. Attempted Synthesis of N-Methylenebenzenamine Monomers......................................... 30
  3.3. Synthesis of Formaldehyde Oxime and Formaldehyde Oxime Derivatives......................... 31
  3.4. Homopolymerization of Azaethylenecarbonitrile Monomers........................................... 34
  3.5. Copolymerization of Azaethylenecarbonitrile Monomers.................................................. 37
  3.6. Attempted Homopolymerizations of Formaldehyde Oxime.............................................. 41
  3.7. Homopolymerization and Copolymerization of Acetaldehyde Oxime............................... 41
  3.8. Homopolymerization of Formaldehyde, O-Benzylxoxime.............................................. 42
      3.8.1. Radical Initiated Homopolymerization.................................................................... 42
      3.8.2. Ionic Initiated Homopolymerization..................................................................... 43
  3.9. Copolymerization of Formaldehyde, O-Benzylxoxime...................................................... 43
      3.9.1. Radical Initiated Copolymerization................................................................... 43
      3.9.2. Ionic Initiated Copolymerization...................................................................... 44
  3.10. "Living Cationic Systems".............................................................................................. 46
      3.10.1. “Living” System-Preformed Strands-Imine Monomer Only.................................... 47
      3.10.2. “Living” System-Preformed Strands-Imine Monomer and IBVE Comonomer............ 48
      3.10.3. “Living” System-No Preformed Strands-Imine Monomer and IBVE Comonomer...... 49

CHAPTER 4  DISCUSSION.................................................................................................................. 50
  4.1. Thermodynamics of Polymerization.................................................................................... 50
      4.1.1. Azaethylenecarbonitrile Monomers........................................................................ 51
4.1.2. Monomers of Formaldehyde Oxime and Formaldehyde Oxime Derivatives ............................................................... 55
4.1.3. Polymer Stability .................................................................................................................................................. 57
4.1.4. Stability of the Trimer; 1,3,5-Hexahydrotriazine .............................................................................................. 59
4.2. Mechanism of Polymerization .................................................................................................................................. 61
4.2.1. Radical Centers .................................................................................................................................................. 61
4.2.2. Ionic Centers ...................................................................................................................................................... 64
4.3. Synthesis of Monomers ............................................................................................................................................... 65
4.4. Polymerization of Monomers ........................................................................................................................................ 65
4.4.1. Polymerization of Azaethylenecarbonitriles........................................................................................................ 66
  4.4.1.1. Radical Homopolymerization ......................................................................................................................... 66
  4.4.1.2. Anionic Homopolymerization ....................................................................................................................... 67
  4.4.1.3. Radical Copolymerization .......................................................................................................................... 68
4.4.2. Polymerization of Formaldehyde Oxime ............................................................................................................ 69
4.4.3. Polymerization of Acetaldehyde Oxime ............................................................................................................ 69
4.4.4. Polymerization of Formaldehyde, O-Benzyloxime ............................................................................................ 70
  4.4.4.1. Radical Homopolymerization ......................................................................................................................... 70
  4.4.4.2. Cationic Homopolymerization ....................................................................................................................... 70
  4.4.4.3. Anionic Homopolymerization ....................................................................................................................... 70
  4.4.4.4. Radical Copolymerization .......................................................................................................................... 71
  4.4.4.5. Cationic Copolymerization .......................................................................................................................... 71
  4.4.4.6. Anionic Copolymerization .......................................................................................................................... 71
  4.4.4.7. “Living” Cationic Polymerizations ............................................................................................................... 72
4.5. Summary .................................................................................................................................................................... 72

CHAPTER 5 EXPERIMENTAL ............................................................................................................................................... 75
5.1. Instrumentation............................................................................................................................................................ 75
5.2. Synthesis of Monomers ............................................................................................................................................... 75
  5.2.1 Synthesis of Azaethylenecarbonitrile Monomers ................................................................................................ 75
    5.2.1.1. Phenylazaethylenecarbonitrile ....................................................................................................................... 77
    5.2.1.2. 3-Thiophenylazaethylenecarbonitrile ............................................................................................................. 77
    5.2.1.3. 2-Thiophenylazaethylenecarbonitrile ............................................................................................................. 78
    5.2.1.4. 2-Furanyazaethylenecarbonitrile .................................................................................................................. 78
    5.2.1.5. 4-Methoxyphenylazaethylenecarbonitrile ..................................................................................................... 79
    5.2.1.6. 4-Cyanophenylazaethylenecarbonitrile ......................................................................................................... 79
    5.2.1.7. Dimethylazaethylenecarbonitrile .................................................................................................................. 79
    5.2.1.8. Cyclopropylazaethylenecarbonitrile trimer .................................................................................................. 81
    5.2.1.9. Attempted Synthesis of methylazaethylenecarbonitrile ................................................................................ 81
    5.2.1.10. Attempted Synthesis of ethylazaethylenecarbonitrile .................................................................................. 82
    5.2.1.11. Attempted Synthesis of 2-methylpropylazaethylenecarbonitrile ................................................................. 82
    5.2.1.12. Ethoxyazaethylenecarbonitrile ................................................................................................................... 83
5.2.2. N-Methylenebenzenamine derivatives ........................................................ 84
  5.2.2.1. N-Methylenebenzenamine Trimer ...................................................... 84
  5.2.2.2. 4-Methoxy-N-methylenebenzenamine Trimer .................................. 85
5.2.3. Formaldehyde Oxime and Formaldehyde Oxime Derivatives ..................... 85
  5.2.3.1. Formaldehyde Oxime.......................................................................... 85
  5.2.3.2. Formaldehyde, O-Methyloxime ........................................................ 86
  5.2.3.3. Formaldehyde, O-Benzylloxime .................................................... 86
  5.2.3.4. Formaldehyde, O-4-Methoxybenzylloxime ...................................... 90
  5.2.3.5. Formaldehyde, O-Benzoyloxime ..................................................... 91
5.3. Polymerization of Monomers ........................................................................ 92
  5.3.1. Homopolymerization of Azaethylenecarbonitrile Monomers .................... 93
    5.3.1.1. Radical Homopolymerization-Benzoyl Peroxide Initiator .................. 93
    5.3.1.2. Radical Homopolymerization-Benzoyl Peroxide Initiator- in the Presence of Inhibitors ................................................................. 95
    5.3.1.3. Radical Homopolymerization-Benzoin Methyl Ether Initiator ............ 95
    5.3.1.4. Radical Homopolymerization-BE\textsubscript{3}, O\textsubscript{2} Initiator ......... 97
    5.3.1.5. Radical Homopolymerization-t-Butylhydroperoxide Initiator .......... 97
    5.3.1.6. Anionic Homopolymerization-KCN Initiator ..................................... 97
    5.3.1.7. Anionic Homopolymerization-Et\textsubscript{2}AICN Initiator .................... 99
  5.3.2. Copolymerization of Azaethylenecarbonitrile Monomers .......................... 99
    5.3.2.1. Radical Copolymerization-Benzoyl Peroxide Initiator- p-Methoxystyrene Comonomer ................................................................. 100
    5.3.2.2. Radical Copolymerization-Benzoin Methyl Ether Initiator- p-Methoxystyrene Comonomer ................................................................. 100
    5.3.2.3. Radical Copolymerization-Benzoyl Peroxide Initiator- Methyl Acrylate Comonomer ................................................................. 101
    5.3.2.4. Radical Copolymerization-Benzoin Methyl Ether Initiator- Methyl Acrylate Comonomer ................................................................. 102
    5.3.2.5. Radical Copolymerization-Benzoyl Peroxide Initiator- Acrylonitrile Comonomer ................................................................. 104
    5.3.2.6. Radical Copolymerization-Benzoyl Peroxide Initiator- Styrene Comonomer ................................................................. 104
    5.3.2.7. Radical Copolymerization-Benzoin Methyl Ether Initiator- Acrylonitrile Comonomer ................................................................. 105
  5.3.3. Attempted Homopolymerization of Formaldehyde Oxime ......................... 105
    5.3.3.1. Radical Initiated Homopolymerization ............................................ 105
    5.3.3.2. Cationic Initiated Homopolymerization ........................................ 105
  5.3.4. Homopolymerization and Copolymerization of Acetaldehyde Oxime .......... 106
    5.3.4.1. Homopolymerization of Acetaldehyde Oxime .................................. 106
    5.3.4.2. Copolymerization of Acetaldehyde Oxime-IBVE Comonomer ............. 106
5.3.5. Homopolymerization of Formaldehyde (O-benzyl) oxime ...................... 107
  5.3.5.1. Radical Homopolymerization-Benzoin Methyl Ether Initiator .......... 107
  5.3.5.2. Radical Homopolymerization-Triethylborane, O₂ Initiator .......... 107
  5.3.5.3. Cationic Homopolymerization-Methyl Triflate Initiator .............. 108
  5.3.5.4. Cationic Homopolymerization-Boron Trifluoride Etherate Initiator 108
  5.3.5.5. Cationic Homopolymerization-Stannic Chloride Initiator ............. 108
  5.3.5.6. Anionic Homopolymerization-Butyl Lithium Initiator ................. 108

5.3.6. Copolymerization of Formaldehyde, O-Benzyl oxime ....................... 108
  5.3.6.1. Radical Copolymerization-Benzoin Methyl Ether Initiator .......... 109
  5.3.6.2. Radical Copolymerization-Triethylborane, O₂ Initiator .......... 110
  5.3.6.3. Cationic Copolymerization-Boron Trifluoride Initiator .......... 111
  5.3.6.4. Cationic Copolymerization-Stannic Chloride Initiator .......... 113
  5.3.6.5. Anionic Copolymerization-Butyl Lithium Initiator .......... 114
  5.3.6.6. Cationic Copolymerization-“Living System” Triflic Acid Initiator. 115

5.4. NMR Studies of Temperature Effects on Structure .................................. 119
  5.4.1. Cyclopropylaazetylenecarbonitrile Trimer ...................................... 119
  5.4.2. N-Methylene-4-methoxybenzenamine Trimer .................................. 119
  5.4.3. Poly-4-cyanophenylalaazetylenecarbonitrile and
           Poly-phenylalaazetylenecarbonitrile ...................................... 120

5.5. Attempted Trimerization of 4-Cyanoazetylenecarbonitrile Monomer ........ 120

REFERENCES ........................................................................................................ 122
| Table 2.1 | Homopolymerization of Simple Imines | 26 |
| Table 3.1 | Homopolymerization of Azaethylenecarbonitrile Monomers | 34 |
| Table 3.2 | Homopolymerization of Azaethylenecarbonitrile Monomers in the Presence of Inhibitors | 36 |
| Table 3.3 | Copolymerization of Azaethylenecarbonitrile Monomers | 38 |
| Table 3.4 | Copolymerization of Azaethylenecarbonitrile Monomers | 39 |
| Table 3.5 | Homopolymerization and Copolymerization of Acetaldehyde Oxime | 42 |
| Table 3.6 | Radical Homopolymerization of Formaldehyde, O-Benzyl oxide | 42 |
| Table 3.7 | Ionic Homopolymerization of Formaldehyde, O-Benzyl oxide | 43 |
| Table 3.8 | Radical Copolymerization of Formaldehyde, O-Benzyl oxide | 44 |
| Table 3.9 | Ionic Copolymerization of Formaldehyde, O-Benzyl oxide | 45 |
| Table 3.10 | "Living System"-Preformed Strands-Imine Monomer Only | 47 |
| Table 3.11 | "Living System"-Preformed Strands-Imine Monomer and IBVE Comonomer | 48 |
| Table 3.12 | "Living System"-No Preformed Strands-Imine Monomer and IBVE Comonomer | 49 |
| Table 4.1 | Heats of Polymerization | 50 |
| Table 4.2 | Calculated Enthalpy of Polymerization | 51 |
| Table 4.3 | Isodesmic Stabilization of Nitrogen Containing Compounds | 60 |
| Table 5.1 | Amounts Used in Polymerization in the Presence of Inhibitors | 95 |
| Table 5.2 | Amounts Used in the Cationic Copolymerization of Formaldehyde, O-Benzyl oxide; IBVE, Comonomer; BF$_3$ Initiator | 112 |
| Table 5.3 | Amounts Used in the Cationic Copolymerization of Formaldehyde, O-Benzyl oxide; 4-Methoxystyrene, Comonomer; BF$_3$ Initiator | 113 |
| Table 5.4 | Amounts Used in the Cationic Copolymerization of Formaldehyde, O-Benzyl oxide; IBVE, Comonomer; Stannic Chloride, Initiator | 114 |
| Table 5.5 | Amounts Used in the Anionic Copolymerization of Formaldehyde, O-Benzyl oxide | 114 |
| Table 5.6 | Amounts Used in "Living" Copolymerization-Preformed Strands | 117 |
| Table 5.7 | Amounts Used in "Living" Copolymerization-No Pre-formed Strands | 118 |
LIST OF SCHEMES

Scheme 3.1  Synthesis of Azaethylenecarbonitrile Monomers................................. 29
Scheme 3.2  Synthesis of Formaldehyde, O-Benzylloxime........................................... 33
Scheme 4.1  Isodesmic Reactions for Cyclopentane and Imidazolidine......................... 59
ABBREVIATIONS USED IN THIS DISSERTATION

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AN</td>
<td>acrylonitrile</td>
</tr>
<tr>
<td>BME</td>
<td>benzoin methyl ether</td>
</tr>
<tr>
<td>BP</td>
<td>benzoyl peroxide</td>
</tr>
<tr>
<td>DMSO</td>
<td>dimethyl sulfoxide</td>
</tr>
<tr>
<td>Elem Anal</td>
<td>elemental analysis</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>IBVE</td>
<td>isobutyl vinyl ether</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>MA</td>
<td>methyl acrylate</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>p-methoxystyrene</td>
</tr>
<tr>
<td>μL</td>
<td>microliter</td>
</tr>
<tr>
<td>mL</td>
<td>milliliter</td>
</tr>
<tr>
<td>mol</td>
<td>mole</td>
</tr>
<tr>
<td>MW</td>
<td>molecular weight</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>% conv</td>
<td>% conversion</td>
</tr>
<tr>
<td>% incorp</td>
<td>% incorporation</td>
</tr>
<tr>
<td>SEC</td>
<td>size exclusion chromatography</td>
</tr>
</tbody>
</table>
ABSTRACT

In this research, the synthesis and polymerization of new simple imine monomers was studied. The work covered three groups of imine monomers; the azaethylenecarbonitriles, the N-methylenebenzenamines, and formaldehyde oxime and its O-alkyl derivatives.

Synthesis of several azaethylenecarbonitrile monomers was attempted. Monomers with carbon aromatic substituents were found to be stable monomers, while those with carbon alkyl substituents were unstable yielding oligomeric or cyclic trimer products. Homopolymerizations by radical and anionic initiation were run on the stable imine monomers and found to produce low molecular weight polymers. Copolymerizations run on the stable monomers with radical initiation gave good results at low monomer:comonomer feed ratios but decreased as the monomer:comonomer feed ratios increased pointing to inhibition of polymerization by the imine monomers. Incorporation of the imine monomer into the copolymer increased with increasing monomer:comonomer feed ratios.

The attempted synthesis of N-methylenebenzenamine and 4-methoxy-N-methylenebenzenamine yielded the cyclic trimer form of the monomer. No polymerization was attempted.

Formaldehyde oxime was synthesized. Because the oxime spontaneously polymerizes below 60 °C, homopolymerization with radical and cationic initiation was attempted above this temperature. However, no polymer was formed.

Homopolymerization of acetaldehyde oxime was attempted with only a trace of low
molecular weight oligomers formed. Copolymerization studies showed only trace amounts of the oxime incorporated into the polymer product.

Synthesis of O-alkyl derivatives of formaldehyde oxime yielded two stable monomers, formaldehyde, O-benzyloxime and formaldehyde, O-4-methoxybenzyloxime. Only the formaldehyde, O-benzyloxime monomer was used in polymerization studies. Homopolymerization and copolymerization using radical or anionic initiation yielded only a trace of product with both modes of initiation. Homopolymerization by cationic initiation gave only the cyclic trimer. Copolymerization by cationic initiation gave polymers whose molecular weights and conversion decreased as the monomer:comonomer feed ratios increased.

The azaethylenecarbonitrile monomers and formaldehyde, O-benzyloxime yielded both homopolymers and copolymers. In homopolymerization, yields were lower with radical initiation than with ionic initiation, although the molecular weights of the polymers formed were comparable with the two types of initiation. In copolymerizations, incorporation of imine into the polymer occurred in both radical and ionic initiation. Despite problems encountered, the future of the new field of imine polymerization remains certain.
CHAPTER 1

INTRODUCTION

Although the chemistry of polymerization of the C=C and C=O functional groups has been studied a great deal, little is known about the chemistry of polymerization of the C=N functional group. The extent of literature references on C=N polymerization consists of two early papers by Smith et al.\(^1\) and Sato et al.\(^2\) and a systematic study by Hall et al.\(^3\)-\(^{11}\) However, the majority of this research which does exist deals with conjugated 1-aza-1,3-butadiene imine systems, \(\text{CH}_2=\text{CR}_1\text{CH} = \text{NR}_2\), while only two research projects have dealt with the simple imines, \(^8\)-\(^{11}\) \(\text{R}_1\text{CH} = \text{NR}_2\). Thus the new field in polymerization of simple imine monomers has been virtually unexplored.

The goal of this research project was therefore to further explore this new area of polymers utilizing the knowledge gained from the two previous research projects.\(^8\)-\(^{11}\) This research includes synthesis of new imine monomers with a variety of substituents on both the carbon and nitrogen atoms to gain insight into which imines can be synthesized as stable imine compounds and also which types of imines will undergo polymerization. Polymerization was run under various conditions of temperature, solvents, and initiators (radical or ionic) to determine the most efficient methods of polymerization. Complete characterization via NMR, IR, and size exclusion chromatography was performed to determine polymer structure and composition. Only preliminary investigation into the physical or stereochemical properties of the polymers formed was performed. This dissertation will discuss experimental procedures used,
results obtained, problems encountered, and new knowledge acquired.
CHAPTER 2
BACKGROUND

The C=N imine bond is very chemically reactive undergoing addition, cycloaddition, hydrolysis, rearrangement, electrochemical, and photochemical reactions. The stability of the C=N bond is highly dependent on the substituents attached to both the carbon and nitrogen atoms. Certain imines are unstable under normal conditions and may exist as dimers or the trimeric hexahydrotriazine ring form. A knowledge of imine stability is paramount in designing stable monomers which are still energetically able to polymerize.

2.1. Stability of C=N Compounds

\[
\begin{array}{c}
\text{H} \\
\text{R}_1 \\
\text{C=N} \\
\text{R}_2
\end{array}
\]

\( \text{R}_1 = \text{R}_2 = \text{H} \)

The parent compound, methanimine has been prepared by flash vacuum thermolysis but decomposes rapidly above -80 °C to hexamethylenetetramine. In attempted preparations using aliphatic aldehydes and ammonia, the addition products, RCHOHNH$_2$, are formed. On heating in a vacuum, H$_2$O is removed. The imine products were found to exist as a mixture of dimers and trimers.

In the vapor phase, the trimers were found to dissociate into the monomeric form. Ethanimine was found to be monomeric, not only in the vapor phase, but also in the
liquid phase on rapid cooling but slowly trimerized on standing.\textsuperscript{15}

\( R_1 = H \quad R_2 = \text{Alkyl} \)

In attempted preparations using formaldehyde and aliphatic amines, the reaction forms only methylolamines, \( \text{RNHCH}_2\text{OH} \). When distilled over KOH to remove \( \text{H}_2\text{O} \), the cyclic trimer of the imine is formed.\textsuperscript{14}

\( R_1 = R_2 = \text{Alkyl} \)

In reactions between the aliphatic aldehydes and aliphatic amines, the product is usually sufficiently stable to be isolated in the imine form.\textsuperscript{14} e.g. \( \text{C}_2\text{H}_5\text{N} = \text{CHCH}_3 \), b.p. 48 °C.

\( R_1 = \text{Aryl} \quad R_2 = H \)

Aromatic aldehydes in general react with aqueous or alcoholic ammonia to give high melting, crystalline substances formed by 3 mol of the aldehyde and 2 mol of ammonia.\textsuperscript{14}

\[
3 \text{ArCHO} + 2 \text{NH}_3 \rightarrow \text{ArCH(N=CHAR)}_2 + 3 \text{H}_2\text{O}
\]

\( R_1 = H \quad R_2 = \text{Aryl} \)

The usual product from the reaction of an aromatic amine with formaldehyde is the trimer product of the imine. For example, a 1:1 molar ratio of formaldehyde and aniline yields the trimer product, 1,3,5-triphenylhexahydrotriazine.\textsuperscript{16}

However, other products can be formed. A 2:1 mixture of aniline and formaldehyde gives exclusively dianilinomethane, \( \text{C}_6\text{H}_4\text{NHCH}_2\text{NHCH}_2\text{H}_5 \), as product.\textsuperscript{16}

\( R_1 = \text{Aryl} \quad R_2 = \text{Alkyl} \)

Almost all products of the reaction of an aromatic aldehyde and an aliphatic amine are the imine product.\textsuperscript{14} e.g. benzylidenenethylimine b.p. 180 °C.
RI = Alkyl  R2 = Aryl

The reaction product of acetaldehyde and aniline in neutral or basic solution give the product, C₆H₅NHCH(CH₃)NHC₆H₅ while in acidic solution a dimer form “Eckstein’s base” is the formed, C₆H₅NHCH(CH₃)CH=CHNHC₆H₅.¹⁴ Higher alkyl aldehyde such as butyraldehyde and heptaldehyde form stable imines.¹⁴

R₁ = Aryl  R₂ = Aryl

Aromatic aldehydes and aromatic amines form very stable imine products in very good yields.¹⁴ e.g. benzylideneaniline m.p. 52-54.

R₁ = H,Alkyl, Aryl  R₂ = OH, NH₂, NHC₆H₅, NHCONH₂

All oximes, hydrazones, phenylhydrazones, and semicarbazones are stable with the notable exceptions of formaldehyde oxime which spontaneously polymerizes at room temperature.¹⁷

From the known literature data, it appears that imines must be at least 1,2-disubstituted to be stable except when strong electron-donating resonance groups are attached to the nitrogen as in the oximes, hydrazones, and semicarbazones.

2.2 Polymerization of Imines

Although the literature contains isolated references to imine polymerization,¹²,¹⁷,¹⁸ no systematic studies were attempted until those by the Hall group.³⁻¹¹

2.2.1 Polymerization of conjugated imine systems

In the conjugated imine systems, the vinyl group would function as a handle for imine group polymerization whose degree of participation would depend on the different
N-substituent groups.

The earliest polymerization experiment was done by Smith et al.\(^1\) on N-cyclohexyl-3-methyl-1-aza-1,3-butadiene monomer.

\[
\text{CH}_3 \quad \text{CH}_2=\text{C}-(\text{CH}_2)_2=\text{CH}=\text{N}
\]

No polymer product was found in homopolymerization or in copolymerization with methyl methacrylate or styrene using the radical initiator benzoyl peroxide or the cationic initiator boron trifluoride etherate. Boron trifluoride was found to precipitate as an imine salt.\(^1\)

Later studies were done by Sato and Tsuruta\(^2\) on a variety of N-alkyl substituted 1-aza-1,3-butadienes, 3-methyl-1-aza-1,3-butadienes, 4-methyl-1-aza-1,3-butadienes, and 4-phenyl-1-aza-1,3-butadienes involving both homopolymerization and copolymerization. While radical or cationic initiators failed to yield polymer products in all cases, some organoalkali and organoalkaline earth anionic initiators gave moderate yields of homopolymer with the 1-aza-1,3-butadienes and 3-methyl-1-aza-1,3-butadienes. Attempted copolymerization of the 1-aza-1,3-butadienes and 3-methyl-1-aza-1,3-butadienes, gave pure poly methyl methacrylate and poly isopropyl crotonate with comonomers methyl methacrylate and isopropyl crotonate and pure poly imine polymer with comonomers styrene and isoprene. Analysis of the imine polymers indicated
4,3 addition in all cases with the imine bond being a non-participant in the reactions. The 4-methyl-1-aza-1,3-butadienes and 4-phenyl-1-aza-1,3-butadienes showed no polymer product under both ionic or radical conditions.²

More recently, polymer research with conjugated systems was expanded by Kitayama and Hall³ with the 1-aza-1,3-butadienes and 3-methyl-1-aza-1,3-butadienes.

\[
\begin{align*}
CH_2=CH-CH=N^+R & \quad CH_2=C-CH=N^+N(CH_3)_2 \\
R = \text{phenyl; 2,4,6-trimethylphenyl; methoxy}
\end{align*}
\]

Polymers were obtained with the N-phenyl and N-2,4,6-trimethylphenyl-1-aza-1,3-butadiene monomers using both anionic and cationic initiators. Results varied greatly with temperature and initiator used with the anionic initiators giving the highest molecular weights and per cent conversions. Analysis of the polymers formed by IR and NMR analysis showed both 4,3 and 4,1 addition had occurred under both cationic and anionic addition giving the first evidence that the imine group could participate in polymerization.³

Attempts at radical homopolymerization or copolymerization of the two N-phenyl derivatives with methyl methacrylate were unsuccessful.³

Attempted polymerization of the N-methoxy-1-aza-1,3-butadiene and N-(dimethylamino)-3-methyl-1-aza-1,3-butadiene monomers using anionic and radical initiators produced no polymer product while cationic initiation resulted in formation of
the imine salt.³

Because of the inactivity of the monomers containing nitrogen substituted electron-donating groups in the previous study, the monomer, N-carbethoxy-3-methyl-1-aza-1,3-butadiene, with a nitrogen substituted electron withdrawing group was synthesized and polymerized by Kim and Hall.⁴

\[
\begin{align*}
\text{CH}_3 \\
\text{CH}_2\text{C} & \text{CH}=\text{CH}\text{N}\text{COOEt}
\end{align*}
\]

Polymers ranging in molecular weight from 800-2100 were obtained in a wide range of yields by both radical and anionic initiation. Analysis of the polymer products by IR and NMR revealed that addition had occurred by all three types of mechanisms; 4,1; 2,1; and 4,3 addition, in both the radical and anionic initiated polymerizations. Surprisingly, in most of the anionic initiated polymerizations, the 4,1 and 2,1 additions greatly dominated over 4,3 addition thought to be due to the greater stabilization of the growing anionic center due to the N-electron withdrawing substituent.⁴

Attempts at copolymerization with styrene produced pure polystyrene while attempted copolymerization with ethyl vinyl ether resulted in pure imine homopolymer. Attempts at copolymerization with the electron-rich comonomers, p-methoxystyrene, p-ethoxystyrene, and isobutyl vinyl ether gave predominantly Diels-Alder type cycloaddition reactions.⁴

In another experiment by Hall et al.,⁵ the effect of the position of the nitrogen atom in
the conjugated system on polymerization was examined using derivatives of 2-aza-1,3-butadiene.

\[
\text{CH}_2=\text{CH}-\text{N}=\text{CH}^\text{R}
\]

\( R = \text{phenyl; 2,4,6-trimethylphenyl; t-buty} \)

The homopolymerization for all three monomers was attempted by cationic, anionic, and radical initiation. The only polymerization observed was with the phenyl derivative under anionic initiation which produced moderate yields of low molecular weight material. Analysis by IR and NMR showed no 2,1 addition had occurred but was unable to distinguish between the amount of 4,1 and 4,3 addition. The authors did conclude that 1-aza-1,3-butadienes are much more efficient monomers than 2-aza-1,3-butadienes.\(^5\)

The most recent work with conjugated imines was done by Bonner and Hall\(^6\) using 3-methyl-N-phenylsulfonyl-1-aza-1,3-butadiene and 3-methyl-N-methylsulfonyl-1-aza-1,3-butadiene monomers.

\[
\text{CH}_3
\]

\[
\text{CH}_2=\text{C}—\text{CH}=\text{N}^\text{SO}_2\text{R}
\]

\( R = \text{methyl, phenyl} \)

In homopolymerization with anionic initiation, low molecular weight polymers below 1000 MW were formed in moderate yields for both monomers. Analysis of the polymer by NMR showed almost exclusive (\(>90\%\)) 4,1 addition. Radical homopolymerization
produced a dimer product.⁶

Radical copolymerization of the N-phenyl monomer with various comonomers gave varying results depending on monomer:comonomer feed ratios used. Incorporation of the imine monomer into the copolymer was observed with all comonomers examined. Addition was however by 4,3 addition with no participation of the imine group.⁶

2.2.2 Polymerization of simple imine systems

Because of the success obtained with 1-aza-1,3-butadienes containing nitrogen substituted electron acceptor groups,⁴ it was hypothesized that the simple imines (shown below) with an acceptor on nitrogen would also undergo polymerization.⁷

![Chemical structures](image)

The first compounds synthesized containing N-acceptor groups were N-cyano monomers.⁸ ⁹

![Chemical structures](image)

It was found that all three compounds could be synthesized in solution but were unstable on isolation and oligomerized. Spontaneous copolymerization of the di and tri-cyano
monomers with p-methoxystyrene comonomer was successful in achieving alternating
copolymers of molecular weights around 2000 gm mol\(^{-1}\).\(^{10}\)

The most recent work with the simple imines was done by Hall et al.\(^{11}\) utilizing several
different electron acceptor substituents attached to the nitrogen atom.

\[
\begin{align*}
1. & \text{ phenylazaethylenecarbonitrile} & 4. & \text{ethyl 2-phenylazaethylenecarboxylate} \\
2. & \text{t-butylazaethylenecarbonitrile} & 5. & \text{ethyl 2-t-butylazaethylenecarboxylate} \\
3. & \text{methyl 2-phenylazaethylenyl sulfone} & & \\
\end{align*}
\]

These imine compounds (azaethylenes) were all found to be stable on isolation of the
pure monomer.

Homopolymerization was attempted on the monomers with a variety of radical and
anionic initiators. The results are shown in Table 2.1.
### Table 2.1
Homopolymerization of Simple Imine Monomers\textsuperscript{11}

<table>
<thead>
<tr>
<th>monomer</th>
<th>initiator(mol%)</th>
<th>solvent(ml)</th>
<th>temp(°C)</th>
<th>time(day)</th>
<th>% conv</th>
<th>MW(SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AIBN (2)</td>
<td>neat</td>
<td>75</td>
<td>3</td>
<td>70</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>DTBP (2)</td>
<td>toluene (1)</td>
<td>100</td>
<td>3</td>
<td>51</td>
<td>950</td>
</tr>
<tr>
<td></td>
<td>KCN (1.5)</td>
<td>DMF (2)</td>
<td>0</td>
<td>2</td>
<td>88</td>
<td>1050</td>
</tr>
<tr>
<td></td>
<td>BuLi (4)</td>
<td>toluene (2)</td>
<td>0</td>
<td>2</td>
<td>76</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>BuLi (4)</td>
<td>THF (2)</td>
<td>0</td>
<td>2</td>
<td>82</td>
<td>780</td>
</tr>
<tr>
<td>2</td>
<td>AIBN (2)</td>
<td>neat</td>
<td>70</td>
<td>3</td>
<td>17</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>BuLi (2)</td>
<td>toluene (1.5)</td>
<td>0</td>
<td>2</td>
<td>4</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>KCN (2)</td>
<td>DMF (1.5)</td>
<td>0</td>
<td>2</td>
<td>17</td>
<td>750</td>
</tr>
<tr>
<td></td>
<td>TEA (4)</td>
<td>neat</td>
<td>28</td>
<td>1.5</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>AIBN (3)</td>
<td>acetone (2)</td>
<td>70</td>
<td>3</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BuLi (3)</td>
<td>toluene (2)</td>
<td>0</td>
<td>2</td>
<td>trace</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BuLi (3)</td>
<td>THF (2)</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>BuLi (3)</td>
<td>THF (2)</td>
<td>-50</td>
<td>2</td>
<td>3</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td>KCN (3)</td>
<td>DMF (2)</td>
<td>0</td>
<td>2</td>
<td>16</td>
<td></td>
</tr>
<tr>
<td></td>
<td>t-BuOK</td>
<td>THF (0.6)</td>
<td>0</td>
<td>2</td>
<td>18</td>
<td>700</td>
</tr>
<tr>
<td></td>
<td>BuLi (3)</td>
<td>THF (2)</td>
<td>28</td>
<td>2</td>
<td>&gt;90</td>
<td>600</td>
</tr>
</tbody>
</table>

From the experiment, it was found that 2-phenylazaethylenecarbonitrile oligomerizes in higher yields and molecular weights. Lower yields and molecular weights were obtained with 2-t-butylazaethylenecarbonitrile and ethyl 2-phenylazaethylenecarboxylate while the other two monomers gave only poor yields.\textsuperscript{11}

Analysis of the polymers obtained from monomers 1 and 2 by IR and NMR analysis confirmed that the polymerization had proceeded through the C=N bond.\textsuperscript{11}

Because of the success of homopolymerization of these simple imines, the possibility of polymerization of other simple imine compounds became of interest.
CHAPTER 3

RESULTS

3.1. Synthesis of Azaethylenecarbonitrile Monomers

The success of Hall et al.\textsuperscript{11} in homopolymerization of simple imine monomers aroused our interest in the possibility of homopolymerization and copolymerization of other simple imine monomers.

Because the best results in homopolymerization by Hall et al.\textsuperscript{11} were obtained with the phenylazaethylenecarbonitrile monomer, it seemed logical to investigate the effect of other aromatic substituents attached to the imine carbon. Aromatic substituent groups which donate electrons should increase the electron density of the imine bond while aromatic substituents groups which are electron-withdrawing should decrease the electron density. The effect of this increase or decrease in electron density of the imine bond should manifest itself in an increased or decreased reactivity of the imine bond towards polymerization. To investigate this hypothesis, the following aromatic substituted monomers were synthesized.
The t-butylazaethylenecarbonitrile monomer in the study by Hall et al.\textsuperscript{11} also gave good results in homopolymerization even though the t-butyl group is a very sterically demanding substituent group. Attempts were made at synthesis of other stable non-aromatic substituted azaethylenecarbonitriles with smaller steric demands.
The azaethylene carbonitrile monomers were synthesized in two steps by a modification of a previous method reported by Hall et al.\textsuperscript{11} and shown in Scheme 3.1.

Scheme 3.1

Synthesis of Azaethylenecarbonitrile Monomers

\[
\begin{align*}
\text{NC-NH}_2\text{Cl} + \text{SiMe}_3\text{Cl} + \text{NEt}_3 \xrightarrow{\text{diethyl ether}} &\text{Me}_3\text{SiN} = C = \text{NSiMe}_3 \\
\hline
\text{O} & \text{RCH} + \text{Me}_3\text{SiN} = C = \text{NSiMe}_3 \xrightarrow{\text{CF}_3\text{SO}_3\text{Si(}\text{CH}_3)_3/\text{CH}_2\text{Cl}_2} \text{RCH} = \text{NC}
\end{align*}
\]

In those monomers which were stable, the yields were good ranging from 38-67%. The yields were in the same range as those reported by Hall et al.\textsuperscript{11} for phenylaazaethylenecarbonitrile (60%).

In the original method by Hall et al.,\textsuperscript{11} TiCl\textsubscript{4} was used as catalyst. However, in our synthesis using TiCl\textsubscript{4} gave a dark brown slurry which made purification of the product difficult and gave low yields of 5-20%. By replacing the TiCl\textsubscript{4} catalyst with CF\textsubscript{3}SO\textsubscript{2}Si(CH\textsubscript{3})\textsubscript{3}, the yields increased as did the purity of the product. In most cases, a single recrystallization from hot, boiling hexane gave a \textsuperscript{1}H NMR pure product.

All aromatic substituted azaethylenecarbonitrile monomers 1-6 were stable under ordinary conditions. Even attempts at trimerization of monomer 5 using trifluoroacetic acid catalyst at low temperatures proved unsuccessful. Only the ethoxyazaethylenecarbonitrile monomer 12 was stable of the non-aromatic azaethylenecarbonitriles. The dimethylazaethylenecarbonitrile monomer 7 was stable for
several hours at room temperature but decomposed in a highly exothermic reaction to give >30 decomposition products as revealed by GC-MS analysis. The molecular weights of the major decomposition products showed them to be different dimer and trimer products of the monomer. The cyclopropylazaethylenecarbonitrile monomer product 8 was found to exist as the cyclic trimer. Attempts at converting the trimer to the monomer by heating in solution with an acid catalyst were unsuccessful as described in 5.4.1. Attempted synthesis of monomers 9, 10, and 11 gave oligomeric products which gave broad peaks in 1H NMR and molecular weights around 400 as determined by SEC analysis.

3.2 Attempted Synthesis of N-Methylenebenzenamine Monomers

Using the method of Miller and Wagner19, attempts were made to synthesize stable monomers of N-methylenebenzenamine 13 and its derivative, 4-methoxy-N-methylenebenzenamine 14. In the procedure, equimolar amounts of formaldehyde from a 37% aqueous formaldehyde solution and freshly distilled aniline or 4-methoxyaniline were added together. Methanol was added until the solution was homogeneous. After a few minutes, a white precipitate formed.
The white precipitate proved to be the cyclic trimer form of the monomer. An attempt was made with the N-methylene-4-methoxybenzenamine 14 trimer to convert the trimer to the monomeric form by heating in DMSO-d₆ and observing by ¹H NMR analysis. A small amount of monomer was formed above 100 °C but total conversion to the monomer did not occur even at 140 °C where the monomer:trimer ratio was 1:6.

### 3.3 Synthesis of Formaldehyde Oxime and Formaldehyde Oxime Derivatives

Because formaldehyde oxime is known to spontaneously polymerize¹⁷, synthesis of formaldehyde oxime and stable derivatives was attempted in order to investigate their polymerization characteristics. The monomers are shown below.

![Monomers](image)

Formaldehyde oxime 15 was synthesized by the method of Andersen and Jensen¹⁷ by reacting equimolar amounts of hydroxylamine hydrochloride and 37% formaldehyde solution. Because the pure product spontaneously polymerizes below 60 °C, the monomer was distilled directly into a diethyl ether solution. The ether solution was
dried with Na$_2$SO$_4$ and ether removed by heating. The resulting pure product was kept at 70 °C until used.

The O-methyl derivative 16 was prepared by the method of Jensen et al., by reacting methoxyamine hydrochloride with a 9X molar excess of 37% aqueous formaldehyde solution. The purified product was collected by distillation. Because its low boiling point, the monomer was not used in polymerization studies.

The formaldehyde, O-benzyloxime monomer 17 and formaldehyde, O-4-methoxybenzyloxime monomer 18 were both synthesized in several steps following known procedures as shown in Scheme 3.2 for the synthesis of formaldehyde, O-benzyloxime 17. The formaldehyde, O-4-methoxybenzyloxime monomer 18 was found to be stable in the monomeric form in step 4. Because both monomers were stable as monomers, either could have been used in polymerization studies. The O-benzyl derivative 17 was thought to be more reactive because of less resonance stability than the O-4-methoxybenzyl derivative 18 and was the monomer used in polymerization studies.

The attempted synthesis of the formaldehyde, O-benzoyloxime monomer 19 was done by reacting equimolar amounts of formaldehyde oxime and benzoyl chloride. The solid product precipitated from the aqueous solution but was found to be the cyclic trimer form of the monomer.
Scheme 3.2
Synthesis of Formaldehyde, O-Benzoxime

\[
\text{Scheme 3.2}
\]

**Synthesis of Formaldehyde, O-Benzoxime**

\[
\begin{align*}
\text{Scheme 3.2} & \\
\text{Synthesis of Formaldehyde, O-Benzoxime} & \\
\end{align*}
\]

\[
\text{Scheme 3.2} & \\
\text{Synthesis of Formaldehyde, O-Benzoxime} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Scheme 3.2} & \\
\text{Synthesis of Formaldehyde, O-Benzoxime} & \\
\end{align*}
\]

\[
\text{Scheme 3.2} & \\
\text{Synthesis of Formaldehyde, O-Benzoxime} & \\
\end{align*}
\]

\[
\text{Scheme 3.2} & \\
\text{Synthesis of Formaldehyde, O-Benzoxime} & \\
\end{align*}
\]
### 3.4 Homopolymerization of Azaethylenecarbonitrile Monomer

#### Table 3.1
Homopolymerization of Azaethylenecarbonitrile Monomers

<table>
<thead>
<tr>
<th>monomer</th>
<th>initiator (mol%)</th>
<th>temp. (°C)</th>
<th>% conversion</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BP (5%)</td>
<td>80</td>
<td>40</td>
<td>880</td>
</tr>
<tr>
<td></td>
<td>BME (5%)</td>
<td>25</td>
<td>5</td>
<td>1040</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>77</td>
<td>1270</td>
</tr>
<tr>
<td></td>
<td>BEt₃O₂ (10%)</td>
<td>-50</td>
<td>NA</td>
<td>1230</td>
</tr>
<tr>
<td></td>
<td>(CH₃)₂COCOOH</td>
<td>110</td>
<td>30</td>
<td>730</td>
</tr>
<tr>
<td>2</td>
<td>BP (5%)</td>
<td>80</td>
<td>8</td>
<td>940</td>
</tr>
<tr>
<td></td>
<td>BME (5%)</td>
<td>25</td>
<td>3</td>
<td>560</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>53</td>
<td>950</td>
</tr>
<tr>
<td>3</td>
<td>BP (5%)</td>
<td>80</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>BME (5%)</td>
<td>25</td>
<td>6</td>
<td>790</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>85</td>
<td>800</td>
</tr>
<tr>
<td>4</td>
<td>BP (5%)</td>
<td>80</td>
<td>5</td>
<td>870</td>
</tr>
<tr>
<td></td>
<td>BME (5%)</td>
<td>25</td>
<td>5</td>
<td>520</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>35</td>
<td>620</td>
</tr>
<tr>
<td>5</td>
<td>BP (5%)</td>
<td>80</td>
<td>18</td>
<td>2100</td>
</tr>
<tr>
<td></td>
<td>BME (5%)</td>
<td>25</td>
<td>6</td>
<td>1280</td>
</tr>
<tr>
<td></td>
<td>Et₂AlCN (5%)</td>
<td>-50</td>
<td>79</td>
<td>2110</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>65</td>
<td>1390</td>
</tr>
<tr>
<td>6</td>
<td>BP (5%)</td>
<td>80</td>
<td>17</td>
<td>906</td>
</tr>
<tr>
<td></td>
<td>Et₂AlCN (5%)</td>
<td>-50</td>
<td>22</td>
<td>840</td>
</tr>
<tr>
<td>7</td>
<td>BME (5%)</td>
<td>-5</td>
<td>67</td>
<td>315**</td>
</tr>
<tr>
<td></td>
<td>KCN (5%)</td>
<td>5</td>
<td>75</td>
<td>340**</td>
</tr>
<tr>
<td>12</td>
<td>BP (5%)</td>
<td>80</td>
<td>trace</td>
<td>370</td>
</tr>
</tbody>
</table>

* sample decomposed at polymerization temperature
** spontaneous decomposition products of monomer
Polymerizations were run at different temperatures and initiators to determine the optimal conditions for homopolymerization. Radical initiators benzoyl peroxide (BP); benzoin methyl ether (BME); BEt₃, O₂, and (CH₃)₂CCOOH and anionic initiators KCN and Et₂AlCN were used.

The 4-cyanophenyl derivative 5 gave the highest molecular weight, followed by the aromatic heteroatom monomers, with the 4-methoxyphenyl derivative and ethoxy derivatives the lowest.

The % conversion ranged widely depending on initiator and temperature. Anionic initiation gave much higher % conversion than radical initiation. Among radical initiators, higher temperatures favored an increase in % conversion.

All polymer samples were yellow to light brown powders with the exception of the benzoyl peroxide initiated polymerization with 2-furanylazaethylenecarbonitrile monomer which turned black due to decomposition of the monomer during the polymerization.

Characterization of the polymer products by IR and NMR analysis gave the predicted structure showing polymerization through the C=N, imine bond. IR analysis of the purified polymers in all samples showed the presence of the C=N stretch above 2000 cm⁻¹ as well as a broad band between 1700-1000 cm⁻¹. The C=N stretch peak near 1600 cm⁻¹ was not evident in the samples indicating polymerization through the imine bond. The IR of 3-thiophenylazaethylenecarbonitrile, for example, gave narrow peaks at 3099, 2990, 2215, 2185, 838, 786, 709 cm⁻¹ and a broad peaks from 1750-1000 cm⁻¹. ¹H NMR
analysis of the purified polymers showed a single broad peak between δ6-8.5 and the absence of the imine proton peak (HC=N) between δ8-9.5 in all samples. An exception was the product of dimethylazaethylenecarbonitrile monomer 7 whose 1H NMR spectrum of both the radical and anionic catalyzed polymerization product was almost identical to that of the spontaneous decomposition product of the monomer discussed in 5.2.1.7. The monomer 7 apparently underwent spontaneous decomposition instead of polymerization.

To test the free radical nature of the radical initiated polymerizations, the 3-thiophenylazaethylenecarbonitrile monomer 1 was polymerized in the presence of inhibitors.

Table 3.2
Homopolymerization of Azaethylenecarbonitrile Monomers in the Presence of Inhibitors

<table>
<thead>
<tr>
<th>sample</th>
<th>initiator</th>
<th>inhibitor</th>
<th>% conversion</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>benzoyl peroxide</td>
<td>-</td>
<td>43</td>
<td>1020</td>
</tr>
<tr>
<td>2</td>
<td>none</td>
<td>-</td>
<td>9</td>
<td>730</td>
</tr>
<tr>
<td>3</td>
<td>benzoyl peroxide</td>
<td>sulfide*</td>
<td>1</td>
<td>850</td>
</tr>
<tr>
<td>4</td>
<td>benzoyl peroxide</td>
<td>TEMPO**</td>
<td>1</td>
<td>540</td>
</tr>
<tr>
<td>5</td>
<td>none</td>
<td>sulfide*</td>
<td>trace</td>
<td>650</td>
</tr>
<tr>
<td>6</td>
<td>none</td>
<td>TEMPO**</td>
<td>2</td>
<td>500</td>
</tr>
</tbody>
</table>

* 5-t-butyl-4-hydroxy-2-methylphenyl sulfide  
** TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy, free radical

The results in Table 3.2 show only a trace of product in the presence of both TEMPO and the sulfide inhibitor.
Some spontaneous free radical polymerization was observed in samples without initiators present but only in those at temperatures of 80 °C and above. The most notable was at 110 °C where spontaneous polymerization resulted in a 10% conversion of monomer with a MW of 800. This compares with a 30% conversion and MW of 730 in the t-butyl hydroperoxide initiated sample. Those blank samples run below 80 °C showed only a trace or no uninitiated polymerization.

3.5. Copolymerization of AzaethyleneCarbonitrile Monomer

Free radical copolymerizations were run on monomers 1-5 with various comonomers using benzoyl peroxide and benzoin methyl ether as initiators.

Because the azaethylenecarbonitrile monomers are electron-poor monomers, copolymerizations were run with at least one electron-poor and one electron-rich comonomer. Two comonomers that were used consistently in the copolymerizations was methyl acrylate, an electron-poor monomer, and p-methoxystyrene, an electron-rich monomer.
Table 3.3
Copolymerization of Azaethylenecarbonitrile Monomers
Benzoyl Peroxide Initiator

<table>
<thead>
<tr>
<th>mon</th>
<th>comon</th>
<th>mon/comon ratio</th>
<th>% conv</th>
<th>MW (SEC)</th>
<th>% incorp of imine into polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-MeOS</td>
<td>0:1</td>
<td>81</td>
<td>51900</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:9</td>
<td>4</td>
<td>2530</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 0:1</td>
<td>86</td>
<td>42300</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:9</td>
<td>17</td>
<td>9900</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:2</td>
<td>19</td>
<td>3490</td>
<td>41 39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AN 0:1</td>
<td>72</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>AN 1:9</td>
<td>10</td>
<td>NA</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>AN 1:2</td>
<td>25</td>
<td>NA</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>Styrene</td>
<td>0:1</td>
<td>65</td>
<td>22580</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Styrene 1:9</td>
<td>4</td>
<td>2530</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>p-MeOS</td>
<td>0:1</td>
<td>45</td>
<td>30400</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:9</td>
<td>8</td>
<td>1660</td>
<td>49 40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 0:1</td>
<td>82</td>
<td>62200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:9</td>
<td>37</td>
<td>9350</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:2</td>
<td>15</td>
<td>2670</td>
<td>41 40</td>
</tr>
<tr>
<td>3</td>
<td>p-MeOS</td>
<td>0:1</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:9</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 0:1</td>
<td>NA</td>
<td>NA</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:9</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:2</td>
<td>*</td>
<td>*</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>p-MeOS</td>
<td>0:1</td>
<td>66</td>
<td>67600</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:9</td>
<td>4</td>
<td>720</td>
<td>trace</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 0:1</td>
<td>83</td>
<td>66200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:9</td>
<td>68</td>
<td>44330</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:2</td>
<td>17</td>
<td>37640</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>p-MeOS</td>
<td>0:1</td>
<td>59</td>
<td>55200</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1:9</td>
<td>24</td>
<td>1840</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 0:1</td>
<td>75</td>
<td>28100</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:9</td>
<td>51</td>
<td>17470</td>
<td>17 13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>MA 1:2</td>
<td>46</td>
<td>16480</td>
<td>28 33</td>
</tr>
</tbody>
</table>
Table 3.4
Copolymerization of Azaethylenecarbonitrile Monomers
Benzoim Methyl Ether Initiator

<table>
<thead>
<tr>
<th>mon</th>
<th>comon</th>
<th>mon/comon ratio</th>
<th>%conv</th>
<th>MW (SEC)</th>
<th>% incorp of imine into polymer</th>
<th>NMR</th>
<th>Elem Anal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>p-MeOS 0:1</td>
<td>62</td>
<td>16580</td>
<td></td>
<td>70</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-MeOS 1:9</td>
<td>4</td>
<td>1070</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AN 0:1</td>
<td>68</td>
<td>NA</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>AN 1:1</td>
<td>14</td>
<td>1210</td>
<td></td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>p-MeOS 0:1</td>
<td>52</td>
<td>31000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-MeOS 1:9</td>
<td>6</td>
<td>910</td>
<td></td>
<td>51</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 0:1</td>
<td>71</td>
<td>77100</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:9</td>
<td>30</td>
<td>9890</td>
<td></td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:2</td>
<td>15</td>
<td>2010</td>
<td></td>
<td>36</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>p-MeOS 0:1</td>
<td>71</td>
<td>14860</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-MeOS 1:9</td>
<td>3</td>
<td>1340</td>
<td></td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 0:1</td>
<td>68</td>
<td>50700</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:9</td>
<td>57</td>
<td>4560</td>
<td></td>
<td>11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:2</td>
<td>29</td>
<td>1770</td>
<td></td>
<td>23</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>p-MeOS 0:1</td>
<td>57</td>
<td>13280</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-MeOS 1:9</td>
<td>8</td>
<td>2050</td>
<td></td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 0:1</td>
<td>77</td>
<td>58200</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:9</td>
<td>54</td>
<td>14000</td>
<td></td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:2</td>
<td>62</td>
<td>12600</td>
<td></td>
<td>trace</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>p-MeOS 0:1</td>
<td>46</td>
<td>12550</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-MeOS 1:9</td>
<td>18</td>
<td>1680</td>
<td></td>
<td>41</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 0:1</td>
<td>59</td>
<td>34000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:9</td>
<td>48</td>
<td>32200</td>
<td></td>
<td>3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>MA 1:2</td>
<td>23</td>
<td>20400</td>
<td></td>
<td>14</td>
<td>16</td>
<td></td>
</tr>
</tbody>
</table>
An examination of Tables 3.3 and 3.4 show several features. First, the copolymerizations gave much lower molecular weights and % conversion than homopolymerizations of the comonomers alone indicating an inhibitory nature of the imine monomer. Second, the 4-methoxyphenylazaethylenecarbonitrile monomer is shown to be a very inactive species due to its low % incorporation into the copolymers formed. Third, copolymerization of the monomers with p-methoxystyrene gave approximately 50 % incorporation of the monomer into the copolymers in all cases indicating a polymer structure of alternating monomer and comonomer. Fourth, copolymerizations with the 4-cyanophenylazaethylenecarbonitrile monomer gave higher results for molecular weight and % conversions in general but were not as consistent in all cases as in homopolymerization of the imine monomers.

All isolated copolymers were brown powders with the exception of the benzoyl peroxide initiated polymerization with 2-furanylazaethylenecarbonitrile monomer which turned black due to decomposition of the monomer during the copolymerization. All blank samples with comonomer, initiator, and solvent were colorless to light yellow granules.

IR analysis showed features consistent with the expected polymer structure, the presence of the C=N stretch and the absence of the C=N stretch. With the methyl acrylate comonomer, the C=O stretch was present around 1730 cm⁻¹. A typical IR (KBr) of the copolymerization product of 2-furanylazaethylenecarbonitrile and methyl acrylate in a 1:2 ratio with benzoin methyl ether initiation gives peaks at 2950, 2222 C=N
stretch, 1729 C=O stretch, 1445, two broad peak from 1150-1300 and 800-1120, 828, 757, 699 cm⁻¹.

¹H NMR analysis revealed a broad peak in the aromatic region (δ6-8.5), a broad OCH₃ peak from methyl acrylate (δ3.60) or p-methoxystyrene (δ3.70), and broad methine and methylene peaks (δ1-2.5). No imine proton (CH=N) peak or alkene proton peaks from the starting monomer or comonomer were present. A typical ¹H spectrum for the copolymerization product of 4-cyanophenylazaethylenecarbonitrile and methyl acrylate in a 1:2 ratio initiated by benzoyl peroxide gave broad phenyl peaks and CH-N peak at δ6.4-8.4, a broad OCH₃ peak at δ3.5-3.7, a broad CH peak at δ2.2-2.4, and a broad CH₂ peak at δ1.4-2.0.

3.6. **Attempted Homopolymerizations of Formaldehyde Oxime**

The polymerization of formaldehyde oxime at 60 °C by both radical and cationic initiation methods gave no precipitate, no discoloration, and no apparent change in viscosity. An ¹H NMR analysis at 60 °C showed only monomer starting material. Lowering of the temperature in the sample below 60 °C resulted in spontaneous polymerization of the sample.

3.7. **Homopolymerization and Copolymerization of Acetaldehyde Oxime**

Homopolymerization and copolymerizations with isobutyl vinyl ether comonomer were run using boron trifluoride cationic initiator.
Table 3.5
Homopolymerization and Copolymerization of Acetaldehyde Oxime

<table>
<thead>
<tr>
<th>tube</th>
<th>mon:comon ratio</th>
<th>temp (°C)</th>
<th>% conv</th>
<th>MW (SEC)</th>
<th>% incorp of imine (Elem Anal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:0</td>
<td>5</td>
<td>trace</td>
<td>480, 320, 260</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>5</td>
<td>29</td>
<td>850, 550, 350, 230</td>
<td>trace</td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>5</td>
<td>18</td>
<td>570, 320</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0:1</td>
<td>5</td>
<td>62</td>
<td>16240</td>
<td></td>
</tr>
</tbody>
</table>

Results indicate low activity of acetaldehyde oxime under these conditions as shown by the low % conversion in homopolymerization and low % incorporation of the imine into the polymer in copolymerizations.

An $^1$H NMR analysis could not be performed on the homopolymerization sample due to the low yield. An $^1$H NMR analysis of the copolymerization samples showed peaks characteristic of poly IBVE only.

3.8. Homopolymerization of Formaldehyde, O-Benzylxime

3.8.1. Radical Initiated Homopolymerization

Table 3.6
Radical Homopolymerization of Formaldehyde, O-Benzylxime

<table>
<thead>
<tr>
<th>initiator</th>
<th>temp (°C)</th>
<th>solvent</th>
<th>time (day)</th>
<th>% conv</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BME, hv</td>
<td>-15</td>
<td>neat</td>
<td>3</td>
<td>trace</td>
<td>630, 410, 280</td>
</tr>
<tr>
<td>BEt$_3$, O$_2$ (5%)</td>
<td>-50</td>
<td>neat</td>
<td>6</td>
<td>trace</td>
<td>450, 260</td>
</tr>
<tr>
<td>BEt$_3$, O$_2$ (10%)</td>
<td>-50</td>
<td>neat</td>
<td>6</td>
<td>trace</td>
<td>690, 460, 260</td>
</tr>
</tbody>
</table>

Homopolymerizations were run at lower temperatures to avoid any ceiling
temperature effects which might be present at higher temperatures. The homopolymerizations gave only a trace of low molecular weight material even at lower temperatures.

The isolated polymers were light yellow powders. $^1$H NMR analysis gave peaks corresponding to oligomeric products. The $^1$H NMR spectrum for the 10 mol% BEt$_3$, O$_2$ initiated polymerization product gave aromatic peaks at $\delta$7.18 (m), a CH$_2$ peak at $\delta$4.73 (s), and a broad N-CH-N peak at $\delta$3.86 (broad s).

### 3.8.2. Ionic Initiated Homopolymerization

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Temp (°C)</th>
<th>Solvent</th>
<th>Time (day)</th>
<th>% Conv</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF$_3$SO$_3$CH$_3$</td>
<td>-15</td>
<td>neat</td>
<td>1</td>
<td>31</td>
<td>430</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>3</td>
<td>49</td>
<td>390</td>
</tr>
<tr>
<td>SnCl$_4$</td>
<td>5</td>
<td>CH$_2$Cl$_2$</td>
<td>3</td>
<td>31</td>
<td>410</td>
</tr>
<tr>
<td>BuLi</td>
<td>-75</td>
<td>THF</td>
<td>2</td>
<td>6</td>
<td>370</td>
</tr>
</tbody>
</table>

The isolated polymers were white powders. $^1$H NMR and SEC analysis showed the product to be the cyclic trimer form of the monomer in all cases.

### 3.9. Copolymerization of Formaldehyde, O-Benzylxime

#### 3.9.1. Radical Initiated Copolymerization

Radical initiated copolymerizations of formaldehyde, O-benzylxime with various comonomers were run.
Table 3.8
Radical Copolymerization of Formaldehyde, O-Benzylloxime

<table>
<thead>
<tr>
<th>comon</th>
<th>initiator (mol%)</th>
<th>mon:comon ratio</th>
<th>temp (°C)</th>
<th>% conv</th>
<th>% incorp (NMR)</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>BME (5%)</td>
<td>0:1</td>
<td>-15</td>
<td>60</td>
<td>-</td>
<td>99500</td>
</tr>
<tr>
<td>MA</td>
<td>BME (5%)</td>
<td>1:9</td>
<td>-15</td>
<td>22</td>
<td>5</td>
<td>1970</td>
</tr>
<tr>
<td>AN</td>
<td>BME (5%)</td>
<td>0:1</td>
<td>-15</td>
<td>99</td>
<td>-</td>
<td>NA</td>
</tr>
<tr>
<td>AN</td>
<td>BME (5%)</td>
<td>1:9</td>
<td>-15</td>
<td>39</td>
<td>3</td>
<td>1540</td>
</tr>
<tr>
<td>Styrene</td>
<td>BME (5%)</td>
<td>0:1</td>
<td>-15</td>
<td>64</td>
<td>-</td>
<td>1919</td>
</tr>
<tr>
<td>Styrene</td>
<td>BME (5%)</td>
<td>1:9</td>
<td>-15</td>
<td>42</td>
<td>trace</td>
<td>1140</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>BME (5%)</td>
<td>0:1</td>
<td>-15</td>
<td>93</td>
<td>-</td>
<td>11300</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>BME (5%)</td>
<td>1:9</td>
<td>-15</td>
<td>22</td>
<td>trace</td>
<td>1290</td>
</tr>
<tr>
<td>MA</td>
<td>BEt₃O₂ (5%)</td>
<td>0:1</td>
<td>-50</td>
<td>88</td>
<td>-</td>
<td>11930</td>
</tr>
<tr>
<td>MA</td>
<td>BEt₃O₂ (5%)</td>
<td>1:9</td>
<td>-50</td>
<td>34</td>
<td>6</td>
<td>1620</td>
</tr>
<tr>
<td>MA</td>
<td>BEt₃O₂ (10%)</td>
<td>0:1</td>
<td>-50</td>
<td>86</td>
<td>-</td>
<td>4930</td>
</tr>
<tr>
<td>MA</td>
<td>BEt₃O₂ (10%)</td>
<td>1:9</td>
<td>-50</td>
<td>24</td>
<td>3</td>
<td>1040</td>
</tr>
</tbody>
</table>

The copolymerizations with only a 1:9 monomer:comonomer ratio give a substantially lower molecular weight and % conversion compared to the results obtained from homopolymerizations of the comonomers in all cases. The % incorporation of the imine into the copolymer as determined by ¹H NMR was only a trace with the styrene and 4-methoxystyrene monomers but was higher in monomers methyl acrylate and acrylonitrile.

3.9.2. Ionic Initiated Copolymerization

The copolymerizations were run at a variety of monomer:comonomer ratios,
temperatures, initiators, and comonomers.

### Table 3.9
Ionic Copolymerization of Formaldehyde, O-Benzoxime

<table>
<thead>
<tr>
<th>comon</th>
<th>mon:comon ratio</th>
<th>initiator</th>
<th>temp (°C)</th>
<th>% conv</th>
<th>% imine incorp (NMR)</th>
<th>MW (SEC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBVE</td>
<td>0:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>55</td>
<td>-</td>
<td>14500</td>
</tr>
<tr>
<td>IBVE</td>
<td>0:1</td>
<td>SnCl$_4$</td>
<td>5</td>
<td>41</td>
<td>-</td>
<td>13320</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:9</td>
<td>BF$_3$</td>
<td>5</td>
<td>31</td>
<td>8</td>
<td>10600</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:9</td>
<td>SnCl$_4$</td>
<td>5</td>
<td>34</td>
<td>8</td>
<td>4470</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>-20</td>
<td>35</td>
<td>26</td>
<td>2500</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>0</td>
<td>46</td>
<td>24</td>
<td>2320</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>5</td>
<td>12</td>
<td>28</td>
<td>1940</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>SnCl$_4$</td>
<td>5</td>
<td>34</td>
<td>20</td>
<td>2200</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>25</td>
<td>39</td>
<td>32</td>
<td>2160</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>50</td>
<td>50</td>
<td>24</td>
<td>1620</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>80</td>
<td>31</td>
<td>14</td>
<td>1710</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:2</td>
<td>BF$_3$</td>
<td>5</td>
<td>10</td>
<td>33</td>
<td>1910</td>
</tr>
<tr>
<td>IBVE</td>
<td>1:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>6</td>
<td>NA</td>
<td>850</td>
</tr>
<tr>
<td>IBVE</td>
<td>2:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>4</td>
<td>NA</td>
<td>1050</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>0:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>94</td>
<td>-</td>
<td>48700</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>1:9</td>
<td>BF$_3$</td>
<td>5</td>
<td>54</td>
<td>trace</td>
<td>12020</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>1:3</td>
<td>BF$_3$</td>
<td>5</td>
<td>34</td>
<td>14</td>
<td>5790</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>1:2</td>
<td>BF$_3$</td>
<td>5</td>
<td>29</td>
<td>17</td>
<td>4200</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>1:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>15</td>
<td>21</td>
<td>2760</td>
</tr>
<tr>
<td>p-MeOS</td>
<td>2:1</td>
<td>BF$_3$</td>
<td>5</td>
<td>10</td>
<td>18</td>
<td>2240</td>
</tr>
<tr>
<td>Styrene</td>
<td>0:1</td>
<td>BuLi</td>
<td>-75</td>
<td>33</td>
<td>-</td>
<td>2900</td>
</tr>
<tr>
<td>Styrene</td>
<td>1:9</td>
<td>BuLi</td>
<td>-75</td>
<td>32</td>
<td>trace</td>
<td>2640</td>
</tr>
<tr>
<td>Styrene</td>
<td>1:3</td>
<td>BuLi</td>
<td>-75</td>
<td>21</td>
<td>trace</td>
<td>4890</td>
</tr>
</tbody>
</table>
The copolymerizations with gave a substantially lower molecular weight and % conversion compared to the results obtained from homopolymerizations of the comonomers in all cases. As the imine monomer:comonomer feed ratio was increased, the % incorporation increased as would be expected, but the % conversions and molecular weights decreased. The % incorporation of imine was significantly higher with isobutyl vinyl ether than with p-methoxystyrene. The effect of temperature and different initiators showed no significant differences in molecular weight, % conversion, or % incorporation. The anionic copolymerizations of the imine monomer with styrene produced only a trace of monomer incorporation.

3.10. "Living Cationic Systems"

A study was performed to examine the effect preformed polymer strands with “living” cationic ends would have on the polymerization of the monomer. It was hoped the preformed “living” polymer strands and the presence of a counter ion would decrease any side reactions and give a larger molecular weight polymer. The study involved creating a living system and utilizing it in 3 different experiments: 1) creating “living” polymer strands of isobutyl vinyl ether (IBVE) and adding formaldehyde, O-benzylloxime monomer 17 only 2) creating “living” polymer strands of IBVE and adding both imine monomer 17 and "fresh" IBVE and 3) having no preformed strands and adding the monomer 17 and IBVE.

The “living” polymerization system was a triflic acid-tetrahydrothiophene system with
IBVE monomer previously reported by Webster et al.\textsuperscript{25} shown below.

\[
\begin{align*}
\text{CH}_2=\text{C} & \cdot \text{OC}_4\text{H}_9 + \text{C}_4\text{H}_9\text{O} = \text{C} & \text{H} + \text{CF}_3\text{SO}_3\text{H} \rightarrow \text{C}_4\text{H}_9\text{O} = \text{C} & \text{S} \cdot \text{H} + \text{H}_3\text{C} \cdot \text{OTf} \\
\text{poly-IBVE} \leftrightarrow \text{CH}_2=\text{C} & \cdot \text{OC}_4\text{H}_9 & \text{C}_4\text{H}_9\text{O} = \text{C} & \text{S} \cdot \text{H} + \text{H}_3\text{C} \cdot \text{OTf}
\end{align*}
\]

3.10.1. "Living" System-Preformed Strands-Imine Monomer Only

The pre-formed strands of "living" IBVE were synthesized and the imine monomer \textsuperscript{17} was added.

<table>
<thead>
<tr>
<th>tube</th>
<th>temperature (°C)</th>
<th>MW (SEC)</th>
<th>%incorp of imine* (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-50</td>
<td>7070, 370, 170</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>-20</td>
<td>6440, 360, 150</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>6740, 370, 140</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>6930, 400, 140</td>
<td>3</td>
</tr>
</tbody>
</table>

* % incorporation of imine monomer into large MW strands

It was found that the monomer did not add exclusively to the "living" end of the pre-formed strands but synthesized trimers through chain transfer from the larger pre-formed
strands. An \textsuperscript{1}H NMR analysis of the two lower MW compounds showed them to be exclusively the imine monomer and its trimer. An \textsuperscript{1}H NMR analysis to measure the %incorporation of the imine monomer into the larger MW strands showed from 1-4% incorporation.

3.10.2. “Living” System-Preformed Strands-Imine Monomer and IBVE Comonomer

The pre-formed strands of “living” IBVE were synthesized and the imine monomer 17 and fresh IBVE were added.

<table>
<thead>
<tr>
<th>Tube</th>
<th>Mon:Comon</th>
<th>Temp (°C)</th>
<th>% Conversion</th>
<th>MW (SEC)</th>
<th>% Incorporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:9</td>
<td>-50</td>
<td>18</td>
<td>7900, 1280, 800</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>-20</td>
<td>23</td>
<td>8570, 1060, 690</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>1:9</td>
<td>5</td>
<td>32</td>
<td>8450, 980, 610</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>1:9</td>
<td>25</td>
<td>35</td>
<td>8330, 1030, 580</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>1:3</td>
<td>-50</td>
<td>14</td>
<td>8380, 710</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>1:3</td>
<td>-20</td>
<td>23</td>
<td>8261, 1110, 650, 410</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>1:3</td>
<td>5</td>
<td>38</td>
<td>8760, 1050, 610</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>1:3</td>
<td>25</td>
<td>45</td>
<td>8830, 1011, 590</td>
<td>14</td>
</tr>
</tbody>
</table>

* % incorporation of imine monomer into smaller MW polymers

It was found that copolymerization did not occur exclusively to the “living” end of the pre-formed strands but synthesized oligomers through chain transfer from the larger pre-formed strands. \textsuperscript{1}H NMR analysis of the MW 8000 material showed a % incorporation
of the imine monomer of <1% in all samples. The % incorporation of imine monomer into the smaller polymers was actually less in some cases to that of non-living systems such as those in 3.9.2.

3.10.3. “Living” System-No Preformed Strands-Imine Monomer and IBVE Comonomer

The imine monomer 17 and IBVE comonomer were added to the “living” catalysts with no preformed “living” IBVE strands present.

Table 3.12
"Living System"-No Preformed Strands-Imine Monomer and IBVE Comonomer

<table>
<thead>
<tr>
<th>tube</th>
<th>mon:comon</th>
<th>temp (°C)</th>
<th>% conv</th>
<th>MW (SEC)*</th>
<th>% incorp of imine (NMR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:9</td>
<td>-50</td>
<td>9</td>
<td>640</td>
<td>21</td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>-20</td>
<td>16</td>
<td>1290, 630</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>1:9</td>
<td>5</td>
<td>26</td>
<td>1080, 550</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>1:9</td>
<td>25</td>
<td>36</td>
<td>1030, 630</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>1:3</td>
<td>-50</td>
<td>11</td>
<td>640</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>1:3</td>
<td>-20</td>
<td>18</td>
<td>1250, 630</td>
<td>24</td>
</tr>
<tr>
<td>7</td>
<td>1:3</td>
<td>5</td>
<td>44</td>
<td>1250, 610</td>
<td>21</td>
</tr>
<tr>
<td>8</td>
<td>1:3</td>
<td>25</td>
<td>46</td>
<td>700, 340</td>
<td>25</td>
</tr>
<tr>
<td>9</td>
<td>0:1</td>
<td>-50</td>
<td>96</td>
<td>7830</td>
<td>-</td>
</tr>
</tbody>
</table>

* area of the lower MW peak in SEC analysis was 10X the higher MW peak

The results using the “living” catalysts were similar to those of the non-living systems previously used such as those described in 3.9.2.
CHAPTER 4

DISCUSSION

The discussion section will cover thermodynamics and mechanism of polymerization as well as synthesis and polymerization of the imine monomers.

4.1. Thermodynamics of Polymerization

A prediction of the heats of polymerization by the simple technique of obtaining the difference between the average bond energy of the monomer (e.g. C=N) and the sum of two single bonds formed in the polymer (e.g. C-N) yield the values given in Table 4.1.26

<table>
<thead>
<tr>
<th>Bond energies (kcal/mole)</th>
<th>Predicted heat of polymerization (ΔHₚ) (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C (145.8) to -C-C- (82.6)</td>
<td>-20</td>
</tr>
<tr>
<td>C=O (178) to -C-O- (85.6)</td>
<td>+5</td>
</tr>
<tr>
<td>C=N (147) to -C-N- (72.6)</td>
<td>+1.4</td>
</tr>
<tr>
<td>C=O (212.6) to -C=N- (147)</td>
<td>-7.2</td>
</tr>
<tr>
<td>C=S (128) to -C-S- (65)</td>
<td>-2</td>
</tr>
</tbody>
</table>

According to the above calculations, both the C=O and C=N bonds would be impossible to polymerize thermodynamically. However, using average bond energies give misleading energies due to the variations in both monomer and polymer stability with different substituents attached to the atoms. Substituents groups which stabilize the monomer or destabilize the polymer decrease the heat of polymerization while groups which destabilize the monomer or stabilize the polymer increase the heat of polymerization.

In spite of the data above, the polymerization of the C=O bond with a limited variety
of substituents is energetically possible and its thermodynamics has been widely studied.\textsuperscript{27} It is also known that the polymerization of the C=N bond is also possible through previous studies with both conjugated systems and simple imines.\textsuperscript{3-6,11} The thermodynamics of C=N polymerization has not been experimentally studied, however, but was addressed in a theoretical study by Leroy et al.\textsuperscript{28} In this study the free radical heat of polymerization was assumed to be equal to the enthalpy of the reaction HABAH + A=B \rightarrow HABABAH. The heat of formation, $\Delta H^\circ$, for HABABH, A=B, and HABABAH were calculated using various ab initio methods. The results for several monomers are given in Table 4.2.\textsuperscript{28}

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$\Delta H^\circ$ (theor.) kcal/mole</th>
<th>$\Delta H^\circ$ (expt.) kcal/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$ = CH$_2$</td>
<td>-22.64</td>
<td>-22.35 (g,g)</td>
</tr>
<tr>
<td>CH$_2$ = CHCN</td>
<td>-16.47</td>
<td>-18.3 (l,c)</td>
</tr>
<tr>
<td>CH$_2$ = O</td>
<td>-11.58</td>
<td>-13.2 (g,c)</td>
</tr>
<tr>
<td>CH$_2$ = NH</td>
<td>-13.67</td>
<td></td>
</tr>
<tr>
<td>CH$_2$ = NCN</td>
<td>-13.76</td>
<td></td>
</tr>
</tbody>
</table>

The theoretical values were generally very close or slightly lower than experimental values. The study shows that the predicted heats of polymerization for the two imine monomers are fairly exothermic, even higher than the formaldehyde monomer. It would therefore seem that a "no man's land" exists between the +1.4 kcal/mol heat of polymerization predicted using average bond energies and -13.76 kcal/mol predicted for the CH$_2$=NCN monomer.

4.1.1. Azaethylenecarbonitrile Monomers

The cyano group on the nitrogen would be a good choice for a substituent for three
reasons: first its large predicted heat of polymerization, second, it was the best N-substituent group on the simple imines polymerized by Kim, and third, it is not a very sterically demanding functional group.

Unfortunately CH₂ = NH and CH₂ = NCN are not stable under normal experimental nor are all other C or N monosubstituted imines with the exception of those with strong resonance electron donating groups attached to the nitrogen, e.g. oxime derivatives, hydrazone derivatives, semicarbazones. Therefore, at least a C and N disubstituted imine (R₁CH=NR₂) must be used to obtain a stable monomer. Carbon substituent groups which are electron-withdrawing tend to destabilize the imine bond and these monomers are not stable such as those whose syntheses were attempted by Ramezanian.

\[
\begin{align*}
\text{NC}_2\text{C}=\text{N(CN)} & \quad \text{CH}_3\overline{\text{O}}-\text{C}\text{C}=\text{N(CN)} & \quad \text{C}_2\text{H}_5\overline{\text{O}}-\text{C}\text{C}=\text{N(CN)} \\
\text{NC}_2\text{C}=\text{N(CN)} & \quad \text{CH}_3\overline{\text{O}}-\text{C}\text{C}=\text{N(CN)} & \quad \text{C}_2\text{H}_5\overline{\text{O}}-\text{C}\text{C}=\text{N(CN)}
\end{align*}
\]

Imines containing imine carbon electron-donating substituents and nitrogen electron-withdrawing substituents such as ethoxyazaethylenecarbonitrile are known to be stabilized through a push-pull resonance effect.
However, this monomer proved to be too stable as radical polymerization gave only a trace of product as described in 3.4. Imines containing mildly electron-donating carbon substituted aliphatic groups such as methyl, ethyl, isobutyl, dimethyl, and cyclopropyl proved to be unstable giving a variety of dimer, trimer, and oligomeric products as described in 3.1. The only aliphatic group which produced a stable imine monomer\textsuperscript{11}, namely t-butyl, has the disadvantage of being very sterically demanding. Our choice of monomers thus came to aromatic carbon substituents in which the degree of electron-donation and electron-withdrawal could be varied. The hope was to create monomers that were stable, yet not be so stable as to be thermodynamically impossible to polymerize. Unfortunately the aromatic groups necessary for stabilization of the monomer decrease the heat of polymerization by the loss of resonance in the polymerization and by steric effects. These effects by the phenyl group in styrene are predicted to lower $\Delta H_p$ by 2-3 kcal/mol as compared to other ethene substituted monomers.$^{26}$

An examination of the behavior of the different azaethylene monomers may provide an insight into the stability of these imines. As described in 3.1., while attempting synthesis of the three monomers below, it was found that only
4-cyanophenylaethylenecarbonitrile was stable as the imine, cyclopropylaethylenecarbonitrile existed as the trimer, and dimethylaethylenecarbonitrile decomposed in time giving several decomposition products.

As described in 3.1., attempts at trimerizing the 4-cyanophenyl derivative using an acid catalyst at low temperatures were unsuccessful as were attempts at monomer formation using an acid catalyst at higher temperature with the cyclopropyl derivative. This would tend to indicate that the conjugation of the aromatic substituent stabilizes the C=N bond so the monomeric form is most thermodynamically stable while this lack of resonance stability in the cyclopropyl derivative would make the trimeric form the more thermodynamically stable.

The presence of β-hydrogens on two of the monomers adds the possibility of tautomerization. The cyclopropyl derivative would be unlikely to tautomerize due to the formation of a double bond exo to the ring which would be higher in energy than the monomer.
The dimethyl derivative would tautomerize easier and likely does as evidenced by the number of decomposition products in the dimer and trimer molecular weight range as described in 3.1.

4.1.2. Monomers of Formaldehyde Oxime and Formaldehyde Oxime Derivatives

The choice of using derivatives of formaldehyde oxime as monomers was based on three factors. First, formaldehyde oxime itself shares similar characteristics with that of formaldehyde in that it is known to spontaneously polymerize and exhibits a ceiling temperature effect. Stable derivatives of formaldehyde oxime might also be predicted to have similar properties. However the polymer of formaldehyde oxime does have OH side chains in which a very large stabilization can occurs which would not be present in O-alkyl derivatives.
Because poly formaldehyde oxime is non-crystalline, X-ray studies could not confirm its structure. However, from vibrational analysis of the IR spectra of poly-formaldehyde oxime and its deuterated analogues support a planar zig-zag backbone. This structure is in contrast to that of the poly aldehydes which are known to exist as helices. This is also in contrast to the predicted helical structure of C-N-C-N polymers as will be discussed in 4.1.3. Second, the monomers would be monosubstituted which should reduce steric interactions in chain propagation and in the polymer product. Third, an equilibrium between the trimeric and monomeric form is known to exist in the formaldehyde O-benzylloxime monomer in solution from 20-60 °C. Below 20 °C and above 60 °C the monomer is in the trimer and monomer form respectively. There must exist a ceiling temperature above which the monomer is the thermodynamically stable form and below which the trimer is the thermodynamically stable form. Therefore if the temperature of pure monomer were lowered below this ceiling temperature and a kinetic pathway to polymer formation rather than trimerization was found, the polymerization should be thermodynamically feasible.

As previously mentioned the stabilization of the formaldehyde oxime derivatives is linked to the resonance donating ability of the O-alkyl group attached to the nitrogen.
In N-substituent groups where the donating ability is less, the temperature range of the monomer-trimer equilibrium increases. This is seen in the compound, N-methylene-4-methoxybenzenamine compound, where only the trimer form is observed in the \(^1\)H NMR spectra with the CH=N peak of the monomer first appearing above 100 °C. Even at 140 °C the monomer-trimer ratio is approximately 1:6 as described in 3.2.

The OCH\(_3\) group through the aromatic ring is not as efficient donating group as the O-alkyl group directly attached directly to the nitrogen.

4.1.3. Polymer Stability

The imine polymers formed should have some added stability over conventional -C-C- polymers through an anomeric stabilization effect which would result in a helical structure for the polymer. Polyoxymethylene is known to favor a 9/5 helical form in
preference to an all trans configuration\textsuperscript{32} with a gauche, gauche configuration. The effect of lone pair-lone pair repulsions was ruled out as a factor by Gorenstein and Kar\textsuperscript{33} in a study on the structure of dimethoxymethane. They found that in the all trans structure, the OCO bond angle was actually smaller than in the more thermodynamically stable gauche, gauche configuration.\textsuperscript{33}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{t,t_structure.png}
\caption{t,t structure}
\end{figure}

The authors concluded that the more stable g,g structure which is also found in polyoxymethylene was due only to anomeric stabilization\textsuperscript{33} which occurs by delocalization of the $n_p$ lone pair into the $\sigma^*$ orbital of the adjacent C-O bond.\textsuperscript{17}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{g,g_structure.png}
\caption{g,g structure}
\end{figure}

These results are also found in methanediol\textsuperscript{32} and methylenediamine.\textsuperscript{34}
4.1.4. Stability of the Trimer; 1,3,5-Hexahydrotriazine

The interactions of the lone pair on nitrogen which stabilize the polymer chain will also occur in a ring system.

Isodesmic reactions are reactions in which a chemical change occurs in which there is retention of the number of bonds of a given formal type, but with a change in their relation to one another. A study using isodesmic reactions to compare this added stabilization in nitrogen containing compounds in both cyclic and non-cyclic systems was done by Politzer et al. The isodesmic stabilization energy was calculated relative to NH₃ which has no lone pair-σ bond conjugation and also relative to the corresponding hydrocarbon. The isodesmic reactions for comparison of stabilization energy of cyclopentane and imidazolidine is shown in Scheme 4.1.

Scheme 4.1
Isodesmic Reactions for Cyclopentane and Imidazolidine

\[
\begin{align*}
5 \text{C}_2\text{H}_6 & \rightarrow \text{C}_5\text{H}_{10} + 5 \text{CH}_4 \\
4 \text{CH}_3\text{NH}_2 + \text{C}_2\text{H}_6 & \rightarrow \text{C}_3\text{N}_2\text{H}_8 + 3 \text{CH}_4 + 2 \text{NH}_3
\end{align*}
\]

The stabilization was believed to be by anomeric stabilization in those cases where N-C-N groups were present or by nitrogen lone pair-σ bond conjugation in the other molecules. Stabilization energies for the different imines are shown in Table 4.3.
The study leads to three main conclusions. First, ring systems containing nitrogen show a large stabilization energy over their hydrocarbon counterparts. Second, nitrogen ring systems show a greater stabilization energy over noncyclic systems containing the same number of nitrogen atoms. Third, even in those rings where anomeric stabilization does not occur (1,4-piperazine), a large stabilization is still seen due to nitrogen lone pair-σ bond conjugation.

Although 1,3,5-hexahydrotriazine was not used in the above study, the same anomeric stabilization effects should occur. This added stabilization may in part account for the instability of some monomers which trimerize. In addition, it could provide a more desirable thermodynamic pathway in competition with polymerization although kinetic
would probably play the major role.

4.2. Mechanism of Polymerization

4.2.1. Radical Centers

The stability of the nitrogen centered radical follows the same general pattern of carbon centered radical. In a theoretical study of carbon radical stability by Leroy et al., it was found that electron-withdrawing substituents destabilize a carbon radical while electron-donating substituents stabilize the radical as compared to a methyl radical. Further, the greatest stability was in those carbon radicals which were stabilized by a captodative push-pull effect of an electron donating and a withdrawing group such as in a \( \text{H}_2\text{N}(<\text{CN})\text{CH}^- \) radical. In another study by Leroy et al. using nitrogen centered radicals, the same trend was observed, electron withdrawing substituents destabilize the nitrogen radical while electron donating substituents stabilize. However, contrary to carbon radicals, the captodative effect of an electron donating and a withdrawing group did not produce stabilization greater than two electron donating groups.

The reactivity of nitrogen radicals with different substituents towards the competitive reactions of hydrogen abstraction vs. addition to alkenes was studied by Neale. In reactions of neutral nitrogen radicals such as a dialkyl aminyl radical, \( \text{R}_2\text{N}^- \), with allylic hydrocarbons, it was found that hydrogen abstraction predominates in both the vapor phase and in solution. However, when the dialkylaminyl radical was protonated, \( \text{R}_2\text{NH}^+ \), creating a electrophilic radical species, addition of olefins predominated and hydrogen abstraction occurred only in the absence of conjugation. In studies with the radical
species of $\text{CH}_3\text{SO}_2\text{CH}_3\text{N}^-$ and $\text{CH}_3\text{(CN)}\text{N}^-$ which radicals are mildly electrophilic, the radical were found to add to several alkenes in good yield.\textsuperscript{40} However, whether hydrogen abstraction still occurred with these mildly electrophilic radicals in the presence of alkenes was not mentioned by Neale.\textsuperscript{40}

The propagating radicals of the two groups of monomers studied would be the radicals shown below.

![Propagating Radicals](image)

$R = 3$-thiophene, 2-thiophene, 2-furan, 4-methoxyphenyl, 4-cyanophenyl

Both radical species are resonance stabilized, but from the studies on nitrogen radicals by Leroy\textsuperscript{38}, the second radical should be much more stable. However, from the standpoint of obtaining copolymers with alkene comonomers, the more electrophilic N-cyano radical should add to alkenes easier with less tendency at hydrogen abstraction.

Although the discussion has centered on the nitrogen radical as the propagating species, for the azaethylenecarbonitrile monomers the possibility exists that the carbon centered radical shown below, resulting from radical addition to nitrogen, could be the more stable radical.
R = 3-thiophene, 2-thiophene, 2-furan, 4-methoxyphenyl, 4-cyanophenyl

The radical would be not only stabilized through resonance with the aromatic ring but also by a three electron bond with the lone pair on nitrogen.

The formaldehyde oxime monomer under radical initiation probably undergoes a hydride shift to form the more stable nitroxy radical.

This rearrangement occurred in all alkyl oximes studied including acetaldoxime by Smith and Fox.\textsuperscript{41}

Formaldehyde oxime derivatives like the azaethylenecarbonitriles should form a stabilized propagating radical species. The nitrogen propagating radical formed would be stabilized by the adjacent oxygen atom to give the three bond resonance form below.
This resonance structure is not the same as that seen in classical nitroxyl radicals below.

The resonance of the 3 electron bond formed with the oxime derivatives would stabilize the propagating radical but its stability would not be as great as for a classical nitroxyl radical, otherwise the hydride shift in oxime radicals would not occur. Unfortunately, the literature contains no information on the relative stability of radicals formed from oximes.

4.2.2. Ionic Centers

It is known that ionic polymerizations have strict requirements for stabilization of the propagating species\textsuperscript{42}. The greatest stabilization of the nitrogen centers should therefore occur with anionic initiated polymerization for the azaethylenecarbonitriles and cationic
initiated polymerization for formaldehyde oxime and its derivatives. The nitrogen centers would be stabilized through resonance delocalization of the positive or negative charge as shown below.

4.3. Synthesis of Monomers

The aim of the synthesis was to produce stable monomers for polymerization studies. As discussed in 4.1.1. and 4.1.2, monomers must not only be stable but also be thermodynamically capable of polymerization. No attempt was made to optimize reaction conditions for maximum yields. The methods used in monomer synthesis followed procedures reported in the literature although adaptation were made in several cases as described in 3.1.-3.3.

4.4. Polymerization of Monomers

The polymerizations of the monomers were performed under varying conditions of temperature, initiator, solvents or neat conditions, and comonomers to study their effects
on polymerization and to find the best conditions for polymerization. Polymerizations were run under neat conditions when possible to minimize any ceiling temperature effects which may be present with solvents used for solid monomers or to make a homogeneous solution.

4.4.1. Polymerization of Azaethylenecarbonitriles

The imine polymerizations was found to occur exclusively through the C=N bond as confirmed by IR and NMR. The IR showed the C=N stretch and C≡N stretching the monomers and only the C≡N stretch in the polymers formed. $^1$H NMR showed the characteristic CH=N peaks between δ8.5-9.5 before polymerization with no peaks visible in the polymers formed.

The dimethylazaethylenecarbonitrile monomer which has limited stability at room temperature was tried in two polymerizations but decomposed under the reaction conditions and will not be discussed further.

4.4.1.1. Radical Homopolymerization

The monomer which gave the highest molecular weight with both benzoyl peroxide and benzoin methyl ether initiation was the 4-cyanophenyl derivative, followed by the aromatic heteroatom monomers, with the 4-methoxyphenyl derivative and ethoxy derivatives the lowest. This was not surprising based on the push-pull stabilization of the electron-donating derivatives while the 4-cyanophenyl would activated the imine bond by pulling electrons out of the double bond.

The % conversion ranged widely but as with the molecular weight, the monomers with
electron-donating groups gave the lowest values. The % conversions were much higher with benzoyl peroxide initiation than with benzoin methyl ether initiation. This is difficult to explain as the initiating phenyl radical (from benzoyl peroxide thermal decomposition) and the benzoyl radical (from benzoin methyl ether photodecomposition) are both $\sigma$ radicals and have roughly the same nucleophilic radical characteristics.  

Possible explanations could be that at higher temperatures the activity of the initiating radical increases, self-initiation in the monomer may occur, or chain transfer reactions increase.

The free radical nature of the polymerizations was confirmed with polymerizations of the 3-thiophenylazaethylenecarbonitrile monomer run in the presence of radical inhibitors as described in Table 3.2. The results show only a 1-2% conversion in the presence of inhibitors while giving 43% conversion in their absence. Surprising radical self-polymerization of the monomer occurred giving 9% conversion at 80 °C.

No ceiling temperature effects was present in this group of monomers. The polymerizations were run in temperatures ranging from -50 to 110 °C with little change in the molecular weight of the polymer.

4.4.1.2. Anionic Homopolymerization

The polymers formed using anionic initiation gave molecular weights in the same range as the radical initiated polymerization. As in the radical initiated polymerizations, the 4-cyanophenyl derivative gave a slightly higher value due to creating a more electrophilic monomer by pulling electrons from the C=N bond.
The % conversions in anionic polymerization were much higher than the radical initiated polymerizations. The stabilization of the nitrogen anion in the growing polymers by the N-cyano group would account for a high efficiency of initiation and thus high % conversion.

4.4.1.3. Radical Copolymerization

The copolymerization experiments were run using the five stable aromatic azaethylenecarbonitriles. Both electron-rich (e.g. p-methoxystyrene) and electron-poor (e.g. methyl acrylate) comonomers were used to study their interaction with the electron-poor imine monomers. In addition, the copolymerizations were run at two different temperatures to study the effects of temperature on the copolymerizations.

On analyzing the results described in 3.5., several observations are noted. First, the copolymerizations gave much lower molecular weights and % conversion than homopolymerizations of the comonomers alone. This would indicate that the imine monomer forms a stable radical which inhibits further propagation or the imine radical undergoes termination reactions readily. Second, the 4-methoxyphenylazaethylenecarbonitrile monomer must be a very inactive species due to its low % incorporation into the copolymers formed. The higher molecular weights and higher % conversion observed in copolymerization with methyl acrylate could be explained as a homopolymerization of methyl acrylate with the imine monomer existing in the solution as a non-participant. Third, copolymerization of the monomers with p-methoxystyrene gave approximately 50 % incorporation of the monomer into the
copolymers in all cases. Because the imine monomers are electron-poor and p-methoxystyrene electron-rich, a complex must form between the two monomers through which the polymer formed would have alternating monomer and comonomer. Fourth, copolymerizations with the 4-cyanophenylazaethylenecarbonitrile monomer gave higher results for molecular weight and % conversions in general but were not as consistent in all cases as in homopolymerization of the imine monomers.

4.4.2. Polymerization of Formaldehyde Oxime

The polymerization of formaldehyde oxime at 60 °C by both radical and cationic initiation methods yielded no polymer product as analyzed by 1H NMR. Analysis of the polymerization by other means such as IR and SEC was not used as the monomer is known to spontaneously polymerize below 60 °C. The lack of polymer product in polymerizations above 60 °C is probably due to a ceiling temperature effect where polymerization is thermodynamically unfeasible.

4.4.3. Polymerization of Acetaldehyde Oxime

Because of the instability of formaldehyde oxime at room temperature, polymerizations with acetaldehyde oxime were attempted by cationic initiation. Homopolymerization gave only a trace of product which peaks in SEC analysis which could be dimer, trimer, and tetramer product. Copolymerizations with isobutyl vinyl ether gave higher % conversions but the % incorporation of the oxime into the copolymer was negligible. Molecular weight of the copolymers were also very low. The low reactivity of the oxime in the copolymerizations where ceiling temperature effects do not
operate would probably rule out a ceiling temperature effect being the sole cause of low yields in homopolymerization. Acetaldehyde oxime does not polymerize like formaldehyde oxime because of steric effects of substitution or extra stabilization of the C=\text{N} bond by the methyl group attached to the carbon.

4.4.4. Polymerization of Formaldehyde, O-Benzylloxime

4.4.4.1. Radical Homopolymerization

The radical homopolymerization were run at low temperatures to minimize any ceiling temperature effects. unfortunately at both -15 °C and -50 °C, only a trace of low molecular weight product was found.

4.4.4.2. Cationic Homopolymerization

The cationic homopolymerizations gave higher % conversions than the radical homopolymerizations but only of the cyclic trimer compound. No indication of any polymer material other than the trimer product was found. The trimer formation probably results from a strictly trimerization reaction rather than a backbiting chain transfer to polymer mechanism because of the absence of small oligomers in the product. In either case, the kinetic rate of trimerization must be much faster than the rate of polymerization.

4.4.4.3. Anionic Homopolymerization

Even though the propagating anion would not be resonance stabilized by the O-benzyl group attached to the nitrogen, anionic initiated polymerization was attempted. Analysis showed the product to be a poor yield of the cyclic trimer. Because the monomer will spontaneously trimerize at lower temperature with time, it cannot be assumed that the
appearance of the trimer is solely the result of anionic initiation.

4.4.4.4. Radical Copolymerization

The copolymerizations with only a 1:9 monomer:comonomer ratio give a substantially lower molecular weight and % conversion compared to the results obtained from homopolymerizations of the comonomers. This would indicate a lack of reactivity of the propagating radical of the imine monomer or an increase in the rate of termination.

The % incorporation was only a trace in the electron-rich styrene and 4-methoxy styrene monomers but was higher in the electron-poor monomers methyl acrylate and acrylonitrile possibly due to complex formation with the electron-rich imine monomers.

4.4.4.5. Cationic Copolymerization

The copolymerizations were run at a variety of monomer:comonomer ratios, temperatures, initiators, and comonomers. As the monomer:comonomer feed ratio was increased, the % incorporation increased as would be expected, but the % conversions and molecular weights decreased indicating either a decreased reactivity towards propagation or increased rate of termination. The % incorporation of imine was significantly higher with isobutyl vinyl ether than with p-methoxystyrene. The effect of temperature and different initiators showed no significant differences in molecular weight, % conversion, or % incorporation.

4.4.4.6. Anionic Copolymerization
The anionic copolymerization of the imine monomer with styrene with BuLi initiation produced only a trace of monomer incorporation which was not surprising due to the lack of resonance stabilization of the propagating anionic center by the O-benzyl group attached to the nitrogen.

4.4.4.7. "Living" Cationic Polymerizations

The "living" cationic system was used to study the effect of long pre-polymerized "living" isobutyl vinyl ether strands on homopolymerization and copolymerization of the imine monomer. The "living" strands could be equated to a long pre-formed initiator. It was hoped the longer pre-formed strands and counter ion would reduce side reactions produce longer strands of imine polymers. Unfortunately, the propagating centers at the end of the pre-formed strands was removed through chain transfer reactions and the formation of small oligomeric products occurred. This occurred with addition of imine monomer only and also with addition of imine monomer and "fresh" IBVE comonomer to the pre-formed "living" strands.

4.5 Summary

As with any research project, this work had its successes, failures, and unanswered questions.

The first goal of this work was the synthesis of stable imine monomers. This in itself does not seem difficult, as many stable imines are known to exist. The goal therefore was not only to synthesize stable imine monomers but to synthesize monomers thermodynamically capable of polymerization. As discussed in 4.1.1 and 4.1.2, imine
monomer stability is very dependent on imine carbon and nitrogen substituents. This is in contrast to the alkenes where most monomers are stable under normal conditions with a wide variety of substituent groups and are thermodynamically capable of polymerization. One of the successes of the work was the synthesis of several stable monomers from the azaethylenecarbonitriles and formaldehyde oxime and its derivatives.

The second goal of this work was the polymerization of the imine monomers. Success was achieved in the formation of both homopolymers and copolymers from both azaethylenecarbonitrile monomers and formaldehyde oxime derivatives. Failure, however, occurred in that the formation of high molecular weight homopolymers and copolymers was not achieved. An explanation for this must come from both thermodynamic and kinetic considerations.

Thermodynamic effects would manifest themselves through $\Delta G_p = \Delta H_p - T\Delta S_p$. Because $\Delta S_p$ is negative and $\Delta H_p$ varies little with temperature, a lowering of the temperature should make $\Delta G_p$ more negative and the molecular weight of the polymer should increase. The effect of different temperatures on polymerization in this study produced a negligible effect on molecular weight. For example, 4-cyanophenylazaethylenecarbonitrile monomer 5 was homopolymerized at 80, 25, 5, and -50 °C. All polymerizations were run in solution with monomer concentration roughly the same. As reported in Table 3.1, all molecular weights fall within the same range. Therefore, thermodynamic effects are probably not the major factor in the low molecular weights observed.
Kinetic effects on polymer molecular weight would manifest themselves by the relative rates of many reactions, namely propagation, chain transfer, trimerization, and termination. It is known that 1,2-disubstituted vinyl monomers do not polymerize well because of steric hindrance to propagation and give lower molecular weights in homopolymerization than monosubstituted monomers. This could be a factor in the polymerization of the azaethylenecarbonitrile monomers. Chain transfer reactions are known to occur in cationic polymerization of the formaldehyde, O-benzyloxime monomer as discussed in 4.4.4.7. Hydrogen abstraction reactions may also be a problem in radical polymerization. Hydrogen abstraction reactions are known to occur with neutral nitrogen radicals while more electrophilic nitrogen radicals undergo addition to alkenes as discussed in 4.2.1. However, no mention of whether hydrogen abstraction still occurs along with addition was mentioned. In addition, a study of hydrogen abstraction vs. addition by Neale dealt with nitrogen radical reactions with alkenes; no study of hydrogen abstraction vs. addition of nitrogen radical reactions with imines has been reported in the literature. Trimerization reactions occurred in homopolymerization of formaldehyde, O-benzyloxime monomer giving only the trimer product as discussed in 4.4.4.2.

The study of the polymerization of imines is still a new field. Many questions about the synthesis of stable yet polymerizable monomers, the thermodynamics and kinetics of imine polymerization, the nature of the nitrogen propagating radicals, the structure of imine polymers, and uses of imine polymers have yet to be answered.
CHAPTER 5
EXPERIMENTAL

5.1. Instrumentation

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AM 250 MHZ or a Varian Unity 300 MHZ nuclear magnetic resonance spectrometer. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are corrected. SEC data was obtained using THF as the eluent, ultra-violet and infrared detectors and a set of three Phenomenex Phenogel 5 columns of 1000, 500, and 100 Å pore size. Molecular weight was calibrated versus polystyrene standards. Elemental analyses were performed by Desert Analytics of Tucson, Az. Mass spectroscopy was performed by The University of Arizona Chemistry Department on a Hewlett Packard Model 5988A spectrometer. Irradiation of photoinitiators was performed in a Rayonet Photochemical Reaction chamber containing 8-3500 Å fluorescent lamps.

5.2. Synthesis of Monomers

All starting materials unless otherwise specified, were obtained from Aldrich Chemical Company.

5.2.1 Synthesis of Azaethylenecarbonitrile Monomers

The azaethylenecarbonitrile monomers were synthesized in two steps by a modification of a previous method reported by Kim and Hall.$^{12}$
Synthesis of 1,3-Bis(trimethylsilyl)carbodiimide

Into a 500 mL RB flask equipped with a mechanical stirrer was placed 25.38 mL (0.2 mol) of chlorotrimethylsilane with 100 mL of anhydrous diethyl ether which was cooled to 0 °C. With stirring, 27.90 mL (0.2 mol) of triethylamine previously diluted with 50 mL of anhydrous diethyl ether was slowly added dropwise. A moderate amount of white, smokey gas was emitted during addition and a white precipitate forms. After addition, stirring was continued for 20 minutes. Then 4.204 g (0.1 mol) of cyanamide dissolved in 50 mL of anhydrous diethyl ether was slowly added dropwise to the RB flask which was continuously cooled in an ice bath. A large amount of white smokey gas evolves and a large amount of thick amine salt precipitate was formed. The reaction was stirred for 3 h after addition of the cyanamide.

The white amine salt precipitate was filtered and washed twice with 25 mL of anhydrous diethyl ether. The ether filtrate was then removed via rota-vap until approximately 25 mL of solution was left. The remaining solution was distilled with the fraction between 158-164 °C collected to yield 14.8 mL (0.065 mol) of product. Yield: 65 %.

Synthesis of Azaethylenecarbonitrile Monomers

In a typical synthesis, 0.1 mol of aldehyde and 25 mL (0.11 mol) of freshly distilled 1,3-bis(trimethylsilyl)carbodiimide were placed in a 100 mL RB flask along with 50 mL of dichloromethane and cooled to -20 °C. Slowly, with stirring, 0.20 mL (0.001 mol, 1% of aldehyde) of the catalyst trimethylsilyl trifluoromethanesulfonate was
added. The flask was allowed to warm to room temperature. The solvent was removed via rota-vap until precipitation occurs and was then cooled at -20 °C. The precipitate was filtered off, more solvent removed until precipitation occurs, cooled at -20 °C, and the precipitate filtered. The precipitate was dried and recrystallized from hot, boiling hexane to a pure product. Yields varied depending on the aldehyde used, ranging from 38-67 %.

The catalyst, trimethylsilyl trifluoromethanesulfonate proved to be a much better catalyst than the titanium tetrachloride catalyst used in a previous method by Kim and Hall. The triflate catalyst gave higher yields, purer products, and shorter reaction time.

5.2.1.1. Phenylazaethylenecarbonitrile

Phenylazaethylenecarbonitrile had been previously prepared by Kim. The structure was confirmed by melting point, \(^1\)H NMR, \(^{13}\)C NMR, and IR analysis.

Literature: mp. 71 °C; IR (KBr) 1607 C=N stretch; \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.00 CH=N; \(^{13}\)C NMR (CHCl\(_3\), decoupled) \(\delta\) 182.5 C=N

Experimental: white solid; mp 69-71 °C; IR (KBr) 3188, 3068, 2190 C=N stretch, 1607 C=N stretch, 1595, 1570, 1450, 1379, 1314, 1233, 1023, 995, 757, 683 cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.02 (s,1H) CH=N; 7.85-8.00 (m,2H), 7.65-7.80 (m,1H), 7.50-7.65 (d,2H) phenyl; \(^{13}\)C NMR (CHCl\(_3\), decoupled) \(\delta\) 182.3 C=N; 135.6 C4, 132.1 C1, 129.7 C2,6, 128.3 C3,5, phenyl; 115.6 C=N;

5.2.1.2. 3-Thiophenylazaethylenecarbonitrile

White solid; Yield 66%; mp 62-65 °C; IR (KBr) 3103, 3083, 2190 C=N stretch, 1574 C=N stretch, 1409, 1345, 1242, 1159, 1012, 995, 879, 803, 737, 715, 630 cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(8.97\) (s,1H) CH=N; 8.20 (m,1H), 7.44-7.62 (m,2H), thiophenyl;
\(^13\)C NMR (CHCl\(_3\), decoupled) \(\delta\) 174.8 C=N; 139.1 C2, 138.7 C3, 128.5 C5, 125.6 C4, thiophenyl; 115.9 C=N; MS \textit{m/z} (intensity) 136.00 (100) molecular ion peak and base peak, 135.00 (48), 108.95 (84), 44.80 (81), 39.00 (61); Elemental Analysis, Calculated for C\(_6\)H\(_4\)N\(_2\)S, %C 52.93, %H 2.96, %N 20.57; Found, %C 53.16, %H 3.05, %N 20.63

5.2.1.3. 2-Thiophenylaethylenecarbonitrile

White solid; Yield 51%; mp 73-75 °C; IR (KBr) 3088, 2186 C=N stretch, 1579 C=N stretch, 1413, 1374, 1317, 1257, 1220, 1047, 1023, 1004, 981, 867, 760, 725 cm\(^{-1}\);
\(^1\)H NMR (CDCl\(_3\)) \(\delta\) 9.06 (s,1H) CH=N; 7.80-8.00 (m,2H), 7.29 (m,1H), thiophenyl;
\(^13\)C NMR (CHCl\(_3\), decoupled) \(\delta\) 173.3 C=N; 139.8 C3, 138.9 C2, 137.4 C5, 129.3 C4, thiophenyl; 115.6 C=N; MS \textit{m/z} (intensity) 136.00 (100)molecular ion peak and base peak, 135.00 (55), 109.00 (53), 45.00 (27), 39.00 (32); Elemental Analysis, Calculated for C\(_6\)H\(_4\)N\(_2\)S, %C 52.93, %H 2.96, %N 20.57; Found %C 53.27, %H 3.10, %N 20.80

5.2.1.4. 2-Furanylazaethylenecarbonitrile

White solid; Yield 48%; mp 88-90 °C; IR (KBr) 3111, 3059, 2194 C=N stretch, 1605 C=N stretch, 1536, 1468, 1396, 1337, 1304, 1022, 977, 934, 774 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 8.98 (s,1H) CH=N; 8.24 (m,1H), 7.44-7.60 (m,2H), furanyl; \(^13\)C NMR (CHCl\(_3\), decoupled) \(\delta\) 174.9 C=N; 139.1 C3, 138.1 C2, 128.1 C5, 125.0 C4, furanyl; 115.9 C=N; MS \textit{m/z} (intensity) 119.95 (100)molecular ion peak and base peak, 118.95 (36), 93.00 (29), 65.00 (19), 53.00 (18), 39.00 (65); Elemental Analysis, Calculated for C\(_6\)H\(_4\)N\(_2\)O, %C 60.00, %H 3.36, %N 23.32; Found, %C 59.85, %H 3.23, %N 23.22
5.2.1.5. 4-Methoxyphenylazaethylenecarbonitrile

White solid; Yield 67%; mp 134-136 °C; IR (KBr) 3021, 2982, 2189 C=N stretch, 1597 C=N stretch, 1559 1511, 1432, 1215, 1166, 1021, 846, 820 cm⁻¹; ¹H NMR (CDCl₃) δ 8.89 (s,1H) CH=N; 7.86 (d,2H) C2,6, 7.02 (d,2H) C3,5, phenyl; 3.93 (s,3H) OCH₃; ¹³C NMR (CDCl₃, decoupled) δ 180.5 C=N; 165.9 C4, 132.9 C2,6, 126.2 C1, 114.8 C3,5, phenyl; 116.5 C=N; 55.7 OCH₃; MS m/z (intensity) 160.15 (100) molecular ion peak and base peak, 159.05 (67), 133.05 (75), 103.00 (12), 90.00 (17), 65.00 (32), 39.00 (27); Elemental Analysis, Calculated for C₉H₇N₂O, %C 67.49, %H 5.03, %N 17.49; Found %C 67.16, %H 4.95, %N 17.34

5.2.1.6. 4-Cyanophenylazaethylenecarbonitrile

White solid; Yield 38%; mp sublimes at 130 °C, 145 °C darkens; IR (KBr) 3090, 2227 C=N stretch, 2196 C N stretch, 1601 C=N stretch, 1557, 1309, 1295, 1226, 998, 831 cm⁻¹; ¹H NMR (DMSO) δ 9.49 (s,1H) CH=N; 8.12 (m,2H) C2,6, 8.05 (m,2H) C3,5, phenyl; ¹³C NMR (CHCl₃, decoupled) δ 181.6 C=N; 136.3 C1, 132.8 C3,5, 130.4 C2,6, 117.3 C4, phenyl; 118.4 p-C=N; 114.6 N-C=N; MS m/z (intensity) 155.05 (63) molecular ion peak, 154.05 (32), 127.95 (100)base peak, 102.00 (23), 76.00 (20), 75.00 (21), 50.00 (24); Elemental Analysis, Calculated for C₉H₇N₃, %C 69.67, %H 3.25, %N 27.08; Found %C 69.36, %H 3.49, %N 26.21

5.2.1.7. Dimethylazaethylenecarbonitrile

The pure product was obtained by a Kugelrohr distillation of the reaction mixture. The compound was stable at room temperature for several hours but decomposed with
Time even at lower temperatures to give a mixture of decomposition products.

Colorless liquid; Yield 35%; IR (neat on NaCl plates) 2997, 2921, 2188 C≡N stretch, 1427, 1369, 1260, 1080, 979, 807, 618 cm⁻¹; ¹H NMR (CDCl₃) δ2.45 (s,3H) CH₃ (cis); 2.32 (s,3H) CH₃ (trans); ¹³C NMR (CHCl₃, decoupled) δ199.6 C≡N; 113.0 C≡N; 28.0 CH₃ (cis) 27.1 CH₃ (trans); MS m/z (intensity) 82.05 (63) molecular ion peak, 154.05 (29), 67.05 (100) base peak, 39.05 (21), 27.00 (14), 15.00 (68); Elemental Analysis, Calculated for C₄H₆N₂, %C 58.52, %H 7.37, %N 34.12; Found %C 58.30, %H 7.54, %N 34.23

An analysis of the decomposition products with thin layer chromatography yielded nine different separated products. ¹H NMR (DMSO-d₆) of all decomposition products together gave several peaks in the methyl region between 0.1-2.5 and a broad peak 4.5-5.5. ¹³C NMR (DMSO-d₆, decoupled) and ¹³C APT NMR (DMSO-d₆, decoupled) showed several CH₃ peaks between δ25.0-35.0, several CH₂ peaks between δ40.0-70.0, several C≡N peaks between δ105.0-120.0, and a few CH₂= peaks in the region between δ110.0-130.0. An IR analysis of the decomposition products showed the presence of saturated and unsaturated carbons with peaks above and below 3000 cm⁻¹ at 3027, 3023, 3019, 3017, 3014, 3011, 3007, and 2971 cm⁻¹; several C≡N stretch peaks at 2227, 2176, and 2140 cm⁻¹; a broad band between 1500-1720; and broad peaks at 1446, 1366, 1247, and 1180. An SEC analysis gave a single broad peak at 310.

MS analysis showed >30 peaks with spectra obtained for the 14 largest peaks whose molecular weights were 94, 122, 163, 163, 164, 164, 179, 188, 186, 202, 204, 246, 286,
and 286. The peaks at 163 and 164 correlate with dimer structure while the 246 peak is the trimer.

5.2.1.8. Cyclopropylazaethylenecarbonitrile Trimer

The compound was found to be unstable as an imine and trimerizes on synthesis.

White solid; Yield 58%; IR (KBr) 3093, 3014, 2925, 2215 C≡N stretch, 1231, 1210, 1185, 159, 1070, 870 cm⁻¹; ¹H NMR (DMSO) δ3.80 (d,1H) N-CH-N; 1.37 (m,1H) C1, 0.85 (m,2H) C2,3 (cis-vicinal), 0.61 C2,3 (trans-vicinal), cyclopropyl; ¹³C NMR (DMSO, decoupled) δ110.7 C=N; 78.0 N-C-N; 11.0 C1, 3.9 C2,3, cyclopropyl; MS m/z(intensity) 282 (1) molecular ion peak, 188 (22), 145 (16), 95 (100) base peak, 68 (66), 53 (46), 41 (82); Elemental Analysis, Calculated for trimer, C₁₅H₁₈N₆, %C 63.81, %H 6.43, %N 29.76; Found %C 63.55, %H 6.29, %N 29.47

5.2.1.9. Attempted Synthesis of Methylazaethylenecarbonitrile

The product was unstable as the imine monomer. From NMR, IR, and SEC analysis the product was thought to be an oligomer made up of imine monomers.

White solid; Yield 53%; IR (KBr) 3196, 2989, 2224 C≡N stretch, 1671, 1505, 1414, 1249, 1164, 1029 ,951, 850, 759, 638 cm⁻¹; ¹H NMR (DMSO) δ4.40-5.50 (broad,1H), 1.10-1.90 (broad,3H); ¹³C NMR (DMSO, decoupled) δ114.0-120.0 (several peaks) C≡N; 70.0-85.0 (several peaks)N-C-N; 15.0-25.0 (several peaks) CH₃; NMR APT and DEPT analysis confirmed the assignment of carbon atoms in the ¹³C spectrum; SEC Analysis gave a single broad peak, Mₙ=590 and Pₒ=1.14; Elemental Analysis was not determined.
5.2.1.10. Attempted Synthesis of Ethylazaethylenecarbonitrile

The product was unstable as the imine monomer. From NMR, IR, and SEC analysis the product was thought to be an oligomer made up of imine monomers. Elemental analysis however does not confirm a compound made up of only C, H, and N. Therefore some incorporation of the aldehyde starting material into the oligomer must be occurring.

White solid; Yield 42%; IR (KBr) 3338, 2969, 2932, 2875, 2344, 2221 cm⁻¹; ¹H NMR (DMSO) δ 4.0-4.8 (broad, 1H), 1.40-2.10 (broad, 2H), 0.7-1.2 (broad, 3H); ¹³C NMR (DMSO, decoupled) δ 1114.0-120.0 (several peaks) C=N; 65.0-70.0 (several peaks) N-C-N; 24.0-32.0 (several peaks) CH₂; 6.0-10.0 (several peaks) CH₃; NMR DEPT analysis confirmed the assignment of carbon atoms in the ¹³C spectrum; SEC Analysis gave a single broad peak, Mₙ=402 and Pₒ=1.38; Elemental Analysis, Calculated for monomer, C₄H₆N₂, %C 58.5, %H 7.32, %N 34.1; Found %C 38.21, %H 6.39, %N 17.30

5.2.1.11. Attempted Synthesis of 2-Methylpropylazaethylenecarbonitrile

The product was unstable as the imine monomer. From NMR, IR, and SEC analysis the product was thought to be an oligomer made up of imine monomers. Elemental analysis however does not confirm a compound made up of only C, H, and N. Therefore some incorporation of the aldehyde starting material into the oligomer must be occurring.

White solid; Yield 58%; IR (KBr) 3265, 2957, 2870, 2222 cm⁻¹; ¹H NMR (DMSO) δ 4.4-5.2 (broad, 1H), 1.30-2.00 (broad, 3H), 0.6-1.2 (broad, 6H); ¹³C NMR (DMSO, decoupled)
δ114.0-122.0 (several peaks) C≡N; 58.0-70.0 (several peaks) N=C=N; 35.0-45.0 (several peaks) CH₂; 15.0-25.0 (several peaks) CH₃; NMR DEPT analysis confirmed the assignment of carbon atoms in the ¹³C spectrum; SEC Analysis gave a single broad peak, Mₙ=417 and P_d=1.92; Elemental Analysis, Calculated for monomer, C₆H₁₀N₂, %C 65.5, %H 9.09, %N 25.5; Found %C 52.16, %H 7.70, %N 22.29

5.2.1.12. Ethoxyazaethylenecarbonitrile

Ethoxyazaethylenecarbonitrile was synthesized by the method of Huffman and Schaefer. In a typical synthesis, 8.32 mL (0.05 mol) of triethyl orthoformate and 2.102 g (0.05 mol) of cyanamide were dissolved into acetic 9.44 mL (0.1 mol) of acetic anhydride and heated to 135 °C, at which time ethyl acetate began to distill rapidly. The heat was removed until the initial vigorous reaction subsided, then reheated at 140 °C for 2 h. The yellow wash solution was distilled under vacuum (0.1 torr) and the fraction from 55-65 °C saved. Redistillation under the same condition removed any remaining impurities. The compound was confirmed by comparison of boiling point, ¹H NMR, and IR was literature values.

Literature: Yield 90%; bp (0.1 torr) 58-63 °C; IR (film,NaCl) 2200 C≡N stretch, 1620 C=N stretch cm⁻¹; ¹H NMR (CDCl₃) δ8.30 (s,1H) CH=N; 4.30 (q,2H) CH₂; 1.37 (t,3H) CH₃.

Experimental: Colorless liquid; Yield 42%; bp (0.1 torr) 55-65 °C; IR (film,NaCl) 2196 C≡N stretch, 1614 C=N stretch cm⁻¹; ¹H NMR (CDCl₃) δ8.50 (s,1H) CH=N; 4.40 (q,2H) CH₂; 1.30 (t,3H) CH₃.
5.2.2. N-Methylenebenzenamine derivatives

The N-methylenebenzenamine derivatives were synthesized by the method of Miller and Wagner\textsuperscript{19} from a reaction of formaldehyde and the aniline derivative.

In a typical synthesis, 0.1 mol of formaldehyde (8.1 mL of a 37% solution in H\textsubscript{2}O) was added to an equimolar amount of the freshly distilled aniline derivative in a 100 mL RB flask at room temperature. Ethanol was added until the two layers become one homogeneous mixture. The solution was stirred overnight. The ethanol was removed via rota-vap. The precipitate which forms was filtered, recrystallized from a 1:1 mixture of ethanol:H\textsubscript{2}O and dried.

5.2.2.1. N-Methylenebenzenamine Trimer

The product had been previously synthesized by Miller and Wagner\textsuperscript{19} and was found to be the trimer form of the monomer.

Literature:\textsuperscript{44} m.p. 141.2 °C

Experimental: white solid; Yield 62%; m.p. 138-141 °C; IR (Kbr) 3062, 3031, 2938, 2844, 2344, 1594, 1502, 1453, 1382, 1332, 1226, 1201, 1161, 1127, 984, 934, 919, 752, 690 cm\textsuperscript{-1}; \textsuperscript{1}H NMR (CDCl\textsubscript{3}) \textdelta 6.7-7.3 (m, 5H), phenyl; 4.90 (s, 2H) CH\textsubscript{2}; \textsuperscript{13}C NMR (CDCl\textsubscript{3}, decoupled) \textdelta 148.3 C1, 128.9 C3,5, 119.9 C4, 116.8 C2,6, phenyl; 67.0 CH\textsubscript{2}; NMR APT analysis confirmed the assignment of carbon atoms in the \textsuperscript{13}C spectrum;

MS m/z (intensity) 315 (2) molecular ion peak, 211 (10), 134 (26), 106 (100) base peak;

Elemental Analysis, Calculated for trimer, C\textsubscript{21}H\textsubscript{21}N\textsubscript{3}, %C 79.96, %H 6.72, %N 13.33;

Found %C 80.01, %H 6.53, %N 13.29
5.2.2.2. 4-Methoxy-N-methylenebenzenamine Trimer

The product was found to be the trimer form of the monomer.

White solid; Yield 70%; m.p. 141-144 °C; IR (Kbr) 3038, 2991, 2946, 2896, 2826, 1503, 1460, 1386, 1292, 1243, 1196, 1181, 1152, 1034, 984, 936, 822, 730 cm⁻¹;

¹H NMR (CDCl₃) δ6.98 (d,2H), 6.75 (d,2H), phenyl; 4.63 (s,2H) CH₂; 3.69 (s,3H) OCH₃;

¹³C NMR (CDCl₃, decoupled) δ154.2 C1, 142.5 C4, 119.8 C3,5, 114.2 C2,6 phenyl; 70.9 CH₂; 55.3 OCH₃; NMR APT analysis confirmed the assignment of carbon atoms in the ¹³C spectrum; MS m/z(intensity) 405 (1) molecular ion peak, 271 (4), 176 (5), 164 (14), 136 (100) base peak; Elemental Analysis, Calculated for trimer, C₂₁H₂₁N₃; %C 71.08, %H 6.72, %N 10.37; Found %C 70.99, %H 6.86, %N 10.34

5.2.3. Formaldehyde Oxime and Formaldehyde Oxime Derivatives

5.2.3.1. Formaldehyde Oxime

Formaldehyde oxime was synthesized by a modification of the method of Andersen and Jensen.¹⁷ In a typical procedure, 13.92 g (0.2 mol) of hydroxylamine hydrochloride and 5.60 g (0.14 mol) of NaOH were dissolved in 20 mL of H₂O, followed by addition of 16.2 mL (0.2 mol) of a 37% formaldehyde solution. The solution was heated to 70 °C for 10 minutes. The pH was adjusted slightly basic (pH=8) and the formaldehyde oxime product distilled (b.p. 84 °C) without cooling directly into an diethyl ether solution cooled by a dry ice-acetone bath. (Cooling the pure product below 60 °C results in spontaneous polymerization.) Any residual H₂O which distills over was dried with Na₂SO₄ and removed. The dried solution was heated to remove the ether solvent and the
resulting pure product kept at a temperature of 70 °C until used. The product was characterized by comparison of boiling point and $^1$H NMR with literature values.

Literature: Colorless liquid; bp 82-83 °C; $^1$H NMR (DMSO-d$_6$) δ 11.01 (s,1H) OH; 6.92 (d,1H) HC (trans); 6.38 (d,1H) HC (cis).

Experimental: Colorless liquid; Yield 56%; bp 82-83 °C; $^1$H NMR (DMSO-d$_6$) δ 11.24 (s,1H) OH; 7.03 (d,1H) HC (trans); 6.50 (d,1H) HC (cis).

5.2.3.2. Formaldehyde, O-Methylxime

The O-methyl derivative was prepared by the method of Jensen, et.al. In a typical synthesis, 1.67 g (0.02 mol) of methoxyamine hydrochloride was placed in a small RB flask and cooled in a dry ice-acetone bath. Then 2 mL (.18 mol) of 37% aqueous formaldehyde was slowly added and the pH adjusted with conc. NaOH until still slightly acidic (pH=6). The mixture was allowed to warm and the distillate was collected until a column temperature of 25 °C. The colorless distillate was redistilled, collecting the product from 10-15 °C. The pure product was confirmed by comparison of boiling point and $^1$H NMR with literature values.

Literature: Colorless liquid; Yield 87%; bp 12-12.5 °C; $^1$H NMR (CCl$_4$) δ 6.92 (d,1H) HC (cis); 6.31 (d,1H) HC (trans); 3.84 (s,3H) CH$_3$.

Experimental: Colorless liquid; Yield 47%; bp 10-15 °C; $^1$H NMR (CDCl$_3$) δ 7.04 (d,1H) HC (cis); 6.39 (d,1H) HC (trans); 3.96 (s,3H) CH$_3$.

5.2.3.3. Formaldehyde, O-Benzylxime

The O-benzyl derivative was prepared by five synthetic steps.
Synthesis of N-Hydroxyphthalimide

In a typical synthesis, 22 g (0.1485 mol) of phthalic anhydride, 13 g (0.2016 mol) of hydroxylamine hydrochloride, and 9.9 g (0.0934 mol) of Na₂CO₃ were added to 50 mL of H₂O. The solution was heated at 60 °C for 2 h, cooled and the colorless crystals filtered off. Recrystallization from ethanol yielded a pure product.

Literature: Yield 70%; m.p. 222-224 °C
Experimental: Yield 40-60%; m.p. 221-224 °C

Synthesis of N-Benzyloxyphthalimide

In a typical synthesis, 8.55 g (0.0524 mol) of phthaloxime, 9.95 g (9.01 mol) of benzyl chloride, and 5.05 g (0.040 mol) of anhydrous K₂CO₃ were placed into 60 mL of DMSO with stirring. After 48 h, the reaction mixture was poured into 170 mL of ice water which precipitates the white crystalline product. Recrystallization from ethanol yielded an NMR pure product.

Literature: Yield 93%; m.p. 142-144 °C; ¹H NMR (DMSO) δ 7.79 C₆H₄; 7.39 C₆H₅; 5.15 (s) CH₂.
Experimental: Yield 93%; m.p. 143-145 °C; ¹H NMR (DMSO) δ 7.75 (m,4H) C₆H₄; 7.30-7.60 (m,5H) C₆H₅; 5.12 (s) CH₂.

Synthesis of O-Benzylhydroxylamine HCl

Preparation was a modification of the method of Fujii, et.al. In a typical synthesis, 1 g (3.9 mmol) of N-benzyloxyphthalimide and 0.25 mL (4.34 mmol) of 55% aqueous hydrazine solution in 50 mL of ethanol was refluxed for 2 h. The reaction was cooled
and 0.5 mL of conc. HCl added. Insoluble hydrazide byproduct was filtered off, and washed 3X with 5 mL of ethanol. The filtrate was removed via roto-vap to yield a white crystalline product which can be further purified by recrystallization from hot ethanol.

Literature: \textsuperscript{22,23} m.p.232 °C; \textsuperscript{1}H NMR (DMSO) $\delta$ 11.00 (broad singlet) NH$_3^+$; 7.37 C$_6$H$_5$; 5.09 (s) CH$_2$.

Experimental: m.p. 232-235 °C; \textsuperscript{1}H NMR (DMSO) $\delta$ 7.30-7.55 (m,5H) C$_6$H$_5$; 5.13 (s,2H) CH$_2$; NH$_3^+$ not detected.

**Synthesis of Formaldehyde, O-Benzylxime Trimer**

The product was synthesized by a modification of the method of Hellmann and Teichmann.\textsuperscript{24} In a typical synthesis, 5 g (.0313 mol) of O-benzyl hydroxylamine HCl and 5.1 mL (.0626 mol) of 37% aqueous formaldehyde were placed in a mortar and ground until a liquid slurry results. The mortar was placed at -50 °C for 12 h where a solid paste was formed. Small amounts of H$_2$O were added while stirring the paste. The trimer product was insoluble while excess formaldehyde and HCl dissolve in the water. The slurry formed was placed in test tubes and spun in a centrifuge to precipitate the product. The H$_2$O layer was discarded, and the solid product washed 3X with cold 0.1M NaHCO$_3$ solution, followed 2X with cold H$_2$O, discarding the liquid portion after each washing. The solid product washed 1X with very cold (-50°C) ethanol to remove H$_2$O and dried. The dried product was recrystallized from hot, boiling hexane to yield a pure product.

Literature: \textsuperscript{24,31} white solid; m.p.108.5-109.5 °C; \textsuperscript{1}H NMR (CDCl$_3$) $\delta$ 7.30 (s,5H) C$_6$H$_5$; 4.73 (s,2H) CH$_2$ (benzyl); 3.83 (broad s),2H)N-CH$_2$-N; \textsuperscript{13}C NMR (CDCl$_3$, not decoupled)
\[ \delta 137.68 \text{ (s) Cl, 128.64 (d) C2, C6, 128.05 (d) C3,5, 127.61 (t)C4, phenyl; 75.20 (t) CH}_2 \text{ (benzyl); 73.71 (t) N-CH}_2\text{-N} \]

Experimental: white solid; m. p. 110-111°C; \(^1\text{H NMR (C}_6\text{D}_6\) \[ \delta 7.40 \text{ (s,5H) C}_6\text{H}_5; 4.62 \text{ (s,2H) CH}_2 \text{ (benzyl); 3.88 (broad s,2H)N-CH}_2\text{-N; \(^1\text{C NMR (C}_6\text{D}_6, decoupled) \delta 137.2 \text{ Cl, 128.3 C2, C6, 127.9 C3,5, 127.3 C4, phenyl; 74.9 CH}_2 \text{ (benzyl); 73.3 N-CH}_2\text{-N} \]}

Synthesis of Formaldehyde, O-Benzylloxime Monomer

In a typical synthesis, 0.5 g (1.23 mmol) of the trimer of formaldehyde, O-benzylloxime was placed in a RB flask with 6.40 mg (0.062 mmol) of malonic acid. The flask was heated gently until the solid melted. The flask was quickly joined to a Kugelrohr apparatus and the pure liquid monomer distilled over into the collecting bulb cooled with a water ice bath. The monomer was found to be stable for several days even at lower temperatures. The literature has not previously reported isolation of the pure monomer however it had been previously reported being observed in an equilibrium mixture of the trimer-monomer in CDCl\(_3\) by \(^1\text{H and \(^1\text{C NMR analysis.}^{31}\]

Literature: \(^1\text{H NMR (CDCl}_3\) \[ \delta 7.30 \text{ (s,5H) C}_6\text{H}_5; 7.01 \text{ (d,J=7.5Hz,1H) and 6.39 (d,J=7.5Hz,1H) CH}_2\text{=N; 5.10 (s,2H) CH}_2 \text{ (benzyl); \(^1\text{C NMR (CDCl}_3, not decoupled) \delta 137.58 \text{ (s) C1, 128.31 (d) C2, C6, 128.12 (d) C3,5, 127.80 (t)C4, phenyl; 137.2 (t) CH}_2\text{=N; 75.20 (t) CH}_2 \text{ (benzyl) \[ \[ \]

Experimental: \(^1\text{H NMR (C}_6\text{D}_6\) \[ \delta 7.10-7.30 \text{ (m,5H) C}_6\text{H}_5; 6.73 \text{ (d,J=8.0Hz,1H) and 6.04 (d,J=8.0Hz,1H) CH}_2\text{=N; 5.03 (s,2H) CH}_2 \text{ (benzyl); \(^1\text{C NMR (C}_6\text{D}_6, decoupled) \]}

\]}
δ138.1 (s) C1, 128.52 C2, C6, 128.0 C3,5, 127.7C4, phenyl; 137.3 CH$_2$=N; 76.2 CH$_2$
(benzyl)

5.2.3.4. Formaldehyde, O-4-Methoxybenzylxime

The O-4-methoxybenzyl derivative was synthesized by the method described above
for the O-benzyl derivative substituting 4-methoxybenzyl chloride for benzyl chloride in
step b. However, in step d the product from the reaction of the amine salt and
formaldehyde was the monomer product and not the trimer as in the benzyl derivative.

Although the final product, formaldehyde, O-4-methoxybenzylxime, has not been
reported in the literature, the products of steps b and c, N-4-
methoxybenzylxophthalimide and O-4-methoxybenzylhydroxlamine HCl have been
previously prepared by Kolasa and Chimiak.$^{47}$

**Synthetic Data for N-4-Methoxybenzylxophthalimide**

*Literature:*$^{47}$ m.p. 129-130 °C

*Experimental:* white solid; Yield 32 %; m.p. 132-135 °C; $^1$H NMR (CDCl$_3$)
δ7.70-7.90 (m,4H) C2-C5, phthalic phenyl; 7.45 (d,2H), 6.87 (d,2H) oxime phenyl;
5.16 (s,2H) CH$_2$; 3.80 (s,3H) CH$_3$; $^{13}$C NMR (CDCl$_3$, decoupled) δ 163.5 C=O, 160.3 C1,
113.8 C3,C5 oxime phenyl; 134.3, 131.6, 128.8, 125.7, 123.4 unassigned aromatic;
79.4 CH$_2$; 55.1 CH$_3$

**Synthetic Data of O-4-Methoxybenzylhydroxlamine HCl**

*Literature:*$^{47}$ m.p. 195-196 °C

*Experimental:* white solid; Yield 41%; m. p. 196-198 °C
Synthesis of Formaldehyde, 0-4-Methoxybenzyloxime

In a typical synthesis, 0.5 g (2.64 mmol) of 0-4-methoxybenzylhydroxylamine HCl was placed in a R B flask with 0.64 mL (7.90 mmol) of 37% aqueous formaldehyde. A small amount of methanol was added to dissolve any solid material. The solution was stirred for 2 h, neutralized with Na₂HCO₃, and the methanol removed via roto-vap. The remaining liquid was distilled via a Kugelrohr distillation twice to yield a pure liquid product in the monomeric form.

Colorless liquid; Yield 23%; IR (Kbr) 3005, 2997, 2932, 2834, 1609 cm⁻¹; ¹H NMR (CDCl₃) δ7.28 (d,2H) C₂,C₆, 6.90 (d,2H) C₃,C₅, phenyl; 7.06 (s,1H) CH=N (cis); 6.58 (s,1H) CH=N (trans); 4.99 (s,2H) CH₂; 3.74 (s,3H) CH₃; ¹³C NMR (CDCl₃, decoupled) δ159.0 C₁, 129.9 C₂,C₆, 129.5 C₄, 113.6 C₃,C₅, phenyl; 138.5 CH₂=N; 74.7 CH₂; 55.0 CH₃; MS m/z (intensity) 165.1 (5)molecular ion peak, 135.00 (6), 121.10 (100)base peak, 91.1 (8), 77.00 (22), 63 (10), 51 (10), 39 (12), 28 (12); Elemental Analysis, Calculated for C₉H₁₁N₂O₂, %C 65.43, %H 6.66, %N 8.48; Found %C 65.05, %H 6.74, %N 8.60

5.2.3.5. Formaldehyde, O-Benzoyloxime

In a typical synthesis, 1 g (0.022 mol) of formaldehyde oxime prepared as described above was added to 10 mL of H₂O. The pH was adjusted to slightly basic (pH=8) with 1M NaOH and 2.55 mL (0.022 mol) of benzoyl chloride added. The reaction mixture was stirred for 1 h. Small amounts of 1M NaOH were added frequently to maintain a slightly basic pH throughout the reaction. After a few minutes, solid product begin to
precipitate. After 1 h. the solid material was filtered off, washed 2X with 10 mL of ethanol, and dried. Recrystallization from chloroform gives the purified product which was found to be the trimer form.

White solid; Yield 56%; M.P. 163-165 °C (slight discoloration); IR (Kbr) 3430, 3057, 2947, 1740 C=O stretch, 1597, 1450, 1313, 1270, 1239, 1084, 1065, 924, 715, 704 cm⁻¹; ¹H NMR (CDCl₃) δ 7.84 (d,2H) C₂,C₆, 7.48 (t,1H) C₄, 7.11 (t,2H) C₃,C₅, phenyl; 5.05 (s,1H), 4.98 (s,1H) CH₂; ¹³C NMR (CHCl₃, decoupled) δ 164.8 C=O; 133.3, C₄, 129.6 C₂,C₆, 128.2 C₃,C₅, phenyl; 70.9 CH₂; MS m/z (intensity) 326 (4), 226 (5), 204 (8), 177 (8), 150 (5), 123 (100) base peak, 82 (30), 79(12); Elemental Analysis, Calculated for trimer, C₂₄H₂₁N₃O₂; %C 64.42, %H 4.73, %N 9.39; Found %C 64.42 , %H 4.69, %N 9.65

5.3. Polymerization of Monomers

All compounds not synthesized as discussed above were obtained from Aldrich Chemical Company unless otherwise specified. All monomers and comonomers used for polymerizations were checked by ¹H NMR for purity. All solid monomers were recrystallized and dried with vacuum for 12 h before polymerization. All liquid monomers were distilled under N₂ just before polymerization. Comonomers used such as styrene, p-methoxystyrene, acrylonitrile, methyl acrylate, and isobutyl vinyl ether were dried over CaH₂ for 48 h and freshly distilled under N₂ before polymerization. Solid initiators were recrystallized and dried under vacuum prior to polymerization. THF was dried over sodium for several days and freshly distilled under N₂ prior to polymerization.
CH$_3$CN and CH$_2$Cl$_2$ were dried over CaH$_2$ for several days and freshly distilled under N$_2$ prior to polymerization.

5.3.1. Homopolymerization of Azaethylenecarbonitrile Monomers

General Procedure

The monomer, initiator, and solvent (some polymerizations were done under neat conditions) were placed in a polymerization tube. Blank samples minus the initiator were also run as a check for uninitiated, spontaneous polymerization. The systems were purged of O$_2$ by a freeze-thaw method under vacuum and placed under argon. The polymerization temperature and time varied with initiator used. After polymerization, the polymers formed were precipitated, centrifuged, and washed with a 1:1 hexane:benzene solution until all monomer was removed as determined by SEC analysis. SEC analysis was also used for MW determination. The samples were dried under vacuum and % conversion determined. IR and $^1$H NMR analysis was done to determine polymer structure.

5.3.1.1. Radical Homopolymerization-Benzoyl Peroxide Initiator

All polymerizations using benzoyl peroxide as initiator were run at 80 °C for 48 h following the general procedure described above.

3-thiophenylazaethylenecarbonitrile

The polymerization was run under neat conditions using 0.5 g (3.68 mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 0.0446 g (0.184 mmol) of benzoyl peroxide initiator.
2-thiophenylazaethylenecarbonitrile

The polymerization was run under neat conditions using 0.5 g (3.68 mmol) of 2-thiophenylazaethylenecarbonitrile monomer and 0.0446 g (0.184 mmol) of benzoyl peroxide initiator.

2-furanylazaethylenecarbonitrile

The polymerization was run under neat conditions using 0.1 g (0.833 mmol) of 2-furanylazaethylenecarbonitrile monomer and 0.0101 g (0.0417 mmol) of benzoyl peroxide initiator.

4-methoxyphenylazaethylenecarbonitrile

The polymerization was run in 1 mL of acetonitrile using 0.15 g (0.937 mmol) of 4-methoxyphenylazaethylenecarbonitrile monomer and 0.0113 g (0.0468 mmol) of benzoyl peroxide initiator.

4-cyanophenylazaethylenecarbonitrile

The polymerization was run in 1 mL of acetonitrile using 0.15 g (0.967 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer and 0.0117 g (0.0483 mmol) of benzoyl peroxide initiator.

phenylazaethylenecarbonitrile

The polymerization was run under neat conditions using 0.5 g (3.84 mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 0.0446 g (0.192 mmol) of benzoyl peroxide initiator.

ethoxyazaethylenecarbonitrile
The polymerization was run under neat conditions using 0.5 g (5.95mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 0.0692 g (0.298mmol) of benzoyl peroxide initiator.

5.3.1.2. Radical Homopolymerization-Benzyol Peroxide Initiator-in the Presence of Inhibitors

An polymerization experiment was run using radical initiation in the presence of inhibitors to confirm a radical process is occurring.

3-thiophenylazaethylenecarbonitrile

The polymerizations were run under neat conditions at 80 °C for 24 hours with benzoyl peroxide as initiator. Two inhibitors, 3-tert-butyl-4-hydroxy-5-methylphenyl sulfide and 2,2,6,6-tetramethylpiperidinooxy radical (TEMPO) were used. Six sample tubes were prepared containing the following amounts:

<table>
<thead>
<tr>
<th>sample</th>
<th>monomer g (mmol)</th>
<th>benzyol peroxide g (mmol)</th>
<th>sulfide inhibitor g (mmol)</th>
<th>TEMPO inhibitor g (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1 (0.740)</td>
<td>0.0178 (0.0740)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.1 (0.740)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>0.1 (0.740)</td>
<td>0.0178 (0.0740)</td>
<td>0.0527 (0.148)</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.1 (0.740)</td>
<td>0.0178 (0.0740)</td>
<td>-</td>
<td>0.0230 (0.148)</td>
</tr>
<tr>
<td>5</td>
<td>0.1 (0.740)</td>
<td>-</td>
<td>0.0527 (0.148)</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>0.1 (0.740)</td>
<td>-</td>
<td>0.0527 (0.148)</td>
<td>0.0230 (0.148)</td>
</tr>
</tbody>
</table>

5.3.1.3. Radical Homopolymerization-Benzoin Methyl Ether Initiator

All polymerizations using benzoin methyl ether as photo-initiator were run using the
Rayonet Photochemical Reaction chamber. All other procedures follow the general procedure described above.

3-thiophenylazaethylenecarbonitrile

The polymerization was run at 25 °C for 48 h in 1 mL acetonitrile using 0.5 g (3.68 mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 0.0416 g (0.184 mmol) of benzoin methyl ether initiator.

2-thiophenylazaethylenecarbonitrile

The polymerization was run at 25 °C for 48 h in 1 mL acetonitrile using 0.3 g (2.21 mmol) of 2-thiophenylazaethylenecarbonitrile monomer and 0.0250 g (0.110 mmol) of benzoin methyl ether initiator.

2-furanylazaethylenecarbonitrile

The polymerization was run at 25 °C for 48 h in 0.5 mL acetonitrile using 0.15 g (1.25 mmol) of 2-furanylazaethylenecarbonitrile monomer and 0.0141 g (0.0625 mmol) of benzoin methyl ether initiator.

4-methoxyphenylazaethylenecarbonitrile

The polymerization was run at 25 °C for 48 h in 1 mL acetonitrile using 0.15 g (0.937 mmol) of 4-methoxyphenylazaethylenecarbonitrile monomer and 0.0106 g (0.0468 mmol) of benzoin methyl ether initiator.

4-cyanophenylazaethylenecarbonitrile

The polymerization was run at 25 °C for 48 h in 1 mL acetonitrile using 0.1 g (0.645 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer and 0.00729 g
(0.0322 mmol) of benzoin methyl ether initiator.

**dimethylazaethylenecarbonitrile**

The polymerization was run at -5 °C for 24 h in 1 mL THF using 1.0 g (12.2 mmol) of dimethylazaethylenecarbonitrile monomer and 0.137 g (0.609 mmol) of benzoin methyl ether initiator.

5.3.1.4. Radical Homopolymerization-BEt$_3$, O$_2$ Initiator

**3-thiophenylazaethylenecarbonitrile**

The polymerization was run in 2.5 mL of THF at -50 °C for 5 days using 0.5 g (3.68 mmol) of 3-thiophenylazaethylenecarbonitrile monomer, 0.368 mL (0.368 mmol) of a 1M solution of BEt$_3$ in THF, and 8.24 mL (0.368 mmol) of dry O$_2$. The O$_2$ was introduced through a rubber septum after removal of an equivalent amount of argon. All other procedures follow the general procedure described above.

5.3.1.5. Radical Homopolymerization-t-Butylhydroperoxide Initiator

**3-thiophenylazaethylenecarbonitrile**

The polymerization was run at 110 °C for 3 h under neat conditions using 0.1 g (0.735 mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 24.5 μL (0.0735 mmol) of a 3M solution of t-butyl hydroperoxide initiator in 2,2,4-trimethylpentane. All other procedures follow the general procedure described above.

5.3.1.6. Anionic Homopolymerization-KCN Initiator

All polymerizations using KCN as initiator were run at 5 °C for 5 days. All other
procedures follow the general procedure described above.

**3-thiophenylazaethylenecarbonitrile**

The polymerization was run in 1 mL THF using 0.3 g (2.21 mmol) of 3-thiophenylazaethylenecarbonitrile monomer and 7.29 mg (0.110 mmol) of KCN initiator.

**2-thiophenylazaethylenecarbonitrile**

The polymerization was run in 1 mL THF using 0.2 g (1.47 mmol) of 2-thiophenylazaethylenecarbonitrile monomer and 4.79 mg (0.0735 mmol) of KCN initiator.

**2-furanylazaethylenecarbonitrile**

The polymerization was run in 1 mL THF using 0.2 g (1.67 mmol) of 2-furanylazaethylenecarbonitrile monomer and 5.42 mg (0.0833 mmol) of KCN initiator.

**4-methoxyphenylazaethylenecarbonitrile**

The polymerization was run in 3 mL THF using 0.3 g (1.87 mmol) of 4-methoxyphenylazaethylenecarbonitrile monomer and 6.10 mg (0.0937 mmol) of KCN initiator.

**4-cyanophenylazaethylenecarbonitrile**

The polymerization was run in 1 mL THF using 0.1 g (0.644 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer and 2.10 mg (0.0322 mmol) of KCN initiator.

**dimethylazaethylenecarbonitrile**
The polymerization was run in 1 mL THF using 1.0 g (12.2 mmol) of dimethylazaethylenecarbonitrile monomer and 0.0397 g (0.609 mmol) of KCN initiator.

5.3.1.7. Anionic Homopolymerization-Et$_2$AlCN Initiator

All polymerizations using Et$_2$AlCN as initiator were run at -50 °C for 3 days. All other procedures follow the general procedure described above.

phenylazaethylenecarbonitrile

The polymerization was run in 0.4 mL THF using 0.1302 g (1.0 mmol) of phenylazaethylenecarbonitrile monomer and 0.05 mL (0.050 mmol) of 1M Et$_2$AlCN initiator in THF.

4-cyanophenylazaethylenecarbonitrile

The polymerization was run in 1.5 mL THF using 0.1241 g (0.80 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer and 0.04 mL (0.040 mmol) of 1M Et$_2$AlCN initiator in THF.

5.3.2. Copolymerization of Azaethylenecarbonitrile Monomers

General Procedure

The monomer, comonomer, initiator, and solvent (some polymerizations were run under neat conditions) was placed in a polymerization tube. A sample with no monomer (comonomer, initiator, and solvent) was also run as a comparison standard for the effect of copolymerization with homopolymerization of the comonomer alone. The systems were purged of O$_2$ by a freeze-thaw method under vacuum and placed under argon. The polymerization temperature and time varied with initiator used. After polymerization, the
polymers formed were precipitated, centrifuged, and washed with methanol until all monomer was removed as determined by SEC analysis. SEC analysis was also used for MW determination. The samples were dried under vacuum and % conversion determined. IR and \(^1\)H NMR analysis was done to determine polymer structure. \(^1\)H NMR analysis and elemental analysis was used to measure % incorporation of the imine monomers in the copolymers formed.

5.3.2.1. Radical Copolymerization-Benzoyl Peroxide Initiator-p-Methoxystyrene Comonomer

All polymerizations were run under neat conditions at 80 °C for 48 hours with a monomer:comonomer ratio of 1:9. The copolymerizations were run using 0.8354 mmol of the azaethylenecarbonitrile monomer, 1 mL (7.519 mmol) of p-methoxystyrene, and 0.1012 g (0.4177 mmol) of benzoyl peroxide initiator. A blank sample was also prepared using 1 mL (7.519 mmol) of p-methoxystyrene and 0.0910 g (0.3760 mmol) of benzoyl peroxide initiator. The copolymerizations were run using the following monomers:

a) 3-thiophenylazaethylenecarbonitrile (0.1136g)
b) 2-thiophenylazaethylenecarbonitrile (0.1136 g)
c) 2-furanylazaethylenecarbonitrile (0.1003 g)
d) 4-methoxyphenylazaethylenecarbonitrile (0.1338 g)
e) 4-cyanophenylazaethylenecarbonitrile (0.1296 g)

5.3.2.2. Radical Copolymerization-Benzoin Methyl Ether Initiator-p-Methoxystyrene Comonomer

The polymerizations were run in 1 mL of CH\(_3\)CN at 25 °C for 48 h with a monomer:comonomer ratio of 1:9. The copolymerizations were run using 0.8354 mmol of the azaethylenecarbonitrile monomer, 1 mL (7.519 mmol) of p-methoxystyrene, and
0.0945 g (0.4177 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 1 mL (7.519 mmol) of p-methoxystyrene and 0.0851 g (0.3760 mmol) of benzoin methyl ether initiator. The copolymerizations were run using the following monomers:

a) 3-thiophenylazaethylenecarbonitrile (0.1136 g)
b) 2-thiophenylazaethylenecarbonitrile (0.1136 g)
c) 2-furanylazaethylenecarbonitrile (0.1003 g)
d) 4-methoxyphenylazaethylenecarbonitrile (0.1338 g)
e) 4-cyanophenylazaethylenecarbonitrile (0.1296 g)

5.3.2.3 Radical Copolymerization-Benzoyl Peroxide Initiator-Methyl Acrylate Comonomer

The polymerizations were run at 80 °C for 48 h with a monomer:comonomer ratio of 1:9 and 1:2. The copolymerizations at the 1:9 ratio were run using 1.233 mmol of the azaethylenecarbonitrile monomer, 1 mL (11.10 mmol) of methyl acrylate, and 0.1493 g (0.6170 mmol) of benzoyl peroxide initiator. The copolymerizations at the 1:2 ratio were run using 1.388 mmol of the azaethylenecarbonitrile monomer, 0.25 mL (2.776 mmol) of methyl acrylate, and 0.0504 g (0.2082 mmol) of benzoyl peroxide initiator. A blank sample was also prepared using 1 mL (11.10 mmol) of methyl acrylate and 0.1344 g (0.5550 mmol) of benzoyl peroxide initiator. The copolymerizations were run using the following monomers:

1:9 ratio
a) 3-thiophenylazaethylenecarbonitrile (0.1679 g)
b) 2-thiophenylazaethylenecarbonitrile (0.1679 g)
c) 2-furanylazaethylenecarbonitrile (0.1481 g)
d) 4-methoxyphenylazaethylenecarbonitrile (0.1975 g)
e) 4-cyanophenylazaethylenecarbonitrile (0.1913 g)
1:2 ratio

a) 3-thiophenylazaethylenecarbonitrile (0.1890 g)
b) 2-thiophenylazaethylenecarbonitrile (0.1890 g)
c) 2-furanylazaethylenecarbonitrile (0.1667 g)
d) 4-methoxyphenylazaethylenecarbonitrile (0.2223 g)
e) 4-cyanophenylazaethylenecarbonitrile (0.2154 g)

Monomers a-c were run under neat conditions while d and e were run in 1 mL of CH₃CN due to the poorer solubility of the monomer into the comonomer.

5.3.2.4. Radical Copolymerization-Benzoin Methyl Ether Initiator-Methyl Acrylate Comonomer

The polymerizations were run at 25 °C for 48 h with a monomer:comonomer ratio of 1:9 and 1:2. Due to the range of solubility of the monomer, different amounts of CH₃CN solvent was used for each monomer.

2-thiophenylazaethylenecarbonitrile

The copolymerization at the 1:9 ratio was run in 0.5 mL of CH₃CN using 0.167 g (1.233 mmol) of 2-thiophenylazaethylenecarbonitrile monomer, 1 mL (11.10 mmol) of methyl acrylate, and 0.1395 g (0.6170 mmol) of benzoin methyl ether initiator. The copolymerizations at the 1:2 ratio was run in 0.5 mL of CH₃CN using 0.3775 g (2.776 mmol) of 2-thiophenylazaethylenecarbonitrile monomer, 0.50 mL (5.552 mmol) of methyl acrylate, and 0.0942 g (0.4164 mmol) of benzoin methyl ether initiator. A blank sample was also prepared in 0.5 mL CH₃CN using 1 mL (11.10 mmol) of methyl acrylate and 0.1256 g (0.5550 mmol) of benzoin methyl ether initiator.

2-furanylazaethylenecarbonitrile

The copolymerization at the 1:9 ratio was run in 0.25 mL of CH₃CN using 0.1480 g
(1.233 mmol) of 2-furanylazaethylenecarbonitrile monomer, 1 mL (11.10 mmol) of methyl acrylate, and 0.1395 g (0.6170 mmol) of benzoin methyl ether initiator. The copolymerizations at the 1:2 ratio was run in 0.50 mL of CH₃CN using 0.1100 g (0.9167 mmol) of 2-furanylazaethylenecarbonitrile monomer, 0.165 mL (1.8333 mmol) of methyl acrylate, and 0.0311 g (0.1375 mmol) of benzoin methyl ether initiator. A blank sample was also prepared in 0.25 mL CH₃CN using 1 mL (11.10 mmol) of methyl acrylate and 0.1256 g (0.5550 mmol) of benzoin methyl ether initiator.

4-methoxyphenylazaethylenecarbonitrile

The copolymerization at the 1:9 ratio was run in 1.0 mL of CH₃CN using 0.1975 g (1.233 mmol) of 4-methoxyphenylazaethylenecarbonitrile monomer, 1 mL (11.10 mmol) of methyl acrylate, and 0.1395 g (0.6170 mmol) of benzoin methyl ether initiator. The copolymerizations at the 1:2 ratio was run in 1.5 mL of CH₃CN using 0.2223 g (1.388 mmol) of 4-methoxyphenylazaethylenecarbonitrile monomer, 0.25 mL (2.776 mmol) of methyl acrylate, and 0.0471 g (0.2082 mmol) of benzoin methyl ether initiator. A blank sample was also prepared in 1.0 mL CH₃CN using 1.0 mL (11.10 mmol) of methyl acrylate and 0.1256 g (0.5550 mmol) of benzoin methyl ether initiator.

4-cyanophenylazaethylenecarbonitrile

The copolymerization at the 1:9 ratio was run in 2.0 mL of CH₃CN using 0.1913 g (1.233 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer, 1 mL (11.10 mmol) of methyl acrylate, and 0.1395 g (0.6170 mmol) of benzoin methyl ether initiator. The
copolymers at the 1:2 ratio was run in 2.0 mL of CH$_3$CN using 0.2154 g (1.388 mmol) of 4-cyanophenylazaethylenecarbonitrile monomer, 0.25 mL (2.776 mmol) of methyl acrylate, and 0.0471 g (0.2082 mmol) of benzoin methyl ether initiator. A blank sample was also prepared in 2.0 mL CH$_3$CN using 1.0 mL (11.10 mmol) of methyl acrylate and 0.1256 g (0.5550 mmol) of benzoin methyl ether initiator.

5.3.2.5. Radical Copolymerization-Benzoic Peroxide Initiator-Acrylonitrile Comonomer

3-thiophenylazaethylenecarbonitrile

All polymerizations were run under neat conditions at 80 °C for 24 hours with a monomer:comonomer ratio of 1:9 and 1:2. The copolymerizations at the 1:9 ratio were run using 0.2296 g (1.688 mmol) of the 3-thiophenylazaethylenecarbonitrile monomer, 1 mL (15.19 mmol) of acrylonitrile comonomer, and 0.2053 g (0.8440 mmol) of benzoic peroxide initiator. The copolymerizations at the 1:2 ratio were run using 1.034 g (7.595 mmol) of the 3-thiophenylazaethylenecarbonitrile monomer, 1.0 mL (15.19 mmol) of acrylonitrile comonomer, and 0.2761 g (1.140 mmol) of benzoic peroxide initiator. A blank sample was also prepared using 1 mL (15.19 mmol) of acrylonitrile and 0.1840 g (0.7595 mmol) of benzoic peroxide initiator.

5.3.2.6. Radical Copolymerization-Benzoic Peroxide Initiator-Styrene Comonomer 3-thiophenylazaethylenecarbonitrile

All polymerizations were run under neat conditions at 80 °C for 24 hours with a monomer:comonomer ratio of 1:9. The copolymerization was run using 0.1318 g
(0.9688) mmol of the 3-thiophenylazaethylenecarbonitrile monomer, 1 mL (8.728 mmol) of styrene comonomer, and 0.1173 g (0.4848 mmol) of benzoyl peroxide initiator. A blank sample was also prepared using 1 mL (8.728 mmol) of styrene and 0.1057 g (0.4364 mmol) of benzoyl peroxide initiator.

5.3.2.7. Radical Copolymerization-Benzoin Methyl Ether Initiator-Acrylonitrile Comonomer

3-thiophenylazaethylenecarbonitrile

All polymerizations were run under neat conditions at 25 °C for 48 hours with a monomer:comonomer ratio of 1:1. The copolymerization was run using 0.50 g (3.67 mmol) of the 3-thiophenylazaethylenecarbonitrile monomer, 0.242 mL (3.67 mmol) of acrylonitrile comonomer, and 0.8327 g (0.368 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 0.242 mL (3.67 mmol) of acrylonitrile and 0.0444 g (0.1835 mmol) of benzoin methyl ether initiator.

5.3.3. Attempted Homopolymerization of Formaldehyde Oxime

Although formaldehyde oxime will self polymerize below 60 °C, attempts were made to initiate polymerization above 60 °C.

5.3.3.1. Radical Initiated Homopolymerization

A homopolymerization was attempted under argon at 60 °C for 2 days using 0.5 g (0.011 mol) of formaldehyde oxime and 0.0903 g (0.550 mmol) of 2,2'-azabisisobutyronitrile (AIBN) initiator.

5.3.3.2. Cationic Initiated Homopolymerization

The attempted homopolymerizations were run under argon at 60 °C for 2 days.
boron trifluoroetherate initiator

The polymerization was run using 0.5 g (0.011 mol) of formaldehyde oxime and 27.1 µL (0.220 mmol) of boron trifluoroetherate initiator.

trifluoroacetic acid initiator

The polymerization was run using 0.5 g (0.011 mol) of formaldehyde oxime and 16.3 µL (0.220 mmol) of trifluoroacetic acid initiator.

5.3.4. Homopolymerization and Copolymerization of Acetaldehyde Oxime

The polymerization were run in dry polymerization tubes under argon in CH₂Cl₂ at -5 °C for 3 days. After polymerization, the tubes were quenched with 0.5 mL of a 1:2 triethylamine:isopropanol solution, and a vacuum applied to remove volatile materials. The sample was then washed 2X with methanol precooled to -50 °C, dried, and analyzed by SEC, NMR, and elemental analysis.

5.3.4.1. Homopolymerization of Acetaldehyde Oxime

The homopolymerization was run using 1 mL (16.4 mmol) of acetaldehyde oxime, 0.101 mL (0.820 mmol) of boron trifluoroetherate, and 0.5 mL CH₂Cl₂.

5.3.4.2. Copolymerization of Acetaldehyde Oxime-IBVE Comonomer

The copolymerizations were run using a monomer:comonomer ratios of 1:9 and 1:3. The 1:9 copolymerization was run using 0.1 mL (1.64 mmol) of acetaldehyde oxime, 1.92 mL (14.76 mmol) of isobutyl vinyl ether, 0.101 mL (0.820 mmol) of boron trifluoroetherate, and 0.5 mL CH₂Cl₂. The 1:3 copolymerization was run using 0.1 mL (1.64 mmol) of acetaldehyde oxime, 0.642 mL (4.92 mmol) of isobutyl vinyl ether,
0.043 mL (0.328 mmol) of boron trifluoroetherate, and 0.5 mL CH$_2$Cl$_2$.

5.3.5. Homopolymerization of Formaldehyde, O-Benzylxime

**General Procedure**

The monomer, initiator, and solvent (some polymerizations were done under neat conditions) were placed in a dry polymerization tube under argon. The polymerization temperature and time varied with initiator used. After polymerization, cationic initiated polymerizations were quenched with 0.5 mL of a 1:2 triethylamine:methanol solution. Anionic initiated polymerizations were quenched with 0.2 mL of butanol. All polymers formed were precipitated, centrifuged, and washed with hexane until all monomer was removed as determined by SEC analysis. SEC analysis was also used for MW determination. The samples were dried under vacuum and % conversion determined. $^1$H NMR analysis was used to determine polymer structure.

5.3.5.1. Radical Homopolymerization-Benzoin Methyl Ether Initiator

The polymerization was run under neat conditions at -15 °C for 3 days using 0.30 g (2.22 mmol) of monomer and 0.0251 g (.1110 mmol) of benzoin methyl ether initiator.

5.3.5.2. Radical Homopolymerization-Triethylborane, O$_2$ Initiator

Two samples were run at a initiator concentration of 5 and 10 mol% of monomer. The polymerizations were run under neat conditions at -50 °C for 6 days. The 5 mol% sample was run using 0.632 g (4.67 mmol) of monomer, 0.233 mL of a 1M solution in THF (0.233 mmol) of triethylborane and 5.22 mL ( 0.233 mol) of dry O$_2$. The 10 mol% sample was run using 0.316 g (2.33 mmol) of monomer, 0.233 mL of a 1M solution in
THF (0.233 mmol) of triethylborane, and 5.22 mL (0.233 mol) of dry O₂. The O₂ was introduced through a rubber septum after removal of an equivalent amount of argon.

5.3.5.3. Cationic Homopolymerization-Methyl Triflate Initiator

The polymerization was run under neat conditions at -50 °C for 24 hours using 0.3137 g (2.32 mmol) of monomer and 14.96 μL (0.116 mmol) of methyl triflate initiator.

5.3.5.4. Cationic Homopolymerization-Boron Trifluoride Etherate Initiator

The polymerization was run under in 0.1 mL CH₂Cl₂ at 5 °C for 3 days using 0.106 g (0.784 mmol) of monomer and 48 μL of a 0.325M solution in CH₂Cl₂ (0.0157 mmol) of boron trifluoride etherate initiator.

5.3.5.5. Cationic Homopolymerization-Stannic Chloride Initiator

The polymerization was run under in 0.15 mL CH₂Cl₂ at 5 °C for 3 days using 0.159 g (1.176 mmol) of monomer and 4.2 μL (0.0353 mmol) of stannic chloride initiator.

5.3.5.6. Anionic Homopolymerization-Butyl Lithium Initiator

The polymerization was run under in 0.10 mL THF at -75 °C for 2 days using 0.106 g (0.784 mmol) of monomer and 9.4 μL of a 2.5M solution in hexanes (0.0235 mmol) of butyl lithium initiator.

5.3.6. Copolymerization of Formaldehyde, O-Benzylxime

General Procedure

The monomer, comonomer, initiator, and solvent (some polymerizations were run
under neat conditions) was placed in a dry polymerization tube under argon. A blank sample with no monomer (comonomer, initiator, and solvent) was also run as a comparison standard for the effect of copolymerization with homopolymerization of the comonomer alone. The polymerization temperature and time varied with initiator used. After polymerization, cationic initiated polymerizations were quenched with 0.5 mL of a 1:2 triethylamine:methanol solution. Anionic initiated polymerizations were quenched with 0.2 mL of butanol. All the polymers formed were precipitated, centrifuged, and washed with specific organic solvents until all monomer was removed as determined by SEC analysis. SEC analysis was also used for MW determination. The samples were dried under vacuum and % conversion determined. In NMR analysis was done to determine polymer structure. In NMR analysis and elemental analysis was used to measure % incorporation of the imine monomers in the copolymers formed.

5.3.6.1. Radical Copolymerization-Benzoin Methyl Ether Initiator

The polymerizations were run under neat conditions at 25 °C for 48 h with a monomer:comonomer ratio of 1:9. After polymerization, all tubes were precipitated, centrifuged, and washed 2X with methanol precooled to -50 °C.

**methyl acrylate comonomer**

The copolymerization was run using 0.0834 g (0.617 mmol) of the monomer, 0.5 mL (5.55 mmol) of methyl acrylate, and 0.0698 g (0.308 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 1 mL (11.1 mmol) of methyl acrylate and 0.1256 g (0.555 mmol) of benzoin methyl ether initiator.
acrylonitrile comonomer

The copolymerization was run using 0.114 g (0.844 mmol) of the monomer, 0.5 mL (7.60 mmol) of acrylonitrile, and 0.0955 g (0.422 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 1 mL (15.2 mmol) of acrylonitrile and 0.1719 g (0.760 mmol) of benzoin methyl ether initiator.

styrene comonomer

The copolymerization was run using 0.0655 g (0.485 mmol) of the monomer, 0.5 mL (4.36 mmol) of styrene, and 0.0549 g (0.242 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 1 mL (8.73 mmol) of styrene and 0.0987 g (0.436 mmol) of benzoin methyl ether initiator.

4-methoxystyrene comonomer

The copolymerization was run using 0.0565 g (0.418 mmol) of the monomer, 0.5 mL (3.76 mmol) of 4-methoxystyrene, and 0.0473 g (0.209 mmol) of benzoin methyl ether initiator. A blank sample was also prepared using 0.5 mL (3.76 mmol) of 4-methoxystyrene and 0.0425 g (0.188 mmol) of benzoin methyl ether initiator.

5.3.6.2. Radical Copolymerization-Triethylborane, O₂ Initiator

methyl acrylate comonomer

The polymerizations were run under neat conditions at -50°C for 6 days with a monomer:comonomer ratio of 1:9 using both a 5 and 10 mol% (of monomer) initiator concentration. The 5 mol% copolymerization was run using 0.0632 g (0.468 mmol) of the monomer, 0.362 mL (4.21 mmol) of methyl acrylate, 0.234 mL of a 1.0 M in THF
solution (0.234 mmol) of triethylborane, and 5.22 mL (0.233 mol) of dry O₂. The 10 mol% copolymerization was run using 0.0316 g (0.234 mmol) of the monomer, 0.180 mL (2.10 mmol) of methyl acrylate, 0.234 mL of a 1.0 M in THF solution (0.234 mmol) of triethylborane, and 5.22 mL (0.233 mol) of dry O₂. A 5 mol% blank sample was prepared using 0.403 mL (4.68 mmol) of methyl acrylate, 0.234 mL of a 1.0 M in THF solution (0.234 mmol) of triethylborane, and 5.22 mL (0.233 mol) of dry O₂. A 10 mol% blank sample was prepared using 0.201 mL (2.34 mmol) of methyl acrylate, 0.234 mL of a 1.0 M in THF solution (0.234 mmol) of triethylborane, and 5.22 mL (0.233 mol) of dry O₂. After polymerization, all tubes were precipitated, centrifuged, and washed 2X with methanol precooled to -50 °C.

5.3.6.3. Cationic Copolymerization-Boron Trifluoride Initiator

isobutyl vinyl ether (IBVE) comonomer

Two different experiment were set up for the IBVE comonomer-the first varying the monomer:comonomer ratio and the second varying the temperature.

The polymerizations for the first experiment were run in CH₂Cl₂ at 5°C for 3 days using various monomer:comonomer ratios. The following were placed in dry polymerization tubes under argon:
Table 5.2

Amounts Used in the Cationic Copolymerization of Formaldehyde, O-Benzylxime IBVE, Comonomer; BF₃ Initiator

<table>
<thead>
<tr>
<th>tube</th>
<th>mon/comon ratio</th>
<th>g (mol)</th>
<th>mL comon</th>
<th>μL initiator*</th>
<th>mL CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:1</td>
<td>-</td>
<td>1.0</td>
<td>472</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(7.67)</td>
<td>(0.153)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>0.106</td>
<td>0.920</td>
<td>482</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(7.06)</td>
<td>(0.157)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>0.106</td>
<td>0.306</td>
<td>193</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(2.35)</td>
<td>(0.063)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1:2</td>
<td>0.106</td>
<td>0.208</td>
<td>145</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(1.57)</td>
<td>(0.047)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>0.106</td>
<td>0.104</td>
<td>97</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(0.784)</td>
<td>(0.031)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2:1</td>
<td>0.106</td>
<td>0.052</td>
<td>72</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(0.392)</td>
<td>(0.024)</td>
<td></td>
</tr>
</tbody>
</table>

* μL amounts of a 0.325M solution of boron trifluoride etherate in CH₂Cl₂

After polymerization, all tubes were precipitated, centrifuged, and washed 2X with methanol precooled to -50 °C.

The copolymerizations for the second experiment were run for 2 days using monomer:comonomer ratios of 1:3 at temperatures of -20, 0, 25, 50 and 80°C. The copolymerization were run using 0.106 g (0.784 mmol) of monomer, 0.306 mL (2.35 mmol) of IBVE, 0.193 mL of a 0.325M solution (0.0627 mmol) of boron trifluoride etherate in CH₂Cl₂, and 0.213 mL toluene. After polymerization, all tubes were precipitated, centrifuged, and washed 2X with methanol precooled to -50 °C.

4-methoxystyrene comonomer

The polymerizations were run in CH₂Cl₂ at 5°C for 2 days using various
monomer:comonomer ratios. The following were placed in dry polymerization tubes under argon:

<table>
<thead>
<tr>
<th>Tube</th>
<th>mon/comon ratio</th>
<th>g mon (mmol)</th>
<th>mL comon (mmol)</th>
<th>μL initiator* (mmol)</th>
<th>mL CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:1</td>
<td>-</td>
<td>1.0 (7.52)</td>
<td>462 (0.150)</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>0.106 (0.784)</td>
<td>0.939 (7.06)</td>
<td>482 (0.157)</td>
<td>1.0</td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>0.106 (0.784)</td>
<td>0.313 (2.35)</td>
<td>193 (0.063)</td>
<td>0.40</td>
</tr>
<tr>
<td>4</td>
<td>1:2</td>
<td>0.106 (0.784)</td>
<td>0.209 (1.57)</td>
<td>145 (0.047)</td>
<td>0.30</td>
</tr>
<tr>
<td>5</td>
<td>1:1</td>
<td>0.106 (0.784)</td>
<td>0.104 (0.784)</td>
<td>97 (0.031)</td>
<td>0.20</td>
</tr>
<tr>
<td>6</td>
<td>2:1</td>
<td>0.106 (0.784)</td>
<td>0.052 (0.392)</td>
<td>72 (0.024)</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* μL amounts of a 0.325M solution of boron trifluoride etherate in CH₂Cl₂

After polymerization, all tubes were precipitated, centrifuged, and washed 2X with hexane.

5.3.6.4. Cationic Copolymerization-Stannic Chloride Initiator

**isobutyl vinyl ether comonomer**

The polymerizations were run in CH₂Cl₂ at 5°C for 3 days using various monomer:comonomer ratios. The following were placed in dry polymerization tubes under argon:
Table 5.4
Amounts Used in the Cationic Copolymerization of Formaldehyde, O-Benzylxime
IBVE, Comonomer; Stannic Chloride, Initiator

<table>
<thead>
<tr>
<th>tube</th>
<th>mon/comon ratio</th>
<th>g mon (mmol)</th>
<th>mL comon (mmol)</th>
<th>μL initiator (mmol)</th>
<th>mL CH₂Cl₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:1</td>
<td>-</td>
<td>1.0</td>
<td>27 (7.67)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.230)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>0.106</td>
<td>0.920</td>
<td>28 (7.06)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(7.06)</td>
<td>(0.235)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>0.106</td>
<td>0.306</td>
<td>11 (2.35)</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(2.35)</td>
<td>(0.094)</td>
<td></td>
</tr>
</tbody>
</table>

After polymerization, all tubes were precipitated, centrifuged, and washed 2X with methanol precooled to -50 °C.

5.3.6.5. Anionic Copolymerization-Butyl Lithium Initiator

styrene comonomer

The polymerizations were run in THF at -75°C for 2 days using various monomer:comonomer ratios. The following were placed in dry polymerization tubes under argon:

Table 5.5
Amounts Used in the Anionic Copolymerization of Formaldehyde, O-Benzylxime

<table>
<thead>
<tr>
<th>tube</th>
<th>mon/comon ratio</th>
<th>g mon (mmol)</th>
<th>mL comon (mmol)</th>
<th>μL initiator* (mmol)</th>
<th>mL THF</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0:1</td>
<td>-</td>
<td>1.0</td>
<td>105 (8.73)</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.261)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>0.106</td>
<td>0.809</td>
<td>94 (7.06)</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(7.06)</td>
<td>(0.235)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:3</td>
<td>0.106</td>
<td>0.270</td>
<td>38 (2.35)</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(0.784)</td>
<td>(2.35)</td>
<td>(0.094)</td>
<td></td>
</tr>
</tbody>
</table>

* μL amounts of a 2.5M solution of butyl lithium in hexanes
After polymerization, all tubes were precipitated, centrifuged, and washed with hexane.

5.3.6.6. Cationic Copolymerization—”Living System” Triflic Acid Initiator

A study was performed to examine what effect preformed polymer strands with "living" cationic ends would have on the polymerization of the monomer. It was hoped the preformed polymer strands and the presence of a counter ion would decrease any side reactions and give a larger MW polymer. The study involved creating a living system and utilizing it in 3 different experiments: 1) creating "living" polymer strands of IBVE and adding monomer only 2) creating "living" polymer strands of IBVE and adding both monomer and IBVE and 3) having no preformed strands and adding the monomer and IBVE.

"living" system

The "living" polymerization system was the triflic acid-tetrahydrothiophene system previously used by Webster et al.\(^2^5\) The "living" polymerizations creating the IBVE strands were run at -50 °C under argon in 8 mL CH\(_2\)Cl\(_2\) using 1 mL (7.67 mmol) of IBVE, 7.70 μL (0.0870 mmol) of triflic acid, and 0.230 mL (2.60 mmol) of tetrahydrothiophene (10 mL total volume). After 6 hours, a portion was taken and the MW determined by SEC analysis was found to be 7900 with a polydispersity of 1.09. The predicted MW value calculated by (7.67 mmol/0.0870 mmol) 100.16 is 8830.

The "livingness" of the system was tested by addition of an 3X molar amount fresh IBVE monomer to a 1.0 mL portion of the system. After 6 additional hours, SEC analysis found a MW of 27640 with a polydispersity of 1.0. There was however a small
peak at a MW of 9780 approximately 5-8 % of the larger MW peak indicating some loss in the "livingness" of the system.

"Living" System-Preformed Strands-Imine Monomer Only

Into 4 dry polymerization tubes under argon at -75 °C were placed 1.0 mL portions of the "living" polymerization system with preformed IBVE strands (originally 0.767 mmol of IBVE) and 97.8 µL (0.767 mmol) of monomer. The tubes were then left at -50, -20, 5, and 25 °C for 3 days. The tubes were quenched and SEC analysis run giving a single high MW peak and two lower MW peaks.

The lower MW products were separated by dissolving in CH₂Cl₂ and precipitating with methanol. An ¹H NMR analysis of the two lower MW compounds showed them to be monomer and its trimer. An ¹H NMR analysis to measure %incorporation of the monomer into the larger MW strands was done.

"Living" System-Preformed Strands-Imine Monomer and IBVE Comonomer

Into 8 dry polymerization tubes under argon at -75 °C were placed 1.0 mL portions of the "living" polymerization system with preformed IBVE strands (originally 0.767 mmol of IBVE) and 0.767 mmol of monomer plus comonomer at different ratios. The tubes were then left at -50, -20, 5, and 25 °C for 3 days. The following amounts of monomer and "fresh" IBVE comonomer were used:
Table 5.6  
Amounts Used in “Living” Copolymerization-Preformed Strands

<table>
<thead>
<tr>
<th>Tube</th>
<th>mon:comon ratio</th>
<th>temp (°C)</th>
<th>mmol IBVE</th>
<th>mmol mon plus</th>
<th>mg. mon (mmol)</th>
<th>µL comon (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:9</td>
<td>-50</td>
<td>0.767</td>
<td>0.767</td>
<td>10.4 (0.0767)</td>
<td>90 (0.690)</td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>-20</td>
<td>0.767</td>
<td>0.767</td>
<td>10.4 (0.0767)</td>
<td>90 (0.690)</td>
</tr>
<tr>
<td>3</td>
<td>1:9</td>
<td>5</td>
<td>0.767</td>
<td>0.767</td>
<td>10.4 (0.0767)</td>
<td>90 (0.690)</td>
</tr>
<tr>
<td>4</td>
<td>1:9</td>
<td>25</td>
<td>0.767</td>
<td>0.767</td>
<td>10.4 (0.0767)</td>
<td>90 (0.690)</td>
</tr>
<tr>
<td>5</td>
<td>1:3</td>
<td>-50</td>
<td>0.767</td>
<td>0.767</td>
<td>26.0 (0.192)</td>
<td>75 (0.575)</td>
</tr>
<tr>
<td>6</td>
<td>1:3</td>
<td>-20</td>
<td>0.767</td>
<td>0.767</td>
<td>26.0 (0.192)</td>
<td>75 (0.575)</td>
</tr>
<tr>
<td>7</td>
<td>1:3</td>
<td>5</td>
<td>0.767</td>
<td>0.767</td>
<td>26.0 (0.192)</td>
<td>75 (0.575)</td>
</tr>
<tr>
<td>8</td>
<td>1:3</td>
<td>25</td>
<td>0.767</td>
<td>0.767</td>
<td>26.0 (0.192)</td>
<td>75 (0.575)</td>
</tr>
</tbody>
</table>

The tubes were quenched, a vacuum used to remove volatile material, and a SEC analysis run.

The lower MW products were separated by dissolving in CH₂Cl₂ and precipitating with a small amount of methanol and confirmed by SEC analysis. ¹H NMR analysis of the MW 8000 material showed a % incorporation of the imine monomer of <1% in all tubes. A % conversion calculation and ¹H NMR analysis for % imine incorporation of the lower MW material was run.
"Living" System-No Preformed Strands-Imine Monomer and IBVE Comonomer

Into a dry tube under argon at -75 °C was prepared a solution containing 8.5 µL (0.09556 mmol) of triflic acid, 0.253 mL (2.867 mmol) of tetrahydrothiophene, and 9.74 mL of CH₂Cl₂ (total volume 10 mL). Using a dry syringe, 0.9 mL of this solution was placed into 9 polymerization tubes at different temperatures into which the following amounts of monomer and comonomer had been previously added:

<table>
<thead>
<tr>
<th>tube</th>
<th>mon:comon ratio</th>
<th>temp (°C)</th>
<th>mg mon (mmol)</th>
<th>μL comon (mmol)</th>
<th>mL catalyst solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1:9</td>
<td>-50</td>
<td>10.4</td>
<td>90</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.0767)</td>
<td>(0.690)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1:9</td>
<td>-20</td>
<td>10.4</td>
<td>90</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.0767)</td>
<td>(0.690)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1:9</td>
<td>5</td>
<td>10.4</td>
<td>90</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.0767)</td>
<td>(0.690)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1:9</td>
<td>25</td>
<td>10.4</td>
<td>90</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.0767)</td>
<td>(0.690)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1:3</td>
<td>-50</td>
<td>26.0</td>
<td>75</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.192)</td>
<td>(0.575)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>1:3</td>
<td>-20</td>
<td>26.0</td>
<td>75</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.192)</td>
<td>(0.575)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1:3</td>
<td>5</td>
<td>26.0</td>
<td>75</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.192)</td>
<td>(0.575)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>1:3</td>
<td>25</td>
<td>26.0</td>
<td>75</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.192)</td>
<td>(0.575)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0:1</td>
<td>-50</td>
<td>-</td>
<td>100</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.767)</td>
<td></td>
</tr>
</tbody>
</table>

The polymerizations were run for 2 days, the samples quenched, and the tubes pulled...
under vacuum to remove volatile material. After washing with cold methanol to remove traces of monomer and drying, the samples were analyzed for % conversion, MW, and % incorporation of imine into the polymer.

5.4. NMR Studies of Temperature Effects on Structure

5.4.1. Cyclopropylazaethylenecarbonitrile Trimer

Approximately 0.1 g of the cyclopropylazaethylenecarbonitrile trimer was placed in an NMR tube in CDCl₃. A drop of trifluoroacetic acid was added, the tube heated to 60 °C, and a ¹H NMR analysis taken at intervals. Even after 24 hours, the ¹H NMR spectrum showed only peaks of the starting trimeric materials with no trace of a CH=N peak which is predicted at δ8-10. No evidence of monomer was found in the ¹H NMR spectrum.

5.4.2. N-Methylene-4-methoxybenzenamine Trimer

Approximately 0.1 g of the N-methylene-4-methoxybenzenamine trimer was placed in an NMR tube in DMSO-d₆ and a ¹H NMR analysis taken at 25, 60, 100, and 140 °C. Twenty minutes were allowed for the sample to equilibrate at each temperature. No change from the starting trimer material was seen at 25 and 60 °C. At 100 °C a small peak was observed at δ9.63 (CH=N peak). At 140 °C the peak at δ9.63 was larger, and new peaks were observed at δ3.75 (OCH₃) and in the aromatic region δ6.50-7.70 (C₆H₄). The spectrum contains peaks of both the monomer and trimer in a ratio of approximately 1:6. The tube was left at 140 °C for an additional hour with no significant change observed in the monomer:trimer ratio. The tube was allowed to cool to room temperature where ¹H NMR analysis showed only peaks of the starting trimer material. All peaks of
the monomer observed at 140 °C had disappeared.

5.4.3. Poly-4-cyanophenylazaethylenecarbonitrile and Poly-phenylazaethylenecarbonitrile

Small amounts of poly-4-cyanophenylazaethylenecarbonitrile (0.05g) and poly phenylazaethylenecarbonitrile (0.05g) were dissolved in two NMR tubes in DMSO-d₆ and ¹H NMR analyses take at 25, 60, 100, and 150 °C. Twenty minutes were allowed for the sample to equilibrate at each temperature.

At 25 °C, the spectrum of poly-4-cyanophenylazaethylenecarbonitrile is a single broad peak from δ6.2-8.0. On heating to 150 °C, the spectrum is still a slightly narrower broad peak from δ6.8-8.0. No evidence of depolymerization is apparent even at 150 °C.

At 25 °C, the spectrum of poly-phenylazaethylenecarbonitrile appears as a single broad peak from δ6.0-8.4. At 100 °C, two broad peaks have resolved; one at δ6.2-6.8 and the other at δ6.8-8.0 at a ratio of approximately 1:4. At 140 °C, the resolution is slightly improved but the spectrum is complicated by the presence of benzaldehyde peaks formed from a reaction of the polymer with H₂O in the DMSO-d₆.

5.5. Attempted Trimerization of 4-Cyanoazaethylenecarbonitrile Monomer

In order to assess the stability of the azaethylenecarbonitrile monomers, trimerization of 4-cyanoazaethylenecarbonitrile using trifluroracetic acid as catalyst was attempted. A small amount of monomer (0.1 g) was dissolved in 1 mL of CHCl₃ at room temperature, a drop of trifluroracetic acid added, and the solution placed at -50 °C for 48 hours. After 48 hours, a small amount of precipitate was present. An ¹H NMR analysis of the precipitate gave peaks characteristic of the monomer with the CH=N imine hydrogen still
present which indicates the precipitate is probably an imine salt. An $^1$H NMR analysis of the solution gave peaks characteristic of the monomer and trifluoroacetic acid.
REFERENCES


