# Thermomechanical Characterization of Thermoplastic Polyimides Containing 4,4'-Methylenebis(2,6-Dimethylaniline) and Polyetherdiamines

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In this work, we synthesized polyimides by incorporating an aromatic diamine monomer with a methylene linker, 4,4'-methylenebis(2,6-dimethylaniline) (MBDMA), to make a robust main chain along with aliphatic polyetherdiamine backbone linkers to reduce rigidity. We designed the polymers to exhibit thermal properties in between those of conventional aromatic polyimides and polymers with wholly aliphatic ether diamine links. Through dynamic mechanical analysis and differential scanning calorimetry, it is shown that control of the molar ratios of the aromatic MBDMA (4,4'-methylenebis(2,6-dimethylaniline)) and the composition and size of the aliphatic polyetherdiamine can be used to tune the glass transition. The polymers were characterized by GPC, FTIR, NMR, thermomechanical and calorimetric analysis, and microhardness testing. POLYM. ENG. SCI., 59:221-232, 2019. © 2018 Society of Plastics Engineers

## INTRODUCTION

A series of thermoplastic polyimides (PI) with tractable properties is synthesized and characterized in this work. Polyimides (PIs), due to their linear, highly ordered aromatic backbones and rigidity, prototypically exhibit high thermal stability, solvent resistance, low coefficients of thermal expansion, low dielectric constants, high glass transition temperatures, and superior mechanical properties [1-3]. These attributes are of interest in the production of high performance products found in electronics, aerospace structural components, thermal insulation, composites, and adhesives [4-8]. More specifically, polyimides exhibit unique properties involving small ion or molecule diffusive transport. Hence, they are used as semi-dry lithium ion transport separator layers for batteries, where short circuiting is eliminated due to low electrical conductivity [9, 10]. Polyimides are also ideal in selective gas transport and fuel cell membranes [11, 12].

Although polyimides are relatively expensive compared to most polymer classes, they can be tailored at the molecular level to produce a broad combination of controllable properties.

Hence, the chemistry of polyimides is rather diverse with a variety of usable monomers and several methodologies available for synthesis. However, there has been considerable debate on the various reaction mechanisms involved in different synthetic methods [13–17].

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The stability found in the conventional, fully aromatic polyimides renders them difficult to process due to highly elevated glass transition and melt temperatures, which range close to their decomposition temperatures [4-6, 18, 19]. To combat this, typically PIs are first synthesized as soluble polyamic acids and coated as thin films on a surface to be later imidized by heat treatment to form the final polyimide [20, 21]. However, these polyamic acid precursors are vulnerable to hydrolysis or solvolysis and the imidization ring closing reaction releases water, which can lead to delamination from volume change and may hydrolyze the polyamic acid intermediate [20, 21]. Such an approach also limits PIs to being cast as thin sheets with little post-synthetic processability for industrial applications. To circumvent these shortcomings, various groups have sought to break up the aromaticity of the polyimide backbone ultimately to impart thermoplastic behavior.

These approaches usually consist of using flexible linkers between the aromatic dianhydride motifs in the forms of ethers (Fig. 1A-C) [7, 22-25], thioethers (Fig. 1B) [14], or sulfones (Fig. 1D) [21]. These linkages serve to increase flexibility and reduce the glass transition temperature. The glass transition temperatures for many of the resulting polymers remain relatively high, ranging from 215°C to over 310°C [7, 21, 23-25]. Although these materials can be processed before decomposition, the temperature requirements remain elevated and reprocessing or recycling is unlikely. The work done by Inoe et al. [16] and Kumagai et al. [17] show the usage of aliphatic precursors in the form of Nylon-Salt-type monomers to synthesize polyimides under high pressure. Their work successfully creates a polyimide with a high T<sub>m</sub>; however, they are only soluble in sulfuric acid. On the other end of the spectrum, Baldwin et al. [10] (Fig. 1) used an entirely aliphatic ether as the diamine and reacted it with pyromellitic dianhydride (PMDA), reducing the glass transition temperature significantly (51°C-75°C). These polymers lacked the highly ordered, stiff backbones of conventional polyimides, and this loss of aromaticity greatly diminished the ability to compete with high performance aromatic polyimides.

In this work, we synthesized polyimides by incorporating an aromatic diamine monomer with a methylene linker, 4,4'-methylenebis(2,6-dimethylaniline) (MBDMA), along with aliphatic polyetherdiamine backbone linkers and pyromellitic dianhydride (PMDA) as seen in Fig. 2. We designed the polymers to exhibit thermal properties in between those of conventional aromatic polyimides and polymers with wholly aliphatic ether diamine links.

Limited studies report the use of MBDMA monomer in polyimide synthesis. Munoz et al. studied a direct polycondensation



FIG. 1. Representative approaches for modifying the glass transition temperature rely on introducing flexible linkers within the aromatic dianhydride monomers.

process for synthesizing polyimides using 4,4'-(hexafluoroisopropylidene)-diphthalic anhydride with a series of aromatic diamines including MBDMA [26]. Both chloro(trimethyl)silane (CTMS) and pyridine (Py) were used as polycondensation promoters. The obtained polyimides exhibited inherent viscosities ranging between 0.27 and 0.81 dL/g. Although physical properties other than inherent viscosities were not presented by appearance, the structures of the polymers in question seemingly reflected a high  $T_{\rm g}$  when the molecular weights were high enough. Additionally, Eastmond et al. synthesized a series of polyimides containing MBDMA and a series of dianhydrides designed to impose constraints, limiting motion in the polymer chains [27]. Diols with varying aromatic substitutions were incorporated into the dianhydrides such that conformational relaxations were restricted in a variety of ways. These dianhydrides were reacted with MBDMA to yield polyetherimides. Glass transition temperatures varied from 245°C to 420°C. Later, dielectric relaxation studies related the effect of the steric constraints to the glass transition relaxation [28].

Ultimately, our polyimides are designed to serve as functional thermoplastic materials, which can be molded or extruded into shapes necessary for diverse uses, negating the need for the highly limiting thin-film polyamic acid casting methodology used with conventional PIs. Furthermore, the glass transition temperatures are tuned by controlling the stoichiometric ratio of MBDMA to aliphatic polyetheramines along with the molecular weight of the polyetheramine itself. The polymers were characterized by GPC, FTIR, NMR, thermomechanical and calorimetric analysis, and microhardness testing.

# **EXPERIMENTAL**

# Materials

Pyromellitic dianhydride (PMDA), 4,4'-methylenebis(2,6dimethylaniline) (MBDMA), and gamma-butyrolactone (GBL) were used as received and donated from BrightVolt, Inc. (Lakeland, FL) [9]. Jeffamine<sup>®</sup> D230, D400, and D2000 were donated by Huntsman, Inc. (The Woodlands, Texas). Tin (II) ethyl hexanoate (catalyst) and HPLC-grade THF were used as received from Sigma Aldrich. Narrow molecular weight polystyrene standards were purchased from Fluka Analytical.

## Methods

**General Procedure for Polymerization.** Methodology was designed to minimize water content since molecular weight can be strongly influenced by residual water content as it acts as a chain stopper during the polymerization process. Polymer batches of approximately 250 g were synthesized in a 1 L three-necked glass reactor. The reactor was equipped with a mechanical mixer with Teflon<sup>®</sup> blades, a nitrogen line for purging and maintaining inert





FIG. 2. Synthetic procedure for the formation of PI formulations.

atmosphere, a thermocouple, and a distillation head. This setup was charged with the Jeffamine<sup>®</sup> aliphatic diamines of interest, MBDMA, and GBL (Table 1). This solution was warmed to 30°C and homogenized for 20 minutes with mechanical stirring and nitrogen purge with Tin (II) ethyl hexanoate was added as catalyst. PMDA was separately dissolved in GBL and charged into the glass reactor, initiating the polymerization, and resulting in an immediate exothermic temperature spike. The reaction was kept under an inert nitrogen atmosphere for 4 hours after which the temperature was increased to 80°C and a vacuum was applied to distill off water, resulting from imidization of the polyamic acid

backbone and excess GBL solvent. This procedure is summarized in Fig. 2. The reaction remained under vacuum at 80°C for 24 hours. The resulting polyimide slurry was placed in a vacuum oven at 100°C to further dry the polymer of residual GBL solvent and ensuring complete imidization.

Fourier Transform Infrared Spectroscopy/Attenuated Total Reflectance and Proton Nuclear Magnetic Resonance. Thin film samples were prepared using a heated Carver hydraulic press. The films were analyzed using a Spectrum One FT-IR (Perkin Elmer) equipped with ATR. The resulting data was collected in reflection mode and it was analyzed using Spectrum software.

Proton Nuclear Magnetic Resonance (<sup>1</sup>H NMR) spectra were collected using a Varian Inova 400 spectrometer at the USF Interdisciplinary NMR Facility. All samples were recorded with a spectral width of 6400 Hz using a standard proton pulse sequences for 1D proton NMR, gCOSY, TOCSY, and NOESY experiments. About 10–20// mg of each sample were prepared in CDCl<sub>3</sub> at 298 K. The data were processed using the VNMRj software. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) relative to the residual protonated solvent signal as a reference.

Gel Permeation Chromatography. Polystyrene narrow molecular weight standards ranging from 1,180 to 1,170,000 MW were used to calibrate a PL-50 GPC (Agilent) with RI detector and PE LC200 chromatograph. The solvent was HPLC grade tetrahydrofuran (THF) at a flow rate of 0.5 mL/min at 25°C. Polymer samples were prepared at 5 mg/mL concentrations in THF and filtered with 0.2  $\mu$ m PTFE syringe filters.

**Thermogravimetric Analysis (TGA).** A 10 mg sample from each polymer formulation was assayed for temperature stability with a TGA Q50 (TA Instruments) under nitrogen atmosphere. The samples were heated from  $25^{\circ}$ C to  $800^{\circ}$ C with a ramp rate of  $10^{\circ}$ C per minute. The results were analyzed using TA Data Analysis software.

Differential Scanning Calorimetry (DSC). Analysis was carried out using a DSC 2920 differential scanning calorimeter (TA Instruments) over the temperature range  $-50^{\circ}$ C to  $300^{\circ}$ C. Temperature was calibrated using an Indium standard. The sample films were cut and weighed; weights ranged from 9 to 10 mg. Samples were first heated from  $25^{\circ}$ C to  $300^{\circ}$ C at  $20^{\circ}$ C min<sup>-1</sup>, cooled to  $-50^{\circ}$ C at  $20^{\circ}$ C min<sup>-1</sup>, and reheated to  $300^{\circ}$ C at  $20^{\circ}$ C min<sup>-1</sup>. The cycle processes were used to erase thermal history due to sample preparation and storage. The results were analyzed using TA universal analysis software and the second heating cycle was reported.

**Dynamic Mechanical Analysis.** Rectangular solid samples (50 mm  $\times$  10 mm  $\times$  3 mm) were molded in a heated Carver<sup>®</sup> hydraulic press at approximately 170°C with quick cooling to room temperature under pressure. Isothermal strain sweeps were performed on the rectangular samples to determine the linear viscoelastic regions (LVR) with an AR2000 rheometer (TA Instruments) at three temperatures (-50°C, 25°C, and 100°C) corresponding with temperature regions of interest as seen during testing. The highest strain percent within the measured LVR, common to the three temperatures, was chosen to characterize the sample with a temperature ramp in oscillation mode. Ramp conditions were -120°C to 150°C at 5°C/min with liquid nitrogen used for cooling. Resulting data were analyzed with software available from TA Instruments.

**Microhardness Testing.** Rectangular solid samples were prepared in a matter analogous to those used in rheology testing; 10 replicate 15 second indentations were obtained (5 per side of rectangular sample) under 500 g force using a Leica VMHT equipped with a Vickers diamond indenter. Averages and their standard deviations were computed and are reported in kgf/mm<sup>2</sup>.

**Tensile Testing.** Films of 0.1 mm thickness were pressed and then cut with a Fremont ASTM D638 Type 5 die with a width of 3.15 mm. A minimum of six replicates were tested in a Shimadzu AGS-J with a model SM-50N-168 load cell. The samples were tested at 25 mm/min at 23°C. The results were analyzed using a TrapeziumX software. Averages and standard deviations for maximum stress, maximum strain, and Young's modulus were computed and are reported in MPa and percentage.

# **RESULTS AND DISCUSSION**

## Infrared Spectroscopy and Proton Nuclear Magnetic Resonance

FT-IR spectroscopy was used to confirm polyimide formation and complete ring closure (imidization) from the polyamic acid backbone. The polyimides studied here exhibited characteristic imide group absorptions around 1.771 and 1.716  $\text{cm}^{-1}$ , typical of imide carbonyl asymmetrical and symmetrical stretching, arising from the anhydride ring of PMDA with 1,355-1,373 cm<sup>-1</sup> being the characteristic C–N aromatic stretch. The disappearance of amide carbonyl absorption around 1,540 cm<sup>-1</sup> (-NHCO- stretch) indicated a virtually complete imidization of the polyamic acid (PAA) precursor into polyimide. There are characteristic bands of aromatic rings at  $1,565 \text{ cm}^{-1}$  for C–C stretching vibrations. Alkyl C-H stretch vibrations are seen at 2.871 and 2,972  $\text{cm}^{-1}$  [29]. The absence of broad peaks in the 3,400 to 3,000 cm<sup>-1</sup> from the carboxylic acid precursor and NH<sub>2</sub> symmetric and asymmetric stretching and deformation vibrations indicate that the ring was fully imidized.

Proton Nuclear magnetic resonance was used to confirm the incorporation of the different monomers into the backbone and complete ring closure. The random organization of the different diamines can be seen in three different singlets from 8.1 to 8.5 ppm of the PMDA aromatic protons, the combinations aliphatic–aliphatic, aliphatic–aromatic, and aromatic–aromatic. The characteristic peaks of the aromatic region at 7.0 ppm and CH<sub>3</sub> at 2.0 ppm of the MBDMA can be identified to ensure that the aromatic diamine was incorporated. However, the CH<sub>3</sub> signals from the linear Jeffamine were 0.7 to 1.1 ppm [30]. The rest of the signals come from the two diamines and they overlap. Furthermore, <sup>1</sup>H NMR confirmed the incorporation of the aliphatic and aromatic units in the polymer structure.

PI-1: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) – 0.74–1.12 (m, 7.62H, Jeffamine CH<sub>3</sub>), 2.07 (s, 3.90H, MBDMA CH<sub>3</sub>), 3.07–4.00 (m, 11.58H, MBDMA and Jeffamine CH/CH<sub>2</sub>), 6.98 (s, 1H, MBDMA), 8.13–8.45 (s, 2H, PMDA). ATR-IR (cm<sup>-1</sup>): 1,770 cm<sup>-1</sup> (asymmetric stretching C = O), 1,709 cm<sup>-1</sup> (symmetric stretching C = O), 1,351 cm<sup>-1</sup> (C–N stretching), and 729 cm<sup>-1</sup> (C = O bending).

PI-2: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) – 0.74–1.12 (s, 10.06H, Jeffamine CH<sub>3</sub>), 2.09 (s, 3.42H, MBDMA CH<sub>3</sub>), 3.09–4.05 (m, 14.58H, MBDMA and Jeffamine CH/CH<sub>2</sub>), 7.01 (s, 1.16H, MBDMA), 8.17–8.48 (s, 2H, PMDA). ATR-IR (cm<sup>-1</sup>): 1,771 cm<sup>-1</sup> (asymmetric stretching C = O), 1,714 cm<sup>-1</sup> (symmetric stretching C = O), 1,355 cm<sup>-1</sup> (C–N stretching), and 730 cm<sup>-1</sup> (C = O bending).

PI-3: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  (ppm) – 0.71–1.06 (s, 8.08H, Jeffamine CH<sub>3</sub>), 2.07 (s, 4.12H, MBDMA CH<sub>3</sub>), 3.02–4.01 (m,

TABLE 1. Feedstock stoichiometry of the PI series.

Polyimide	PMDA mol%	MBDMA mol%	D230 mol%	D400 mol%	D2000 mol%
PI-1	50.0%	11.0%	38.8%	0.0%	0.2%
PI-2	50.0%	11.0%	35.4%	3.0%	1.4%
PI-3	50.0%	11.0%	39.4%	0.0%	0.0%
PI-4	50.0%	11.0%	0.0%	39.4%	0.0%
PI-5	50.0%	25.0%	0.0%	23.8%	1.4%

11.72H, MBDMA and Jeffamine CH/CH<sub>2</sub>), 6.98 (s, 1.22H, MBDMA), 8.13–8.46 (s, 2H, PMDA). ATR-IR (cm<sup>-1</sup>): 1,771 cm<sup>-1</sup> (asymmetric stretching C = O), 1,709 cm<sup>-1</sup> (symmetric stretching C = O), 1,350 cm<sup>-1</sup> (C–N stretching), and 729 cm<sup>-1</sup> (C = O bending).

PI-4: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) – 0.83–1.37 (s, 8.08, Jeffamine CH<sub>3</sub>), 2.06 (s, 4.12H, MBDMA CH<sub>3</sub>), 3.05–4.00 (m, 11.72H, MBDMA and Jeffamine CH/CH<sub>2</sub>), 6.99 (s, 1.22H, MBDMA), 8.14–8.40 (s, 2.00H, PMDA). ATR-IR (cm<sup>-1</sup>): 1,771 cm<sup>-1</sup> (asymmetric stretching C = O), 1,714 cm<sup>-1</sup> (symmetric stretching C = O), 1,354 cm<sup>-1</sup> (C–N stretching), and 730 cm<sup>-1</sup> (C = O bending).

PI-5: <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) – 0.87–1.10 (s, 14.86H, Jeffamine CH<sub>3</sub>), 2.08 (s, 8.36H, MBDMA CH<sub>3</sub>), 3.18–4.04 (m, 17.06H, MBDMA and Jeffamine CH/CH<sub>2</sub>), 6.99 (s, 2.62H, MBDMA), 8.14–8.46 (s, 2H, PMDA). ATR-IR (cm<sup>-1</sup>): 1,772 cm<sup>-1</sup> (asymmetric stretching C = O), 1,716 cm<sup>-1</sup> (symmetric stretching C = O), 1,355 cm<sup>-1</sup> (C–N stretching), and 730 cm<sup>-1</sup> (C = O bending).

#### Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) data were obtained and yielded weight-average molecular weights ( $M_w$ ) ranging from approximately 28,500 to 35,000 Da, number-averaged molecular weights ( $M_n$ ) ranging from approximately 12,000 to 15,900 Da, and polydispersity indices ( $M_w/M_n$ ) ranging from 2.21 to 2.38 (Table 2).

TABLE 2. M<sub>w</sub>, M<sub>n</sub>, and PD of the polyimides \*PI-5 was insoluble.

Polyimide	M <sub>w</sub> (Da)	M <sub>n</sub> (Da)	Polydispersity (PD)	
PI-1	31,062	13,026	2.3846	
PI-2	33,301	14,428	2.3081	
PI-3	28,533	11,992	2.3793	
PI-4	35,182	15,887	2.2145	
PI-5*	N/A	N/A	N/A	

#### Thermogravimetric Analysis

The thermal stability and residual solvent retention of the polyimide were evaluated by TGA measurements under nitrogen atmosphere. The thermograms of the PIs are shown in Fig. 3. The corresponding temperature at 3% weight loss and the onset temperature are reported in Table 3. The stability at the onset temperature represents a relation between the lengths of the different aliphatic diamines in the repeat unit versus the temperature [5, 10]. Fully aromatic polyimides typically have higher temperature stability [5, 6, 16] as their backbone is linear, well-ordered, rigid, and aromatic. The polyimides synthesized in this article exhibit thermal onset stabilities that decrease as the glass transition temperatures decrease and range from 362°C to 378°C.

As the aliphatic linkers increase in length, the temperature stability decreases due to the presence of longer aliphatic linkages imparting flexibility and decreasing heat resistance. Though there is a decrease in thermal stability, the difference is not large between the higher molecular weight of the links of PI-4 and the lower molecular weight links of PI-3. The results provided by the TGA show that the majority of the samples have conserved 97% of their mass up to 300°C. The diamine monomers and the lactone solvent used in processing both have boiling points around 205°C, which may explain the minimal loss of mass around that temperature. The onset temperature was above 360°C for each formulation. The information provided by TGA testing also allows the determination of appropriate temperature regimes for dynamic mechanical analysis.



FIG. 3. Stacked TGA thermograms for the polyimides studied. [Color figure can be viewed at wileyonlinelibrary. com]



FIG. 4. DSC thermograms of polyimide in the glass transition region, ran at  $20^{\circ}$ C min<sup>-1</sup> with a range from  $-50^{\circ}$ C to  $300^{\circ}$ C. The endotherm direction points down in the heat flow. [Color figure can be viewed at wileyonlinelibrary. com]



FIG. 5. DSC thermograms of polyimide at  $20^{\circ}$ C min<sup>-1</sup> with a range from  $-50^{\circ}$ C to  $300^{\circ}$ C representing the crystalline peak. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 6. Storage, loss, and damping moduli versus temperature (varying polyetheramine amount). [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 7. Storage, loss, and tan  $\delta$  versus temperature (varying aromatic MBDMA amount). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3. Onset temperature at 97% starting weight for the polyimides studied.

Polyimide	Onset temperature (°C) 3%		
PI-1	367.0		
PI-2	363.0		
PI-3	377.9		
PI-4	362.0		
PI-5	363.0		

TABLE 4. Glass transition temperatures determined by DSC and DMA measured at 2.6 Hz, from inflection point of Tan  $\delta$  and G".

Polyimide	<i>T</i> <sub>g</sub> from DSC (20°C/min) (°C) –50°C to 300°C	$T_{\rm g}$ from DMA at 2.6 Hz (°C) (G")	$T_{\rm g}$ from DMA at 2.6 Hz (°C) (Tan $\delta$ )	
PI-1	92.5	80.0	114.9	
PI-2	22.3	69.8	90.0	
PI-3	101.1	100.0	120.0	
PI-4	24.3	15.1	40.1	
PI-5	37.0	45.1	100.0	

#### Differential Scanning Calorimetry

The glass transition temperature  $(T_g)$  manifests as a step decrease in the heat capacity of the polymer and will be defined here as the mid-point of the curve between the original baseline heat capacity and the resulting heat capacity. The  $T_g$  is encountered in the temperature region where slipping of the long chain segments occurs. Samples were first heated and then quenched to erase thermal history of the material resulting from synthesis, drying, and storage. The second run is reported in Fig. 4 for the heating rate of 20°C min<sup>-1</sup>. The glass transitions proceed in the following order: PI-3 > PI-1 > PI-5 > PI-4 > PI-2.

The results confirmed that the increase in length of the aliphatic diamine decreases the glass transition temperature. A small crystallization exotherm in the region from 180°C to 190°C is evident. In the region from 190°C to 205°C, a small melting transition is noted for all the samples (Fig. 5). These polyimides appear to exhibit a low degree of crystallinity. This is further discussed in the dynamic mechanical studies.

## Dynamic Mechanical Analysis

Dynamic mechanical analysis was performed on rectangular solid samples under linear viscoelastic (LVE) strains determined from isothermal strain sweeps as described in the Methods Section. Temperature sweeps at various frequencies under these LVE-determined strains yielded both  $\alpha$  and  $\beta$  transitions as frequency dependent peaks in Tan  $\delta$  and G" with the glass ( $\alpha$ ) transitions showing as precipitous drops in the storage modulus (G') and peaks in both the loss modulus (G") and damping (Tan  $\delta$ ). It can be seen in Figs. 6 and 7 that the storage modulus, representing the elastic properties of the material and its recoverable energy after deformation, drops as the sample nears its  $\alpha$ transition and becomes more rubbery (viscous), representing the glass transition  $(T_{g})$ . The concomitant increase in the loss modulus (G") and decrease in the storage modulus (G') during the  $\alpha$ transition is due to a shift from structured elastic material below the glass transition to one that is rubbery as the polymer chains obtain enough thermal energy to exhibit long range segmental slippage. The ratio of the loss to storage modulus (known as damping or Tan  $\delta$ ) is a measure of how the material dissipates energy, and its width is related to molecular weight distribution and branching. All relevant data is tabulated in Table 4. Due to the constraints of the rectangular solid sample geometry, dynamic mechanical data after the glass transition  $(T_{o})$  cannot be obtained because of a loss of rigidity and sample integrity within the geometry.

From these data, it can be elucidated that the size of the aliphatic diamine in addition to its molar composition relative to the aromatic diamine and aromatic dianhydride influences the glass transition. For this study, the molar concentration is kept the same for the aromatic diamine MBDMA across all samples except for PI-5, which sees a large increase of this aromatic



FIG. 8. Loss modulus (G") versus temperature illustrating the two sub-glass transitions typical of polyimides. The glass transition ( $\alpha$  transition) is located to the right of the  $\beta$  relaxation, at higher temperature. A rubbery plateau and melt are also visible after the alpha transition. [Color figure can be viewed at wileyonlinelibrary.com]



FIG. 9. Tan delta  $(\tan \delta)$  versus temperature illustrating the frequency dependence of the  $\alpha$  and  $\beta$  transitions, implying a relaxation process is occurring. [Color figure can be viewed at wileyonlinelibrary.com]

diamine. However, the molar contribution of the aromatic dianhydride (PMDA) is kept the same for all samples with samples PI-1 through PI-4 varying only in the concentrations of the various aliphatic diamines. As seen in Table 4, the order of both G" and Tan  $\delta$  based on glass transitions proceed in the following order: PI-3 > PI-1 > PI-2 > PI-5 > PI-4.

Polyimides PI-1 and PI-3 are composed of the smallest aliphatic diamines, which manifest the two highest glass transition temperatures (Table 4). It can be postulated that because of PI-3's composition of solely the smallest aliphatic amine of 230 MW (D230) exhibited, one of the highest glass transitions of 100°C is due to the less flexible diamine linker. Departure from the expected glass transition ordering for PI-2 in Differential Scanning Calorimetric data but not in dynamic mechanical data may be due to differences in the mechanistic aspects of what those techniques measure and the polymeric time dependence inherent to dynamic mechanical analysis. PI-1 contains approximately the same mol% of D230 as PI-3 but has 0.2 mol% of the largest diamine (D2000), which decreases the overall rigidity of the backbone and would decrease its glass transition temperature. PI-4 and PI-5 show the next lowest glass transitions at approximately 15.1°C and 45.1°C, respectively, and are composed of moderate levels of the larger molecular weight diamines, with PI-2 composed of 35 mol% D230, 3 mol% D400, and 1.4 mol% D2000, and PI-5 composed of 23.8 mol% D400 and 1.4 mol% D2000, and an increased aromatic diamine percentage (25.0 mol% vs. 11.0 mol%) of MBDMA. The lowest glass transition was exhibited by PI-4 of only 15.1°C because it contained 39.4 mol% of the large aliphatic diamine D400 as the sole aliphatic diamine. Polyimide PI-5 exhibits a higher glass transition than PI-4 because even though it contains more and larger molecular weight aliphatic diamines, it contains a larger contribution of the aromatic diamine MBDMA (25 mol% vs. 11 mol%).

In addition to the  $\alpha$  transition (assigned to the glass transition), there are two additional transitions occurring at lower temperatures as shown in Fig. 8. These transitions are labeled as  $\beta$  and  $\gamma$  in order of decreasing temperature and show Arrhenius frequency dependence. This suggests time-dependent localized relaxation processes [31, 32] as seen in Fig. 9. The mechanism of the  $\beta$  relaxation is rather debated in the literature but appears to be related to rotations and conformational shifts of both the diamine and dianhydride [31]. The peak frequencies shift both in intensity and temperature in the polyimide series studied here depending on diamine molecular weight utilized. For instance, PI-1, PI-3, and PI-4 show reduced  $\beta$  transitions in terms of magnitude and variable  $\beta$  transitions falling within a range of  $-15^{\circ}$ C to  $-30^{\circ}$ C as seen in Fig. 10. These polymers alternate the amount of aliphatic diamine present whilst retaining identical compositions of the aromatic dianhydride PMDA and aromatic amine 4,4'-methylenebis(2,6-dimethylaniline). In PI-1, the 230 MW aliphatic diamine D230 is approximately 39 mol% and



FIG. 10. Non-logged plots of loss modulus versus temperature for the five polyimides which illustrate the relative positions and magnitudes of the three relaxations at 2.6 Hz. [Color figure can be viewed at wileyonlinelibrary.com]

also contains 0.2 mol% of the 2,000 MW aliphatic diamine D2000, whereas PI-3 is composed of approximately 39 mol% of the 230 MW D230 with no D2000. Both of these polymers show highly reduced  $\beta$  transitions in terms of intensity; PI-1 has a lower temperature,  $T_{\beta}$ , at  $-15^{\circ}$ C versus  $T_{\beta}$  of  $+30^{\circ}$ C for PI-3 (at 2.6 Hz). The  $\beta$  transition of PI-1 has a lower intensity transition than PI-3. Note that PI-4 is composed of approximately 39 mol% of the larger aliphatic diamine at 430 MW (D400) as seen in Table 1. PI-4, whose aliphatic diamine content consists entirely of the second largest MW amine (D400), exhibits no detectable  $\beta$  transition, although the merging of the  $\beta$  within the  $\alpha$  transition cannot be ruled out. Therefore, the largest aliphatic diamine, D2000, appears to produce large  $\beta$  intensities within the polyimide series, but the  $\beta$  transition appears to be controlled more holistically in terms of stoichiometric composition of all diamines present. For example, PI-5 exhibits large  $\beta$  intensities in Fig. 7 as they contain the highest percentage of D2000 and have the lowest glass transitions of all samples. Although these general trends can be garnered from this data, a more systematic assay of structure-property relationships is needed to thoroughly tease out the causal mechanistic relationship between the beta relaxation and polymer structure.

The  $\gamma$  transition, the lowest temperature relaxation, is thought to involve crankshaft motions of the main chain with solvent molecules affecting intensity [31, 33]. There is no discernible relationship between polymer composition and  $T_{\gamma}$  and minimal temperature variation between compositions as depicted in Fig. 10.

#### Microhardness

Multiple indentations were performed on multiple sides of the sample to account for sample anisotropy. The random conformations

TABLE 5. Microhardness data for the polyimides studied \*PI-4 was too soft for microhardness analysis.

TABLE 6. Tensile information for the polyimides studied.

Polyimides	HV (kgf/mm <sup>2</sup> )	Standard deviation (±)	Polyimides	Maximum stress (MPa)	Maximum strain (%)	Young's modulus (MPa)
PI-1	17.6	0.95	PI-1	$65.69 \pm 12.94$	$2.91 \pm 0.44$	$20.33 \pm 1.71$
PI-2	14.4	1.25	PI-2	$34.57\pm2.49$	$4.77\pm0.51$	$9.95 \pm 1.01$
PI-3	17.6	1.37	PI-3	$51.03 \pm 5.96$	$2.87\pm0.38$	$18.39 \pm 1.31$
PI-4*	N/A	N/A	PI-4	$9.88\pm0.97$	$328.21 \pm 14.46$	$0.94\pm0.18$
PI-5	9.8	0.85	PI-5	$38.63 \pm 3.88$	$4.90\pm0.61$	$10.20 \pm 1.16$

of the polymer do not appear to show regions of varying hardness, implying a relative isotropic composition. The results of the indentations are presented in Table 5. Overall, those samples with larger mol% of the low molecular weight Jeffamine D230 show higher hardness, ranging from 17.6 to 14.4 Hv (PI-1 through PI-3) as compared to the sample with a large molar composition of the relatively high molecular weight Jeffamine D400 (PI-5) with a hardness of 9.8 Hv. Particularly, PI-1 and PI-3 both composed of the shorter Jeffamine D230, the major diamine of those polymers, appear to have similar Vickers Hardness values of 17.6 Hv. However, once the higher weight amine is added, the value decreases to 14.4 Hv as was seen in PI-2. Thus, the hardness appears to be governed by both the aliphatic diamine size and concentration and is thus also related to the glass transition due to polymer chains' mobility and segmental slippage with applied force [34]. A trend approximately mirroring that for the glass transition is observed with PI-1 = PI-3 > PI-2 > PI-25 > PI-4 (is too soft to measure). The results for PI-4 and PI-5, in particular, are governed by the large size of the aliphatic Jeffamine D400. In this case, PI-4 was too soft to be measured using a Vickers indenter and when related to the glass transition, the value dropped from 100°C in PI-5 to 40.1°C in PI-4.

## Tensile Testing

The tensile testing corroborates the idea that the shorter diamine D230 linkers provide a higher stress resistance but a lower strain elongation. This is illustrated with the maximum stress value for PI-1 of 65.69 MPa compared to the Kapton® films' maximum stress of 231 MPa at 23°C. On the other hand, the longer Jeffamine D400 proves to lower the stress resistance but increase the strain elongation as shown with the maximum elongation for PI-4 of 328.21%, which is three times the initial length (Table 6). When comparing the effects of the MBDMA (25 mol% for PI-5 vs. 11 mol% PI-4), it can be seen that the overall tensile properties of the material are governed by the aromatic diamine. The aromatic and shorter aliphatic links govern the initial behavior of the material as it can be illustrated by the Young's modulus. The stiffness is 20 times higher for PI-3 compared to PI-4, showing the effects of doubling the length of the aliphatic diamine. The same comparison applies for the MBDMA aromatic linker between PI-4 and PI-5, showing a one-fold increase in the stiffness when the aromatic linker is increased from 11 to 25 mol%.

## CONCLUSIONS

Fully aromatic polyimides are well known to exhibit high thermal stability and resistance to solvents, and as a consequence, they are typically unable to be processed with conventional thermoplastic equipment. By using long chain aliphatic polyetherdiamines, we were able to impart into the backbone flexible components, making our polyimides melt processable using typical thermoplastic techniques, such as compression molding, injection molding, and extrusion. The synthesis and subsequent characterization of polyimides in this work prove that thermoplastic polyimides with tunable glass transition temperatures are possible. Thermal and mechanical properties, such as microhardness and decomposition temperatures, were also characterized. The molecular weight and polydispersities were elucidated from gel permeation data and are low relative to industrial polyimides. This works provides an expansion in the area of aliphatic polyimides with the objective to be used in semidry lithium ion polymer batteries [9]. The larger forms of processability of the material provide the elimination or reduction of the solvent used for the separator layer/electrolyte composite. The advantage of the flexible polyimide with a lower  $T_g$  comes from the manufacturing process because different options could be used and at lower energy expenses.

Rheological analysis showed glass transition temperatures  $(T_g)$  ranging from approximately 15.1°C to 100.0°C according to G" peaks at 2.6 Hz. It was demonstrated that with approximately equivalent amounts of Jeffamine D230, the glass transitions can be tuned by the addition of varying sizes of the aliphatic polyetherdiamines, with larger, higher MW aliphatic diamines reducing the glass transition temperature. Conversely, the aromatic diamine shows a significant influence on glass transition temperature and can increase it even when large molecular weight aliphatic diamines are present. The flexible component came from the diamine portion of the polyimide, but the modifications at the dianhydride side could impart different ranges in the properties targets.

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