

POLYIMIDES FROM CYCLIC ALIPHATIC DIAMINE MONOMER

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by

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## **ABSTRACT**

### **POLYIMIDES FROM CYCLIC ALIPHATIC DIAMINE MONOMER**

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**SUPERVISING PROFESSOR: CHAD BOOTH**

Polyimides are of interest because of their characteristic thermal properties such as high glass transition and decomposition temperatures and chemical resistance to many conventional solvents. The synthesis of polyimides from cyclic aliphatic diamine monomers would ideally incorporate enhanced rigidity and toughness to the typically brittle films while maintaining excellent clarity. Similar work has been shown by Kelsey and co-workers where terephthalate-based copolyesters have been found to “exhibit high impact resistance combined with good thermal properties, ultraviolet stability, optical clarity, and low color.”<sup>1</sup> The low color property is a result of the aliphatic monomer disrupting the aromaticity of the polymer backbone which could reduce some of the yellow tint common to most polyimides. The improvement in mechanical properties such as impact resistance, toughness, and modulus, while observed, are inexplicable at this point in the research of polymers incorporating cyclic aliphatic monomers.<sup>2,3</sup> A series of polyimides was synthesized with 1,4-bis(aminomethyl)cyclohexane, a cyclic, aliphatic diamine monomer, and four commercially available dianhydrides. The polymers showed good thermal properties, excellent chemical resistance, and fair mechanical properties consistent with similar polyimides.

## 1.0 INTRODUCTION

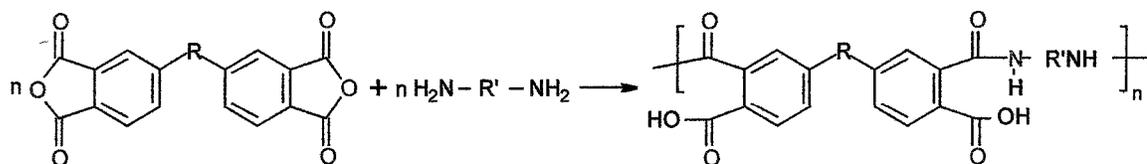
### 1.1 POLYIMIDES

#### 1.1.1 BACKGROUND

Polyimides are of particular interest because of their peculiar thermal, optical, and chemical properties which can be customized by varying the composition of the monomers.<sup>4</sup> Good mechanical properties can be achieved if the number average molecular weight,  $M_n$ , of the polymers is between 10,000 and 30,000 g/mol.<sup>5</sup> Often, it is difficult to determine the molecular weight of polyimides as they are resistant to many conventional organic solvents and oxidation (although they do not wear well in alkaline environments).<sup>6,7</sup> The combination of insolubility and poor processability is commonly referred to as intractability. Polyimides are mostly amorphous with glass transition temperatures above 150 °C and decomposition temperatures up to 300 °C or higher.<sup>6</sup> The glass transition temperature,  $T_g$ , is a first order transition temperature above which the amorphous regions of the polymer are able to undergo long-range segmental motion. The decomposition temperature is typically recorded as the temperature at which the material has lost ten percent of its initial mass. The low dielectric constant of polyimides, in addition to their other properties, make polyimides particularly suitable to function in many applications, such as wiring insulation materials, membranes for separating gases, and optical sensors.<sup>4,6</sup>

### 1.1.2 SYNTHESIS

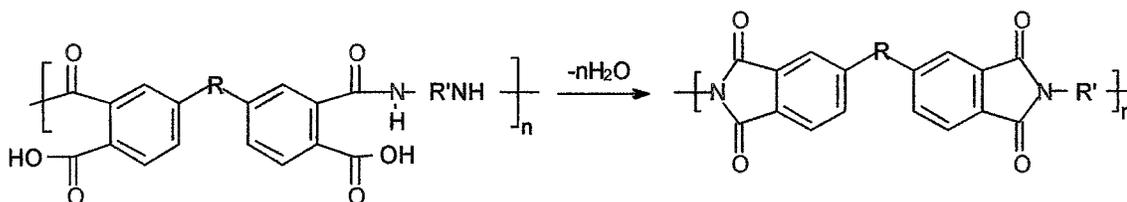
Polyimides are classically synthesized by the polymerization of aromatic dianhydrides with either aromatic or aliphatic diamines. It is important to note that this synthesis cannot occur in a simple one step process because of the poor solubility of polyimides which would cause the polymer to precipitate at relatively low molecular weights; therefore, polyimides must be synthesized in two steps. The first step in the condensation polymerization is an amidation reaction performed in a polar aprotic solvent, typically *N*-methylpyrrolidone (NMP) or *N,N*-dimethylacetamide (DMAc), at room temperature to form the soluble, high molecular weight poly(amic acid) intermediate as shown in Scheme 1.<sup>6</sup>



Scheme 1: Amidation Reaction Between a Dianhydride and a Diamine

It is after this first step in the synthesis that the polymer is most easily processed into films, fibers, laminates, coatings, *etc.* since it is still soluble and fusible due to the hydrogen bonding to the polar solvent.<sup>6</sup> Less polar, more volatile solvents can be used (to allow ease of solvent removal from the final product), but a catalyst is required since the reaction rate decreases in less polar solvents.<sup>6</sup> Catalysts can also be used for diamines with an acid dissociation constant,  $\text{p}K_a$ , greater than 4.5.<sup>5</sup> These catalyst systems usually consist of a mixture of an imidization catalyst, usually a tertiary or aromatic amines such as tributylamine or pyridine respectively, and a dehydration catalyst represented by anhydrides of lower fatty acids, such as acetic anhydride.<sup>5,8</sup>

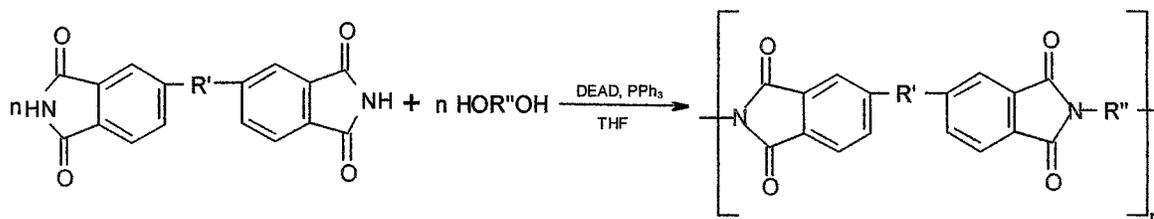
The second step in the polyimide synthesis is cyclodehydration of the intermediate poly(amic acid) to form the polyimide (Scheme 2). This step can occur thermally by heating the intermediate to temperatures typically above 150 °C or in solution, if catalysts such as acetic anhydride and pyridine are used.<sup>5</sup> A second solvent which forms a minimum boiling azeotrope with water, *i.e.* toluene, can be added to remove water by azeotropic distillation.<sup>5</sup>



Scheme 2: Cyclodehydration of Poly(amic acid) to Form the Polyimide

This two-step polymerization process is the one utilized in this research in order to characterize the poly(amic acid) intermediates by infrared spectroscopy and inherent viscosity since the polyimides are insoluble. However, it is important to note that in 2000, T.D. Kim *et al.* published an article describing a novel, one-step approach to synthesizing polyimides by employing a Mitsunobu reaction (Scheme 3) on a diimide and a diol; thereby, eliminating the need for imidization at high temperatures.<sup>9</sup>

Diethylazodicarboxylate (DEAD) and triphenylphosphine ( $\text{PPh}_3$ ) form an intermediate which acts as a catalyst to deprotonate the diimide, making it a nucleophile which undergoes substitution with the alcohol.



Scheme 3: Polyimide Mitsunobu Reaction

## 1.2 POLYIMIDES INCORPORATING AROMATIC MOIETIES

One of the most common commercial examples of a wholly aromatic polyimide is the DuPont™ Kapton® polyimide film (shown in Figure 1\*).

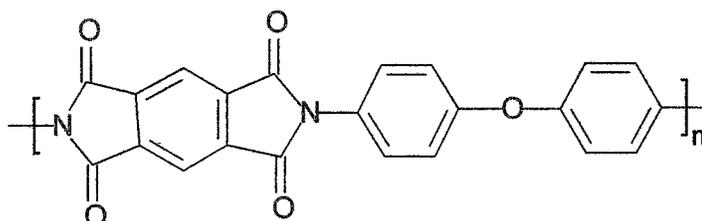


Figure 1: General Structure of DuPont™ Kapton® Polyimide Film

Kapton® is synthesized from pyromellitic dianhydride and 4,4'-oxydiphenylamine according to traditional methods mentioned above, where the ring closure occurs at temperatures between 200 °C and 300 °C. DuPont™ has shown the polyimide film to possess excellent chemical resistance (there are no known organic solvents for the film) and thermal resistance (it does not melt or burn). Kapton® polyimide film has been used in electrical and magnetic wiring insulation for various applications including electronics and civil and military avionics.<sup>10</sup> The resistance to gamma and neutron radiation demonstrated by Kapton® polyimide film makes it ideal for solar arrays and incorporation into the outer layer of space suits.<sup>10</sup>

## 1.3 POLYIMIDES INCORPORATING PARTIALLY ALIPHATIC MOIETIES

Although wholly aromatic polyimides display excellent thermal stability over wide ranges of temperatures (as evident by the fact that they can be used for applications ranging from cryogenic temperatures to around 200 °C), electrical resistance, and chemical resistance, they do suffer from prolonged exposure to ultraviolet light.<sup>13</sup>

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\* DuPont™ and Kapton® are registered trademarks of E.I. du Pont de Nemours & Company.

Additionally, polyimides are typically too stiff and brittle for many applications and are extremely difficult to process due to their poor solubility and lack of melt flow at reasonable temperatures.<sup>6</sup> A simple solution to these problems is to customize the dianhydride and/or diamine monomers by adding flexible or bulky segments to the polymer backbone. However, the improvement in solubility and processability generally diminishes thermal properties of the polyimide except in cases of partially fluorinated species, like 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane (Figure 4). One example of introducing bulky segments to the polymer backbone is a partially fluorinated aromatic polyimide consisting of 2,2-bis(3,4-anhydrodicarboxyphenyl)hexafluoropropane (6FDA) and 4,4'-diaminodiphenyl ether (ODA), which has a rigid structure resulting in expanded molecular packing, reduced local segmental motion, and greater diffusion coefficients relative to other non-fluorinated polyimides.<sup>13,14</sup> The 6FDA-based polyimides demonstrate good solubility in common organic solvents while maintaining good mechanical and thermal properties.<sup>13</sup>

The current thermoplastic polyimide commercial leader in gas separation is Matrimid<sup>®</sup> bismaleimides by Huntsman Advanced Materials, produced by Ciba Geigy and shown in Figure 2\*.

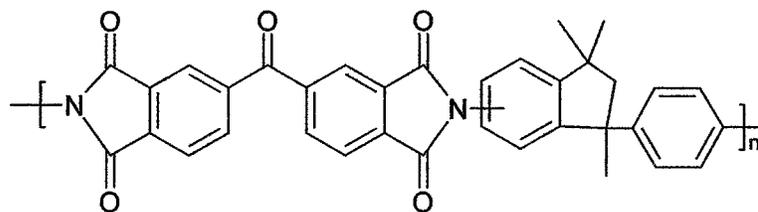


Figure 2: Matrimid<sup>®</sup> 5218 Structure

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\* Matrimid<sup>®</sup> is a registered trademark of Huntsman Corporation or an affiliate thereof in one or more, but not all, countries.

Matrimid<sup>®</sup> 5218 is made from a proprietary diamine and is soluble in numerous organic solvents.<sup>11</sup> Matrimid<sup>®</sup> has a glass transition temperature of 265-280 °C, tensile modulus of 420,000 psi, and 48.6% elongation at break. Matrimid<sup>®</sup> possesses the desired structure-property relationships of loosely packed glassy polymers with sufficient cohesive energy and rigid, plasticization-resistant backbones necessary for high permeability and selectivity owing to the high aromatic content in the backbone constrained by the rigid, aliphatic segment.<sup>12</sup>

#### 1.4 THESIS PROPOSAL

The cyclic, aliphatic monomer in this study is a *cis*-/*trans*- mixture of 1,4-bis(aminomethyl)cyclohexane (BAMC). Figure 3 shows the two different conformations of BAMC.

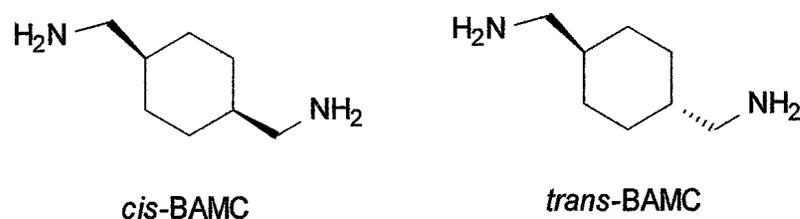
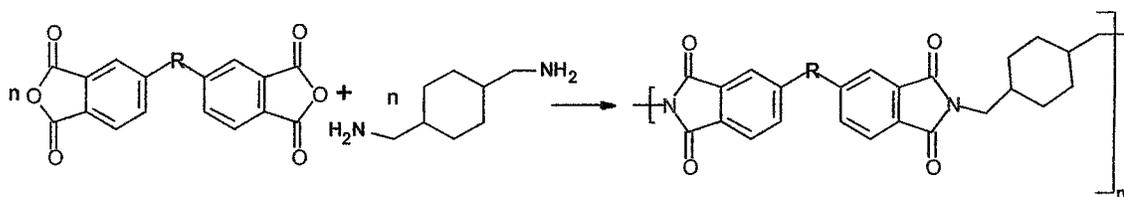


Figure 3: Isomers of BAMC

BAMC is less torsionally constrained than smaller cyclic rings because it can assume a chair configuration. The synthesis of polyimides from cyclic, aliphatic diamines ideally incorporates enhanced rigidity and toughness into the typically brittle films while maintaining excellent clarity owing to the disruption in aromaticity. This project identifies the properties of polyimides synthesized with 1,4-bis(aminomethyl)cyclohexane. These polyimides have the general structure (Scheme 4), where R can be an aryl group (4,4'-bipthalic anhydride, BPDA), an ether linkage (4,4'-oxydiphthalic anhydride, ODPA), a carbonyl (3,3',4,4'-

benzophenonetetracarboxylic dianhydride, BTDA), or a fluorinated linkage (4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 6FDA) (Figure 4).



Scheme 4: General Polyimide Synthesis

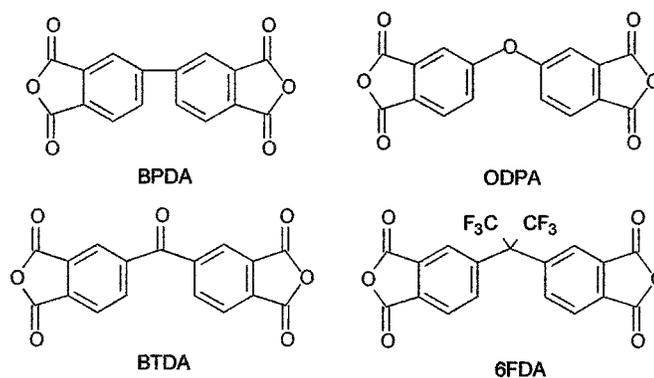


Figure 4: Dianhydride Structures

The two-step approach to the condensation of the polyimide will be utilized to produce high molecular weight polyimide. While the BAMC group is expected to improve mechanical properties, it may result in decreased thermal stability relative to wholly aromatic polyimides due to the presence of the incorporated aliphatic segment.

The resulting poly(amic acid) intermediates were characterized using Fourier transform infrared spectroscopy (FTIR) and viscosity to determine inherent viscosities. The polyimides were also analyzed using infrared spectroscopy. Differential scanning calorimetry (DSC) was performed to determine the glass transition temperature and any crystallinity that is present, although the polyimides were not expected to display melting behavior temperature because of the aliphatic diamine monomer. Thermogravimetric analysis (TGA) was performed in order to determine the decomposition temperature at

ten percent weight loss. Additionally, dynamic mechanical analysis (DMA) was performed to estimate the glass transition temperature for comparison with the DSC values and determine the storage modulus and loss modulus.

## 2.0 EXPERIMENTAL

### 2.1 MATERIALS

1,4-Bis(aminomethyl)cyclohexane (*cis/trans* mixture) (98%) was purified by fractional vacuum distillation. 4,4'-Biphthalic anhydride (97%, TCI), 4,4'-oxydiphthalic anhydride (98%, TCI), and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (95%, TCI) were purified by sublimation. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride was donated by Daiken Chemical Company and purified by sublimation twice.

### 2.2 POLYMER SYNTHESIS

A typical procedure for the polymerization is as follows. Dimethylacetamide (2 mL) (DMAc) was added to a three-neck round-bottom flask equipped with a magnetic stir bar and purged with argon at room temperature for 15 minutes. BAMC (4-6 mmol) was added to the solvent and allowed to disperse for 15 minutes while an equimolar amount of BTDA was weighed in a beaker. Approximately 2 mL of DMAc was added to the beaker to dissolve the dianhydride, and then this was added intermittently with a glass pipette over a period of two hours with stirring. The beaker was rinsed with DMAc for a total volume of 10 mL of solvent. The flow of argon was slowed, and the solution was allowed to stir overnight. Then the solution was precipitated into cold methanol and filtered. The precipitated poly(amic acid) was re-dissolved in DMAc and then cast onto a level polytetrafluoroethylene plate adhered to an aluminum plate. The solvent was then allowed to slowly evaporate in the hood for 24 hours before the plate was placed in a vacuum oven. Once in the vacuum oven, the polymer was heated at 53 °C for 24 hours.

The heat was gradually raised to 60 °C, and then the vacuum was applied slowly to decrease the pressure over a four hour time period. After an additional hour, the polymer was thermally cured in a high temperature, digital oven where the temperature was gradually increased from 85 °C to 115 °C over a four hour period. This synthesis process was repeated with the other three dianhydrides.

## 2.3 CHARACTERIZATION METHODS

### 2.3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

Infrared spectra were obtained using a Perkin Elmer Spectrum One FT Infrared Spectrometer. The poly(amic acid) was dissolved in minimal dimethyl sulfoxide and placed on a potassium bromide (KBr) pellet. The subtracted background consisted of dimethyl sulfoxide and the KBr pellet. The polyimide films were analyzed by themselves without any support material. An average of five scans was obtained for each spectrum.

### 2.3.2 INHERENT VISCOSITY

Inherent viscosities were determined for the poly(amic acid) precursors at a concentration of 0.25 g/dL in DMAc which was stirred for 24 hours prior to analysis to ensure dissolution of polymer. The measurements were taken in a Julabo constant temperature bath maintained at 30 °C using a Cannon-Fenske 50 bore viscometer. The solutions were placed in the viscometer and allowed to equilibrate in the bath for thirty minutes before analysis. Two polystyrene standards were analyzed for comparison: PS5000 ( $M_w = 5,480$  g/mol and  $M_n = 5,450$  g/mol) and PS14000 ( $M_w = 14,800$  g/mol and  $M_n = 13,300$  g/mol). The inherent viscosities were calculated using the following

formula:  $\eta_{inh} = \frac{\ln(\frac{t}{t_o})}{c}$ , where  $t$  is the time in seconds it takes the solution to travel the distance,  $t_o$  is the time in seconds it takes the pure solvent to travel the distance, and  $c$  is

the concentration of the polymer solution in g/dL. Five measurements were taken for each sample. The highest and lowest measurements were discarded, and the values reported are an average of remaining three measurements.

### 2.3.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analyses were performed using a TA Instruments Q50 Thermogravimetric Analyzer. The analyses were performed in air from ambient temperature to 800 °C at a ramp rate of 20 °C/min. on 10 – 20 mg samples in a platinum pan. TGA measures the weight loss and decomposition temperatures of the polymer.

### 2.3.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimetry was performed using a TA Instruments Q200 Differential Scanning Calorimeter using a heat/cool/heat cycle at 10 °C/min on 5 – 10 mg samples under argon. Data collected from the DSC provided information on the glass transition temperature ( $T_g$ ) and any crystalline melting temperatures ( $T_m$ ).

### 2.3.5 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analyses were performed using a TA Instruments Q800 Dynamic Mechanical Analyzer with tension clamp designed for thin films. DMA provides mechanical information on the materials' storage and loss modulus and  $\tan \delta$ . The variable  $\tan \delta$  is the loss modulus divided by the storage modulus which can provide an estimation of the glass transition temperature based on mechanical properties. The samples were cut into bars measuring approximately 22.0 x 7.00 x 0.2 mm. The samples were analyzed at temperatures from ambient to 225 °C at a ramp rate of 3 °C/min.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 POLYMER SYNTHESIS

Four different polyimides were synthesized from the reaction of the diamine, 1,4-bis(aminomethyl)cyclohexane (BAMC), and four different dianhydrides namely 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-biphthalic anhydride (BPDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), and 4,4'-oxydiphthalic anhydride (OPDA). The polyimides were prepared by conventional two-step polymerization method involving the formation of the poly(amic acid) intermediate followed by thermal cyclodehydration conversion into the polyimide.

Yields for the BTDA/BAMC, BPDA/BAMC, ODPA/BAMC, and 6FDA/BAMC polyimide films were 1.87g (93%), 1.93g (90%), 1.29g (96%), and 2.33g (87%), respectively. The solubilities of the poly(amic acid) precursors and polyimides in common polar, aprotic solvents, chloroform, methanol, and ether were investigated by attempting to dissolve a small amount of polymer (~ 0.1g) per deciliter of solvent in a test tube with subsequent heating. The poly(amic acid) precursors were soluble only in dimethylacetamide, dimethylformamide, and dimethyl sulfoxide. The polyimides were insoluble in all solvents investigated which may be a result of the compact aggregation of the polymer chains which occurred during the thermal imidization.<sup>16</sup> Having an ether linkage or a partially fluorinated linkage in the backbone of the polymer did not appear to enhance the solubility of the polyimides which may be due to the rigid phenyl groups surrounding the flexible moieties.<sup>16</sup>

## 3.2 CHARACTERIZATION

### 3.2.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY

The FTIR spectra of the poly(amic acid) precursors (dissolved in DMSO and cast on KBr pellets) provide evidence for the presence of all expected functional groups. Characteristic absorptions of poly(amic acid)s include: the amide I (C=O) absorption near  $1650\text{ cm}^{-1}$ , the amide II (N-H bending) absorption at a lower frequency under the envelope of amide I band, and the strong overlapping N-H and O-H stretching absorptions between  $3564\text{-}3000\text{ cm}^{-1}$ . The IR spectra of the poly(amic acid)s also demonstrate the aromatic C-H stretch above  $3000\text{ cm}^{-1}$  and the aliphatic C-H stretch below  $3000\text{ cm}^{-1}$  which confirms presence of the alicyclic group in the polymer. The band assignments for several major IR absorption peaks for the poly(amic acid) precursors and polyimides are shown in Table 1. The IR spectra for the poly(amic acid) precursors can be found in Appendix I, No's. 1-4.

Alternatively, the polyimides (analyzed as freestanding films) exhibit characteristic peaks in the regions  $1787\text{-}1710\text{ cm}^{-1}$  (imide carbonyl asymmetric and symmetric stretch) and  $1357\text{-}1330\text{ cm}^{-1}$  (C-N stretch).<sup>16</sup> The overlapping N-H and O-H stretching frequencies are significantly diminished, although not totally as the amount of heat necessary to complete imidization would likely begin to degrade the polymer, in relation to the aromatic and aliphatic C-H stretching vibration absorptions. The IR spectra for the polyimides can be found in Appendix I, No's. 5-8.

Table 1 – FTIR of Synthesized Poly(amic acid)s and Polyimides by Spectra Number (cm<sup>-1</sup>)

Band Assignment	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
Amide, C=O	1645	1651	1651	1645	-	-	-	-
N-H/O-H str.	3400, 3210	3543, 3243	3543, 3270	3564, 3207	3350	3465	3472	3475
sp <sup>3</sup> C-H str.	2927	2921	2920	2920	2782	2924	2926	2851
C-N str.	1440	1437	1437	1437	1555	1555	1555	1555
imide C=O asym.	-	-	-	-	1787	1768	1772	1769
imide C=O sym.	-	-	-	-	1722	1715	1718	1710

*str.* stretching, *asym.* asymmetric stretching, *sym.* symmetric stretching

### 3.2.2 INHERENT VISCOSITY

Gel permeation chromatography could not be performed to determine the molecular weight of the polyimides and the poly(amic acid) intermediates because they were all insoluble in both tetrahydrofuran and chloroform; therefore, inherent viscosity was determined for the poly(amic acid) precursors. The results of the viscosity experiment are tabulated in Table 2.

Table 2 – Inherent Viscosities of Poly(amic acid) Precursors

Sample	$\eta_{inh}$ (dL/g)
6FDA/BAMC PAA	0.087
BPDA/BAMC PAA	0.122
BTDA/BAMC PAA	0.104
OPDA/BAMC PAA	0.081
PS5000	0.045
PS14000	0.116

Inherent viscosity can be used as an indicator of molecular weight. The OPDA/BAMC poly(amic acid) had the lowest inherent viscosity of 0.081 dL/g and the BPDA/BAMC poly(amic acid) had the highest inherent viscosity of 0.122 dL/g. The polystyrene standards with  $M_w$  of 5,480 g/mol (PS5000) and 14,800 g/mol (PS14000) had inherent

viscosities of 0.045 and 0.116 dL/g, respectively. Based on the evidence that films were cast and the thermal properties of the polyimides are similar to other polyimide systems, a comparison between the inherent viscosities of the polyimides and the polystyrene standards indicates that the molecular weight of the polyimides is between 5,500 and 15,000 g/mol, although polystyrene is inherently different than the condensation polymers studied in this research. Low molecular weights of the polyimides did affect the mechanical and thermal properties some as seen in the following sections, but not as much as it would affect other polymer classes, because of the incredibly strong intermolecular dipole-dipole interactions among the polyimide chains.

### 3.2.3 THERMOGRAVIMETRIC ANALYSIS (TGA)

Thermogravimetric analysis was performed in air to determine the decomposition temperature of each polyimide. The decomposition temperature,  $T_d$ , was taken as the temperature at which the polymer has lost ten percent of its initial weight by mass. Char yield is the amount of polymer sample remaining at 700 °C. Table 3 summarizes the ten percent decomposition temperatures for the four polyimides under investigation. The TGA thermograms can be seen in Appendix II, No's. 1-4.

Table 3 – TGAs of Polyimide Series

<b>Polyimide</b>	<b><math>T_d</math> (°C)</b>	<b>Char Yield (%) at 700 °C</b>
6FDA/BAMC	467	2
BPDA/BAMC	485	30
BTDA/BAMC	470	18
ODPA/BAMC	485	1

The 6FDA/BAMC polyimide has the lowest  $T_d$  of 467 °C. The decomposition temperatures varied by less than 20 °C which is evidence that the aliphatic portion of the

polyimide is the most thermally susceptible region relative to the dianhydride moiety. The TGA thermograms for BPDA/BAMC and BTDA/BAMC show a more gradual weight loss due to a loss of either moisture or solvent above the glass transition temperature of the polyimides. The moisture and/or solvent may have become trapped in the polyimide during the curing process. The 6FDA/BAMC and OPDA/BAMC samples were dried more thoroughly prior to thermogravimetric analysis. William Blackley synthesized the BTDA/BAMC polyimide using a different procedure and reported a ten percent weight loss at 459 °C and a fifty percent weight loss at 490 °C as determined by TGA in air at a rate of 5 °C/min.<sup>17</sup> This value is slightly lower compared to the ten percent weight loss at 470 °C and a fifty percent weight loss at 498 °C as determined for the same polyimide in this study. The difference could be a result of higher molecular weight obtained in this study or more extensive drying of the polyimide film.

### 3.2.4 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Differential scanning calorimetry was performed to determine the glass transition temperature of the polyimide as well as to determine the degree of crystallinity, if any. Glass transition temperatures ( $T_g$ ) and crystalline melting temperatures ( $T_m$ ) were taken as the midpoint of the step transition during the second heating. Table 4 summarizes the  $T_g$  and  $T_m$  for each polymer. The differential scanning calorimetry analyses can be seen in Appendix III, No's 1-4.

Table 4 – DSCs of Polyimide Series

<b>Polyimide</b>	<b><math>T_g</math> (°C)</b>	<b><math>T_m</math> (°C)</b>
6FDA/BAMC	229	None
BPDA/BAMC	225	377 °C
BTDA/BAMC	214	None
ODPA/BAMC	203	None

Although the ODPA/BAMC polyimide has the highest  $T_d$ , it has the lowest  $T_g$  of 203 °C because of the flexible ether linkage between the benzene rings of the dianhydride. The 6FDA/BAMC polyimide which has the lowest  $T_d$ , has the highest  $T_g$  of 229 °C. The BPDA/BAMC polyimide displays a crystalline melting transition temperature at 377 °C. This is due to the ability of the polymer strains to pack more closely and form crystalline regions because of the absence of a flexible functional group between the two benzene rings of the dianhydride. These results are comparable to the  $T_g$  of Matrimid<sup>®</sup> 5218/graphite prepreg which is 265 °C wet and 280 °C dry.<sup>11</sup> Matrimid<sup>®</sup> 5218 has more aromatic character in the diamine portion of the polymer backbone which likely accounts for its higher thermal properties. The  $T_g$  of the BTDA/BAMC polyimide synthesized in this study was 214 °C as determined by DSC in air. William Blackley's BTDA/BAMC polyimide has a  $T_g$  of 137-156 °C, determined by differential thermal analysis in helium.<sup>17</sup> As consistent with this study, the Blackley polymer does not show a crystalline melting transition.

### 3.2.5 DYNAMIC MECHANICAL ANALYSIS (DMA)

Dynamic mechanical analysis (DMA) was performed to determine the storage and loss modulus and  $\tan \delta$ , which correlates to  $T_g$ , for each polyimide. Table 5 contains the data obtained from DMA. The analyses from DMA can be seen in Appendix IV, No's.

1-3. Table 5 – DMAs of Polyimide Series

Polyimide	Estimated $T_g$ (°C) from $\tan \delta$	$T_g$ (°C) from DSC	Storage Modulus at 50 °C (MPa)	Loss Modulus at 50 °C (MPa)
BPDA/BAMC	202	225	677	13
BTDA/BAMC	200	214	1347	38
ODPA/BAMC	124	203	2240	73

DMA could not be performed on the 6FDA/BAMC polyimide because the film was too brittle to undergo mechanical testing, which is likely a result of low molecular weight polymer or limited free rotation resulting from the large trifluoromethyl groups of the 6FDA monomer. The  $T_g$ , as determined from DMA as the peak maximum of the  $\tan \delta$  curve, was significantly lower for all the polyimides compared to the distinctive  $T_g$  as determined by DSC. This may be a result of solvent trapped in the matrix of the polymer film which affects the mechanical, but not thermal, analyses of the polyimides. The ODPA/BAMC polyimide contained approximately ten percent solvent as determined by TGA; however, this additional drying step could not be performed on the test bars for DMA because bubble formation occurs as the solvent escapes during the drying process. Both the BTDA/BAMC and the BPDA/BAMC polyimides likely had considerably less solvent trapped within the polymer because the molecular structures of the polymers have less affinity for trapping the solvent than the ODPA/BAMC polyimide. DMA revealed that the polyimides had decent storage moduli ranging from 677 MPa to 2240 MPa compared to other cyclic aliphatic polyimides such as Matrimid<sup>®</sup> 5218 which has a tensile modulus of 2896 MPa.<sup>11</sup>

Table 6 combines all the thermal and physical properties of the polyimides in this study.

Table 6 – Properties of Polyimide Series

Polymer	$\eta_{inh}$ of PAA (dL/g)	Bond Angle*	$T_d$ (°C)	DSC $T_g$ (°C)	$T_m$ (°C)	DMA $T_g$ (°C)
6FDA/BAMC	0.087	109°	467	229	-	-
BPDA/BAMC	0.122	120°	485	225	377	202
BTDA/BAMC	0.104	120°	470	214	-	200
OPDA/BAMC	0.081	105°	485	203	-	124

\*Bond angle around functional group between diphthalic groups.

#### 4.0 CONCLUSIONS

A series of polyimides were synthesized with an alicyclic diamine monomer (1,4-bis(aminomethyl)cyclohexane) and varying aromatic dianhydrides. Thermal analysis of the polymers using DSC revealed the glass transition temperatures range from 203 °C to 229 °C. TGA revealed decomposition temperatures in the range of 467 °C to 485 °C. Adversely, solvent played a major role in the mechanical testing of the polyimides. DMA revealed that the polyimides had decent storage moduli ranging from 677 MPa to 2240 MPa compared to other cyclic aliphatic polyimides such as Matrimid<sup>®</sup> 5218 which has a tensile modulus of 2896 MPa.<sup>11</sup>

Based on the comparison between the inherent viscosities of the polyimides and the polystyrene standards, it can be assumed that the molecular weight of the polyimides is between 5,500 and 15,000 g/mol. The molecular weights of the polyimides were high enough to cast films and achieve thermal properties similar to other polyimide systems. The polyimides exhibited good solvent resistance since they were insoluble in virtually every organic solvent, including dimethylacetamide.

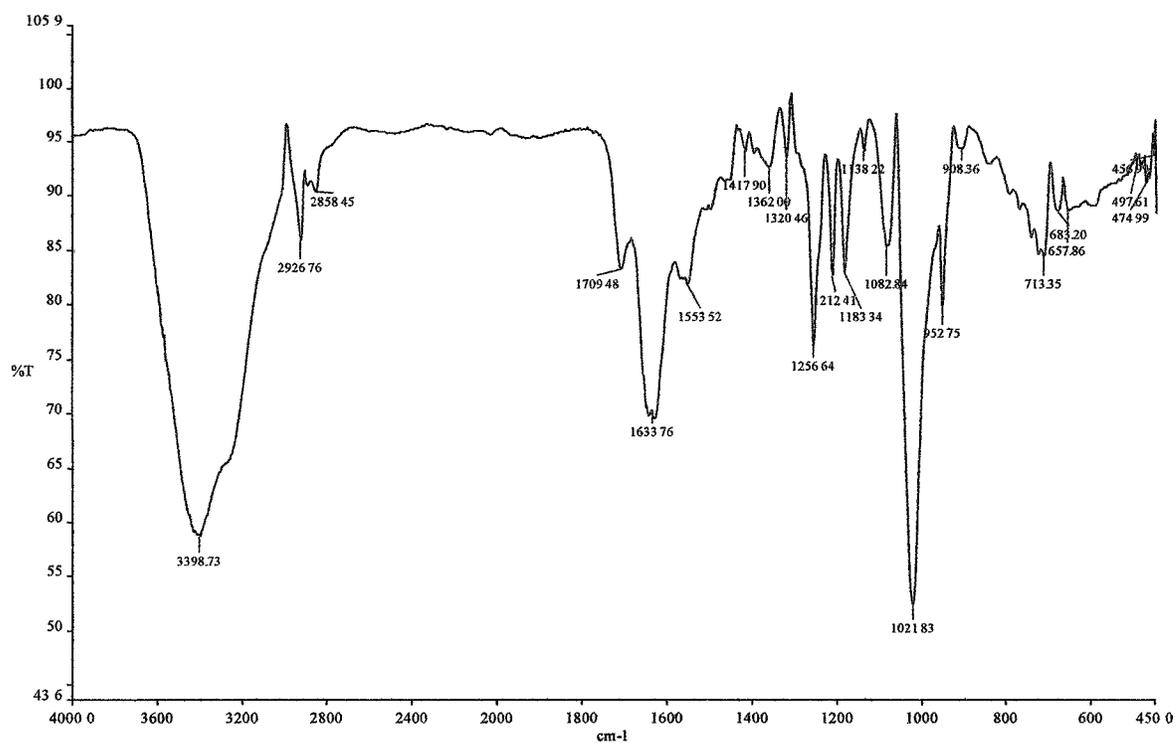
Thus, the series of polyimides synthesized from the cyclic aliphatic monomer BAMC showed high glass transition temperatures and decomposition temperatures characteristic of polyimides but suffered mechanically from solvent trapped in the matrix of the polymer once cured. This issue could be resolved by performing the cyclodehydration step chemically (with catalysts) instead of thermally. Also, a

copolymer could be made incorporating straight-chain aliphatic diamines into the polymer backbone to improve solubility as demonstrated in related work by our group.

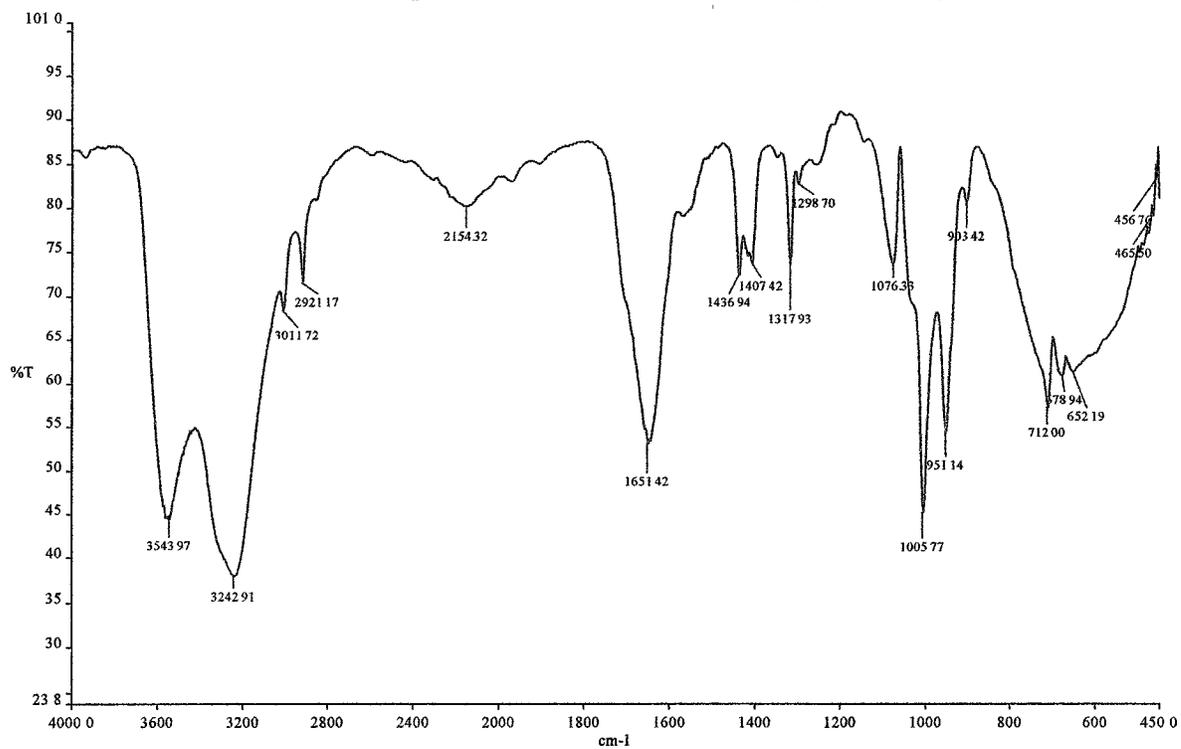
## APPENDIX I: FTIR SPECTRA

### Index for Appendix I

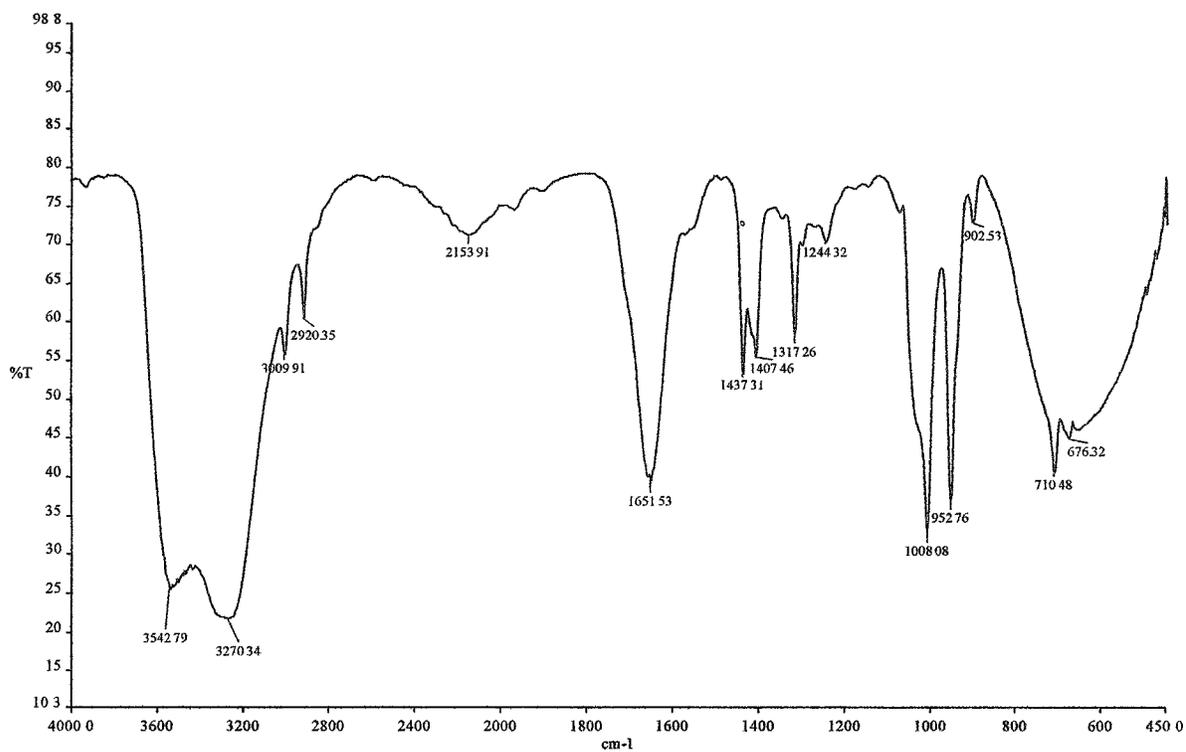
<u>Spectra</u>	<u>Spectra Number</u>
I.R. Spectrum of 6FDA/BAMC Poly(amic acid) .....	1
I.R. Spectrum of BPDA/BAMC Poly(amic acid).....	2
I.R. Spectrum of BTDA/BAMC Poly(amic acid) .....	3
I.R. Spectrum of OPDA/BAMC Poly(amic acid) .....	4
I.R. Spectrum of 6FDA/BAMC Polyimide .....	5
I.R. Spectrum of BPDA/BAMC Polyimide.....	6
I.R. Spectrum of BTDA/BAMC Polyimide .....	7
I.R. Spectrum of OPDA/BAMC Polyimide .....	8



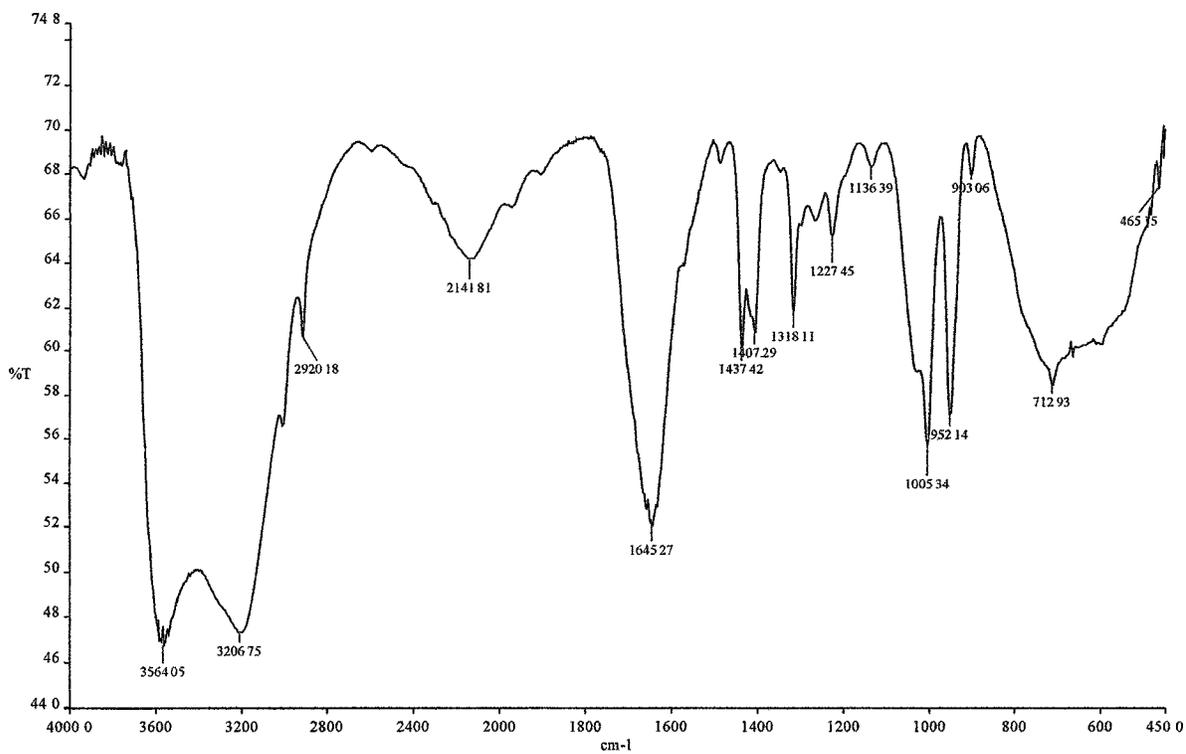
1. I.R. Spectrum of 6FDA/BAMC Poly(amic acid)



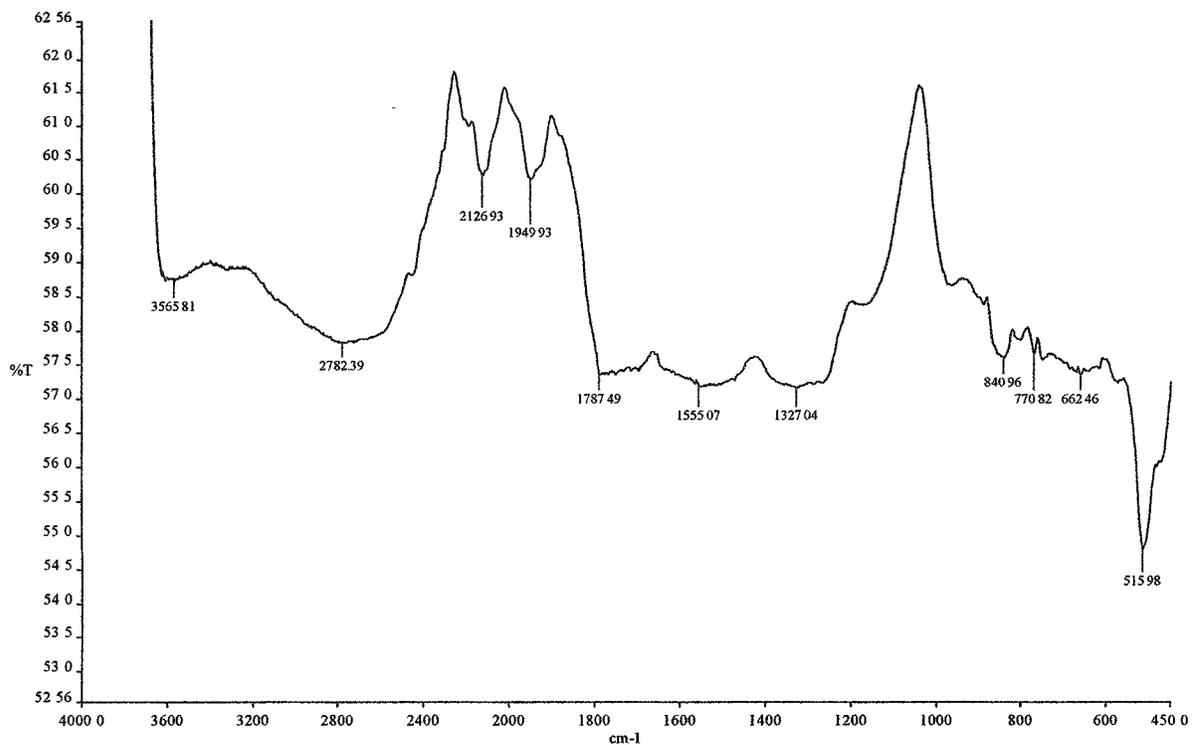
2. I.R. Spectrum of BPDA/BAMC Poly(amic acid)



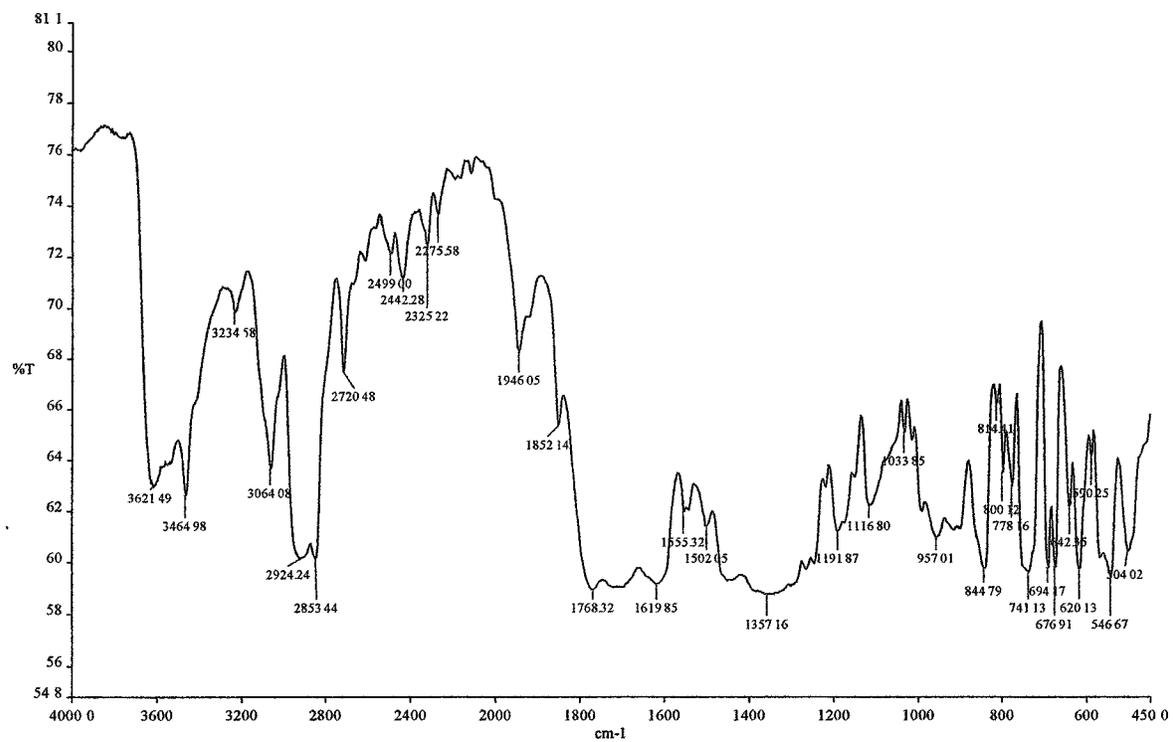
### 3. I.R. Spectrum of BTDA/BAMC Poly(amic acid)



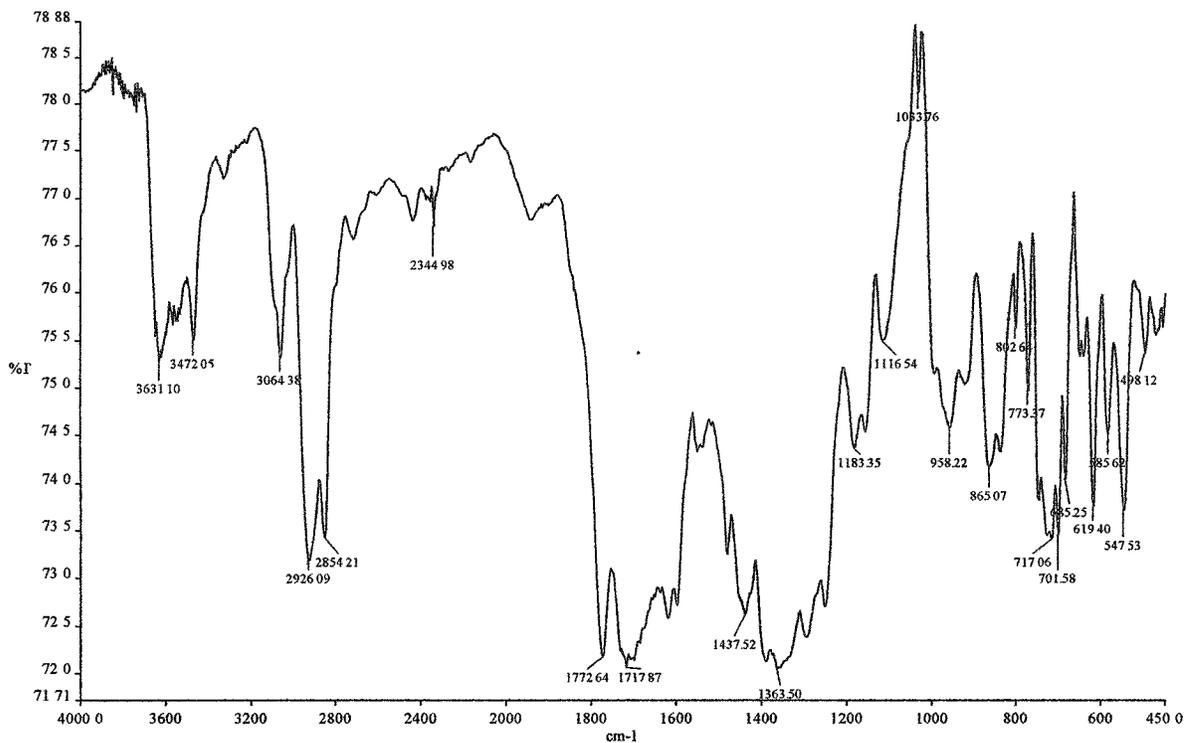
### 4. I.R. Spectrum of OPDA/BAMC Poly(amic acid)



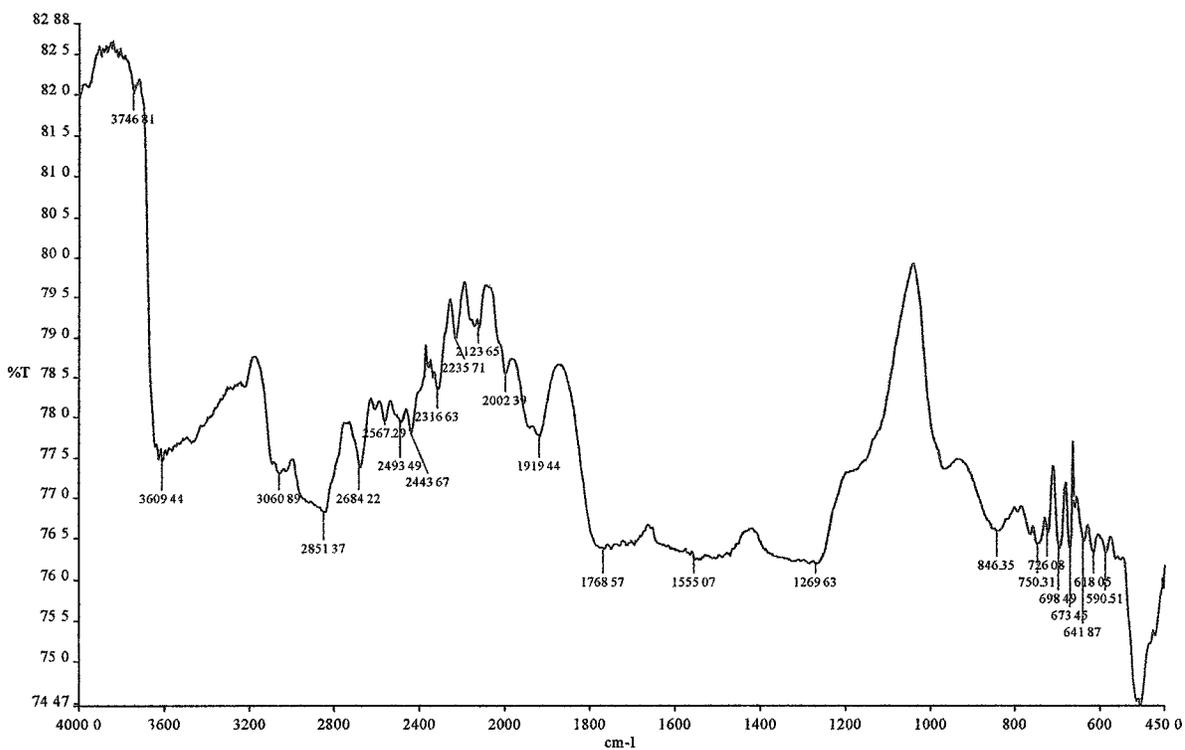
5. I.R. Spectrum of 6FDA/BAMC Polyimide



6. I.R. Spectrum of BPDA/BAMC Polyimide



7. I.R. Spectrum of BTDA/BAMC Polyimide

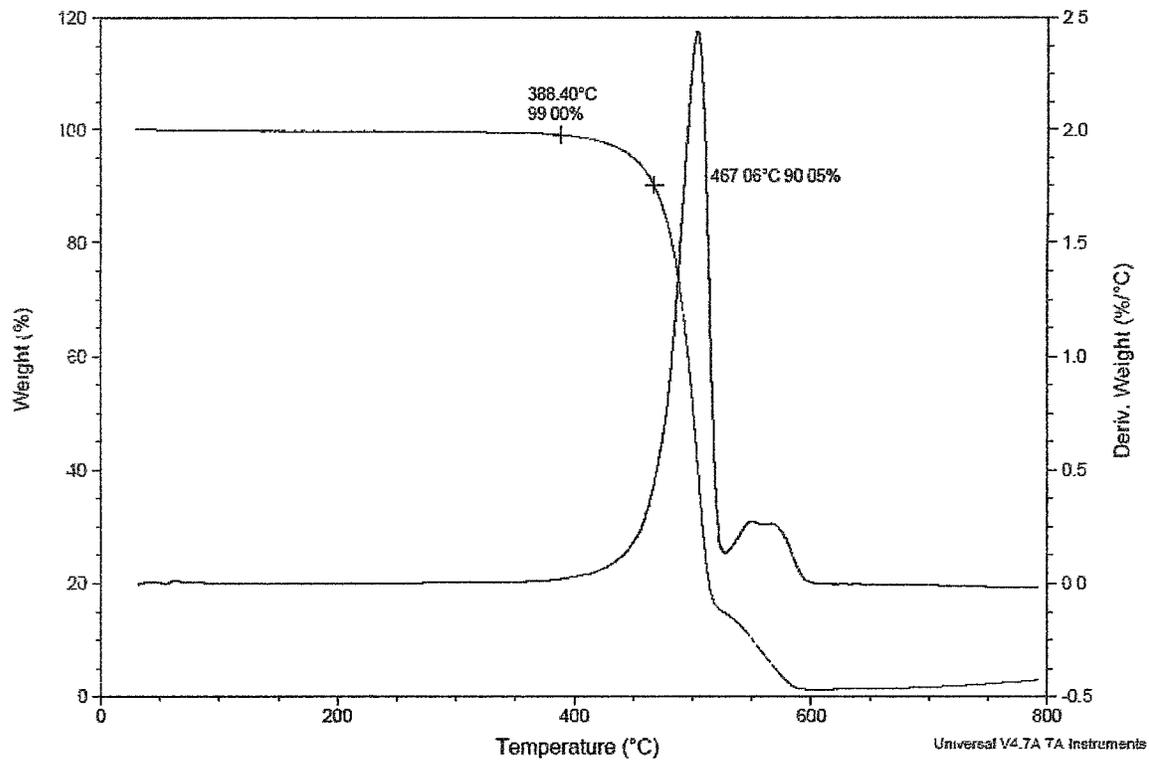


8. I.R. Spectrum of OPDA/BAMC Polyimide

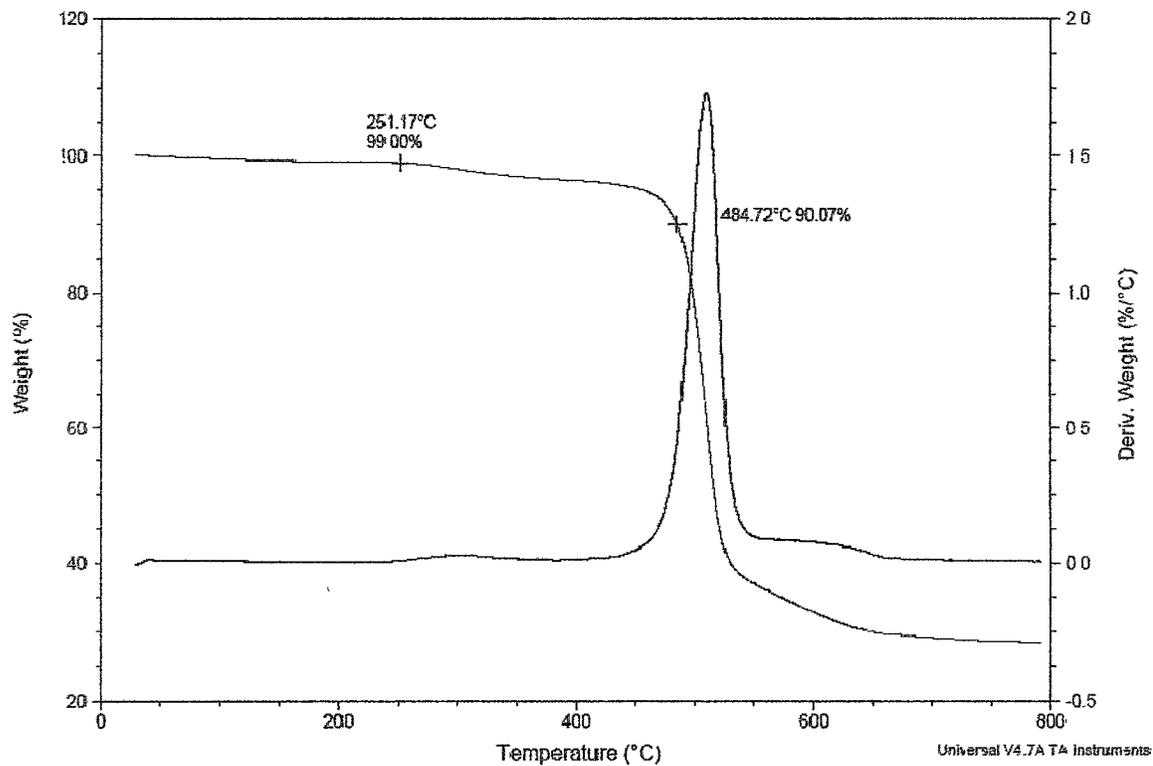
## APPENDIX II: THERMOGRAVIMETRIC ANALYSES

### Index for Appendix II

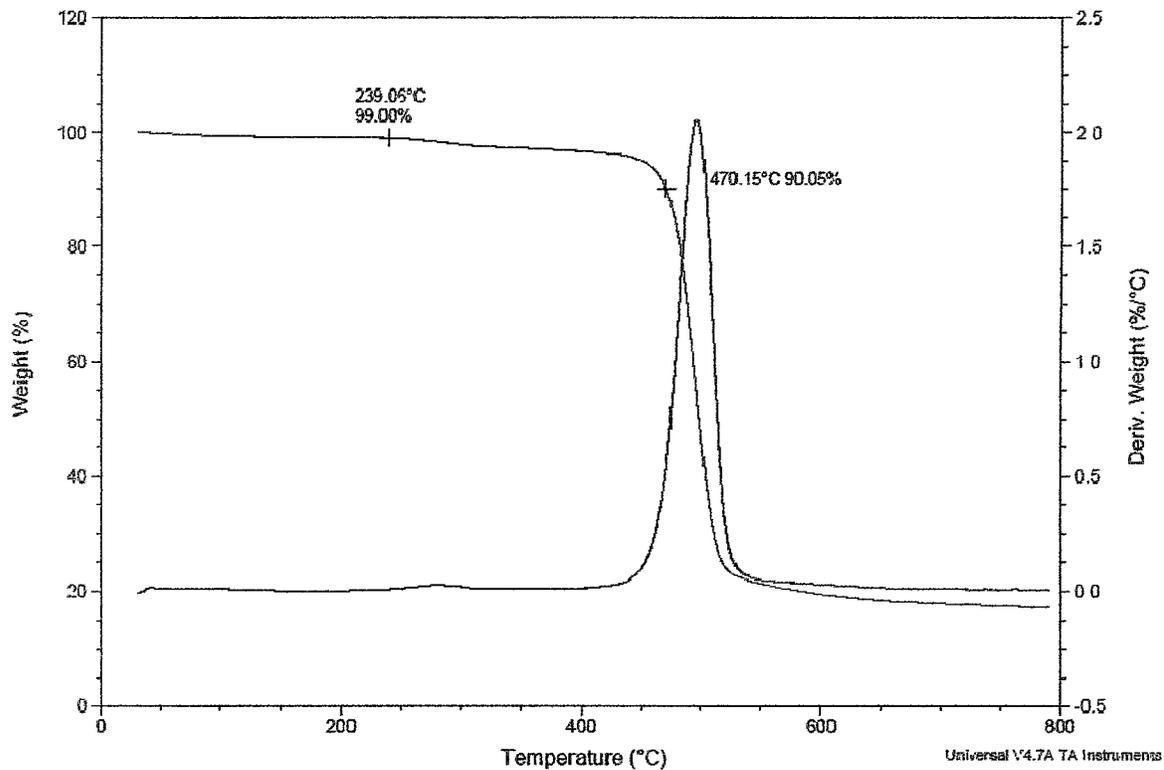
<u>Compound</u>	<u>Number</u>
TGA of 6FDA/BAMC Polyimide .....	1
TGA of BPDA/BAMC Polyimide.....	2
TGA of BTDA/BAMC Polyimide.....	3
TGA of OPDA/BAMC Polyimide.....	4



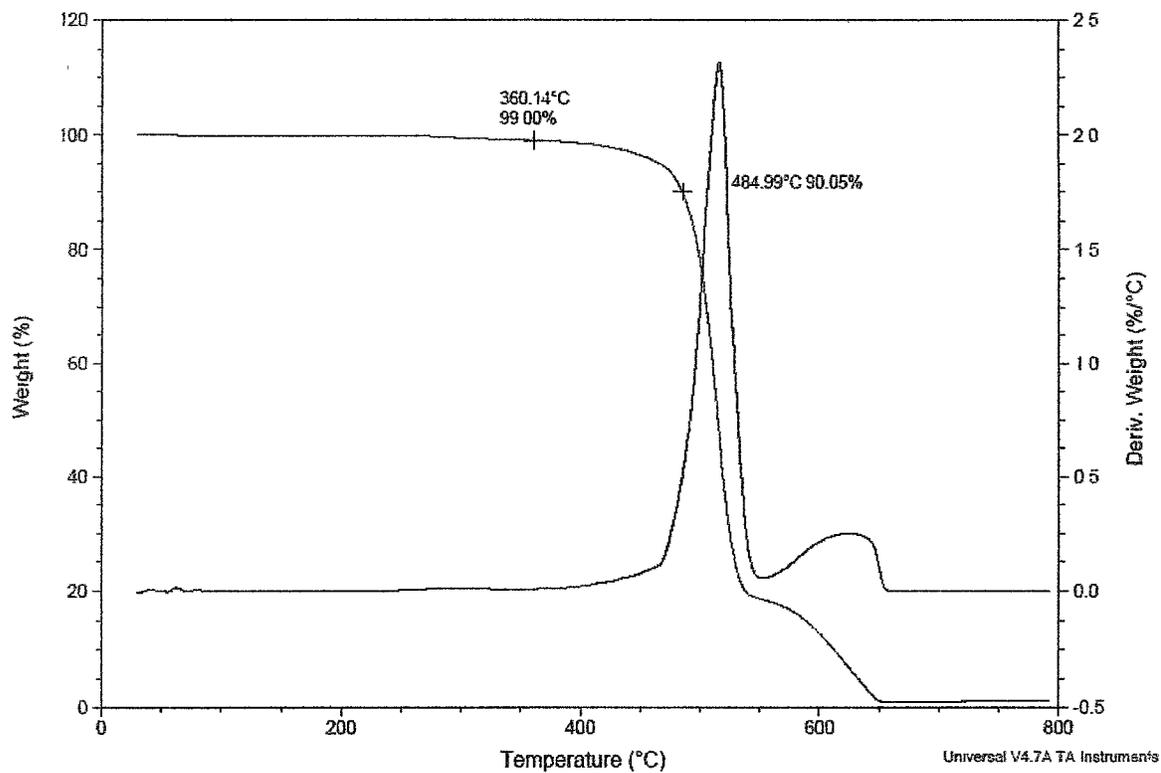
### 1. TGA of 6FDA/BAMC Polyimide



### 2. TGA of BPDA/BAMC Polyimide



3. TGA of BTDA/BAMC Polyimide

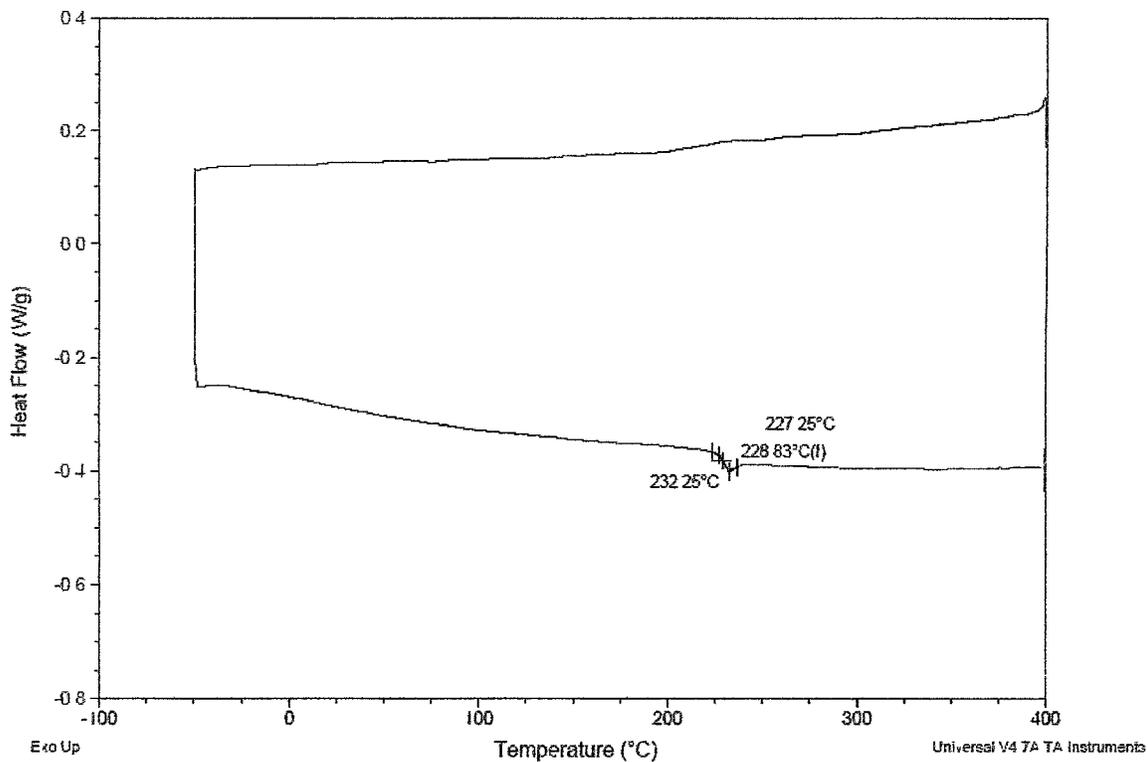


4. TGA of OPDA/BAMC Polyimide

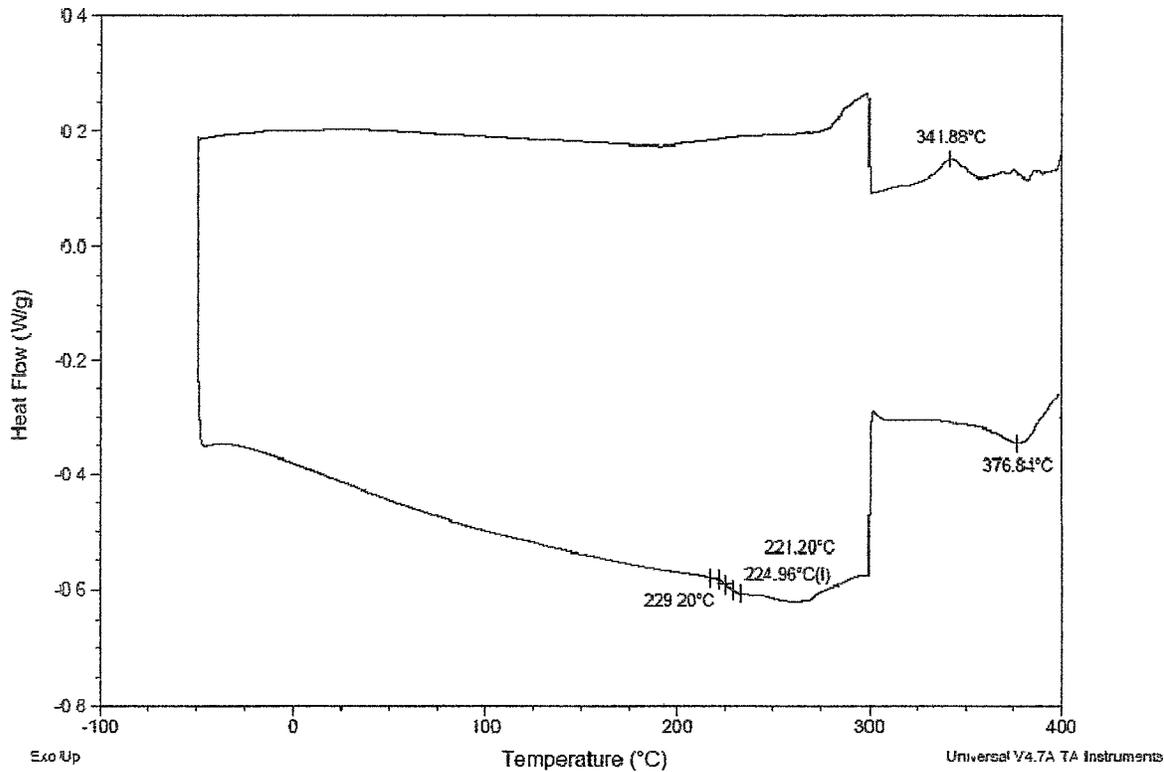
**APPENDIX III: DIFFERENTIAL SCANNING CALORIMETRY  
THERMOGRAMS**

Index for Appendix III

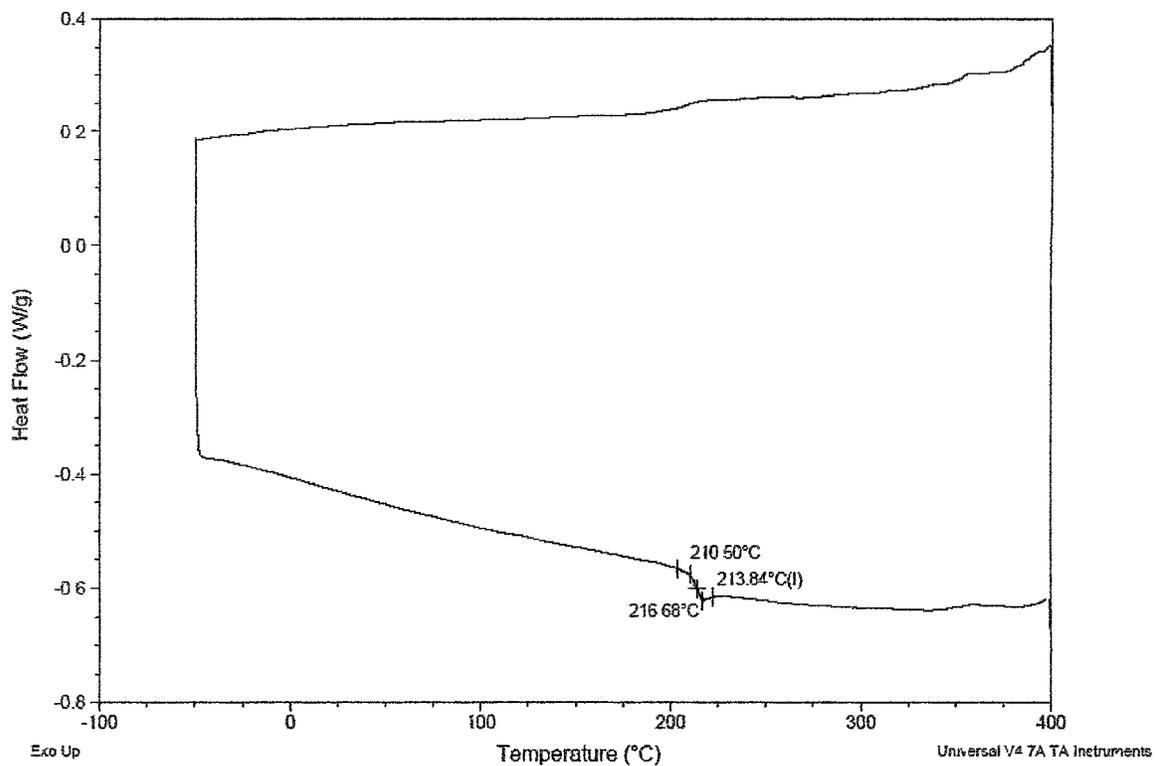
<u>Compound</u>	<u>Number</u>
DSC of 6FDA/BAMC Polyimide.....	1
DSC of BPDA/BAMC Polyimide.....	2
DSC of BTDA/BAMC Polyimide.....	3
DSC of OPDA/BAMC Polyimide.....	4



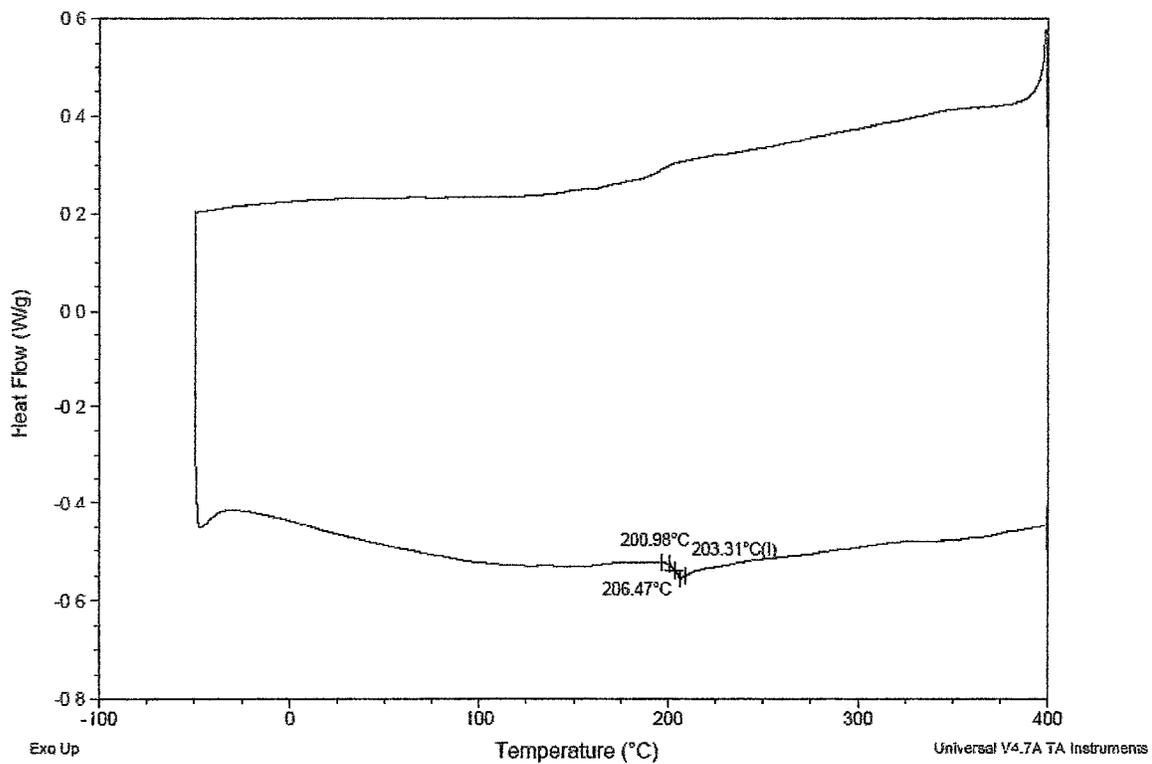
### 1. DSC of 6FDA/BAMC Polyimide



### 2. DSC of BPDA/BAMC Polyimide



### 3. DSC of BTDA/BAMC Polyimide

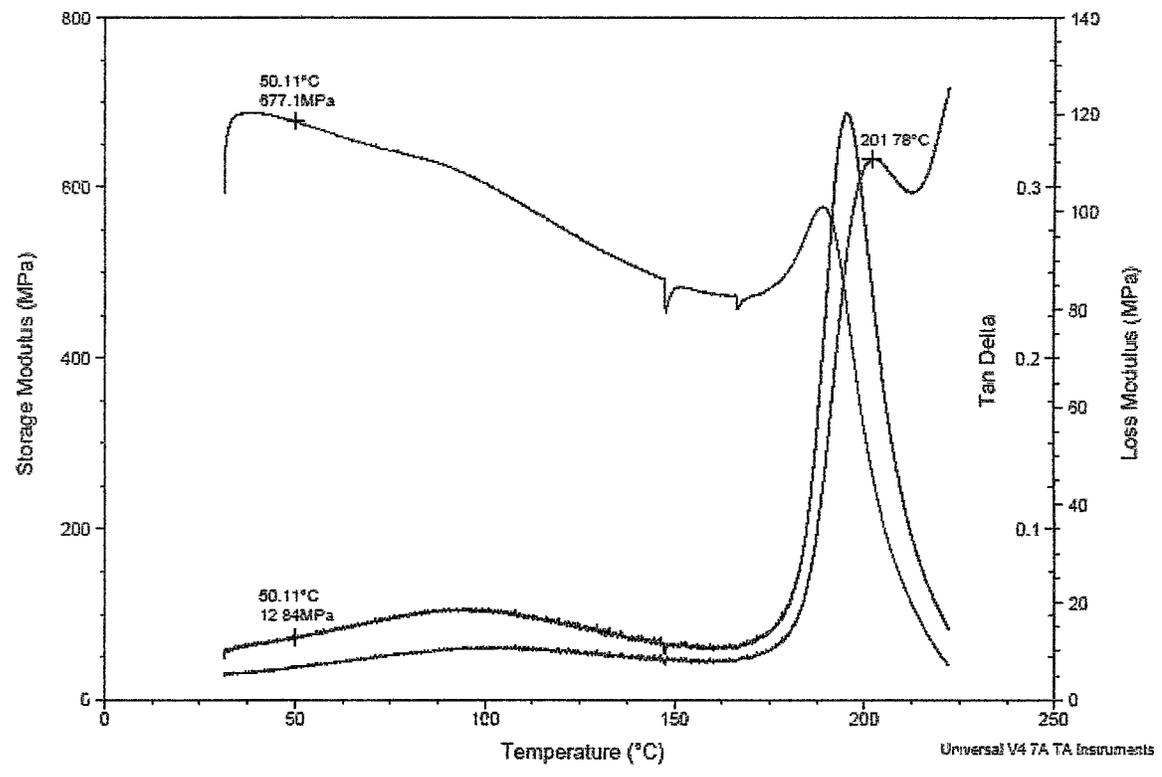


### 4. DSC of OPDA/BAMC Polyimide

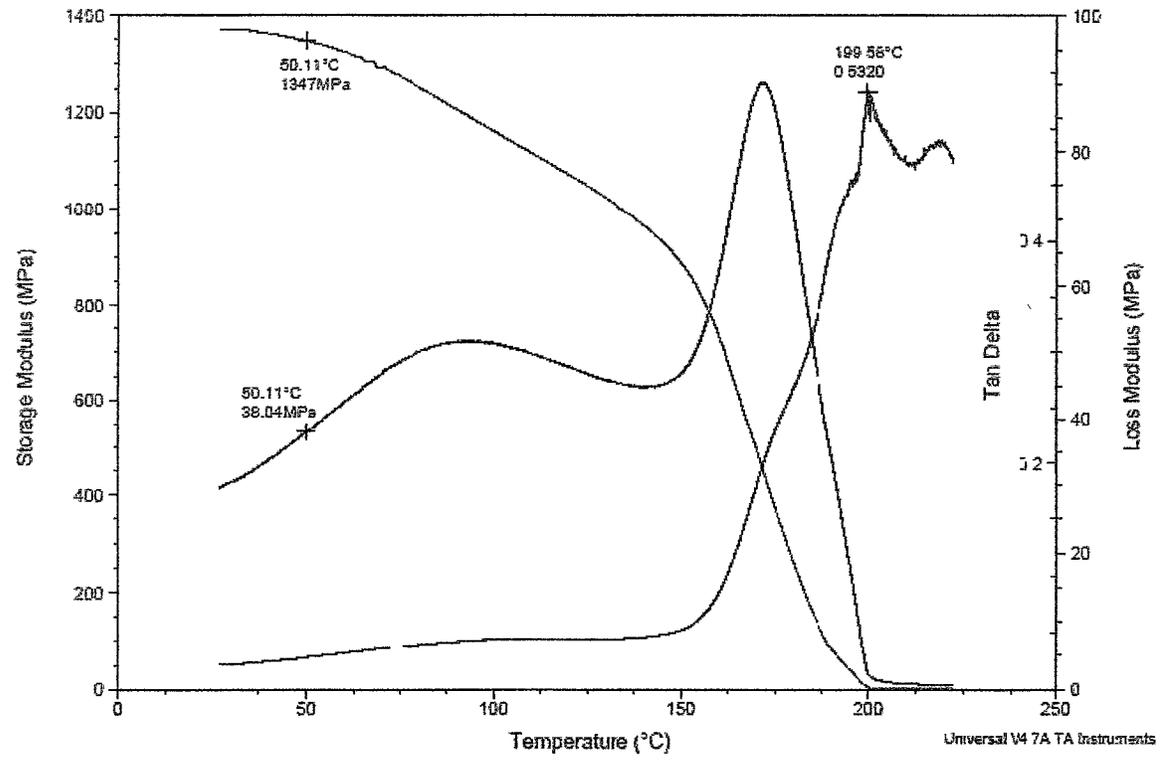
## APPENDIX IV: DYNAMIC MECHANICAL ANALYSES

### Index for Appendix IV

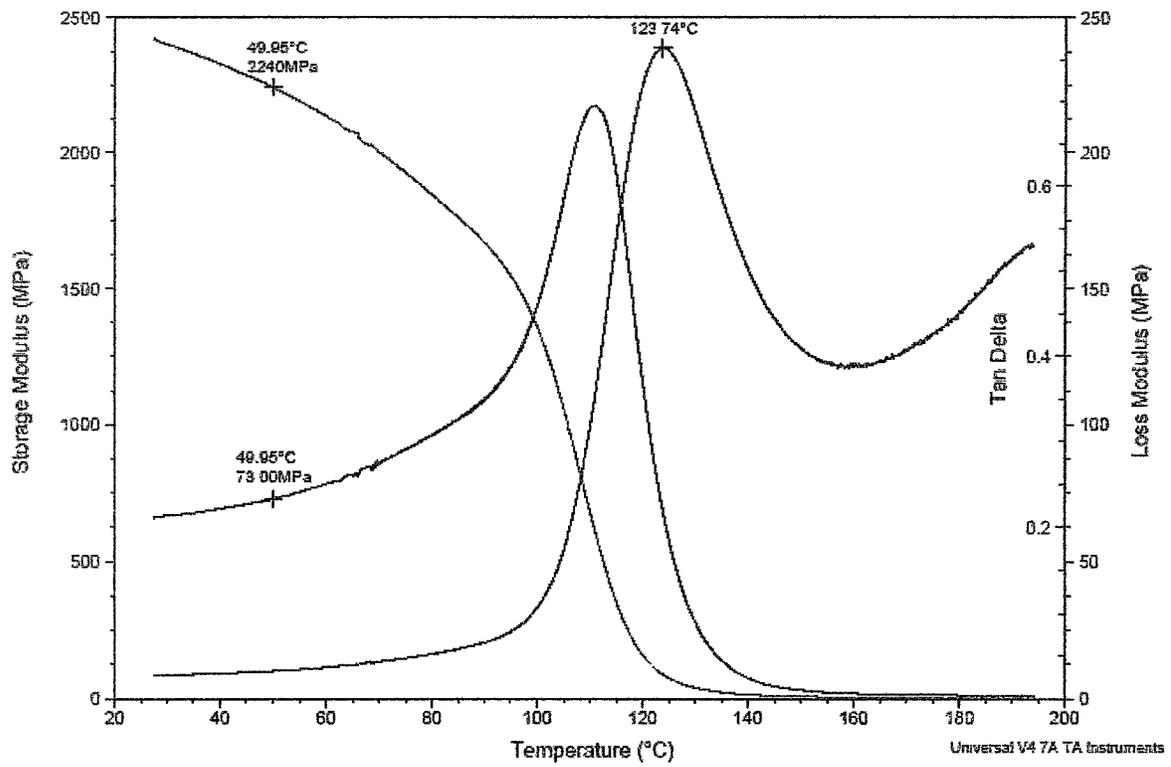
<u>Compound</u>	<u>Number</u>
DMA of BPDA/BAMC Polyimide.....	1
DMA of BTDA/BAMC Polyimide .....	2
DMA of OPDA/BAMC Polyimide .....	3



### 1. DMA of BPDA/BAMC Polyimide



### 2. DMA of BTDA/BAMC Polyimide



### 3. DMA of OPDA/BAMC Polyimide

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## VITA

Kristen Elaine Truett was born in San Angelo, Texas, on April 2, 1985, the daughter of Thomas and Sandra Truett. After graduating valedictorian from Central High School, San Angelo, Texas, in 2003, she attended Angelo State University. She received her Bachelor of Science from Angelo State in May 2007 as the Presidential Award recipient with summa cum laude and highest honors on her dual chemistry and mathematics majors. In June 2007, she married Perwira Joshua Suprobo and became Kristen Elaine Suprobo. She was employed as an inorganic chemist at Cardinal Laboratories in Hobbs, New Mexico. In September 2008, she entered the Graduate College of Texas State University-San Marcos.

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