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Synthesis and characterization of maleimide-based polymers

Hua-Chin Chen

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SYNTHESIS AND CHARACTERIZATION
OF MALEIMIDE–BASED
POLYMERS

by
Hua–Chin Chen

Submitted to the Graduate School
of the Rochester Institute of Technology
in partial fulfillment of the Requirements
for the Degree of

Master of Science

November 1991

Dr. Andreas Langner
Project Advisor

Dr. Gerald A. Takacs
Chair, Department of Chemistry

Rochester Institute of Technology
Rochester, New York 14623
Department of Chemistry
Statement of Authorization

Title of thesis: Synthesis and Characterization of Maleimide-Based Polymers

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Date: November 27, 1991
to Mr. and Mrs. Chen,

my parents
Acknowledgements

My sincerest appreciation and gratitude goes to Dr. Andreas Langner for his support, encouragement, guidance and confidence in me.

I would like to thank Frank C. Hu, Hua-Wei Chen and friends for their support and understanding, especially during the final period of writing the thesis.

This thesis is dedicated to my parents, Mr. and Mrs. Yun-Liang Chen. They always stand by me. Thanks for their love.
SYNTHESIS AND CHARACTERIZATION OF MALEIMIDE-BASED POLYMERS

Abstract

This study concerns the synthesis and characterization of maleimide-based monomers and polymers. N-phenylmaleimide, 4’-N-maleimido-2,3’-dimethylazobenzene and N-p-chlorophenylmaleimide monomers were formed by imidizing maleic anhydride with aniline, 4’-amino-2,3’-dimethylazobenzene and p-chloroaniline, respectively. But N-nitrophenylmaleimide monomer was produced from the nitration of N-phenylmaleimide monomer. The two homopolymers, poly-(N-p-chlorophenylmaleimide) and poly-(N-nitrophenylmaleimide), were synthesized by solution polymerization in toluene solvent. Poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene), each with compositions of [50:50] and [92:8], were produced by imidizing maleic anhydride constructing commercial poly-(Styrene-co-maleic anhydride); [50:50] and [92:8]. Styrene and N-phenylmaleimide monomers were copolymerized in both solution and emulsion to form poly-(Styrene-co-N-phenylmaleimide). Likewise, styrene and 4’-N-maleimido-2,3’-dimethylazobenzene were copolymerized in both solution and emulsion to form poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene). In all, four maleimide monomers, two maleimide homopolymers, and eight maleimide copolymers were synthesized in this study.
Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis and Differential Scanning Calorimetry techniques were utilized to carry out qualitative and quantitative analyses. The yields of the four monomers were not as high as expected, since toluene was not as good a solvent as either xylene or ethyl ether. However, the purities of the four monomers were considered to be very high. In addition, it is seen that the nitro group was a stronger electron-withdrawing group and led to a less thermally stable polymer compared to the chloro group. Based on the FTIR spectra of these copolymers, the following observations were made: (1) the formation of N-phenylmaleimide products from the imidization of maleic anhydride was more complete than the 4’-N-maleimido-2,3’-dimethylazobenzene products, (2) the imidization of maleic anhydride was complete for the [92:8] copolymers, but incomplete for the [50:50] copolymers, (3) polymerization reactions including both emulsion and solution polymerizations were preferred over imidization reaction, and (4) solution polymerization was more favorable in the incorporation of imide than emulsion polymerization. From the analogy of TGA and DSC characteristics, the [50:50] and [92:8] polymers were alternating and random copolymers, respectively. Polymers synthesized by emulsion and solution polymerizations were random copolymers. The emulsion polymerized materials decomposed at higher temperatures than the solution polymerized materials. Most of the copolymer products were amorphous copolymers as no crystallization or melting behavior was observed on their DSC thermograms.
# Table of Contents

**Introduction** .......................................................... 1

**Experimental** .......................................................... 14

- Apparatus and Reagents ............................................. 14
- Preparations .......................................................... 14
  - Table 1. Reagents Used ........................................... 16
  - Table 2. Products Synthesized .................................. 17
  - Table 2a. Page Numbers of Analysis Graphs ................. 18
- Characterization ..................................................... 29
  - FT-IR ................................................................... 29
  - Figures 2-12 ......................................................... 34
- TGA ........................................................................ 45
- DSC ........................................................................ 46

**Results** .................................................................. 49

- FT-IR Analysis ......................................................... 49
- Thermal Analysis ...................................................... 53
- Table 3. Frequency and Coefficient B for Polystyrene .... 56
- Table 4. θ 1 (l/mole) Values .................................... 57
- Table 5. Constituents of Various Copolymers ............... 58
- Table 6. Constituents of Various Copolymers ............... 59
- Table 7. Decomposition Temperatures of Various Copolymers .. 60
- FT-IR Absorption Spectra (Figures 13-26) .................. 64
- TGA Thermograms (Figures 27-40) ............................. 78
- DSC Thermograms (Figures 41-51) ............................. 92

**Discussion** ............................................................. 103

**Conclusions** .......................................................... 117

**Appendix** .............................................................. 119

**References** ............................................................ 124
INTRODUCTION

Maleimide derivatives have been found to be easily copolymerized with a number of monomers such as styrene, methyl methacrylate and maleic anhydride. Maleimides, in addition to their traditional role in the synthesis of polymers, have also been investigated as potential antifungal substances.\(^1\) This study focused on maleimide-based polymers which were synthesized by imidization of maleic anhydride-based polymers or polymerization reactions.

N-substituted maleimides can be obtained by treatment of maleic anhydride with primary amines in an inert solvent. N-phenylmaleimide has also been prepared by mixing maleic anhydride and aniline in ethyl ether at room temperature, and by treating the maleanilic acid with a mixture of acetic anhydride and anhydrous sodium acetate.\(^2\) However, when the ethyl ether solvent was substituted by xylene; this yielded 90.3% N-phenylmaleimide.\(^3\) N-phenylmaleimide was not only synthesized by the reaction of maleanilic acid with acetic anhydride and sodium acetate as catalysts,\(^4,5\) but also by reaction with phosphorus pentoxide\(^6\) or phosphorus trichloride.\(^7\) Originally, in experiments where all the maleic anhydride was added at the start of the reaction sequence, yields were low as compared to adding additional maleic anhydride when the maleanilic acid had undergone partial dehydration.\(^8\)
Maleimides have been polymerized by addition polymerization with either free radical or anionic initiation. Anionic polymerization of N-phenylmaleimide was initiated with alkali metal tert-butoxides in THF, a so-called “slow-initiation” system.\(^{(9,10)}\) Polymerization took place only at the C=C bond although the monomer had a carbonyl group.\(^{(11)}\) Propagation occurred via a “living” mechanism without appreciable termination or chain-transfer reactions. The free radical polymerized homopolymers showed excellent thermal stability. Introduction of meta or para electron-donating substituents on N-phenylmaleimide enhanced its polymerization reactivities; substitution of electron-withdrawing groups at the ortho position decreased reactivities.\(^{(12)}\)

The free radical-initiated copolymerization of N-phenylmaleimide with styrene yielded a nearly equimolar alternating copolymer, and the monomer feed ratios was found not to be a factor.\(^{(13,14)}\) The maleimides form alternating copolymers with styrene; reactivity of the maleimides decreased with increasing substituent bulkiness.\(^{(12)}\) N-phenylmaleimide was polymerized with maleic anhydride to produce a 1:1 copolymer,\(^{(15)}\) and with maleic anhydride and styrene to form a terpolymer.\(^{(16)}\)

An imidization reaction is a process in which amines are reacted with carboxylic acids or anhydrides to produce imides. In this study, the syntheses of
N-phenylmaleimide, 4'-N-maleimido-2,3'-dimethylazobenzene and N-p-chlorophenylmaleimide are carried out by imidization reactions. Maleic anhydride is the starting material. That reacts with aniline, 4'-amino-2,3'-dimethylazobenzene and p-chloroaniline to form N-phenylmaleimide, 4'-N-maleimido-2,3'-dimethylazobenzene and N-p-chlorophenylmaleimide, respectively.

The imidization reaction of maleic anhydride is a two-step condensation reaction. In the first step, maleic anhydride is dissolved in a toluene solvent which then reacts with the primary amine to produce an intermediate product, N-substituted maleamic acid. In the second step which is performed at an elevated temperature in a mixture of sodium acetate and acetic anhydride, the intermediate product undergoes dehydration and ring closure to produce N-substituted maleimide.

The mechanism of the imidization reaction is given by the following sequence:

\[
\begin{align*}
\text{CH}_3 \quad \text{CH}_3 \\
\begin{array}{c}
\text{O} \\
\text{H}_2 \text{N}-\text{R} \\
\text{O} \\
\end{array}
& \quad \begin{array}{c}
\text{CH}_3 \\
\text{NH}-\text{R} \\
\text{H}_2 \text{O} \\
\end{array}
\begin{array}{c}
\text{O} \\
\text{O}_2 \text{C} \\
\text{H}_2 \text{O} \\
\end{array}
& \quad \begin{array}{c}
\text{CH}_3 \\
\text{NH}-\text{R} \\
\text{H}_2 \text{O} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{NH}-\text{R} \\
\text{H}_2 \text{O} \\
\text{O}_2 \text{C} \\
\end{array}
& \quad \begin{array}{c}
\text{O} \\
\text{O}_2 \text{C} \\
\text{OH} \\
\end{array}
\end{align*}
\]
The N-nitrophenylmaleimide monomer is produced by nitrating N-phenylmaleimide. The reaction proceeds according to the following sequence:

\[
\begin{align*}
\text{N-H} - \text{R} \quad &\xrightarrow{\triangle} \quad \text{CH}_3\text{COONa} + (\text{CH}_3\text{CO})_2\text{O} \quad \rightarrow \\
&\quad \text{N-R} + 2\text{CH}_3\text{COOH} \quad (2)
\end{align*}
\]

\[ R = \begin{array}{c}
\text{C} \\
\text{H}_3
\end{array} ,
\begin{array}{c}
\text{C} \\
\text{H}_3 \\
\text{N}=\text{N}
\end{array} \begin{array}{c}
\text{C} \\
\text{H}_3
\end{array} ,
\begin{array}{c}
\text{C} \\
\text{Cl}
\end{array}
\]

The maleimides homopolymerize easily in the presence of either azobisisobutyronitrile (AIBN) or benzoyl peroxide which acts as an initiator. This is because the olefinic bond of a maleimide is reactive in addition polymerization with either free radical or anionic initiation. In the preparations of poly-(N-nitrophenylmaleimide) and poly-(N-p-chlorophenylmaleimide), benzoyl peroxide is used as the initiator. Here a free radical polymerization occurs. It proceeds by the following reaction mechanism:
Initiation.

\[
\text{Initiation.} \\
\begin{align*}
2 \text{Ph-C-O-O-Ph} & \xrightarrow{\Delta} 2 \text{Ph-C-O-} & \xrightarrow{} 2 \text{Ph} + 2 \text{CO}_2 \\
\text{Ph-} & + \text{M} \rightarrow \text{Ph-M-}
\end{align*}
\]  

Propagation.

\[
\text{Propagation.} \\
\begin{align*}
\text{Ph-M-} + \text{M} & \rightarrow \text{Ph-M-M-} \\
\text{Ph-M-M-} & \overset{n \text{M}}{\rightarrow} \text{Ph-} (\text{M})_{n+1} \text{-M-}
\end{align*}
\]  

Termination.

(1) Combination:

\[
\begin{align*}
\text{Ph-M-} + \cdot \text{M} & \rightarrow \text{Ph-M-M-} \\
\end{align*}
\]  

(2) Disproportionation:

\[
\begin{align*}
\text{Ph-M-} + \cdot \text{M} & \rightarrow \text{Ph-M-} \cdot \text{H} + \text{M=}_\text{C-}
\end{align*}
\]
In the above reaction, M represents either the N-nitrophenylmaleimide monomer or the N-p-chlorophenylmaleimide monomer. During a polymerization reaction, both termination mechanisms may occur together or singularly. The occurrence of termination mechanisms depends on the experimental conditions and the monomers involved. Disproportionation is favored at higher temperatures.

For copolymerization of two monomer types, there are four possible ways the propagation step can take place:

\[ \text{M}_{1}\text{.} + \text{M}_{1} \xrightarrow{k_{11}} \text{M}_{1}\text{M}_{1}\text{.} \]  \hfill (10)

\[ \text{M}_{1}\text{.} + \text{M}_{2} \xrightarrow{k_{12}} \text{M}_{1}\text{M}_{2}\text{.} \]  \hfill (11)

\[ \text{M}_{2}\text{.} + \text{M}_{1} \xrightarrow{k_{21}} \text{M}_{2}\text{M}_{1}\text{.} \]  \hfill (12)

\[ \text{M}_{2}\text{.} + \text{M}_{2} \xrightarrow{k_{22}} \text{M}_{2}\text{M}_{2}\text{.} \]  \hfill (13)

\( \text{M}_{1} \) and \( \text{M}_{2} \) represent monomer 1 and monomer 2. The reactivity ratios of \( \text{M}_{1} \) and \( \text{M}_{2} \) are defined as \( r_{1} = \frac{k_{11}}{k_{12}} \) and \( r_{2} = \frac{k_{22}}{k_{21}} \), respectively. The copolymer structure can be predicted according to the \( r_{1} \) and \( r_{2} \) values.\(^{(17)}\)
In the system of styrene \((M_1)\) and N-phenylmaleimide \((M_2)\) copolymer, as an example, \(r_1 = 0.0066\) and \(r_2 = 0.1615\); the copolymer is predicted to be an alternating copolymer.\(^{(13)}\)

In this investigation, poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene) are copolymerized by both emulsion and solution free radical polymerization. These two polymerization methods have their differences as will be described below.

In emulsion polymerization two immiscible liquid phases are present; these are usually an aqueous continuous phase and a nonaqueous discontinuous phase. The latter consists of monomer and polymer. The essential ingredients in an emulsion polymerization are water, a monomer which is not soluble in water, an oil-in-water surfactant, and an initiator which can provide a small amount of free radicals to the monomer phase. As an example, the recipe of poly-(Styrene-co-N-phenylmaleimide) is given as follows:

\[
\begin{array}{c|c|c|c|c}
 r_1 & r_2 & r_1r_2 & \text{Copolymer structure} \\
\hline
 r_1 = \frac{1}{r_2} & r_2 = \frac{1}{r_1} & 1 & \text{Random (ideal)} \\
<< 1 & << 1 & --> 0 & \text{Alternating} \\
>> 1 & < 1 & < 1 & \text{Tends to be homopolymer of } M_1 \\
\end{array}
\]
<table>
<thead>
<tr>
<th>Component</th>
<th>Weight, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SDS (sodium dodecyl sulfate); surfactant</td>
<td>0.50</td>
</tr>
<tr>
<td>HPLC water</td>
<td>670.00</td>
</tr>
<tr>
<td>N-phenylmaleimide; monomer</td>
<td>5.00</td>
</tr>
<tr>
<td>Styrene; monomer</td>
<td>13.64</td>
</tr>
<tr>
<td>Sodium persulfate; initiator</td>
<td>0.03</td>
</tr>
<tr>
<td>Sodium metabisulfite; initiator</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The initiator is miscible in the aqueous phase.

At the beginning of the reaction the surfactant surrounds a small pool of monomer to form a micelle. However, most of the monomer exists as suspended droplets. The polymerization takes place in the micelles, thus the reaction is determined by the degree of diffusion of monomers into the micelles. Very little initiator is activated in the micelle at any given time. As polymer is formed, the micelles grow by the addition of monomer dispersed in the aqueous phase and ultimately from the suspended monomer droplets. The terminated product contains, in addition to polymer, surfactant, initiator and monomer. Dialysis is generally required to purify the material.

In solution polymerization, the monomer is dissolved in a solvent prior to polymerization. The solvent facilitates contact of monomer with a reaction initiator, which may or may not be soluble in the solvent, and assists in the dissipation of the heat of the exothermic reaction. As an example, toluene is the
solvent and AIBN is used as the initiator for both the preparations of poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-co-4′-N-maleimido-2,3′-dimethylazobenzene) discussed in this study. AIBN is activated by heating it to produce free radicals as is depicted below,

\[
\begin{align*}
\text{C}_2\text{H}_3 - \text{C} - \text{N} = \text{N} - \text{C} - \text{C}_2\text{H}_3 & \xrightarrow{\Delta} 2 \text{C}_2\text{H}_3 - \text{C}^* + \text{N}_2
\end{align*}
\]

Chain transfer is a possible pathway of terminating the polymerization in solution free radical polymerization; it could take place with solvent, initiator and monomer to depress molecular weight of polymer in polymerization reaction.

A comparison of the advantages and disadvantages of emulsion and solution polymerization is given in the following table.\(^{(18)}\)

<table>
<thead>
<tr>
<th>Type</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emulsion</td>
<td>Rapid polymerization to high molecular weight and narrow distribution, with ample heat control.</td>
<td>Contamination with surfactant, leading to poor color and color stability.</td>
</tr>
</tbody>
</table>
Solid product readily obtainable. Washing, drying may be required.

Solution

Ample control of the heat of polymerization. Difficulty of complete solvent removal.

Solution may be directly usable.

In this study, Fourier Transform Infrared Spectroscopy, Thermogravimetric Analysis and Differential Scanning Calorimetry instrumentation is utilized to confirm the identity of specific polymer products, to determine the constituent concentrations of the copolymers, and to study the polymer products’ thermal properties such as decomposition temperatures and glass transition temperatures.

The application of FT-IR spectroscopy is normally associated with the spectrum range between 625 and 4000 cm\(^{-1}\). And the FT-IR spectrum is often utilized in the qualitative application of characterizing a polymer’s structure. After a spectrum has been obtained, the functional groups corresponding to those absorption bands are identified. Since characteristic frequencies often overlap, a complete analysis is difficult. Thus, the Sadtler reference literature spectra of
maleic anhydride, maleanilic acid, N-phenylmaleimide, N-o-nitrophenylmaleimide and N-p-chlorophenylmaleimide are presented to provide information about product purity. The quantitative application of FT-IR spectroscopy is based on the Beer-Lambert law. In the low concentration range the more simplified Beer’s law is appropriate. The relationship between absorbance and concentration in Beer’s law is linear. The constituent concentrations of various copolymers can generally be established by using Beer’s law.

Thermogravimetric analysis is a dynamic method in which the weight loss of a sample is measured continuously as a function of temperature at a constant rate. Heating rate is a factor to affect the appearance of a thermogram. When a faster heating rate is applied, the thermogravimetric curve shifts to lower temperatures. A thermogram can be used to study the decomposition mechanism referred to the weight loss of the sample; also, it is useful to study the thermal stability of a polymer according to the decomposition temperature. In addition, a thermogram can give information of the monomer sequence on a copolymer chain. One weight loss shoulder obtained on a thermogram indicates that the copolymer is a random copolymer and the weight loss is due to the bond breakage between two monomers. For a block copolymer, two shoulders which result from the bond breakage between like monomers will be obtained on a thermogram. However, some pendent groups such as nitro and carbon dioxide may liberate from polymer chain; this takes place at a lower temperature compared to the decomposition temperature of polymer. This also leads to two
weight loss transitions.

The change between rubbery liquid and glassy behavior is known as the glass transition. The glass transition is a characteristic phenomenon of amorphous polymers; it can be detected by using the DSC technique. The glass transition is a second-order transition and it causes abrupt changes in the slope of a DSC thermogram. The temperature of glass transition can be affected by the degree of cross-linking and crystallinity, molecular weight, polymer structure and heating rate. The Fox equation\(^{(19)}\) derived for random copolymers is presented as the following:

\[
\frac{1}{T_g} = \frac{M_1}{T_{g1}} + \frac{M_2}{T_{g2}} \tag{15}
\]

here, \(T_g\) = glass transition temperature of copolymer
\(T_{g1}\) = glass transition temperature of monomer 1
\(T_{g2}\) = glass transition temperature of monomer 2
\(M_1\) = weight fraction of monomer 1
\(M_2\) = weight fraction of monomer 2

this equation usually predicts a too high value of \(T_g\) for random copolymers. If a copolymer is a block copolymer, two distinguishable glass transitions from each monomer will be obtained. A random copolymer; however, has only one glass
transition which occurs between the two individual transitions of the respective monomers; the glass transition temperature can be approximated by the Fox equation prior to the analysis of the copolymer by DSC. A DSC thermogram can also give information about polymers, such as the melting point, decomposition temperature, heat of fusion, heat of crystallization, specific heat and entropy of transition.

The objectives of this study were to: (1) study the influence of solvent such as toluene on the product yield of imidization reaction, (2) study the reaction reactivities of different structural materials such as N-phenylmaleimide and 4′-N-maleimido-2,3′-dimethylazobenzene with styrene, (3) determine the thermal stabilities of N-phenylmaleimide that has nitro substituent attached to the ring structure with N-phenylmaleimide that has chloro substituent attached to the ring structure, (4) compare imidization with polymerization reaction in the synthesis of poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-co-4′-N-maleimido-2,3′-dimethylazobenzene), (5) compare emulsion with solution polymerization reaction in the synthesis of poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-co-4′-N-maleimido-2,3′-dimethylazobenzene), and (6) apply FT-IR spectra in the quantitative analyses by Beer’s Law of all the synthesized copolymer products.
EXPERIMENTAL APPARATUS and REAGENTS:

The apparatus used in the synthesis of all fourteen products is schematically illustrated in Figure 1. The system consisted of a 1-liter three-necked round-bottom flask. Nitrogen was continuously fed into the flask through neck B during the entire synthesis period. This provided a constant nitrogen blanket, intended to prevent oxidation of the reactants. A thermometer was inserted in neck C to monitor the reaction temperature. Reactants were also injected into the flask through this neck. Neck A had a reflux condenser connected to it to condense the vaporized reactant and solvent back into the flask. A heating mantle maintained a constant temperature with a fluctuation of ±5°C in the flask and provided the heat necessary to drive and maintain the reaction. A magnetic stirrer provided the constant agitation needed to keep the reactants in suspension to promote uniform reaction conditions throughout the flask. All apparatus were kept dry, because the imidization reaction is sensitive to water. The reagents used in this synthesis are listed in Table 1.

PREPARATIONS:

Of the fourteen products synthesized in this study, four were monomers, two were homopolymers, and eight were copolymers. Table 2 lists the name, the type of polymerization, and the solvent used in the synthesis of each product. The detailed procedures regarding the synthesis of these fourteen products are given in the following pages.
Figure 1. Apparatus for Polymer Synthesis

1. 1-Liter Three-Necked Round-Bottom Flask with Necks A, B, and C (24/40 fittings)
2. Heating Mantle
3. Magnetic Stirrer
4. Stirrer Bar
5. Thermometer
6. Pipette with Drying Reagent (Calcium Chloride) on the Top
7. Nitrogen
8. Reflux Condenser
9. Drying Tube with Calcium Chloride
Table 1. Reagents Used

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Manufacturer: Cat No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic anhydride</td>
<td>A; 0018-01</td>
</tr>
<tr>
<td>AIBN (2,2'-azobis(2-methylpropionitrile))</td>
<td>B; 6400</td>
</tr>
<tr>
<td>Aniline</td>
<td>A; 9110-01</td>
</tr>
<tr>
<td>Benzoyl peroxide</td>
<td>F; B-274</td>
</tr>
<tr>
<td>p-Chloroaniline</td>
<td>B; 106 4849</td>
</tr>
<tr>
<td>Chloroform</td>
<td>A; 9180-01</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>A; 9206-01</td>
</tr>
<tr>
<td>Ethanol</td>
<td>C; 200 Proof</td>
</tr>
<tr>
<td>Fast garnet GBC base (4’-amino-2,3’-dimethylazobenzene)</td>
<td>D; 97-56-3</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>B; 112 4650</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>A; 9324-01</td>
</tr>
<tr>
<td>Nitric acid, Fuming, 90%</td>
<td>A; 9624-02</td>
</tr>
<tr>
<td>Poly-(Styrene-co-maleic anhydride); [50:50]</td>
<td>E; 9182</td>
</tr>
<tr>
<td>Poly-(Styrene-co-maleic anhydride); [92:8]</td>
<td>E; 8821</td>
</tr>
<tr>
<td>Sodium acetate anhydrous</td>
<td>A; 3470-01</td>
</tr>
<tr>
<td>SDS (sodium dodecyl sulfate)</td>
<td>D; 151-21-3</td>
</tr>
<tr>
<td>Sodium metabisulfite</td>
<td>D; 7681-57-4</td>
</tr>
<tr>
<td>Sodium persulfate</td>
<td>D; 7775-27-1</td>
</tr>
<tr>
<td>Styrene</td>
<td>D; 100-42-5</td>
</tr>
<tr>
<td>Sulfuric acid, 95-98%</td>
<td>A; 9681-01</td>
</tr>
<tr>
<td>Toluene ‘Photrex’</td>
<td>A; 9456-1</td>
</tr>
</tbody>
</table>

B= Eastman Kodak Co.                                                      
C= AAPER Alcohol & Chemical Co.                                           
D= Aldrich Chemical Co.                                                   
E= Monomer-Polymer and Dajac Laboratories, Inc.
### Table 2. Products Synthesized

<table>
<thead>
<tr>
<th>Name</th>
<th>Type of Polymerization</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-phenylmaleimide</td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>4’-N-maleimido-2,3’-dimethylazo-benzene</td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>N-nitrophosphynmaleimide</td>
<td></td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>N-p-chlorophosphynmaleimide</td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>Poly-(N-nitrophosphynmaleimide)</td>
<td>Solution</td>
<td>Toluene</td>
</tr>
<tr>
<td>Poly-(N-p-chlorophosphynmaleimide)</td>
<td>Solution</td>
<td>Toluene</td>
</tr>
<tr>
<td>Poly-(Styrene-co-N-phenylmaleimide); [50:50]</td>
<td></td>
<td>Toluene</td>
</tr>
<tr>
<td>Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [50:50]</td>
<td></td>
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Table 2a. Page Numbers of Analysis Graphs

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<th>Name</th>
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<th>DSC</th>
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**N-phenylmaleimide**

Maleic anhydride, in the amount of 23.3 g (0.24 mole) in 500 ml of toluene, was placed into the 1-liter flask and stirred under nitrogen. A solution consisting of 22.15 ml (0.24 mole) of aniline in 75 ml of toluene was then added to the same flask. The resulting solution, in the presence of a nitrogen blanket, was stirred at room temperature for 2 hours and then cooled to 0\(^\circ\)C in an ice bath. Product (maleanilic acid) precipitated during cooling was suction filtered, then washed with 100 ml of toluene, and finally dried for 24 hours under vacuum. The dried maleanilic acid was next recrystallized from ethanol cooled from 50\(^\circ\)C.

To synthesize N-phenylmaleimide, 5 g (0.061 mole) of sodium acetate in 40 ml of acetic anhydride was placed into the 1-liter flask, stirred continuously at 70\(^\circ\)C under a nitrogen blanket. To this was added 20 g (0.105 mole) of the maleanilic acid, obtained as described above. The mixture was stirred for 1 hour at 70\(^\circ\)C while under a nitrogen blanket; then it was cooled to 0\(^\circ\)C in an ice bath. The precipitated product was first suction filtered, then washed with 0\(^\circ\)C distilled water, and lastly dried for 12 hours in a vacuum oven maintained at 70\(^\circ\)C. Recrystallization from cyclohexane cooled from 70\(^\circ\)C yielded 18 g (0.104 mole) of bright yellow-colored N-phenylmaleimide, m.p. 90-92\(^\circ\)C. (mp 89-89.8\(^\circ\)C, Merck II, 7270)
4'-N-maleimido-2,3’-dimethylazobenzene

A solution of 25.34 g (0.26 mole) of maleic anhydride in 400 ml of toluene was stirred and heated to 40°C under nitrogen in the 1-liter flask. A solution consisting of 60 g (0.27 mole) of fast garnet GBC base (4’-amino-2,3’-dimethylazobenzene), in 350 ml of toluene was then added to the same flask. The reaction mixture was stirred at 40°C under nitrogen for 2 hours and then cooled in an ice bath. The product N-substituted maleamic acid was suction filtered, washed with 100 ml of toluene, and then dried for 24 hours under vacuum.

To execute the ring closure of the maleamic acid, 15 g (0.18 mole) of sodium acetate in 150 ml of acetic anhydride was placed into the 1-liter flask, stirred and heated to 70°C under a nitrogen blanket. All of the maleamic acid prepared above was added to the flask. The mixture was continuously stirred for 3 hours at 70°C; then it was poured into 400 ml of cold distilled water and stirred vigorously with a glass rod. The cooled suspension was filtered, then washed with 0°C distilled water, and dried for 12 hours in a vacuum oven maintained at 70°C. After recrystallization from cyclohexane cooled from 70°C, 20 g (0.066 mole) of dark red-colored 4’-N-maleimido-2,3’-dimethylazobenzene, m.p. 97-100°C, was obtained, for a product yield of 24%.

N-nitrophenylmaleimide

Ten grams (0.058 mole) of N-phenylmaleimide were put in the 1-liter flask
set in an ice/acetone bath. 20 ml of concentrated sulfuric acid were added slowly to the flask; then the solution was stirred vigorously for 15 minutes. A solution (nitrating agent) of 4.5 ml of concentrated nitric acid and 4.5 ml of concentrated sulfuric acid was added dropwise into the same flask while maintaining constant mixing. The temperature of the reaction mixture was maintained below 5°C and the mixture was continuously stirred for 30 minutes. After the reaction was finished, the solution was poured into 200 ml of 0°C distilled water. The cooled solution was suction filtered, washed with 0°C distilled water till the filtrate was neutral, and dried under vacuum for 24 hours. Recrystallization from cyclohexane cooled from 70°C resulted in 10.1 g (0.046 mole) of orange yellow-colored N-nitrophenylmaleimide, m.p. 125-130°C, for a crude product yield of 80%.

**N-p-chlorophenylmaleimide**

Maleic anhydride, in the amount of 23.3 g (0.24 mole) in 500 ml of toluene, was placed into the 1-liter flask and stirred under nitrogen. A solution consisting of 30.62 g (0.24 mole) of p-chloroaniline in 75 ml of toluene was then added to the same flask. The resulting solution, in the presence of a nitrogen blanket, was stirred at 40°C for 2 hours and then cooled to 0°C in an ice bath. Product (4-chloro-maleanilic acid) precipitated during cooling was suction filtered, then washed with 100 ml of toluene, and finally dried for 24 hours under vacuum. The dried 4-chloro-maleanilic acid was next recrystallized from
To synthesize N-p-chlorophenylmaleimide, 5 g (0.061 mole) of sodium acetate in 40 ml of acetic anhydride was placed into the 1-liter flask, stirred continuously at 70°C under a nitrogen blanket. To this was added 20 g (0.089 mole) of the maleanilic acid, obtained as described above. The mixture was stirred for 1 hour at 70°C while under a nitrogen blanket; then it was cooled to 0°C in an ice bath. The precipitated product was first suction filtered, then washed with 0°C distilled water, and lastly dried for 12 hours in a vacuum oven maintained at 70°C. Recrystallization from cyclohexane cooled from 70°C resulted in 16.6 g (0.08 mole) of bright yellow green-colored N-p-chlorophenylmaleimide, m.p. 113-115°C, for a product yield of 90%.

**Poly-(N-nitrophenylmaleimide): Solution Polymerization**

N-nitrophenylmaleimide, in the amount of 2 g in 100 ml of toluene, was placed into the 1-liter flask and stirred under nitrogen then heated to 90°C. After the desired temperature of 90°C was reached, 0.02 g of benzoyl peroxide, acting as the initiator, was added to the 1-liter flask. The resulting solution, in the presence of a nitrogen blanket, was stirred at 90°C for 4 hours and then cooled to 0°C in an ice bath. The product, poly-(N-nitrophenylmaleimide), precipitated during cooling and was suction filtered, then washed with 100 ml of toluene, and finally dried for 24 hours under vacuum. The dried poly-(N-nitrophenylmaleimide) was light yellow in color, and 0.4 g of this powder-like
material was obtained, for a crude product yield of 20%. The low yield may have been due to the redissolution of low molecular weight polymer by the toluene used to wash the filtrate product.

Poly-(N-p-chlorophenylmaleimide): Solution Polymerization

N-p-chlorophenylmaleimide, in the amount of 2 g in 100 ml of toluene, was placed into the 1-liter flask and stirred under nitrogen then heated to 90°C. After the desired temperature of 90°C was reached, 0.02 g of benzoyl peroxide acting as the initiator was added to the 1-liter flask. The resulting solution, in the presence of a nitrogen blanket, was stirred at 90°C for 4 hours and then cooled to 0°C in an ice bath. The product, poly-(N-p-chlorophenylmaleimide), precipitated during cooling and was suction filtered, then washed with 100 ml of toluene, and finally dried for 24 hours under vacuum. The dried poly-(N-p-chlorophenylmaleimide) was white in color and 0.8 g of this powder-like material was obtained, for a crude product yield of 40%. As in the previous case of poly-(N-nitrophenylmaleimide), the low yield was due to the redissolving of the low molecular weight polymer during the washing process with toluene, thus leaving only the high molecular weight polymer in the product.

Poly-(Styrene-co-N-phenylmaleimide): [50:50]

A solution of 25 g of poly-(Styrene-co-maleic anhydride); [50:50] in 260 ml of toluene was deoxygenated by the bubbling of nitrogen through the stirred
solution at room temperature. A solution of aniline (11.5 ml) in 39 ml of toluene was added to the same flask kept under a nitrogen blanket. This yielded a 1:1 molar ratio of aniline and maleic anhydride. The reaction mixture was continuously stirred at room temperature for 4 hours and then quench cooled to 0 °C in an ice bath. The precipitate was first suction filtered, then washed with 100 ml of toluene, and then finally dried under vacuum for 24 hours. The maleanilic acid copolymer was purified by recrystallization from toluene cooled from 80°C.

Ten grams of the maleanilic acid copolymer was added to a stirred solution of acetic anhydride (20 ml) and sodium acetate (2.5 g) kept under nitrogen at 70°C. The mixture was stirred for 3 hours, then it was poured into 250 ml of HPLC water in an ice bath. The cooled mixture was filtered then washed with 100 ml of cold HPLC water and vacuum dried for 24 hours. After recrystallization from cyclohexane cooled from 70°C, 4.7 g of orange-colored poly-(Styrene-co-N-phenylmaleimide); [50:50] was obtained.

Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]

A solution consisting of 26 g of poly-(Styrene-co-maleic anhydride); [50:50] in 200 ml of toluene was stirred and heated to 40°C under nitrogen. A solution of 30 g of fast garnet GBC base (4'-amino-2,3'-dimethylazobenzene) in 175 ml of toluene was added to the copolymer solution. This yielded a 1:1 molar ratio of the azo dye and maleic anhydride. The reaction mixture was continuously stirred under nitrogen for 4 hours and then cooled in an ice bath.
The quenched solution was suction filtered, washed with 200 ml of toluene, and then dried for 24 hours under vacuum. 24.36 g of maleamic acid copolymer was obtained.

To perform the ring closure of the maleamic acid, 3.75 g of sodium acetate in 30 ml of acetic anhydride was placed into the 1-liter flask, stirred and heated to 70°C under a nitrogen blanket. 15 g of the maleamic acid copolymer prepared above was added to the flask. The mixture was continuously stirred for 4 hours at 70°C; then it was poured into 200 ml of cold distilled water and stirred vigorously with a glass rod. The cooled suspension was suction filtered, then washed with 0°C distilled water, and dried for 12 hours in a vacuum oven maintained at 70°C. After recrystallization from ethanol cooled from 50°C, 3.5 g of dark red-colored poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50] was obtained.

Poly-(Styrene-co-N-phenylmaleimide); [92:8]

A solution of 25 g of poly-(Styrene-co-maleic anhydride); [92:8] in 300 ml of toluene was deoxygenated by the bubbling of nitrogen through the stirred solution at room temperature. A solution of aniline (11.5 ml) in 39 ml of toluene was added to the same flask kept under a nitrogen blanket. The reaction mixture was continuously stirred at room temperature for 3 hours and then quench cooled to 0 °C in an ice bath. The quenched solution was first distilled to evaporate toluene out of the solution at 100°C for 24 hours and then dried in a vacuum oven.
maintained at 70°C for 48 hours. The maleanilic acid copolymer was brittle and light brown.

An amount of 8.7 g of the maleanilic acid copolymer was added to a stirred solution of acetic anhydride (60 ml) and sodium acetate (5.0 g) kept under nitrogen at 70°C. The mixture was stirred for 4 hours, then it was poured into 150 ml of iced distilled water in an ice bath and stirred vigorously with a glass rod. The cooled mixture was filtered, then washed with cold distilled water and dried in a vacuum oven at 70°C for 24 hours. The resulting dark yellow-colored product was dissolved in methylene chloride and stored as a solution. For the characterization step, the product was dried under vacuum prior to being analyzed with FT-IR, TGA, and DSC.

Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene): [92:8]

A solution consisting of 26 g of poly-(Styrene-co-maleic anhydride); [92:8] in 200 ml of toluene was stirred and heated to 40°C under nitrogen. A solution of 30 g of fast garnet GBC base (4’-amino-2,3’-dimethylazobenzene) in 70 ml of toluene was added to the copolymer solution. The reaction mixture was continuously stirred under nitrogen for 4 hours and then cooled in an ice bath. The quenched solution was first distilled to remove toluene from the solution at 100°C for 6 hours, then the sticky and thick liquid was dried in a vacuum oven maintained at 70°C for 24 hours.

To perform the ring closure of the maleamic acid, 12.5 g of sodium acetate in 150 ml of acetic anhydride was placed into the 1-liter flask, stirred and heated
to 70°C under a nitrogen blanket. 30 g of the maleamic acid copolymer prepared above was added to the flask. The mixture was continuously stirred for 4 hours at 70°C; then it was poured into 200 ml of cold distilled water and stirred vigorously with a glass rod. The cooled suspension was suction filtered, then washed with 0°C distilled water, and dried for 24 hours in a vacuum oven maintained at 100°C. 36.65 g of dark red-colored poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [92:8] was obtained. The increase in mass of more than 6.65 g was due to undissolved acetic anhydride that remained with the polymer product.

**Poly-(Styrene-co-N-phenylmaleimide): Emulsion Polymerization**

A solution of 0.5 g of SDS (surfactant) in 670 ml of HPLC water was deoxygenated by bubbling nitrogen through the stirred solution at room temperature for 8 minutes. A solution of 5 g (0.029 mole) of N-phenylmaleimide (monomer) in 15 ml (0.131 mole) of styrene (monomer) was added to the same flask kept under nitrogen and heated to 60°C. After the desired temperature of 60°C was reached, a solution consisting of 0.06 g of sodium metabisulfite (initiator) and 0.03 g of sodium persulfate (initiator) in 5 ml of HPLC water was added to the flask. The reaction mixture was continuously stirred at 60°C for 3 hours and then quench cooled to 0 °C in an ice bath. The quenched solution was a white-colored milk-like emulsion. It was dialyzed in distilled water for 12 hours and subsequently stored in a brown bottle.
Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Emulsion Polymerization

A solution of 0.5 g of SDS (surfactant) in 670 ml of HPLC water was deoxygenated by bubbling nitrogen through the stirred solution at room temperature for 8 minutes. A solution of 2 g (0.0066 mole) of 4'-N-maleimido-2,3'-dimethylazobenzene (monomer) in 8 ml (0.0699 mole) of styrene (monomer) was added to the same flask while under nitrogen and heated to 60°C. After the desired temperature of 60°C was reached, a solution consisting of 0.06 g of sodium metabisulfite (initiator) and 0.03 g of sodium persulfate (initiator) in 5 ml of HPLC water was added to the flask. The reaction mixture was continuously stirred at 60°C for 3 hours and then quench cooled to 0 °C in an ice bath. The quenched solution was a dark orange-colored emulsion. It was dialyzed in distilled water for 24 hours, then stored in a brown bottle.

Poly-(Styrene-co-N-phenylmaleimide); Solution Polymerization

A solution consisting of 2 g (0.012 mole) of N-phenylmaleimide (monomer) in 100 ml of toluene was stirred and heated to 85°C under nitrogen. When the temperature of 85°C, the working temperature of the initiator, was reached, a solution of 0.1 g of AIBN (initiator) and 5 ml (0.044 mole) of styrene (monomer) in 15 ml of toluene was added to the monomer solution. The reaction mixture was continuously stirred under nitrogen for 3 hours and then quench cooled in an ice bath. The quenched solution was first suction filtered,
washed with 100 ml of toluene, and then dried under vacuum for 24 hours. White-colored precipitates were obtained.

Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Solution Polymerization

A solution consisting of 2 g (0.0060 mole) of 4’-N-maleimido-2,3’-dimethylazobenzene (monomer) in 100 ml of toluene was stirred and heated to 85°C under nitrogen. When the temperature of 85°C, the working temperature of the initiator, was reached, a solution of 0.06 g of AIBN (initiator) and 6 ml (0.0524 mole) of styrene (monomer) in 15 ml of toluene was added to the monomer solution. The reaction mixture was continuously stirred under nitrogen for 3 hours and then quench cooled in an ice bath. The quenched solution was a dark orange-colored solution kept in a brown bottle.

CHARACTERIZATION:

This section includes the three techniques that were utilized to confirm products, to determine the composition of copolymers, and to characterize polymers based on thermal properties.

FT-IR (Fourier Transform Infrared Spectroscopy)

FT-IR is useful for both qualitative and quantitative analyses. All fourteen
products were analyzed as solutions using a Perkin Elmer 1760X FT-IR Spectrometer. The PE 1760X FT-IR is a computer-interfaced single-beam instrument capable of storing spectra in a background and three data registers. Chloroform was chosen as the solvent for preparing solution samples, since it could dissolve all of the products. The spectrum of each solution sample was recorded using a sealed NaCl cell placed in the FT-IR.

Prior to recording a spectrum, each sealed salt cell was cleaned by feeding chloroform into the cell followed by drying with a nitrogen purge. This cleaning process was repeated four times to ensure the sealed cell was thoroughly cleaned.

Prior to any solvent or sample analysis, a cleaned and empty sealed salt cell was scanned as the background spectrum. Next, a sealed salt cell containing the pure chloroform solvent was scanned. The resultant transmission spectrum was transformed into an absorption spectrum and stored in one of the data registers for later use. Then each product sample was scanned, transformed into an absorption spectrum and also stored in computer memory. Since the chloroform solvent could interfere with the characteristic group absorptions of the products' absorption spectra, the chloroform spectrum was subtracted from the absorption spectra of the various products. This subtraction of the chloroform solvent spectrum from a particular product spectrum was conveniently done by the computer, with the resultant spectrum displayed on the computer screen ready to be printed out as hardcopy. The absorption band at 2400 cm\(^{-1}\) was taken as
representative of the chloroform spectrum, Figure 2. Its presence in each of the product spectra was used as an indicator of the intensity of the solvent spectrum. The intensity of the 2400 cm$^{-1}$ peak in the product spectra was minimized by subtracting varying proportions of the solvent spectrum from those of the products. Inherent errors in this method will be discussed later.

Sadtler reference literature spectra for maleic anhydride, maleanilic acid, N-phenylmaleimide, N-(o-nitrophenylmaleimide), and N-(p-chlorophenylmaleimide) are given in the following figures. These figures are interspersed with the respective spectra of the product monomers. A Sadtler IR spectrum was not available for N-(p-nitrophenylmaleimide); in addition, 4'-N-maleimido-2,3’-dimethylazobenzene is a new compound, hence no reference literature spectrum is available to compare with its product spectrum. The characteristic absorptions of the four monomers are listed as follows:

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<th>Compound</th>
<th>Frequency</th>
<th>Absorption</th>
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<td>N-phenylmaleimide</td>
<td>1719 cm$^{-1}$</td>
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<td>1601 cm$^{-1}$</td>
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<tr>
<td></td>
<td>1394 cm$^{-1}$</td>
<td>C-N (imide)</td>
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<tr>
<td>4’-N-maleimido-2,3’-dimethylazobenzene</td>
<td>1719 cm$^{-1}$</td>
<td>C=O</td>
</tr>
<tr>
<td></td>
<td>1631 cm$^{-1}$</td>
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<td></td>
<td>1390</td>
<td>C-N (imide)</td>
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Figure 2. Absorption Spectrum of Chloroform

Figure 3. Sadtler Transmission Spectrum of Maleic Anhydride

Figure 4. Absorption Spectrum of Maleic Anhydride; 0.1 g product in 10 ml chloroform

Figure 5. Sadtler Transmission Spectrum of Maleanilic Acid

Figure 6. Sadtler Transmission Spectrum of N-phenylmaleimide

Figure 7. Absorption Spectrum of N-phenylmaleimide; 0.1 g product in 10 ml chloroform

Figure 8. Absorption Spectrum of 4’-N-maleimido-2,3’-dimethylazobenzene; 0.1 g product in 10 ml chloroform

Figure 9. Sadtler Transmission Spectrum of N-o-nitrophenylmaleimide

Figure 10. Absorption Spectrum of N-nitrophenylmaleimide; 0.0099 g product in 1 ml chloroform

Figure 11. Sadtler Transmission Spectrum of N-p-chlorophenylmaleimide

Figure 12. Absorption Spectrum of N-p-chlorophenylmaleimide; 0.009 g product in 1 ml chloroform
Figure 2. Absorption Spectrum of Chloroform
Figure 3. Sadtler Transmission Spectrum of Maleic Anhydride
Figure 4. Absorption Spectrum of Maleic Anhydride; 0.1 g product in 10 ml chloroform.
Figure 5. Sadlier Transmission Spectrum of Maleanilic Acid
PHENYLMALEIMIDE

Figure 6. Sadtler Transmission Spectrum of N-phenylmaleimide
Figure 8. Absorption Spectrum of 4'-N-maleimido-2,3'-dimethyl-azobenzene; 0.1 g product in 10 ml chloroform
Figure 9. Sadtler Transmission Spectrum of N-o-nitrophenylmaleimide
Figure 10. Absorption Spectrum of N-nitrophenylmaleimide; 0.0099 g

product in 1 ml chloroform
Figure 11. Sadtler Transmission Spectrum of N-p-chlorophenylmaleimide
Figure 12. Absorption Spectrum of N-p-chlorophenylmaleimide; 0.009 g product in 1 ml chloroform
TGA (Thermogravimetric Analysis)

TGA is used to study the thermal stability of polymers. Thermogravimetry is a technique that records the weight gain or loss of a substance heated in a gaseous environment at a controlled rate as a function of time or temperature. A Perkin Elmer TGS-2 Thermogravimetric Analyzer was used to determine the decomposition temperature of the polymer products with the operating conditions as follows:

- Gas: Nitrogen
- T Final: 500°C
- T Min: 100°C
- T Increment: 40°C
- T Initial: 100°C
- Y-Range: 100
- Heating rate: 20 °C/min
- Cooling rate: 200 °C/min
- Sample weight: 0.647-10 mg
- Plot: N

The TGA was primarily used to measure the decomposition temperature of each sample; the decomposition temperature then in turn specified the operating conditions for the DSC for that specific polymer sample. Prior to placing the polymer sample into the sample pan, the pan was cleaned by burning it with a Bunsen burner. If a sample is not a powder but rather a liquid, it should be dried.
under vacuum to volatilize the solvent completely. Otherwise, a weight loss will be observed at the beginning of the thermogram as a consequence of solvent volatilization.

Each polymer sample was placed into the sample pan and weighed automatically by the TGS-2 with no counter weight in the reference pan. The sample was exposed to N₂ before heating for five minutes, and then heated to 500°C under N₂. However, there was a problem with the temperature calibration of the TGS-2. For a programmed load temperature of 100°C, the thermocouple reading was 108°C. However, the auto calibration procedure of the TGS-2 was centered at 400°C. The accuracy of the temperature reading of the TGS-2 in this range was estimated to be ±5°C.

**DSC (Differential Scanning Calorimetry)**

DSC is useful in studying polymer thermal properties, such as the glass transition temperature, the melting temperature, and the heat of fusion. In DSC, the power necessary to maintain a constant temperature between a sample and a reference material is measured as a function of temperature or time, as the two specimens are subjected to a controlled heating or cooling rate. A Perkin Elmer DSC-4 was used to test for the glass transition temperature of the polymer products. Since the melting temperature is at least 50°C lower than the decomposition temperature and, the glass transition temperature is between one-half and two-thirds of the melting temperature, all physical changes in the
polymer samples could be observed without interference from sample degradation. To optimize the thermograms, the DSC-4 was operated under the following conditions:

- Gas: Nitrogen
- T Final: 250 or 350°C
- T Min: 50°C
- T Increment: 20 or 30°C
- T Initial: 50°C
- Y-Range: 10
- Heating rate: 20 °C/min
- Cooling rate: 320 °C/min
- Sample weight: 2.2-10 mg
- Plot: N
- S. A. Z.: B

The calorimeter was first adjusted to establish an acceptable baseline. Then an Indium standard was used to calibrate the instrument. The melting temperature of Indium is 156.8°C and its heat of fusion is 6.8 cal/g. Prior to heating the polymer products, each powder sample was weighed by using a Mettler AJ 100 balance. Next, the weighed sample was placed into an aluminum pan and the pan was sealed with an aluminum cap by using a crimper. An empty pan with a cap was used as a reference. Each polymer product along with a reference pan was heated above its softening point, then quickly cooled, and reheated again at a controlled rate to a final temperature. This was done to
insure that the sample had maximum contact with the base of the sample pan. The accuracy of the DSC-4 temperature reading was determined to be ±1°C.

During the course of this study it was difficult to obtain a reproducible baseline from the DSC-4. Consequently, the thermograms for the polymer samples varied considerably. Only qualitative results could be obtained.
RESULTS

This section contains the FT-IR absorption spectra, TGA thermograms, and DSC thermograms of the polymers studied. The spectra presented on Figure 13 to Figure 16 are representative of homopolymers. Figure 17 to Figure 22 are representative of the spectra of copolymers based on the two commercial copolymers. Figure 23 to Figure 26 give spectra of the copolymer products listed in Table 2. In this study, FT-IR spectra were used for both qualitative and quantitative analyses; the quantitative analyses were especially important. By employing Beer’s law estimates of the constituent concentrations of various copolymers based on their absorption spectra could be obtained. The TGA and DSC thermograms of the studied polymer products are presented on Figure 27 to Figure 40 and Figure 41 to Figure 51, respectively.

FT-IR ANALYSIS:

The FT-IR absorption spectra are presented on Figure 2 to Figure 26; the spectra of the monomers on Figures 2 to 12 are presented in the experimental section.

To use a FT-IR spectrum to determine the concentration of a sample, Beer’s law is commonly used. The general relation between absorbance A and concentration C from which Beer’s law is derived, is given by the equation
A = B(1-exp\(^{-kC}\)). The relation can be simplified as A = BkC = \(\varepsilon lC\) for small kC, thus yielding Beer’s law. Here \(\varepsilon\) is the molar extinction coefficient, \(l\) is the cell path length and \(C\) is the molar concentration.

On a spectrum, the intensity of an absorption peak is related to both the concentration of a sample and the extinction coefficient of a vibration of a representative structure in the sample molecules. In addition, the height of an absorption peak is proportional to absorbance if the peak is sharp and well resolved, and can therefore be used to represent the absorbance. In order to correct errors resulted from partial scattering of the infrared radiation and the overlap of neighboring absorption peaks, a baseline must be constructed. The absorbance of the baseline should be subtracted from the absorbance of an absorption peak. This has been done in the results that follow.

Figure 13 and X1-X3 of Appendix represent the spectra of polystyrene that were obtained by placing 0.1 g, 0.2 g, 0.3 g and 0.4 g, respectively, of polystyrene in 10 ml of chloroform. Upon plotting graphs of absorbance versus concentration for the six characteristic absorption bands at 2929 cm\(^{-1}\), 2852 cm\(^{-1}\), 1602 cm\(^{-1}\), 1494 cm\(^{-1}\), 1454 cm\(^{-1}\) and 1029 cm\(^{-1}\), it was observed that a nonlinear relationship existed between absorbance and concentration. Consequently, the general relation, A = B(1-exp\(^{-kC}\)), rather than Beer’s law was required to fit the data. A nonlinear least squares fitting procedure established a
value of $k = 0.985$, appropriate for all six absorption bands. The values for the $B$ coefficients are given in Table 3. Particular care was taken to perform the polystyrene analysis since styrene is the main component of most of the samples studied. In addition, since the extinction coefficients for the absorption bands are quite small, any appreciable styrene signal would not obey Beer’s law.

To analyze the spectra of maleic anhydride, N-phenylmaleimide, and 4’-N-maleimido-2,3’-dimethylazobenzene, it was established that Beer’s law, $A = \varepsilon l C$, was the proper relationship between absorbance and concentration. (please refer to Figures 3, 7 and 8). The strongest absorption band in these samples resulted from the C=O double bond stretching vibration and was observed at 1783 cm$^{-1}$, 1719 cm$^{-1}$ and 1719 cm$^{-1}$, respectively. The following illustrates how these samples were analyzed. A solution sample of N-phenylmaleimide was prepared by placing 0.1 g of sample into 10 ml of chloroform; thus the concentration of the solution was 0.0578 mole/l. Using Beer’s law a value of $\varepsilon l = 30.08 \, l/mole$ was obtained for an absorbance value of 1.739. In performing these calculations careful accounting of the baseline of the spectra must be maintained. Table 4 lists the stronger absorption bands and the related $\varepsilon l$ values for maleic anhydride, N-phenylmaleimide, and 4’-N-maleimido-2,3’-dimethylazobenzene. These $\varepsilon l$ values were used to determine the constituent concentrations of the copolymer products.

Table 5 and Table 6 list the results of the quantitative analysis of the copolymer compositions. As an example calculation, Figure 19 gives the
absorption FT-IR spectrum of poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]. The two prominent absorptions at 2918 cm\(^{-1}\) and 2849 cm\(^{-1}\) are due to the existence of styrene and they were used to establish the concentration of styrene in the copolymer. The absorbance of the baseline was 0.024, and the baseline-subtracted absorbance of the 2918 cm\(^{-1}\) and 2849 cm\(^{-1}\) absorptions were 0.0777 and 0.0268, respectively. From Table 3, the B values for the equation \(A = B(1 - \exp^{-0.985C})\) were 0.7816 and 0.2448, yielding an average value of the concentration of styrene in this sample of 0.112 mole/l; as listed in Table 5, for the fourth copolymer. One broad absorption between 1700 cm\(^{-1}\) and 1800 cm\(^{-1}\) indicated that both maleic anhydride and 4'-N-maleimido-2,3'-dimethylazobenzene were in the copolymer. Thus, the absorptions at 1378 cm\(^{-1}\) and 1159 cm\(^{-1}\) were chosen to measure the concentration of 4'-N-maleimido-2,3'-dimethylazobenzene and the absorption at 1274 cm\(^{-1}\) for the unimidized maleic anhydride. The absorbance (baseline subtracted) for the peaks at 1378 cm\(^{-1}\), 1159 cm\(^{-1}\), and 1274 cm\(^{-1}\) were 0.0213, 0.0074, and 0.0038, respectively. The concentrations shown in Table 5 were derived by substituting the absorbance and the \(e_1\) values (see Table 4) into the equation \(A = e_1C\).

The accuracy of this analysis was estimated by using the commercial poly-(Styrene-co-maleic anhydride); [50:50] and [92:8] samples. A 4% difference was obtained between measured and theoretical concentrations.
Inspection of Table 6 reveals the following trends: the reactions were carried to a higher conversion for the [92:8] copolymers than the [50:50] copolymers. The imidization of maleic anhydride to form N-phenylmaleimide was greater when compared to that of 4'-N-maleimido-2,3'-dimethylazobenzene. In addition, solution polymerization favored the incorporation of imide into the copolymer when compared to emulsion polymerization.

**THERMAL ANALYSIS:**

Figures 27 to 40 are the TGA thermograms of the polymer products synthesized in this study. Table 7 lists the respective decomposition temperatures of these polymers based on their thermograms. These values were obtained by using the TGS-2 under the operating conditions given in the experimental section. On individual thermogram, the decomposition temperature was determined by first making two tangent lines along the shoulder of the weight loss which was caused by the breaking of the polymer chain, and the intersect of the two lines was termed as the decomposition temperature of the polymer.

A number of interesting phenomena can be seen from these thermograms. As an example, the decomposition temperature for polystyrene on Figure 27 is 413°C and the decomposition took place from 326°C to 429°C. In some cases, multiple decompositions also took place. Figure 31 exemplifies multiple decompositions where the first shoulder represents the escape of the carbonyl groups from maleic anhydride, and the second shoulder at a higher temperature
is due to the breaking of the polymer backbone. A unique phenomenon where weight loss at the beginning of heating was also observed in this investigation. This weight loss is resulted from solvent desorption. On Figure 35, the solvent desorption took place in a small temperature range; the temperature is very close to the boiling point of 110°C for the solvent toluene used in the polymer synthesis.

In Table 7, it is seen that some of the polymers have more than one decomposition temperatures; this was caused by the departure of the carbonyl group, nitro group and azo group from the polymers prior to the polymer backbone breakage. The percent values in Table 7 were obtained from the thermograms of the respective polymers. The percent value quantifies the weight loss at the corresponding temperature, thus the mechanism of the decomposition can be studied. A higher decomposition temperature indicates that the polymer has a stronger backbone and more stable thermal properties, and conversely, a lower decomposition temperature means that the polymer backbone is not as strong and their thermal properties are not as stable.

The DSC thermograms of the various polymers are presented on Figures 41 to 51. On Figures 41, 42, 43, 46 and 47, the glass transitions of poly-(Styrene), poly-(N-phenylmaleimide), poly-(Styrene-co-maleic anhydride); [50:50], poly-(Styrene-co-maleic anhydride); [92:8], and poly-(Styrene-co-N-phenylmaleimide); [92:8] are well resolved and the respective temperatures are reasonable. The glass transition is simply the location on a thermogram where a
change in the slope of the curve takes place. A broad glass transition is obtained on the thermogram of poly-(Styrene-co-maleimide); [50:50], Figure 44. This phenomenon is due to the unconverted maleic anhydride on the [50:50] copolymer chain. The broad peaks on Figures 44, 45 and 51 indicate the decomposition that took place during the heating process. No glass transitions are seen on Figures 49 and 50, since the polymers have no regular structure and have large molecular weight distribution.
Table 3. Frequency and Coefficient B for Polystyrene

<table>
<thead>
<tr>
<th>Frequency (cm(^{-1}))</th>
<th>Coefficient, B</th>
</tr>
</thead>
<tbody>
<tr>
<td>2929</td>
<td>0.7816</td>
</tr>
<tr>
<td>2852</td>
<td>0.2448</td>
</tr>
<tr>
<td>1602</td>
<td>0.2890</td>
</tr>
<tr>
<td>1494</td>
<td>0.8992</td>
</tr>
<tr>
<td>1454</td>
<td>0.8355</td>
</tr>
<tr>
<td>1029</td>
<td>0.2282</td>
</tr>
</tbody>
</table>

\[ A = B(1 - \exp^{-0.985 \cdot C}) \]

A= absorbance
B= coefficient
C= concentration
Table 4. ε l (l/mole) Values

<table>
<thead>
<tr>
<th>Frequency (cm⁻¹)</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1852</td>
<td>2.151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1783</td>
<td>15.142</td>
<td>0.457</td>
<td></td>
</tr>
<tr>
<td>1775</td>
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</tr>
<tr>
<td>1756</td>
<td>1.992</td>
<td></td>
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</tr>
<tr>
<td>1719</td>
<td>1.139</td>
<td>30.08</td>
<td>25.06</td>
</tr>
<tr>
<td>1631</td>
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<td></td>
<td>0.848</td>
</tr>
<tr>
<td>1601</td>
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</tr>
<tr>
<td>1585</td>
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<td></td>
<td>0.936</td>
</tr>
<tr>
<td>1505</td>
<td>5.529</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1494</td>
<td></td>
<td></td>
<td>2.652</td>
</tr>
<tr>
<td>1477</td>
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<td>1.524</td>
</tr>
<tr>
<td>1412</td>
<td></td>
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<td>2.091</td>
</tr>
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<td>1394</td>
<td>6.519</td>
<td>5.134</td>
<td></td>
</tr>
<tr>
<td>1381</td>
<td>4.998</td>
<td></td>
<td>3.771</td>
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<td>1282</td>
<td>2.011</td>
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<td></td>
</tr>
<tr>
<td>1263</td>
<td>1.196</td>
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</tr>
<tr>
<td>1239</td>
<td>3.061</td>
<td></td>
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</tr>
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<td>1154</td>
<td></td>
<td></td>
<td>3.506</td>
</tr>
<tr>
<td>1148</td>
<td>4.967</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A= maleic anhydride  
B= N-phenylmaleimide  
C= 4’-N-maleimido-2,3’-dimethylazobenzene
Table 5. Constituents of Various Copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>A (mole/l)</th>
<th>B (mole/l)</th>
<th>C (mole/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.1225</td>
<td>0.1063</td>
<td>0.0000</td>
</tr>
<tr>
<td>2</td>
<td>0.6473</td>
<td>0.0265</td>
<td>0.0000</td>
</tr>
<tr>
<td>3</td>
<td>0.0137</td>
<td>0.0080</td>
<td>0.0008</td>
</tr>
<tr>
<td>4</td>
<td>0.1120</td>
<td>0.0019</td>
<td>0.0039</td>
</tr>
<tr>
<td>5</td>
<td>0.1284</td>
<td>0.0004</td>
<td>0.0082</td>
</tr>
<tr>
<td>6</td>
<td>0.0423</td>
<td>0.0002</td>
<td>0.0053</td>
</tr>
<tr>
<td>7</td>
<td>0.0169</td>
<td>----------</td>
<td>0.0045</td>
</tr>
<tr>
<td>8</td>
<td>0.0115</td>
<td>----------</td>
<td>0.0057</td>
</tr>
<tr>
<td>9</td>
<td>0.6013</td>
<td>----------</td>
<td>0.2271</td>
</tr>
<tr>
<td>10</td>
<td>0.0630</td>
<td>----------</td>
<td>0.0140</td>
</tr>
</tbody>
</table>

A = styrene
B = maleic anhydride
C = imide
1 = poly-(Styrene-co-maleic anhydride); [50:50]
2 = poly-(Styrene-co-maleic anhydride); [92:8]
3 = poly-(Styrene-co-N-phenylmaleimide); [50:50]
4 = poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]
5 = poly-(Styrene-co-N-phenylmaleimide); [92:8]
6 = poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [92:8]
7 = poly-(Styrene-co-N-phenylmaleimide); Emulsion
8 = poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Emulsion
9 = poly-(Styrene-co-N-phenylmaleimide); Solution
10 = poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Solution
Table 6. Constituents of Various Copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>% of A</th>
<th>% of B</th>
<th>% of C</th>
<th>Theoretical % of A</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>54</td>
<td>46</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>96</td>
<td>4</td>
<td>0</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>61</td>
<td>36</td>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>95 (50)*</td>
<td>2 (20)</td>
<td>3 (30)</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>94</td>
<td>0</td>
<td>6</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>89</td>
<td>0</td>
<td>11</td>
<td>92</td>
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<tr>
<td>7</td>
<td>79</td>
<td>---</td>
<td>21</td>
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<td>8</td>
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<td>---</td>
<td>27</td>
<td>79</td>
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<tr>
<td>10</td>
<td>82</td>
<td>---</td>
<td>18</td>
<td>89</td>
</tr>
</tbody>
</table>

* The subtraction of chloroform was incomplete in analysis.
Table 7. Decomposition Temperatures of Various Polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Decomposition Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>413 98%</td>
</tr>
<tr>
<td>B</td>
<td>411 98%</td>
</tr>
<tr>
<td>C</td>
<td>153 98% 327 88%</td>
</tr>
<tr>
<td>D</td>
<td>397 98%</td>
</tr>
<tr>
<td>1</td>
<td>287 98% 350 69%</td>
</tr>
<tr>
<td>2</td>
<td>399 100%</td>
</tr>
<tr>
<td>3</td>
<td>237 95% 334 73%</td>
</tr>
<tr>
<td>4</td>
<td>251 95% 331 78%</td>
</tr>
<tr>
<td>5</td>
<td>378 90%</td>
</tr>
<tr>
<td>6</td>
<td>263 95% 373 43%</td>
</tr>
<tr>
<td>7</td>
<td>390 99%</td>
</tr>
<tr>
<td>8</td>
<td>200 100% 402 75%</td>
</tr>
<tr>
<td>9</td>
<td>372 97%</td>
</tr>
<tr>
<td>10</td>
<td>199 90% 400 68%</td>
</tr>
</tbody>
</table>

A= poly-(Styrene)  
B= poly-(N-phenylmaleimide)  
C= poly-(N-nitrophenylmaleimide)  
D= poly-(N-p-chlorophenylmaleimide)  
1= poly-(Styrene-co-maleic anhydride); [50:50]  
2= poly-(Styrene-co-maleic anhydride); [92:8]  
3= poly-(Styrene-co-N-phenylmaleimide); [50:50]  
4= poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [50:50]  
5= poly-(Styrene-co-N-phenylmaleimide); [92:8]  
6= poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [92:8]  
7= poly-(Styrene-co-N-phenylmaleimide); Emulsion  
8= poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Emulsion  
9= poly-(Styrene-co-N-phenylmaleimide); Solution  
10= poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Solution
Figure 13. Absorption Spectrum of Poly-(Styrene); 0.4 g product in 10 ml chloroform.

Figure 14. Absorption Spectrum of Poly-(N-phenylmaleimide); 0.1006 g product in 10 ml chloroform.

Figure 15. Absorption Spectrum of Poly-(N-nitrophenylmaleimide); 0.0038 g product in 0.5 ml chloroform.

Figure 16. Absorption Spectrum of Poly-(N-p-chlorophenylmaleimide); 0.0096 g product in 1 ml chloroform.

Figure 17. Absorption Spectrum of Poly-(Styrene-co-maleic anhydride); [50:50]

Figure 18. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide); [50:50]

Figure 19. Absorption Spectrum of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [50:50]

Figure 20. Absorption Spectrum of Poly-(Styrene-co-maleic anhydride); [92:8]

Figure 21. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide); [92:8]

Figure 22. Absorption Spectrum of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [92:8]

Figure 23. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide); Emulsion

Figure 24. Absorption Spectrum of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Emulsion
Figure 25. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide); Solution

Figure 26. Absorption Spectrum of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Solution

Figure 27. TGA Thermogram of Poly-(Styrene)

Figure 28. TGA Thermogram of Poly-(N-phenylmaleimide)

Figure 29. TGA Thermogram of Poly-(N-nitrophenylmaleimide)

Figure 30. TGA Thermogram of Poly-(N-p-chlorophenylmaleimide)

Figure 31. TGA Thermogram of Poly-(Styrene-co-maleic anhydride); [50:50]

Figure 32. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide); [50:50]

Figure 33. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]

Figure 34. TGA Thermogram of Poly-(Styrene-co-maleic anhydride); [92:8]

Figure 35. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide); [92:8]

Figure 36. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [92:8]

Figure 37. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide); Emulsion

Figure 38. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Emulsion
Figure 39. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide); Solution
Figure 40. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Solution
Figure 41. DSC Thermogram of Poly-(Styrene)
Figure 42. DSC Thermogram of Poly-(N-phenylmaleimide)
Figure 43. DSC Thermogram of Poly-(Styrene-co-maleic anhydride); [50:50]
Figure 44. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide); [50:50]
Figure 45. DSC Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]
Figure 46. DSC Thermogram of Poly-(Styrene-co-maleic anhydride); [92:8]
Figure 47. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide); [92:8]
Figure 48. DSC Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [92:8]
Figure 49. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Emulsion
Figure 50. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Solution
Figure 51. DSC Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Solution

63
Figure 13. Absorption Spectrum of Poly-(Styrene); 0.4 g product in 10 ml chloroform.
Figure 14. Absorption Spectrum of Poly-(N-phenylmaleimide); 0.1006 g product in 10 ml chloroform
Figure 15. Absorption Spectrum of Poly-(N-nitrophenylmaleimide);

0.0038 g product in 0.5 ml chloroform
Figure 16. Absorption Spectrum of Poly-(N-p-chlorophenylmaleimide).

0.0096 g product in 1 ml chloroform
Figure 18. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide); [50:50]
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Figure 20. Absorption Spectrum of Poly-(Styrene-co-maleic anhydride);
Figure 21. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide);

[92:8]
Figure 22. Absorption Spectrum of Poly-(Styrene-co-4'-N-maleimido-2,3’-dimethylazobenzene); [92:8]
Figure 23. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide);

Emulsion Polymerization
Figure 24. Absorption Spectrum of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Emulsion Polymerization
Figure 25. Absorption Spectrum of Poly-(Styrene-co-N-phenylmaleimide);

Solution  Polymerization
Figure 26. Absorption Spectrum of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Solution Polymerization
Figure 27. TGA Thermogram of Poly-(Styrene)
Figure 28. TGA Thermogram of Poly-(N-phenylmaleimide)
Figure 29. TGA Thermogram of Poly-(N-nitrophenylmaleimide)
Figure 30. TGA Thermogram of Poly-(N-p-chlorophenylmaleimide)
Figure 31. TGA Thermogram of Poly-(Styrene-co-maleic anhydride);

DATE: 90/12/13

[50:50]
Figure 32. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Figure 33. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [50:50]
Figure 35. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide);

DATE: 91/06/05
Figure 36. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [92:8]
Figure 37. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Emulsion Polymerization
DATE: 90/12/13

P (STYRENE-MALEIMIDE). Emulsion WT: 1.7452 mg RATE: 20.00 deg/min

FROM: 300.75
TO: 409.4
ONSET AT: 388.67
% WT: 98.93

% WEIGHT
Figure 38. TGA Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); Emulsion Polymerization
Figure 39. TGA Thermogram of Poly-(Styrene-co-N-phenylmaleimide);

Solution Polymerization
Figure 40. TGA Thermogram of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); Solution Polymerization
P (STYRENE)

\[ N = 7.50 \text{ mg} \]

SCAN RATE: 40.00 deg/min

PEAK FROM: 100.21
\[ T_{\text{O}} = 127.04 \]
ONSET: 105.48
CAL/GRAM: .66

MAX: 112.26

Figure 41. DSC Thermogram of Poly-(Styrene)
P (MALEIMIDE)

$\Delta T_s = 4.50$ mg

SCAN RATE = 20.00 deg/min

T/G FROM = 248.62
TO = 274.1
ONSET = 251.65
CAL/GDEG = 6.1336E-02
MIDPOINT = 257.01

Figure 42. DSC Thermogram of Poly-(N-phenylmaleimide)
P[ (50/50) STYRENE-MALEIC ANHYDRIDE ]

\( N_t = 5.60 \text{ mg} \)

SCANT RATE = 20.00 deg/min

\( T/G \text{ FROM} = 150.11 \)

\( T_o = 171.98 \)

ONSET = 155.83
CAL/GDEG = 1.14535
MIDPOINT = 180.43

Figure 43. DSC Thermogram of Poly-(Styrene-co-maleic anhydride);
P (STYRENE-MALEIMIDE); [50:50]

#T: 8.40 mg
SCAN RATE: 20.00 deg/min

T/G FROM: 95.22
TO: 139.52
ONSET: 106.8
CAL/GDEG: 2.05394E-02
MIDPOINT: 115

Figure 44. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Figure 45. DSC Thermogram of Poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene); [50:50]
P (92/8) STYRENE-MALEIMIDE

\[ T_\text{i} \quad 6.50 \text{ mg} \]

SCAN RATE: 20.00 deg/min

\[ T/G \text{ FROM: } 109.79 \]
\[ T_o: 129.89 \]
ONSET: 112.51
CAL/GDEG: 4.65023E-02
MIDPOINT: 116.73

Figure 47. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);
Figure 48. DSC Thermogram of Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); [92:8]
Figure 49. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);

**P (STYRENE-MALEIMIDE). Emulsion**

- **WT:** 2.20 mg
- **SCAN RATE:** 20.00 deg/min

Emulsion Polymerization
P (STYRENE-MALEIMIDE); SOLUTION

\( \#T_i \) 6.70 mg
SCAN RATE: 20.00 deg/min

Figure 50. DSC Thermogram of Poly-(Styrene-co-N-phenylmaleimide);

Solution Polymerization
DISCUSSION

Synthesis of Monomers

Four monomers were synthesized in this study: N-phenylmaleimide, 4’-N-maleimido-2,3’-dimethylazobenzene, N-nitrophenylmaleimide, and N-p-chlorophenylmaleimide.

Both N-phenylmaleimide and 4’-N-maleimido-2,3’-dimethylazobenzene were synthesized by imidizing maleic anhydride. The respective amines for these two reaction were aniline and 4’-amino-2,3’-dimethylazobenzene. The imidization process is a two-step reaction; the intermediate product being an amide acid. When comparing the IR spectrum of N-phenylmaleimide (see Figure 7) with its literature spectrum on Figure 6, it is seen that the two are almost identical, especially the absorption range from 1400 cm\(^{-1}\) to 1800 cm\(^{-1}\). In addition, there was no evidence of an amide acid intermediate left in the N-phenylmaleimide final product. This can be seen when comparing Figure 7 with Figure 5, the literature spectrum of maleanilic acid. The absence of the strong, broad carbonyl absorption band of Figure 7 on the spectrum of the maleimide indicates the lack of an intermediate product. Thus, the purity of synthesized N-phenylmaleimide was considered to be very high.

The structure of 4’-N-maleimido-2,3’-dimethylazobenzene is more
complex than that of N-phenylmaleimide. The structural differences are evident when comparing their IR spectra as depicted on Figures 8 and 7, respectively. First of all, the absorption band at 1600 cm\(^{-1}\) on Figure 7 is split into a 1631 cm\(^{-1}\) and a 1587 cm\(^{-1}\) absorption peaks on Figure 8. This absorption arises from the N-C stretch between the maleimide ring and the phenyl group. All three 1600, 1500 and 1400 cm\(^{-1}\) are split in the azo. The IR spectrum of the monomer displays no amide acid absorptions (see Figure 5) nor maleic anhydride absorptions (see Figure 3); the latter would have been identified by absorption peaks at 1780 cm\(^{-1}\) and 1850 cm\(^{-1}\).

The preparation of N-nitrophenylmaleimide calls for the nitration of the phenyl group on the N-phenylmaleimide monomer synthesized before. The nitro groups were attached to both the para and ortho positions referenced to the phenyl-maleimide linkage. The spectrum for the N-nitrophenylmaleimide monomer on Figure 10 is very similar to the literature spectrum for N-o-nitrophenylmaleimide represented on Figure 9. The absorption peak at 1150 cm\(^{-1}\) is stronger than the peak at 1200 cm\(^{-1}\) on Figure 9, the Sadtler spectrum of N-o-nitrophenylmaleimide. This is an indicative of an ortho-dominated material. Conversely, the 1200 cm\(^{-1}\) peak is stronger than the 1150 cm\(^{-1}\) peak on the spectrum of the N-nitrophenylmaleimide product, Figure 10. It is thought that the product is more para-dominated according to its FT-IR spectrum. The most
pronounced difference between the spectra of N-phenylmaleimide and N-nitrophosphenylnmaleimide is the additional absorption at 1530 cm\(^{-1}\) for the nitro compound which can be attributed to the nitro group (see Figures 7 and 10).

The synthesis of N-p-chlorophosphenylnmaleimide was similar to that of N-phenylmaleimide. The imidization of maleic anhydride was completed by adding p-chloroaniline, thus, the chloro groups were only attached to the para position. When comparing the literature spectrum of Figure 11 and the product spectrum of Figure 12, they are found to be very similar. Therefore, the purity of the N-p-chlorophosphenylnmaleimide monomer was considered to be very high.

The nitro and chloro substituents are strong electron-withdrawing groups. They stabilize the phenyl group and intensify the C=O stretch vibration characteristic. This influence can be seen by comparing the absorption at 1719 cm\(^{-1}\) for N-phenylmaleimide with the absorptions at 1727 cm\(^{-1}\) and 1722 cm\(^{-1}\) for N-nitrophosphenylnmaleimide and N-p-chlorophosphenylnmaleimide, respectively. The stronger the electron-withdrawing group, the greater the frequency shift of C=O stretch vibration.

Comparison of the Thermal Stability of Poly-(N-phenylmaleimide), Poly-(N-nitrophosphenylnmaleimide) and Poly-(N-p-chlorophosphenylnmaleimide)

Figures 29 and 30 are the TGA thermograms of poly-(N-
nitrophenylmaleimide) and poly-(N-p-chlorophenylmaleimide), respectively. Figure 30 shows a sharp weight loss similar to those observed on Figures 27 and 28 for polystyrene and poly-(N-phenylmaleimide), respectively. The weight loss in these figures is thought to be caused by the random breaking of the polymer chains in these polymers. The first weight loss observed on Figure 29 is indicative of the liberation of nitro free radicals away from the polymer, and the broad weight loss at higher temperature is thought to be due to the depolymerization of the polymer backbone. The repeating unit weight of poly-(N-nitrophenylmaleimide) is 218 and the weight of poly-(N-phenylmaleimide) is 173. When all nitro free radicals escape from the polymer chain, the weight should be 79% of the original polymer. The experimental value listed in Table 7 is 88%, thus the first weight loss on Figure 29 is probably due to the liberation of nitro free radicals. The free radicals then attached to the polymer chain initiating the depolymerization process. It should be noted that for Figure 30, the almost horizontal slope at low temperatures gives an indication that free chloro radical formation was minute, and that the narrow weight loss region suggests that random scission rather than depolymerization is the dominant decomposition mechanism for poly-(N-p-chlorophenylmaleimide).

Comparison of [50:50] Polymer and [92:8] Polymer

The IR spectrum of the poly-(Styrene-co-maleic anhydride); [50:50] polymer is given on Figure 17. As can be seen from the figure, there are two strong absorptions occurring in the spectrum at 1780
cm$^{-1}$ to 1857 cm$^{-1}$. These strong absorptions are due to the characteristic asymmetric and symmetric C=O stretch vibrations of the maleic anhydride.

Poly-(Styrene-co-maleic anhydride); [50:50] used in this study is a commercial polymer purchased from an outside supplier. From the TGA and DSC thermograms of Figure 31 and Figure 43, respectively, it can be established that it is an alternating copolymer. Figure 31 exhibits two decomposition temperatures, a feature normally associated with block copolymers. However, in this particular case the two shoulders are not thought to be caused by the breakage of the respective chains in each block of the polymer. For the poly-(Styrene-co-maleic anhydride); [50:50] polymer, the low temperature shoulder on Figure 31 results from the loss of carbon dioxide from the maleic anhydride. Comparing the weight loss percentage, 69%, listed in Table 7 with the theoretical value 64%, the low temperature shoulder observed on Figure 31 can be attributed to the loss of carbon dioxide from maleic anhydride. The other shoulder, which occurred at a higher temperature, results from the decomposition of the polymer backbone between styrene and maleic anhydride monomer units. The decomposition temperature of poly-(Styrene) is higher than the [50:50] copolymer in Table 7; this represents that the strength of the poly-(Styrene) backbone is stronger than the copolymer backbone constructed by the bond between styrene and maleic anhydride monomers. The DSC thermogram on Figure 43 only exhibits one glass transition, indicative of an alternating copolymer.
Table 5 presents the calculated quantitative results based on the spectrum on Figure 17. The calculated results indicate that the amount of styrene in the purchased poly-(Styrene-co-maleic anhydride); [50:50] polymer to be 54%, compared to the theoretical value of 50% styrene. The 4% difference between the experimental and theoretical values suggests that the acceptable error range of the analytical methods is ±5%. For the other commercially purchased polymer, poly-(Styrene-co-maleic anhydride); [92:8], the difference in styrene between the experimental and theoretical values was 4%, this reinforces the finding that the error range is ±5%.

The difference between the experimental and theoretical styrene values resulted from errors in the analysis method. For example, the baseline of the IR spectrum did not stay constant throughout the scanning. This inconsistent baseline necessitated the subtraction of the baseline from each specific absorption band. Since no two absorption peaks are alike, and human judgement must be exercised in deciding where the baselines lie, errors were introduced when calculating the experimental styrene values. In addition, the process of eliminating the solvent peaks from the IR spectra also introduced errors. For example, on Figure 18, the absorption peak at 2400 cm\(^{-1}\) and the negative peaks at 3050 cm\(^{-1}\) and 1220 cm\(^{-1}\) are due to the presence of the solvent. To eliminate the solvent peaks means making adjustment to the spectrometer by a factor of either greater than one or less than one. In making the adjustment to the solvent peak, all other peaks were also affected and hence a new source of error was introduced.
Figure 34 gives the TGA thermogram of poly-(Styrene-co-maleic anhydride); [92:8], which shows a sharp weight loss due to the decomposition of the polymer chain. Figure 34 differs from Figure 31 in the relative amount of maleic anhydride in both materials, 50% versus 8%. The TGA and DSC thermograms of the [92:8] polymer on Figures 34 and 46 are very similar to those of 100% polystyrene on Figures 27 and 41, as would be expected. In addition, both the TGA and DSC thermograms of the [92:8] commercial polymer give evidence that this material is a random copolymer.

The copolymer compositions resulting from the imidization of poly-(Styrene-co-maleic anhydride); [50:50] and poly-(Styrene-co-maleic anhydride); [92:8] to form poly-(Styrene-co-N-substitutedmaleimide); [50:50] and poly-(Styrene-co-N-substitutedmaleimide); [92:8] are listed in Tables 5 and 6. The quantitative results of the [92:8] copolymer products, which were calculated based on the IR spectra of Figures 21 and 22 indicate that the imidization of maleic anhydride is complete for this copolymer. The imidization of the [50:50] copolymer was incomplete. This is because the imidization of maleic anhydride becomes more difficult to bring to full conversion as the relative amount of the maleic anhydride increases in the copolymers. In addition, the stoichiometry of the [50:50] reaction with the respective amines limits the theoretical yield to 50%, based on maleic anhydride units. This is a consequence of the formation of an amide acid- ammonium salt complex during the initial stage of the imidization reaction. The IR spectrum of the poly-(Styrene-co-N-phenylmaleimide); [50:50]
on Figure 18 shows a strong absorption at $1780 \text{ cm}^{-1}$ due to the residual maleic anhydride. The same result was also seen in the IR spectrum of poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene) on Figure 19. This then confirms that a considerable amount of maleic anhydride in the [50:50] polymers was indeed not imidized.

The residual maleic anhydride in the [50:50] products resulted in more complicated thermal behavior when compared to the [92:8] products. It is seen from Figure 32 that there are two broad transitions in the TGA thermogram of poly-(Styrene-co-N-phenylmaleimide); [50:50]. The low temperature transition can be attributed to the loss of the carbon dioxide from the maleic anhydride. Figure 32 is also different from the TGA thermogram for poly-(Styrene-co-N-phenylmaleimide); [92:8] on Figure 35, where a sharp drop is seen at the chain decomposition temperature. The small weight loss at the beginning of the heating on Figure 35 was caused by the vaporization of the toluene solvent. The glass transition of the [50:50] product, seen on Figure 44, is broad due to the complicated arrangement of the three repeating units of styrene, maleic anhydride, and maleimide. Also observed on Figure 44 is a large endothermic peak centered at $200^\circ\text{C}$ resulting from the release of carbon dioxide from the maleic anhydride units.

Comparison of Poly-(Styrene-co-N-phenylmaleimide) and Poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene)
The results of the poly-(Styrene-co-N-phenylmaleimide) polymers are closer to the theoretical values than those of the poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene) polymers (see Tables 5 and 6). For convenience reasons, the poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene) polymer shall be referred to as the N-azo substituted polymer. The difference between the experimental value and the theoretical value for poly-(Styrene-co-N-phenylmaleimide); [92:8] is 2%, and for N-azo substituted copolymer the difference between the experimental and the theoretical values is 3%. The better results for the N-phenylmaleimide polymers are in part due to the smaller molecules of aniline compared to 4’-amino-2,3’-dimethylazobenzene. Both compounds reacted with the maleic anhydride that were attached to styrene units to form the polymer chain; thus, the steric hindrance from the pendent phenyl groups of styrene is a factor affecting imidization. The same reason also can be used to explain the results for the [50:50] copolymers. As a result, it is easier for smaller molecules to get into the polymer coil to latch on to the reactive sites. As can be seen, the compositions of the polymerized N-phenylmaleimide copolymers are closer to the reaction stoichiometry than the polymerized N-azo substituted copolymers. The difference between the theoretical value and the experimental value for the emulsion polymerized N-phenylmaleimide copolymer is 3%, and the difference for the emulsion polymerized N-azo substituted copolymer is 24%.

All of the quantitative results calculated from the IR spectra are given in
Table 5. In comparing the IR spectra of Figures 21 and 22, the absorption between 1600 cm\(^{-1}\) and 1650 cm\(^{-1}\) is due to the N-C stretch vibration between the nitrogen-phenyl group, and is more complicated and broader in the N-azo substituted polymer. The same phenomenon was observed when comparing the spectrum of N-phenylmaleimide with the spectrum of 4'-N-maleimido-2,3'-dimethylazobenzene (see Figures 7 and 8). This is caused by the greater nitrogen-phenyl group stretch vibration in the N-azo substituted material (see Figures 23, 24, 25 and 26). The difference between N-phenyl and N-azo substituted polymers is more pronounced when seen from the TGA thermograms. Figure 35 is the TGA thermogram for a N-phenyl product, which shows a sharp weight loss that was caused by the decomposition of the polymer chain. Conversely, there are two shoulders in the TGA thermogram of a N-azo substituted product on Figure 36. The first broad shoulder was caused by losing the azo groups during the heating and also by the attachment of the fragment free radicals to the polymer mainchain. However, the second shoulder was not obvious; this maybe an indication that both depolymerization and decomposition took place. This phenomenon is also observed on Figure 39, the thermogram of poly-(Styrene-co-4'-N-maleimido-2,3'-dimethylazobenzene); solution.

**Emulsion Polymerization vs. Solution Polymerization**

Two different techniques of polymerization, emulsion and solution, were utilized in this study. Poly-(Styrene-co-N-phenylmaleimide) and poly-(Styrene-
co-4’-N-maleimido-2,3’-dimethylazobenzene) were copolymerized by both techniques, and the resulting composition data are listed in Tables 5 and 6. For poly-(Styrene-co-N-phenylmaleimide), the experimental compositions are close to the theoretical values; emulsion polymerization slightly favors incorporation of imide. Figure 37 is the TGA thermogram for the emulsion polymerized polymer and Figure 39 is that for the solution polymerized polymer; both figures indicate the poly-(Styrene-co-N-phenylmaleimide) polymers are random copolymers (i.e. no multiple transitions). In addition, the only sharp weight loss, which was caused by the random breaking of the polymer chain, indicates the N-phenylmaleimide monomer used contained no detectable maleic anhydride (see the IR spectrum, Figure 7). The emulsion polymerized material degraded at a higher temperature than the solution polymerized material.

The composition results for poly-(Styrene-co-4’-N-maleimido-2,3’-dimethylazobenzene) which was polymerized by the emulsion technique indicate that incorporation of imide is favored. The solution polymerized polymer composition is close to the reaction stoichiometry. One reason for this may be that there was too much subtraction of the solvent signal from Figure 24 compared to Figure 26. Excessive solvent subtraction could result in a lower absorbance of styrene than the actual values. The solution polymerization was performed with styrene and initiator being combined before addition to the maleimide. Based on the reactivity ratios of the monomers, styrene is less reactive than maleimide; therefore, in the solution polymerization, styrene was mixed with the initiator prior to reacting with the maleimide monomer.
However, in emulsion polymerization, styrene and maleimide were placed in the emulsion at the same time, and the initiator was added later to the emulsion. Both monomers are expected to diffuse readily to the reaction micelle. Thus, the relative amount of styrene in the solution polymerized products were higher than that of the emulsion polymerized products. In conclusion, the difference between the two techniques can be seen by comparing the relative amount of styrene in the polymer products polymerized by the emulsion and solution techniques.

Imidization vs. Polymerization

The [50:50] and [92:8] styrene-co-maleimide polymer products were synthesized by imidizing the maleic anhydride repeating units that were already linked to the styrene repeating units in the copolymer chain. Only the [50:50] and [92:8] commercial copolymers were converted to N-substituted maleimide by imidization of maleic anhydride. This procedure led to the formation of a ternary copolymer. The preparation of all other poly-(Styrene-co-N-substitutedmaleimide) copolymers were performed by the traditional polymerization technique. In the traditional technique, the two monomers of styrene and N-substitutedmaleimide were prepared prior to polymerization, therefore, these are the only two species which get incorporated into the polymer chain.

Figure 18 and Figure 23 are the IR spectra for poly-(Styrene-co-N-phenylmaleimide); [50:50] imidized after polymerization and poly-(Styrene-co-
N-phenylmaleimide) produced by emulsion polymerization, respectively. Figure 18 displays a strong absorption occurring at 1780 cm\(^{-1}\) due to C=O stretch vibration of maleic anhydride, which indicates that the imidization on the polymer chain was not complete. This feature is absent on Figure 23, indicating that the imide monomer, once formed, is stable. Tables 5 and 6 list all of the composition results for the two different preparation methods. The TGA thermogram of poly-(Styrene-co-N-phenylmaleimide) polymerized by the solution technique also indicates that the imidization of maleic anhydride monomer was almost complete. Therefore, the results for the polymerized products are cleaner than those of the imidized polymer products.

The polymer chain of poly-(Styrene-co-maleic anhydride); [50:50] was in a random coil conformation when the polymer was dissolved in toluene. Some of the reactive maleic anhydride sites were hindered by the pendent phenyl groups of styrene and by the free volume effect of the polymer chain within the coil. This made it more difficult for the reactants (aniline or 4’-amino-2,3’-dimethylazobenzene) to diffuse into the coil to attack the reactive maleic anhydride sites, thus resulted in an incomplete imidization of maleic anhydride. The same explanation also applies to the cause of the difference between the [50:50] and the [92:8] products. The greater hindrance from styrene in the [50:50] polymer resulted from the alternating sequence between styrene and maleic anhydride. As a result, the imidization of an alternating copolymer is not as complete as that of the random copolymer. In addition, toluene is a better
solvent for the [92:8] polymer than the [50:50] polymer. Consequently, the coil on the latter case has less free volume available to diffusing reactant than in the [92:8] polymer.
CONCLUSIONS

Based on the results of this study, several conclusions can be drawn:

1. The purities of the four monomers, N-phenylmaleimide, 4’-N-maleimido-2,3’-dimethylazobenzene, N-nitrophenylmaleimide and N-p-chlorophenylmaleimide, were high.

2. Nitro group was a stronger electron-withdrawing group and yielded a polymer having a low thermal stability.

3. Poly-(Styrene-co-maleic anhydride); [50:50] and [92:8] were alternating and random copolymers, respectively.

4. The imidization of maleic anhydride was complete for the [92:8] copolymers, but incomplete for the [50:50] copolymers.

5. The imidization of maleic anhydride to form the N-phenylmaleimide products was more complete than the 4’-N-maleimido-2,3’-dimethylazobenzene products.

6. The polymers synthesized by emulsion and solution polymerizations were random copolymers; the emulsion polymerized materials displayed higher thermal decomposition temperatures than the solution polymerized materials.
7. Emulsion polymerization slightly favored incorporation of imide compared to solution polymerization.

8. The copolymers polymerized from the imide monomers contained two constituent groups, while the imidized copolymers contained at least three constituent groups (styrene, maleic anhydride and maleimide).

9. Most of the polymer products were determined by the DSC thermograms to be amorphous polymers, as evidenced by the lack of crystallization, melting behavior.
APPENDIX

Three Absorption Spectra of Poly-(Styrene)
Figure X-1. Absorption Spectrum of Poly-(Styrene); 0.1 g product in 10 ml chloroform

Figure X-2. Absorption Spectrum of Poly-(Styrene); 0.2 g product in 10 ml chloroform

Figure X-3. Absorption Spectrum of Poly-(Styrene); 0.3 g product in 10 ml chloroform
Figure X-1. Absorption Spectrum of Poly-(Styrene); 0.1 g product in 10 ml chloroform
Figure X-2. Absorption Spectrum of Poly-(Styrene); 0.2 g product in 10 ml chloroform
Figure X-3. Absorption Spectrum of Poly-(Styrene); 0.3 g product in 10 ml chloroform.
REFERENCES


