The Imidization Reactions of PMR-15 Polyimide

Kerri Ann Robillard

College of William & Mary - Arts & Sciences

Follow this and additional works at: https://scholarworks.wm.edu/etd

Part of the Polymer Chemistry Commons

Recommended Citation

https://dx.doi.org/doi:10.21220/s2-j9yp-2s64

This Thesis is brought to you for free and open access by the Theses, Dissertations, & Master Projects at W&M ScholarWorks. It has been accepted for inclusion in Dissertations, Theses, and Masters Projects by an authorized administrator of W&M ScholarWorks. For more information, please contact scholarworks@wm.edu.
THE IMIDIZATION REACTIONS OF PMR-15 POLYIMIDE

A Thesis

Presented to

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

by

Kerri Ann Robillard

1992
APPROVAL SHEET

This thesis is submitted in partial fulfillment of the requirements for the degree of

Master of Arts

Kerri Ann Robillard

Approved, July 1992

David Kranbuehl
Christopher Abelt
David Thompson
TABLE OF CONTENTS

Page

Acknowledgements ......................................................................................................... iv

List of Tables .................................................................................................................. v

List of Figures ................................................................................................................. vi

Abstract ......................................................................................................................... ix

Chapter I. Introduction ................................................................................................. 2

Chapter II. Determination of the Kinetics of PMR-15 Imidization Reactions .......... 9

Chapter III. Exploration of the Imidization of PMR-15 ............................................. 31

Chapter IV. Conclusions ............................................................................................. 82

Appendix ......................................................................................................................... 85

Bibliography ................................................................................................................... 86
ACKNOWLEDGEMENTS

The writer wishes to express her sincere appreciation to Dr. David Kranbuehl for his guidance, understanding, and patience throughout this project. The author would like to thank Dr. Chris Abelt, for his patient advice on the aspects of organic chemistry included in this thesis. The author also wishes to thank Dr. David Thompson for his careful reading and criticism of the manuscript. A thank you is also owed to my family for supporting me throughout this endeavor.
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Amount Reacted</td>
<td>12</td>
</tr>
<tr>
<td>2-2</td>
<td>Rate constants: NE:4-aminodiphenylmethane</td>
<td>13</td>
</tr>
<tr>
<td>2-3</td>
<td>Entropy and enthalpy of activation for NE:4-aminodiphenylmethane</td>
<td>14</td>
</tr>
<tr>
<td>2-4</td>
<td>Rate constants: 2:1 NE:MDA</td>
<td>15</td>
</tr>
<tr>
<td>2-5</td>
<td>Entropy and enthalpy of activation for 2:1 NE:MDA</td>
<td>15</td>
</tr>
<tr>
<td>2-6</td>
<td>Rate constants: BTDE:4-aminodiphenylmethane</td>
<td>18</td>
</tr>
<tr>
<td>2-7</td>
<td>Entropy and enthalpy of activation for BTDE:4-aminodiphenylmethane</td>
<td>19</td>
</tr>
<tr>
<td>3-1</td>
<td>Rate constants of variations of NE reacting with 4-aminodiphenylmethane</td>
<td>38</td>
</tr>
<tr>
<td>3-2</td>
<td>Initial rates of reaction</td>
<td>41</td>
</tr>
</tbody>
</table>


LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>PMR-15 monomers</td>
<td>2</td>
</tr>
<tr>
<td>1-2</td>
<td>PMR-15 polymerization</td>
<td>3</td>
</tr>
<tr>
<td>1-3</td>
<td>Crosslinking of NE end groups</td>
<td>3</td>
</tr>
<tr>
<td>1-4</td>
<td>4-Aminodiphenylmethane</td>
<td>4</td>
</tr>
<tr>
<td>1-5</td>
<td>Wolfe-Kishner reduction of 4-aminobenzophenone</td>
<td>5</td>
</tr>
<tr>
<td>1-6</td>
<td>Proton NMR of 4-aminodiphenylmethane</td>
<td>7</td>
</tr>
<tr>
<td>2-1</td>
<td>Proton NMR of NE</td>
<td>20</td>
</tr>
<tr>
<td>2-2</td>
<td>NE</td>
<td>10</td>
</tr>
<tr>
<td>2-3</td>
<td>Imide formed by NE and 4-aminodiphenylmethane</td>
<td>11</td>
</tr>
<tr>
<td>2-4</td>
<td>Proton NMR of unreacted mixture of NE and 4-aminodiphenylmethane</td>
<td>21</td>
</tr>
<tr>
<td>2-5</td>
<td>Proton NMR of mixture of NE and 4-aminodiphenylmethane, 83% reacted</td>
<td>22</td>
</tr>
<tr>
<td>2-6</td>
<td>Plot of 1/(1-(\alpha)) vs. Time for NE and monoamine</td>
<td>21</td>
</tr>
<tr>
<td>2-7</td>
<td>Plot of In (k) vs. 1/T for NE and 4-aminodiphenylmethane</td>
<td>22</td>
</tr>
<tr>
<td>2-8</td>
<td>Plot of (\alpha) vs. Time for 2:1 NE:MDA new and old data</td>
<td>23</td>
</tr>
<tr>
<td>2-9</td>
<td>Plot of 1/(1-(\alpha)) vs. Time for 2:1 NE:MDA</td>
<td>23</td>
</tr>
<tr>
<td>2-10</td>
<td>Plot of In (k) vs. 1/T for 2:1 NE:MDA</td>
<td>24</td>
</tr>
<tr>
<td>2-11</td>
<td>Proton NMR of BTDE</td>
<td>25</td>
</tr>
<tr>
<td>2-12</td>
<td>BTDE</td>
<td>16</td>
</tr>
<tr>
<td>2-13</td>
<td>'H NMR of unreacted mixture of 1:2 BTDE: 4-aminodiphenylmethane</td>
<td>26</td>
</tr>
<tr>
<td>2-14</td>
<td>'H NMR of reacted 1:2 BTDA:4-aminodiphenylmethane</td>
<td>27</td>
</tr>
<tr>
<td>2-15</td>
<td>'H NMR of reacted 1:1 BTDA:4-aminodiphenylmethane</td>
<td>27</td>
</tr>
<tr>
<td>2-16</td>
<td>'H NMR of mixture of BTDE and 4-aminodiphenylmethane, 93% reacted</td>
<td>28</td>
</tr>
<tr>
<td>2-17</td>
<td>Plot of 1/(1-(\alpha)) vs. Time for 1:2 BTDE: 4-aminodiphenylmethane</td>
<td>29</td>
</tr>
<tr>
<td>2-18</td>
<td>Plot of In (k) vs. 1/T for 1:2 BTDE: 4-aminodiphenylmethane</td>
<td>29</td>
</tr>
<tr>
<td>3-1</td>
<td>Reaction Pathway of PMR-15</td>
<td>31</td>
</tr>
<tr>
<td>3-2</td>
<td>Two Schemes for the Reaction Mechanism of PMR-15 Imidization</td>
<td>32</td>
</tr>
<tr>
<td>3-3</td>
<td>Carbon-13 NMR of NA</td>
<td>44</td>
</tr>
<tr>
<td>3-4</td>
<td>Carbon-13 NMR of NE diacid</td>
<td>45</td>
</tr>
<tr>
<td>3-5</td>
<td>Carbon-13 NMR of NE acid ester</td>
<td>46</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (continued)

3-6 Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, unreacted ................................................................. 47
3-7 Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 20 minutes at 100C .......................................................... 48
3-8 Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 40 minutes at 100C .......................................................... 49
3-9 Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 60 minutes at 100C .......................................................... 50
3-10 Proton NMR of 4-aminodiphenylmethane in xylene ................................................................. 51
3-11 Proton NMR of NE in xylene ................................................................. 52
3-12 'H NMR of 1:1 NE:4-aminodiphenylmethane, unreacted in xylene ................................................................. 53
3-13 'H NMR of 1:1 NE:4-aminodiphenylmethane, 15 minutes in xylene ................................................................. 53
3-14 'H NMR of 1:1 NE:4-aminodiphenylmethane, 30 minutes in xylene ................................................................. 54
3-15 'H NMR of 1:1 NE:4-aminodiphenylmethane, 60 minutes in xylene ................................................................. 54
3-16 'H NMR of 1:1 NE:4-aminodiphenylmethane, 90 minutes in xylene ................................................................. 55
3-17 'H NMR of 1:1 NE:4-aminodiphenylmethane, 120 minutes in xylene ................................................................. 55
3-18 'H NMR of 1:1 NE:4-aminodiphenylmethane, 170 minutes in xylene ................................................................. 56
3-19 'H NMR of 1:1 NE:4-aminodiphenylmethane, 215 minutes in xylene ................................................................. 56
3-20 'H NMR of 1:1 NE:4-aminodiphenylmethane, 105 minutes in xylene ................................................................. 57
3-21 'H NMR of 1:1 NE:4-aminodiphenylmethane, 105 minutes plus 88% imide in xylene ................................................................. 57
3-22 'H NMR of NE diester in xylene ................................................................. 58
3-23 'H NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted in xylene ................................................................. 59
3-24 'H NMR of 1:1 NE diester:4-aminodiphenylmethane, 25 hours in xylene ................................................................. 59
3-25 'H NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted in DMSO-d$_6$ ................................................................. 60
3-26 'H NMR of 1:1 NE diester:4-aminodiphenylmethane, 23 hours in DMSO-d$_6$ ................................................................. 60
3-27 'H NMR of 1:1 NA:4-aminodiphenylmethane in DMSO-d$_6$, unreacted ................................................................. 61
<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-28</td>
<td>H NMR of 1:1 NA:4-aminodiphenylmethane in DMSO-d$_6$, 60 minutes at 90°C</td>
</tr>
<tr>
<td>3-29</td>
<td>H NMR of 1:1 NA:4-aminodiphenylmethane in DMSO-d$_6$, 300 minutes at 90°C</td>
</tr>
<tr>
<td>3-30</td>
<td>Proton NMR of NA</td>
</tr>
<tr>
<td>3-31</td>
<td>Proton NMR of NE diacid in DMSO-d$_6$</td>
</tr>
<tr>
<td>3-32</td>
<td>Proton NMR of NE diester</td>
</tr>
<tr>
<td>3-33</td>
<td>Proton NMR of NE ethyl ester</td>
</tr>
<tr>
<td>3-34</td>
<td>Proton NMR of NE isopropyl ester</td>
</tr>
<tr>
<td>3-35</td>
<td>Proton NMR of NE isobutyl ester</td>
</tr>
<tr>
<td>3-36</td>
<td>H NMR of 1:1 NA:4-aminodiphenylmethane, unreacted</td>
</tr>
<tr>
<td>3-37</td>
<td>H NMR of 1:1 NA:4-aminodiphenylmethane, 60 min at 80°C</td>
</tr>
<tr>
<td>3-38</td>
<td>H NMR of 1:1 NE diacid:4-aminodiphenylmethane, 15 min at 80°C</td>
</tr>
<tr>
<td>3-39</td>
<td>H NMR of 1:1 NE diacid:4-aminodiphenylmethane, 35 min at 80°C</td>
</tr>
<tr>
<td>3-40</td>
<td>H NMR of 1:1 NE diacid:4-aminodiphenylmethane, 240 min at 80°C</td>
</tr>
<tr>
<td>3-41</td>
<td>H NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted</td>
</tr>
<tr>
<td>3-42</td>
<td>Carbon-13 NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted</td>
</tr>
<tr>
<td>3-43</td>
<td>H NMR of 1:1 NE diester:4-aminodiphenylmethane, 300 minutes at 80°C</td>
</tr>
<tr>
<td>3-44</td>
<td>Carbon-13 NMR of 1:1 NE diester:4-aminodiphenylmethane, 300 minutes at 80°C</td>
</tr>
<tr>
<td>3-45</td>
<td>H NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, unreacted</td>
</tr>
<tr>
<td>3-46</td>
<td>H NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, 28 minutes at 80°C</td>
</tr>
<tr>
<td>3-47</td>
<td>H NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, 235 minutes at 80°C</td>
</tr>
<tr>
<td>3-48</td>
<td>H NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, unreacted</td>
</tr>
<tr>
<td>3-49</td>
<td>H NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, 30 minutes at 80°C</td>
</tr>
<tr>
<td>3-50</td>
<td>H NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, 125 minutes at 80°C</td>
</tr>
<tr>
<td>3-51</td>
<td>H NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, unreacted</td>
</tr>
</tbody>
</table>
LIST OF FIGURES (continued)

3-52 'H NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, 
30 minutes at 80C ................................................................. 75
3-53 'H NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, 
125 minutes at 80C ................................................................. 76
3-54 4-Aminobenzophenone ...................................................... 41
3-55 Plot of 1/(1-α) to compare k_{\text{initial}} with k ....................... 77
3-56 Proton NMR of 4-Aminobenzophenone ............................... 78
3-57 'H NMR of 1:1 NE:4-aminobenzophenone, 60 minutes at 80C ... 79
3-58 'H NMR of 1:1 NE:4-aminobenzophenone, 210 minutes at 80C .. 79
3-59 'H NMR of 1:1 NE:4-aminobenzophenone, 300 minutes at 80C .. 80
The Imidization Reactions of PMR-15 Polyimide

ABSTRACT

Reaction kinetics of the chain propagating and chain terminating reactions in the polymerization of aromatic polyimides have been investigated using model reactions which were monitored by NMR spectroscopic techniques. Reactions between the PMR-15 chain propagating component, the dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE) and the chain terminating component, the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) with the model compound, 4-aminodiphenylmethane, were studied in order to simulate these two critical steps in the polymerization reaction.

A stable intermediate in the formation of imide in either the form of anhydride or amide has been suggested. No evidence for this intermediate is observed in the melt flow reaction of the powdered state of the resin, the conventional prepreg cure process. However, in solution (xylene) the presence of an asymmetric intermediate which appears to be amide based on NMR spectra was observed. Other NMR studies indicate that, both in solution and in the melt flow state, the reaction mechanism proceeds via anhydride formation.

The results demonstrate that the polymerization occurs via second order rate kinetics and more importantly that the activation energy for NE is greater than that of BTDE. As a result, the ratio of the rate constants $k_{(NE-amine)}/k_{(BTDE-amine)}$ varies by factors of 10 from storage to a typical cure temperature. These results suggest the morphology of the fully cured, crosslinked aromatic polyimide will vary significantly with the cure processing temperature and the previous handling-storage conditions of the resin.
THE IMIDIZATION REACTIONS OF PMR-15 POLYIMIDE
CHAPTER I

Introduction

PMR-15, which stands for polymerization of monomer reactants with a formulated molecular weight of 1500, is an aromatic polyimide. It was developed by NASA to provide a high temperature composite matrix resin which was easier to synthesize and process than polyimides previously produced by amide-acid prepolymer. It is used in military engines and aircraft and may be utilized in commercial aircraft engines. The three monomers of PMR-15 are the dimethyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE), 4,4'-methylene dianiline (MDA), and the monomethyl ester of 5-norbornene-2,3-dicarboxylic acid (NE). The structures of the monomers are shown in Figure 1-1.

![Figure 1-1 PMR-15 Monomers](image)

In order to achieve a molecular weight of 1500 for PMR with these monomers, they are combined in a ratio of \( n \text{ BTDE} : n + 1 \text{ MDA} : 2 \text{ NE} \). Where
n is equal to 2.087. As depicted in Figure 1-2, BTDE and MDA react to form long chains while NE caps the ends of these chains during PMR-15 polymerization.

\[ \text{4,4'-Methylene dianiline} + \text{BTDE dimethyl ester} + \text{NE monomethyl ester} \]

At elevated temperatures, the NE end groups undergo a reverse Diels-Alder reaction to cross-link the chains by a mechanism illustrated in Figure 1-3.

The goals of this project are to determine the kinetics of the chain
formation during PMR-15 polymerization and to learn about the reaction mechanism. Previous studies of the kinetics of PMR-15 using Thermo-Gravimetric Analysis (TGA)\(^2\) and Gel Permeation Chromatography (GPC)\(^3\) were unable to provide complete results and led to experimentation with proton and 13-Carbon Nuclear Magnetic Resonance (NMR). The reaction between the monomers NE and MDA was studied by \(^1\)H NMR and was found to have an order of two.\(^3\) Efforts to analyze the reaction between BTDE and MDA were made but the long chains formed by these two difunctional monomers were insoluble in d-chloroform and DMSO-d$_6$. In order to study the imide formation of BTDE and amine, a molecule identical to MDA but containing only one amine, 4-aminodiphenylmethane, was used in place of MDA. The structure of 4-aminodiphenylmethane is shown in Figure 1-4.

![4-Aminodiphenylmethane](image)

**Figure 1-4  4-Aminodiphenylmethane**

This molecule was not commercially available and had to be synthesized from 4-aminobenzophenone by a Wolff-Kishner reduction,\(^4,5,6\) outlined in Figure 1-5.
The reduction procedure was as follows:

Use 1 equivalent ketone
2.5 equivalents 85% hydrazine hydrate
3 equivalents NaOH
370 mL of diethylene glycol per mole of NaOH

Pour diethylene glycol and NaOH into a 250 ml round bottom flask equipped with thermometer and condenser.

Add boiling chips.

Using bunsen burner, heat flask intermittently since when the NaOH dissolves, it exotherms.

When NaOH is completely dissolved, remove the condenser and let the flask cool to 80-100°C.

Add ketone and hydrazine hydrate, replace the condenser.

Heat cautiously using a heating mantle.

Reflux for 1 hour.

Set up a distillation apparatus and distill until the temperature of the liquid in the pot reaches 205-210°C or until 30 mL of distillate have been collected.

Replace the condenser and reflux 3 hours, the temperature will be 190-200°C.

Cool to 100-110°C.

Pour liquid from round bottom into 150 mL H₂O; rinse round bottom with H₂O.

Extract at least three times with dichloromethane; the product will be in the organic layer.

Dry the organic layer with calcium chloride and filter into a round bottom flask.

Rotovap the solvent away.

Distill the product under vacuum with sodium metal.

This procedure resulted in a low melting solid which was verified by 'H
NMR to be 4-aminodiphenylmethane. $^1$H NMR (d-chloroform): δ 7.24 (d, 4H), δ 7.16 (t, 1H), δ 6.98 (d, 2H), δ 6.62 (d, 2H), δ 3.87 (s, 2H), δ 3.5 (s, 2H). The $^1$H NMR spectrum of 4-aminodiphenylmethane in d-chloroform is presented in Figure 1-6. The methylene hydrogens located at 3.87 ppm are used throughout the experiments to monitor the progress of the reaction; they are shifted to 3.98 ppm when the molecule has reacted with NE to form imide and to 4.05 ppm when it has reacted with BTDE.

Although MDA is commercially available, preparation of the monomers NE and BTDE was necessary. NE and BTDE are available in the anhydride forms, NA and BTDA. To obtain the acid ester from anhydride, the anhydride is dissolved in a volume of methanol based on the density of the solvent and the weight, in grams, of anhydride used. This mixture is refluxed for three hours, dried under vacuum without heat and stored in the freezer, under nitrogen gas.
Figure 1-6  Proton NMR of 4-aminodiphenylmethane
NOTES FOR CHAPTER I


CHAPTER II

Determination of the Kinetics of PMR-15 Imidization Reactions

1:1 NE : 4-Aminodiphenylmethane

In the previous studies in our laboratory, the reaction of NE and MDA was monitored by proton NMR and the kinetic analysis gave a reaction order of two. Since each MDA can react with two NE molecules, it was necessary to account for unreacted amine, mononadimide, and bisnadimide. Each of these species had a distinct shift but it was impossible to distinguish the rate of reaction of the first amine from the second. By reacting the monoamine, 4-aminodiphenylmethane, with NE, it was possible to monitor the first imide formation exclusively and to compare the kinetic data from this reaction with the data from MDA to determine whether the second imidization has any effect on the reaction rate.

A one:one molar ratio mixture of NE and 4-aminodiphenylmethane is prepared from the dry compounds. The two solids are ground together into a fine, well-mixed paste. This sample is then divided into a number of separate aluminum pans and placed in a preheated Delta Design 5900 Type IV μ/C Controller oven. A portion of the sample is reserved as the unreacted sample. At specific time intervals, a pan is removed from the oven and stored in the freezer.
until it can be transferred to an NMR tube, dissolved in solvent, usually d-chloroform, and analyzed by NMR. All NMR spectra were taken on a General Electric QE-300 NMR Spectrometer.

The $^1$H NMR spectrum (see Figure 2-1) for unreacted NE monomer shows nine types of hydrogens labeled a-g in Figure 2-2 below.

Figure 2-2 NE

The two bridge hydrogens labeled H$_{a1}$ and H$_{a2}$ are different and split each other to give two doublets centered around 1.4 ppm. Hydrogens H$_b$, H$_c$, H$_d$, and H$_e$ are all different due to the asymmetry of the NE molecule. These hydrogens give rise to the signals in the 3.2 to 3.4 ppm area. The singlet at 3.6 ppm can be attributed to the hydrogens from CH$_3$. The two doublets around 6.3 ppm are due to the olefin hydrogens, H$_f$ and H$_g$. These doublets arise because while each hydrogen splits the other, they are also split by the H$_e$ and H$_b$ hydrogens.

When NE reacts with 4-aminodiphenylmethane, a dimer is produced and NE becomes symmetric; this imide is drawn in Figure 2-3. When NE has reacted to form imide, the methoxy and hydroxy hydrogens are lost as methanol and water, respectively, and the peaks for these hydrogens in the NMR spectrum
should disappear.

![Diagram of molecule](image)

**Figure 2-3** Imide formed by NE and 4-aminodiphenylmethane

Since the reacted molecule is symmetric, the H\textsubscript{t} and H\textsubscript{a} hydrogens are equivalent and are seen predominantly as a singlet around 6.3 ppm. The reacted molecule can be detected from the appearance of two doublets centered around 1.7 ppm and a singlet peak at 3.98 ppm. The \textsuperscript{1}H NMR spectra of an unreacted mixture of NE and 4-aminodiphenylmethane and of this mixture when the reaction has proceeded to 83 percent of completion, each in d-chloroform, are shown in Figures 2-4 and 2-5, respectively. For Figure 2-5, showing the NE imide with unreacted NE and 4-aminodiphenylmethane present: \textsuperscript{1}H NMR (d-chloroform): \( \delta \) 7.18-7.4 (m,3H), \( \delta \) 7.03 (d,2H), \( \delta \) 6.99 (d,2H), \( \delta \) 6.62 (d,2H), \( \delta \) 6.3 (s,2H), \( \delta \) 3.98 (s,2H), \( \delta \) 3.87 (s,2H), \( \delta \) 3.58 (s,3H), \( \delta \) 3.2-3.5 (m,4H), \( \delta \) 1.7 (dd,2H), \( \delta \) 1.4 (dd,2H). The shifted doublet of doublets is the signal from the two H\textsubscript{a} hydrogens on a reacted NE. This shift is due to the proximity of the bridge hydrogens to the aromatic rings in 4-aminodiphenylmethane. The singlet at 3.98 ppm is from the methylene, which joins the two aromatic rings of 4-aminodiphenylmethane, when it has reacted with NE. It is shifted from the unreacted position of 3.87 ppm.

The extent of reaction can be monitored by comparing the peak areas of reacted to unreacted methylene on the monoamine. The amount reacted (\( \alpha \)) is equal to the peak area for the reacted molecules divided by the sum of the peak
areas for the reacted plus the unreacted species. Using this method and the data
on the peaks for CH$_2$ on the monoamine, it is easy to see, in Table 2-1, that the
reaction of NE and 4-aminodiphenylmethane at 100°C has come to completion in
60 minutes.

Table 2-1
Calculation of Alpha (α)

<table>
<thead>
<tr>
<th>Time</th>
<th>Unreacted Area</th>
<th>Reacted Area</th>
<th>Amount Reacted(α)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 min.</td>
<td>25.06</td>
<td>0.00</td>
<td>0/(0+25.06) = 0.00</td>
</tr>
<tr>
<td>4 min.</td>
<td>22.31</td>
<td>3.04</td>
<td>3.04/(3.04+22.31) = .12</td>
</tr>
<tr>
<td>7 min.</td>
<td>21.76</td>
<td>6.96</td>
<td>6.96/(6.96+21.76) = .24</td>
</tr>
<tr>
<td>15 min.</td>
<td>14.93</td>
<td>16.64</td>
<td>16.6/(16.6+14.93) = .53</td>
</tr>
<tr>
<td>30 min.</td>
<td>12.35</td>
<td>31.58</td>
<td>31.6/(31.6+12.35) = .72</td>
</tr>
<tr>
<td>45 min.</td>
<td>12.10</td>
<td>41.58</td>
<td>41.6/(41.6+12.10) = .77</td>
</tr>
<tr>
<td>60 min.</td>
<td>0.00</td>
<td>33.22</td>
<td>33.2/(33.2+0) = 1.00</td>
</tr>
</tbody>
</table>

A plot of 1/(1-α) vs. Time results in a straight line, indicating that this
reaction is second order. The plots for NE : 4-aminodiphenylmethane at 80°C,
100°C, and 120°C are shown in Figure 2-6. The rate constant, k, can be
calculated from the relation

$$k't = \frac{1}{1-\alpha}$$

where k' is the slope of the line and α is the amount of amine reacted. This
equation gives a rate constant where the concentration of the amine is assumed to
be one. The true rate constant, which is reported, is this rate constant divided by
the concentration, or $k'/a_0$. The calculation of the concentration, $a_0$, is described
in the Appendix. For the reaction between NE and 4-aminodiphenylmethane, the
rate constants are listed in Table 2-2.
By manipulating the Arrhenius equation

\[ k = A e^{-\frac{E_a}{RT}} \]

and the rate equation

\[ k = \kappa k_b T/h e^{\frac{\Delta H^*}{RT}} e^{\frac{\Delta S^*}{R}} \]

the activation energy \( (E_a) \), Arrhenius constant \( (A) \), and entropy \( (\Delta S^*) \) and enthalpy \( (\Delta H^*) \) of activation for the reaction can be calculated. In these two equations, \( k \) is the rate constant of the reaction, \( \kappa \) is the transmission coefficient and is usually 1, \( k_b \) is Boltzman's constant \((1.38 \times 10^{-23} \text{ J K}^{-1})\), \( T \) is the temperature in Kelvin, \( R \) is the universal gas constant \((8.314 \text{ J K}^{-1} \text{ mol}^{-1})\), and \( h \) is Planck's constant \((6.63 \times 10^{-34} \text{ Js})\).

Using the rate constants from the three temperatures and the Arrhenius equation, a plot of \( \ln k \) vs. \( 1/T \) can be constructed (Figure 2-7) and the activation energy and Arrhenius constant can be calculated. The slope of the line is equal to \(-E_a/R\), which yields an activation energy of 66 kJ/mol for the reaction between NE and 4-aminodiphenylmethane. The natural log of the Arrhenius constant \((\ln A)\) is equal to the y-intercept, \( A \) is \( 5.6 \times 10^7 \text{ mol}^{-1} \text{ min}^{-1} \). The Arrhenius constant is related to the entropy of activation in that \( A \) corresponds to \( \kappa k_b T/h e^{\Delta S^*/R} \) when the Arrhenius and rate equations are compared; a small Arrhenius constant implies a large negative entropy of activation for the reaction. The enthalpy of activation

---

### Table 2-2
Rate Constants for 1:1 NE:4-Aminodiphenylmethane

<table>
<thead>
<tr>
<th>( k \text{ (mol}^{-1} \text{ min}^{-1}) )</th>
<th>Temperature ( (^\circ \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0092</td>
<td>80</td>
</tr>
<tr>
<td>.029</td>
<td>100</td>
</tr>
<tr>
<td>.096</td>
<td>120</td>
</tr>
</tbody>
</table>
also can be calculated from the relationship of the rate and Arrhenius equations by relating \( E_a \) and \( \Delta H^* \):

\[
E_a = \Delta H^* + RT.
\]

Rearranging the rate equation to solve for \( \Delta S^* \) yields

\[
\Delta S^* = \frac{\Delta H^*}{T} + R \ln \left( \frac{\hbar k}{k_B T} \right).
\]

Once \( \Delta H^* \) is calculated by substituting the activation energy obtained from the slope of the \( \ln k \) vs. \( 1/T \) plot for \( E_a \), the enthalpy of activation can be used in the equation for \( \Delta S^* \) to yield the entropy of activation for each temperature. The enthalpies and entropies of activation for NE : 4-aminodiphenylmethane are listed in Table 2-3.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( \Delta H^* )</th>
<th>( \Delta S^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>80°C</td>
<td>63.2 kJ/mol</td>
<td>-67.5 J/Kmol</td>
</tr>
<tr>
<td>100°C</td>
<td>63.1 kJ/mol</td>
<td>-68.8 J/Kmol</td>
</tr>
<tr>
<td>120°C</td>
<td>62.9 kJ/mol</td>
<td>-68.3 J/Kmol</td>
</tr>
</tbody>
</table>

From the data obtained by repeating these experiments with MDA in place of 4-aminodiphenylmethane, the effect of the second imidization on the rate of reaction can be observed. Proton NMR spectra from the previous studies were used and provided data at 80°C, 90°C, and 120°C. New samples were monitored at 90°C and 100°C in order to ensure the precision of the first set of data. It can be seen from a plot of alpha (\( \alpha \)) vs. time, Figure 2-8, for 2:1 NE : MDA at 90°C that the old and the new data are comparable. The degree of reaction was then calculated based on the amount of MDA that had reacted. Figure 2-9 is the \( 1/(1-\alpha) \) vs. time plot for 2:1 NE : MDA. A least squares fit line shows that the plot is linear for each of the three reaction temperatures; this reaction, as expected, is
second order. The rate constants which are obtained from the slopes are listed in Table 2-4 and agree with those for NE : 4-aminodiphenylmethane imidization.

**Table 2-4**
Rate Constants for 2:1 NE:MDA

<table>
<thead>
<tr>
<th>k (mol⁻¹min⁻¹)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.010</td>
<td>80</td>
</tr>
<tr>
<td>.015</td>
<td>90</td>
</tr>
<tr>
<td>.037</td>
<td>100</td>
</tr>
<tr>
<td>.085</td>
<td>120</td>
</tr>
</tbody>
</table>

Using these rate constants to plot ln k vs. 1/T (Figure 2-10) gives an activation energy of 64 kJ/mol, which is reasonably close to 66 kJ/mol calculated for NE : 4-aminodiphenylmethane. This $E_a$ also agrees with the activation energy of 55 kJ/mol which T. Prettyman obtained using TGA and the $E_a$ which J. Smith calculated from NMR studies. The enthalpies and entropies of activation for 2:1 NE : MDA, listed in Table 2-5, and 1:1 NE : 4-aminodiphenylmethane, from Table 2-3, are also similar.

**Table 2-5**
Entropy and Enthalpy of Activation for 2:1 NE:MDA

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$\Delta H^\circ$ (kJ/mol)</th>
<th>$\Delta S^\circ$ (J/Kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80°C</td>
<td>60.8</td>
<td>-74.1</td>
</tr>
<tr>
<td>90°C</td>
<td>60.7</td>
<td>-75.9</td>
</tr>
<tr>
<td>100°C</td>
<td>60.6</td>
<td>-73.4</td>
</tr>
<tr>
<td>120°C</td>
<td>60.5</td>
<td>-75.6</td>
</tr>
</tbody>
</table>

From these comparative calculations, it may be concluded that the imidization rates for forming the monoimide and bisimide are approximately equal.
Studies of PMR-15 have shown that the imidizations of NE and BTDE occur at different rates, with NE reacting more rapidly than BTDE. In this experiment, a 1:2 molar ratio of BTDE : 4-aminodiphenylmethane was prepared so that, theoretically, every functional group would react to reveal an alpha (α) equal to one. The 1:2 BTDE : 4-aminodiphenylmethane samples were prepared, stored, and analyzed in the same fashion as NE : 4-aminodiphenylmethane so that the rates of reaction could be compared.

The 'H NMR spectrum of BTDE monomer alone is depicted in Figure 2-11, the structure of BTDE is shown in Figure 2-12.

The -OH and -OCH₃ groups are interchangeable, thus BTDE has four isomers. This results in the H₆ and H₇ from the methyl esters appearing as a doublet at 3.95 ppm. Methanol appears at 3.5 ppm. Excluding the hydroxy hydrogens, the remaining hydrogens are aromatic. All but two, H₆ and H₇, are doublets; H₆ and H₇ are singlets since there are no other protons nearby.

Figure 2-13 shows an unreacted mixture of BTDE and 4-aminodiphenylmethane. The methylene peak on 4-aminodiphenylmethane is discernable at 3.87 ppm and can be seen to shift to 4.05 ppm when the sample is heated and reacts. This peak represents both the monoadduct and the diadduct of BTDE-imide formation. In a 2:1 mixture of BTDA and monoamine, using the
anhydride to simplify the spectrum around 4 ppm, it is assumed that all the functional groups are reacted and bisimide has formed. On the other hand, a 1:1 mixture may result in monoimide or bisimide formation since there are unequal numbers of reactive groups. The methylene on the monoamine appears at 4.05 ppm in both the 2:1 mixture (Figure 2-14) and the 1:1 sample (Figure 2-15). However, by comparing the aromatic regions of these $^1$H NMR spectra, differences can be detected which indicate that the aromatic hydrogens are affected by the differences between monoimide and bisimide, though the methylene is not. The NMR detects no difference in the methylene when it is part of this mono- or diadduct: thus, the area under the peak at 4.05 ppm should be considered the total reacted amine. Therefore, degree of reaction is calculated in the same manner as for NE: 4-aminodiphenylmethane. In Figure 2-16, a sample which has been held at 100°C for 210 minutes and has reached an alpha ($\alpha$) of 93 percent is shown. For this spectrum, $^1$H NMR (d-chloroform): $\delta$ 7.83-8.28 (m, 10H aromatic), $\delta$ 7.34 (s,4H), $\delta$ 7.30 (d,2H), $\delta$ 7.21 (d,2H), $\delta$ 4.05 (s,2H), $\delta$ 3.92-3.98 (m,4H), $\delta$ 3.87 (s,2H), $\delta$ 3.50 (s,3H).

The plots of $1/(1-\alpha)$ vs. time, for 1:2 BTDE: 4-aminodiphenylmethane at 100°C, 120°C, and 140°C, shown in Figure 2-17, are linear and indicate that this imidization, as well as that of NE, is second order. Again, the rate constant is equal to the slope of the least squares fit line. The rate constants for 1:2 BTDE: 4-aminodiphenylmethane are listed in Table 2-6.
Table 2-6
Rate Constants for 1:2 BTDE:4-Aminodiphenylmethane

<table>
<thead>
<tr>
<th>(k \text{ (mol}^\text{−1}\text{·min}^\text{−1}))</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.016</td>
<td>100</td>
</tr>
<tr>
<td>.021</td>
<td>120</td>
</tr>
<tr>
<td>.069</td>
<td>140</td>
</tr>
</tbody>
</table>

Upon comparison with the rate constants for NE, the BTDE reaction is seen to be slower at any given temperature, which is in agreement with previous research.

Continuing the mathematical analysis, the activation energy, Arrhenius constant, and entropy and enthalpy of activation can be calculated for the 1:2 BTDE : 4-aminodiphenylmethane reaction. \(E_a\) is equal to \(-R\) multiplied by the slope of an \(\ln k\) vs. \(1/T\) plot which is 46 kJ/mol, while \(A\) is \(3.95 \times 10^4\) mol\(^{−1}\) min\(^{−1}\). This \(\ln k\) vs. \(1/T\) plot is shown in Figure 2-18. Using these values to obtain \(\Delta H^*\) and \(\Delta S^*\), it can be seen from its larger negative entropy that the transition state for BTDE and 4-aminodiphenylmethane is more ordered than that of NE and the monoamine. Table 2-7 lists the entropies and enthalpies of activation for 1:2 BTDE : 4-aminodiphenylmethane.

Table 2-7
Entropy and Enthalpy of Activation for 1:2 BTDE:4-Aminodiphenylmethane

<table>
<thead>
<tr>
<th>Temperature</th>
<th>(\Delta H^*) (kJ/mol)</th>
<th>(\Delta S^*) (J/Kmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100°C</td>
<td>43.0</td>
<td>-127.5</td>
</tr>
<tr>
<td>120°C</td>
<td>42.8</td>
<td>-132.0</td>
</tr>
<tr>
<td>140°C</td>
<td>42.7</td>
<td>-128.2</td>
</tr>
</tbody>
</table>

Through the analysis of the reactions of BTDE and NE with amine it has been determined that each of these reactions is second order. Additionally, the reaction of BTDE with amine proceeds more slowly, and through a more ordered transition state than does the reaction of NE with amine at each of the temperatures studied. Based on comparisons of the kinetic data for the reactions
of 2:1 NE : MDA and 1:1 NE : 4-aminodiphenylmethane, it can be concluded that the formation of monoimide and bisimide occur at approximately the same rate. These results are consistent with findings obtained through other methods of analysis.
Figure 2-1  "H NMR of NE
Figure 2-4  $^1$H NMR of unreacted mixture of NE and 4-aminodiphenylmethane

Figure 2-5  $^1$H NMR of mixture of NE and 4-aminodiphenylmethane, 83% reacted
Figure 2-6  Plot of $1/(1-\alpha)$ vs. Time for NE and 4-aminodiphenylmethane

$1/(1-\alpha)$ vs. Time

1:1 NE:MMDA

- 80°C
- 100°C
- 120°C

Figure 2-7  Plot of ln k vs. 1/T for NE and 4-aminodiphenylmethane

Determination of Ea

△ 1:1 NE:MMDA

\[ \frac{1}{T} \text{ vs. ln } k \]
Figure 2-8  Plot of $\alpha$ vs. Time for 2:1 NE:MDA New and Old Data at 90°C
Figure 2-9  Plot of $1/(1-\alpha)$ vs. Time
for 2:1 NE:MDA

$1/(1-\alpha)$ vs. Time
2:1 NE:MDA

- 80°C
- 90°C
- 100°C
- 120°C

Figure 2-10  Plot of ln $k$ vs. $1/T$
for 2:1 NE:MDA

Determination of $E_a$
Figure 2-11 'H NMR of BTDE
Figure 2-13  \(^1\)H NMR of unreacted mixture of 1:2 BTDE:4-aminodiphenylmethane

![NMR Spectrum](image)
Figure 2-14 $^1$H NMR of reacted 1:2
BTDA:4-aminodiphenylmethane

Figure 2-15 $^1$H NMR of reacted 1:1
BTDA:4-aminodiphenylmethane
Figure 2-16  $^1$H NMR of mixture of BTDE and 4-aminodiphenylmethane, 93% reacted
Figure 2-17  Plot of $1/(1-\alpha)$ vs. Time
for 1:2 BTDE:4-aminodiphenylmethane

$1/(1-\text{alpha})$ vs. Time
1:2 BTDE:MMDA

• 140°C  △ 120°C  ○ 100°C

![Graph showing $1/(1-\alpha)$ vs. Time with data points at 140°C, 120°C, and 100°C.]

Figure 2-18  Plot of ln k vs. 1/T
for 1:2 BTDE:4-aminodiphenylmethane

Determination of Ea

○ 1:2 BTDE:MMD

![Graph showing ln k vs. 1/T with a linear relationship and data points for 1:2 BTDE:MMD.]
NOTES FOR CHAPTER II


CHAPTER III

Exploration of the Imidization of PMR-15

The reaction mechanism of the imidization to form pre-polymer chains for PMR-15 is controversial. Several mechanisms have been proposed. One proposal is a mechanism involving an isola ble amide intermediate\(^1\) which is outlined in Scheme I. A mechanism based on an anhydride intermediate\(^1,2\) is shown in Scheme II. It has also been suggested that anhydride formation may also be a competing reaction to imide formation; thus during the cure, reversion to the anhydride is related to a decrease in molecular weight prior to achieving the final molecular weight\(^3\). The general proposed reaction pathway is shown in Figure 3-1. The two mechanistic schemes are outlined in Figure 3-2.

![Figure 3-1 Reaction Pathway of PMR-15](image-url)
Figure 3-2  Two Schemes for the Reaction Mechanism of PMR-15 Imidization
The reaction of 1:1 NE : 4-aminodiphenylmethane was monitored by $^{13}$C NMR in an attempt to observe an amide or anhydride intermediate to the formation of imide. NE and 4-aminodiphenylmethane were measured in a 1:1 molar ratio, ground together into a fine powder and heated in a preheated Delta Design 5900 Type IV $\mu$/C controller oven at constant temperature for varying lengths of time, in a procedure identical to the one described in Chapter II of this thesis regarding kinetic analysis. The $^{13}$C NMR spectra of unreacted NE acid ester, NE diacid, and NA were also obtained in order to facilitate peak identification. Only the carbonyl carbons of NE are identified, as these carbons are most directly affected by the formation of imide. The NA, NE diacid, and NE acid ester $^{13}$C NMR spectra are shown in Figures 3-3 to 3-5, respectively. NA: $^{13}$C NMR (d-chloroform): $\delta$ 171.4. NE diacid: $^{13}$C NMR (DMSO-d$_6$): $\delta$ 173.6. NE acid ester: $^{13}$C NMR (d-chloroform): $\delta$ 177.7, $\delta$ 173.0.

From looking at Figures 3-6 to 3-9, the $^{13}$C spectra of 1:1 NE : 4-aminodiphenylmethane at 100$^\circ$C from the unreacted to fully reacted state the progress of the reaction can be viewed. It can be seen that the acid and ester carbonyls become smaller, then disappear, and a new peak grows in at 177.1 ppm. This is the only peak present in the fully reacted sample and, thus, must be the imide. From the spectrum of NA (Figure 3-2), the carbonyl peak on the anhydride, were it present, would appear at 171.4 ppm and according to the studies performed by British Petroleum, an amide carbonyl would appear at 173.8 ppm. Clearly, neither of these peaks is visible and no intermediates, either amide or anhydride, appear to be present via this method of analysis.
Since efforts to find an isolable intermediate to the formation of imide in the dry state were unproductive, the reaction of NE and 4-aminodiphenylmethane in solution was explored.

Again, a 1:1 molar mixture of NE : 4-aminodiphenylmethane was made and this time was placed in an NMR tube and dissolved in xylene. It was then placed into a preheated oil bath and removed at various time intervals to obtain \(^1\text{H}\) NMR spectra. These spectra, for a reaction temperature of 105°C along with the spectra for the unreacted monomers, are shown in Figures 3-10 to 3-19.

Unreacted \(^1\text{H}\) NMR (xylene): \(\delta 6.25 \text{ (d,1H)}, \delta 6.18 \text{ (d,1H)}, \delta 3.70 \text{ (s,2H)}, \delta 3.40 \text{ (s,3H)}, \delta 3.04-3.20 \text{ (m,4H).} \)

Reacted (Figure 3-19) \(^1\text{H}\) NMR (xylene): \(\delta 6.36 \text{ (d,2H)}, \delta 6.27 \text{ (d,1H)}, \delta 6.21 \text{ (d,1H)}, \delta 5.95 \text{ (s,2H)}, \delta 5.56 \text{ (s,2H)}, \delta 3.70 \text{ (d,2H)}, \delta 3.41 \text{ (s,3H)}, \delta 2.90-3.18 \text{ (m,4H).} \)

As in the previous experiments, the methylene hydrogens of the monoamine were monitored. After 15 minutes, peaks at 3.70 and 3.72 ppm represent the unreacted and a reacted form of monoamine. By 30 minutes a third peak due, as will be shown, to the imide begins to appear at 3.69 ppm.

Following the progression of the peaks through time shows the disappearance of the original unreacted \(\text{CH}_2\), the formation and gradual disappearance of an intermediate and finally, the appearance of the final reacted product, the imide.

To be certain that the third peak is imide and that the peak at 3.72 ppm is an intermediate, fully reacted 1:1 NE : 4-aminodiphenylmethane (ie. imide) was added to the sample. This is shown in Figures 3-20 and 3-21. It is clear that by adding 88% imide, the peak at 3.69 ppm definitely increases; therefore it is
obviously the imide peak.

The intermediate represented by the peak at 3.72 ppm can also be observed from the olefinic hydrogens on NE. In the unreacted form, these two hydrogens are different due to the asymmetry of NE and give rise to a doublet of doublets centered at 6.24 ppm. Once the ester has reacted with amine to form amide, as in Scheme II, the resulting molecule is also asymmetric, but is different than NE. When the imide forms, the molecule is symmetric and these olefin hydrogens are identical; they appear as a singlet at 5.95 ppm. The appearance of this singlet can be seen in conjunction with the imide represented by the peak at 3.69 ppm, indicating that each of these peaks represents the imide.

From this reaction, an asymmetric intermediate has been identified as evidenced by the olefinic hydrogens of NE. In this path from amine to imide, the necessary asymmetric intermediate is amide. However, because both Schemes I and II contain amide intermediate, it is yet undetermined which reaction scheme this amide appears in or whether an anhydride intermediate exists as well. In the reaction pathway of acid ester and amine to form imide, the first step may be the attack of either the amine or the acid on the ester. If the amine attacks the ester, amide is formed; attack by the acid will produce anhydride. The amine is more nucleophilic than the acid; this implies that the amine may attack the ester before the acid does, creating amide as the first intermediate in the path to imide formation. However, the acid has an entropic advantage over the amine. The acid is sterically close to the ester while the amine must maneuver to be within reacting distance of the ester, supporting the idea of the anhydride as the first
intermediate. Johnston's work with isophthalic acid methyl ester and amine, provided evidence that the nucleophilic attack on an ester by amine is slower than the formation of anhydride. With this in mind, reacting the diester of NE with amine (4-aminodiphenylmethane) should not produce imide. The NE acid ester may form anhydride as a result of the attack of ester by acid. In the diester, one ester will not attack the other to produce anhydride without the presence of water to hydrolyze one ester, but the amine is still free to attack the ester to form amide. Therefore, if imide is generated in the reaction of NE diester and 4-aminodiphenylmethane, it must mean that the amide is the first intermediate. Conversely, if no imide is formed, the first intermediate must be something other than amide, presumably anhydride.

The reaction of NE diester and 4-aminodiphenylmethane in xylene at 100°C shows no product formation for 25 hours. The proton spectra for the NE diester and for this solution at time zero and after 25 hours are shown in Figures 3-22 to 3-24. To ensure that this inactivity was reproducible, 1:1 NE diester : 4-aminodiphenylmethane were also reacted in DMSO-d₆. Once again, no reaction occurred over a period of 23 hours. The proton spectra of the time zero and 23 hour samples are shown in Figures 3-25 and 3-26. The lack of reaction strongly implies that the amide is not the first intermediate.

Furthermore, if the anhydride is the first intermediate, reacting NA and amine in solution should rapidly produce amide since, presumably, the first intermediate is, in this case, the starting material. A sample of 1:1 NA: 4-aminodiphenylmethane was dissolved in DMSO-d₆ and placed into an oil bath at a
temperature of 90°C. The $^1$H NMR spectra in Figures 3-27 through 3-29 show that NA and amine do react rapidly. In fact even the unheated sample has reacted and contains very little unreacted NA. At first, the unreacted amine, monitored via the methylene hydrogens, can be seen at 3.74 ppm and reacted amine is located slightly downfield at 3.85 ppm. Later, a third peak emerges at 3.94 ppm. Based on the studies of the reaction between NA and 4-aminodiphenylmethane in the melt form, two peaks are present, one at 3.87 and the other at 3.96 when the solvent is d-chloroform. These peaks represent the amine and imide, respectively. The imide formed in the solid melt by the diacid of NE and 4-aminodiphenylmethane appears at 3.94 in DMSO-d$_6$. Thus, it can be concluded that the amine reacts very rapidly with the anhydride to form amide and then goes on to form imide. In fact, the amide may form so rapidly that no anhydride intermediate is seen by NMR at the temperatures we have studied; in other words, once the anhydride forms, it reacts immediately and anhydride formation is the rate limiting step of the reaction.

Also of interest is the effect upon the kinetics of the reaction by altering either the acid or amine molecule. Reactions of 4-aminodiphenylmethane with NE in the diacid, di-methyl ester, ethyl ester, and anhydride forms were compared with the reaction between the monoamine and regular NE acid ester. The NA for these reactions is commercially available and was used without further preparation. Refluxing NA with excess water then drying the solution under vacuum yielded the diacid. The ethyl ester was made by refluxing NA with the appropriate volume of ethanol based on the density of ethanol and the weight,
in grams, of NA which were used. After refluxing, the solution was dried under vacuum. Each of these variations of NE was solid and was handled in the same way as the NE acid ester (described in Chapter I). The preparation of the NE diester required the use of acid catalyst in addition to the methanol reflux. The acid catalyst was needed to protonate the carbonyl carbon and make it more susceptible to attack by the alcohol so that the diester could be formed. To 30 g NA dissolved in 200 mL methanol in an ice bath was added 5 mL concentrated sulfuric acid slowly with constant stirring. This mixture was heated and allowed to reflux for 24 hours. The solution was then extracted three times with dichloromethane and the organic layer washed with a solution of water saturated with sodium bicarbonate until no gas was evolved and the pH of the aqueous layer was basic. The organic layer was dried with calcium chloride and filtered, then placed on a Buchi rotavap to remove the solvent. This procedure yielded a liquid containing NE diester plus impurities which was then distilled to give pure NE diester.

The 'H NMR spectra for NA and the diacid, diester, and ethyl, isopropyl and isobutyl ester forms of NE can be seen in Figures 3-30 to 3-35. For each reaction, procedures outlined in Chapter II for the mixing and heating of NE and 4-aminodiphenylmethane were followed. Proton NMR spectra were obtained and a similar mathematical analysis the one detailed in Chapter II was performed. Representative spectra for each reaction are shown in Figures 3-36 to 3-53. The rate constants of each of these reactions at 80°C can be seen and compared in Table 3-1.
Table 3-1
Melt Flow Rate Constants at 80°C (Substitutions for NE)

<table>
<thead>
<tr>
<th>Substance</th>
<th>k_mol⁻¹min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>NA</td>
<td>0.076</td>
</tr>
<tr>
<td>NE acid ester</td>
<td>0.0092</td>
</tr>
<tr>
<td>NE diacid</td>
<td>0.00096</td>
</tr>
<tr>
<td>NE diester</td>
<td></td>
</tr>
<tr>
<td>NE ethyl ester</td>
<td>0.0034</td>
</tr>
<tr>
<td>NE isopropyl ester</td>
<td>0.0078</td>
</tr>
<tr>
<td>NE isobutyl ester</td>
<td>0.0013</td>
</tr>
</tbody>
</table>

Altering the reactive groups on NE not only changes the kinetics of the imidization, but provides some insight into the reaction mechanism. The rate constant for the reaction of NA and 4-aminodiphenylmethane may not be entirely reliable because even at room temperature, NA reacts immediately to form imide. This phenomenon in the reaction of BTDA and amine has been observed by others. The reaction of the NE diacid proceeds one tenth as quickly as the reaction of acid ester with amine. This would be the result whether the amide or anhydride is the first intermediate. The formation of anhydride and amide from diacid is slower than the formation of these intermediates from an acid ester. This rate can be explained with regard to the reaction mechanism. If the amide is the first intermediate, an amine is more reactive with an ester than is an acid; the amine prefers to attack the ester. In the diacid, there is no ester and imidization is comparatively slower than NE acid ester. The diacid is capable of forming anhydride, but again, not as favorably as the acid ester. This also results in a slowed reaction and explains the small rate constant for imidization of NE diacid.

The reaction of the NE diester with 4-aminodiphenylmethane is immensely slow, even after five hours at 80°C there is no reaction. This is not surprising
given the fact that after 25 hours this system in solution at 100°C had not reacted. No rate constant is available for this reaction since there is no progression of the reactants from the unreacted form. The ethyl ester reacts more slowly than the NE acid methyl ester. Since the ethyl is both larger and more electron donating than the methyl, either steric or electronic effects could result in the difference in the rates of reaction. To distinguish between the steric and electronic effects, 4-aminodiphenylmethane was reacted with the NE isopropyl and isobutyl esters. The isopropyl ester is of similar size to the ethyl ester but, as a secondary alcohol, it is more electron donating than the ethyl. This means that the carbonyl is less electrophilic. Since the carbonyl is no longer a strong electrophile, it is less receptive to an attack by the amine, resulting in a slow reaction when the leaving group is electron donating. To investigate the steric factor, NE isobutyl ester and amine were reacted. The isobutyl ester is similar to the isopropyl ester electronically, as a secondary alcohol it is electron donating, but it is sterically larger. The reaction of the isobutyl ester will be slow, compared to the isopropyl ester if a steric factor is involved in determining the rate of reaction.

Referring to Table 3-1, it is evident from this data that the isopropyl ester reacts faster than the ethyl ester, and that the isobutyl ester is slower than each of these. The effects of the electronic factor are unclear. It would be expected that the isopropyl ester would react more slowly than the ethyl ester since it is more electron donating. This data, where the isopropyl ester reacts faster than the ethyl ester, is indeterminate as to the effects of the electronic factor. The data regarding the steric effect are consistent; the larger isobutyl ester is slower than
the electronically similar isopropyl ester. Thus, this set of data suggests that although the electronic effect plays some role in the rate of imidization as determined by the alcohol leaving group, the steric effect appears to be the dominant factor.

It is clear that altering the reactive groups on NE has undeniable effects on the rate of imidization. Through the comparative experiments on MDA and 4-aminodiphenylmethane with NE acid ester described in Chapter II, we found that the rate of forming the mono- and bisimides are approximately equal. However, it has not been shown whether the structure of the amine molecule, either monofunctional or bifunctional, has any effect on the rate of the reaction.

![Figure 3-54 4-Aminobenzophenone](image_url)

Reaction of NE with 4-aminobenzophenone (Figure 3-54) should be slower than its reaction with 4-aminodiphenylmethane, the reduced form of 4-aminobenzophenone, with NE. The electronegativity of the oxygen of the carbonyl connecting the two aromatic rings in the amine should decrease the nucleophilicity of the amine on 4-aminobenzophenone and as a result, slow the reaction.

Again, well mixed 1:1 molar ratios of NE acid ester and 4-aminobenzophenone were prepared and heated in the oven at 80°C. Since 4-aminobenzophenone does not contain the methylene joining the two aromatic rings
which MDA and 4-aminodiphenylmethane have, it was necessary to monitor the progress of the reaction by some other method. As noted in Chapter II, the bridge hydrogens of NE appear as a doublet of doublets centered at 1.4 ppm which move to 1.7 ppm when NE has reacted. Using these NE hydrogens, an initial rate constant can be calculated using the same mathematical methods described in Chapter II. The initial rate constant, as defined by the amount of NE which has reacted agrees quite well with the rate constant obtained from the amount of reacted amine, as depicted in Figure 3-55, for a sample of 1:1 NE : 4-aminobenzophenone reacted at 80°C. The 'H NMR spectra of the reaction of NE acid ester with 4-aminobenzophenone plus the spectrum of the unreacted amine are shown in Figures 3-56 to 3-59. The rate constants obtained from calculations performed on these spectra are given in Table 3-2.

Table 3-2
Initial Rates of Reaction at 80°C
(Substitution for 4-aminodiphenylmethane)

<table>
<thead>
<tr>
<th></th>
<th>( k_{\text{initia}} ) (( \text{mol}^{-1}\text{min}^{-1} ))</th>
<th>( k ) (( \text{mol}^{-1}\text{min}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NE:4-aminobenzophenone</td>
<td>.00062</td>
<td>----</td>
</tr>
<tr>
<td>NE:4-aminodiphenylmethane</td>
<td>.0092</td>
<td>.0092</td>
</tr>
</tbody>
</table>

Indeed, the rate of reaction of 4-aminobenzophenone with NE is appreciably slower, demonstrating that the structure of the reactants in PMR-15 is vital to their reactivity.

To sum up the experiments dealing with the reaction mechanism of imide formation in PMR-15, (1) a stable amide intermediate is present in solution but not in melt flow reaction and (2) evidence for the formation of a rate limiting anhydride intermediate exists. The inability of NE diester to react with amine
demonstrates the necessity of an anhydride intermediate as the first intermediate in the reaction pathway. This finding supports the mechanism of imidization proposed by Johnston. Additionally, since no anhydride is detected by $^{13}$C or $^1$H NMR, it must be the rate limiting step of the formation of imide; as soon as it forms, it reacts to give amide. Also of interest is the significant change in the rate of imidization when the structure of the acid ester or the amine molecule is altered; as demonstrated, for example, by the inactivity of the NE diester towards amine.
Figure 3-3 Carbon-13 NMR of NA
Figure 3-4  Carbon-13 NMR of NE diacid

<table>
<thead>
<tr>
<th>Peak</th>
<th>Δν (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20.34</td>
</tr>
<tr>
<td>2</td>
<td>32.66</td>
</tr>
<tr>
<td>3</td>
<td>47.93</td>
</tr>
<tr>
<td>4</td>
<td>63.12</td>
</tr>
<tr>
<td>5</td>
<td>105.14</td>
</tr>
<tr>
<td>6</td>
<td>140.14</td>
</tr>
<tr>
<td>7</td>
<td>165.32</td>
</tr>
<tr>
<td>8</td>
<td>177.54</td>
</tr>
<tr>
<td>9</td>
<td>197.77</td>
</tr>
</tbody>
</table>

PPM
Figure 3-5  Carbon-13 NMR of NE acid ester
Figure 3-6  Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, unreacted
Figure 3-7  Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 20 minutes at 100°C
Figure 3-8  Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 40 minutes at 100°C
Figure 3-9  Carbon-13 NMR of 1:1 NE:4-aminodiphenylmethane, 60 minutes at 100°C
Figure 3-10  $^1$H NMR of 4-aminodiphenylmethane in xylene
Figure 3-11  'H NMR of NE in xylene
Figure 3-12 \( ^1H \) NMR of 1:1 NE:4-aminodiphenylmethane, 0 minutes in xylene

Figure 3-13 \( ^1H \) NMR of 1:1 NE:4-aminodiphenylmethane, 15 minutes in xylene at 100°C
Figure 3-14 \( ^1H \) NMR of 1:1 NE:4-aminodiphenylmethane, 30 minutes in xylene at 100°C

Figure 3-15 \( ^1H \) NMR of 1:1 NE:4-aminodiphenylmethane, 60 minutes in xylene at 100°C
Figure 3-16  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 90 minutes in xylene at 100°C

Figure 3-17  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 120 minutes in xylene at 100°C
Figure 3-18  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 170 minutes in xylene at 100°C

Figure 3-19  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 215 minutes in xylene at 100°C
Figure 3-20  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 105 minutes in xylene at 100°C

Figure 3-21  $^1$H NMR of 1:1 NE:4-aminodiphenylmethane, 105 minutes plus 88% imide in xylene at 100°C
Figure 3-22 $^1$H NMR of NE diester in xylene
Figure 3-23  $^1$H NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted in xylene

Figure 3-24  $^1$H NMR of 1:1 NE diester:4-aminodiphenylmethane, 25 hours in xylene at 100°C
Figure 3-25  $^1$H NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted in DMSO-$d_6$.

Figure 3-26  $^1$H NMR of 1:1 NE diester:4-aminodiphenylmethane, 23 hours in DMSO-$d_6$, at 90°C.
Figure 3-27  $^1$H NMR of 1:1 NA:4-aminodiphenylmethane, 0 minutes in DMSO-$d_6$ at 90C

Figure 3-28  $^1$H NMR of 1:1 NA:4-aminodiphenylmethane, 60 minutes in DMSO-$d_6$ at 90C
Figure 3-29  $^1$H NMR of 1:1 NA:4-aminodiphenylmethane, 300 minutes in DMSO-d$_6$ at 90°C
Figure 3-30 Proton NMR of NA

Figure 3-31 Proton NMR of NE diacid
Figure 3-32 Proton NMR of NE diester

Figure 3-33 Proton NMR of NE ethyl ester
Figure 3-34  Proton NMR of NE isopropyl ester

Figure 3-35  Proton NMR of NE isobutyl ester
Figure 3-36 Proton NMR of 1:1 NA:4-aminodiphenylmethane

Figure 3-37 Proton NMR of 1:1 NA:4-aminodiphenylmethane, 60 minutes at 80°C
Figure 3-38 Proton NMR of 1:1 NE diacid:4-aminodiphenylmethane, 15 minutes at 80C

Figure 3-39 Proton NMR of 1:1 NE diacid:4-aminodiphenylmethane, 35 minutes at 80C
Figure 3-40  Proton NMR of 1:1 NE diacid:4-aminodiphenylmethane, 240 minutes at 80C
Figure 3-41  Proton NMR of 1:1 NE diester:4-aminodiphenylmethane, 0 minutes

Figure 3-42  Carbon-13 NMR of 1:1 NE diester:4-aminodiphenylmethane, unreacted
Figure 3-43 Proton NMR of 1:1 NE diester:4-aminodiphenylmethane, 300 minutes at 80°C

Figure 3-44 Carbon-13 NMR of 1:1 NE diester:4-aminodiphenylmethane, 300 minutes at 80°C
Figure 3-45 Proton NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, 0 minutes

Figure 3-46 Proton NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, 28 minutes at 80°C
Figure 3-47 Proton NMR of 1:1 NE ethyl ester:4-aminodiphenylmethane, 235 minutes at 80°C
Figure 3-48  Proton NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, 0 minutes

Figure 3-49  Proton NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, 30 minutes at 80°C
Figure 3-50  Proton NMR of 1:1 NE isopropyl ester:4-aminodiphenylmethane, 125 minutes at 80°C
Figure 3-51  Proton NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, 0 minutes

Figure 3-52  Proton NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, 30 minutes at 80°C
Figure 3-53  Proton NMR of 1:1 NE isobutyl ester:4-aminodiphenylmethane, 125 minutes at 80°C
Figure 3-55 Plot of $1/(1-\alpha)$ vs. time to compare $k_{\text{inial}}$ with $k$

$1/(1-\alpha)$ vs. Time

NE: MMDA initial rate

+ by NE

Δ by MMDA

0  12  24  36  48  60  72  84  96  108  120

Time (min)
Figure 3-56 Proton NMR of 4-Aminobenzophenone
Figure 3-57  Proton NMR of 1:1 NE:4-Aminobenzophenone, 60 minutes at 80°C

Figure 3-58  Proton NMR of 1:1 NE:4-Aminobenzophenone, 210 minutes at 80°C
Figure 3-59 Proton NMR of 1:1 NE:4-Aminobenzophenone, 300 minutes at 80°C
NOTES FOR CHAPTER III


CHAPTER IV

Conclusions

Using NMR spectroscopy, much information has been gained about the kinetics and reaction mechanism of the PMR-15 polyimide. From model experiments analyzed by proton and 13-carbon NMR it has been determined that the imidization of both NE and BTDE with amine occurs via second order kinetics. In the temperature range observed in this study, the rate of reaction of NE with amine exceeds that of BTDE with amine. However, based on the activation energies obtained for these imidizations and their use in the Arrhenius equation, the rates of formation of NE-imide and BTDE-imide differ by orders of magnitude with temperature. At -20°C the rate of reaction for BTDE is greater than the rate for NE, but at higher temperatures NE reacts faster. This indicates that a large difference in chain lengths will occur depending on the reaction temperature and resin age. That is, the amount of short relative to long NE terminated chains can vary greatly with polyimide processing conditions. Additionally, BTDE imidization occurs through a more ordered transition state than the NE as demonstrated by its large, negative entropy of activation. Also of interest is the fact that NE reacts with MDA, a diamine, and 4-aminodiphenylmethane, a monoamine, with approximately the same rate. The first and second imidizations between MDA and an acid ester occur at
approximately equal rates.

Through other NMR studies, some information regarding the mechanism of the imidization of PMR-15 has been gained. One general proposed mechanism allows for one stable intermediate in the form of amide. Another mechanism, proposed by Johnston, involves an anhydride intermediate preceding the formation of amide. Our results support the Johnston mechanism. Through no reaction in mixtures of the NE diester and amine, it was determined that the amide is not the first intermediate in the imidization pathway. Also, reaction of nadic anhydride with amine results in immediate formation of amide. Each of these reactions leads to the conclusion that the anhydride must be the first intermediate. Since no anhydride was observed in the course of these reactions, it seems evident that the formation of the anhydride must be the rate determining step in the imidization. As soon as the anhydride forms, it reacts with amine to give amide, water is then displaced and the imide is formed.

Studies on the effect of molecular structure on the rate of imidization of NE with amine were also carried out. It was determined that changes in the structure of either the acid ester or the amine results in a considerable change in the rate of reaction. The NE acid ester reacts more quickly than the NE diacid does with amine in each of our experiments. However, varying the type of ester also alters the rate of reaction. It seems there is a balance between electronic and steric effects on the rapidity of reaction, with steric hindrance outweighing electronic effects to slow the reaction when the ester is larger than the methyl ester.

Future research may include experimentation with the NE and BTDE diesters
and a computer program designed to monitor the imidization reactions of PMR-15 polymer as a whole, rather than just the NE or BTDE reactions. The diesters will be reacted with amine at increasingly high temperatures in an effort to see if the diester will react, given a sufficiently high temperature. It is intended that this computer program will identify the mole fractions of any size mer when the temperature and rate constant for the two imidizations are provided. For example, the rate constants obtained through analysis described in Chapter I should be used in this program to determine the amount of NE-MDA-NE chains as opposed to the number of NE-\((\text{MDA-BTDE})_n\) chains in a PMR-15 sample at a given temperature. Conceivably, this program would propose chain lengths for PMR-15 based on the handling, storage, and reaction temperature of the resin, providing the optimum conditions for any desired composition of polymer.
The rate equation for a second order reaction,

\[ k_t = \frac{1}{1 - a(t)} \]

is equivalent to the expression

\[ k_t = \frac{l}{a[1-a(t)]} \]

where \( a_0 \) is the concentration of a given functional group and \( a(t) \), which is equivalent to \( \alpha \), is the amount reacted when \( a_0 \) is assumed to be one. However, in this system, the concentration is not one and the rate equation is

\[ \frac{k}{a_0}t = \frac{l}{1-\alpha} \]

thus, the true \( k \) is equal to \( k/a_0 \). The following shows the calculation of \( a_0 \) for MDA, 4-aminodiphenylmethane, and NE, the three species which are used to calculate alpha (\( \alpha \)), from sample weights used in the experiments.

\( a_0 \) (MDA):
\[
\frac{(.0669 \ g \ MDA)}{(198.27 \ g/mol)} = 3.37 \times 10^{-4} \ mol \ MDA
\]

\[
3.37 \times 10^{-4} \ mol \ MDA \times 2 \ functional \ groups/MDA = 6.74 \times 10^{-4} \ mol \ functional \ groups
\]

\[
\frac{(6.74 \times 10^{-4} \ mol \ functional \ groups)}{(0.0669 \ g \ MDA + .1324 \ g \ NE) / 1150 \ g/L} = 3.9 \ mol/L
\]

\( a_0 \) (4-aminodiphenylmethane) when reacted with NE:
\[
\frac{(.0441 \ g \ amine)}{(183.25 \ g/mol)} = 2.40 \times 10^{-4} \ mol \ amine
\]

\[
\frac{(2.40 \times 10^{-4} \ mol \ amine)}{(0.0441 \ g \ amine + .0471 \ g \ NE) / 1100 \ g/L} = 2.6 \ mol/L
\]

\( a_0 \) (4-aminodiphenylmethane) when reacted with BTDE:
\[
\frac{(.0485 \ g \ amine)}{(183.25 \ g/mol)} = 2.65 \times 10^{-4} \ mol \ amine
\]

\[
\frac{(2.65 \times 10^{-4} \ mol \ amine)}{(0.0485 g \ amine + .0511 \ g \ BTDE) / 1100 \ g/L} = 2.9 \ mol/L
\]

\( a_0 \) (NE):
\[
\frac{(.0041 \ g \ NE)}{(196.2 \ g/mol)} = 2.07 \times 10^{-4} \ mol \ NE
\]

\[
\frac{(2.07 \times 10^{-4} \ mol \ NE)}{(0.0041 \ g \ NE + .0038 \ g \ monoamine) / 1100 \ g/L} = 2.6 \ mol/L
\]
BIBLIOGRAPHY


Young, P.R., and A.C. Chang, in *Proceedings of Second International Conference on Polyimides, October 30 - November 1, 1985, Ellenville, New York.*

Young, P.R., and A.C. Chang, 30th National SAMPE Symposium, 30, 889 (1985).
VITA

Kerri Ann Robillard