

## New Polyimides Based On Epiclon

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**Abstract:** Two new polyimides containing epiclon moieties have been synthesized. These polyimides were prepared by high-temperature polycondensation of epiclon, an alicyclic dianhydride with two diamines, 4,4'-methylenedianiline (DDM) and 1,6-hexamethylenediamine (HMDA). The polymers had good solubility, thermal stability up to 345 °C and glass transition temperatures in the range of 122-235 °C. Both polyimides formed flexible films with high transmission above 80% in the wavelength of 400-700 nm. The correlation between the polymers structure and their properties has been discussed.

**Keywords:** 3-5 soluble polyimides, alicyclic dianhydride, thermal stability, high transparency.

### Introduction

Polyimides have received special attention in the electronics field due to their excellent thermal, mechanical and electrical properties, associated with their good adhesion and low dielectric constant. These polymers are useful in a variety of applications in microelectronics and photoelectronics industries due to their advantageous balance between thermal stability,

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chemical resistance mechanical and electric properties.<sup>1-3</sup> In spite of that, there are some problems that hinder extending the applications of the aromatic polyimides as optoelectric materials: the insolubility in common solvents in the fully imidized form, the intra- and intermolecular charge transfer (CT) interactions which cause the color of the aromatic polyimide films and their dielectric constants. These drawbacks determined investigations into polyimides concentrated on fully or semi - aliphatic systems. The polyimides containing aliphatic and alicyclic moieties have a higher transparencies and lower dielectric constants in relation to the aromatic polyimides, derived from their low molecular density and polarity and low probability of undergoing interior intramolecular CT. Is the reason for that they are being considered for the applications in optoelectronics and interlayer dielectric materials.<sup>4,5</sup>

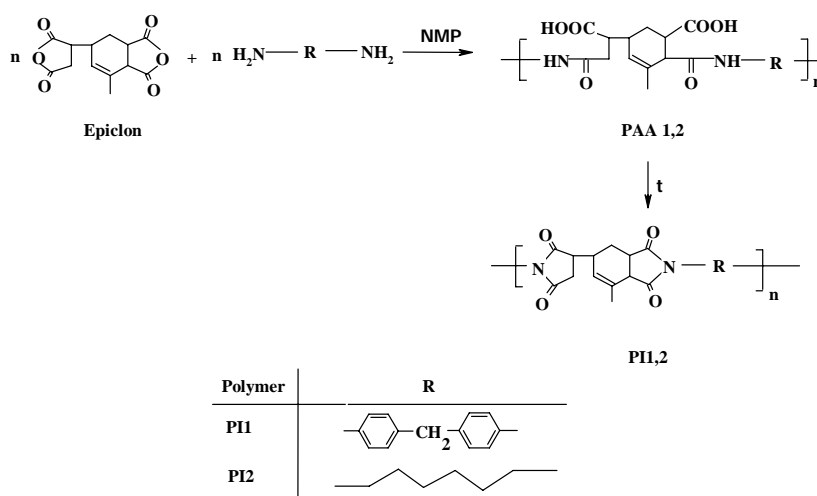
The paper presents the synthesis and characterization of two polyimides from 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon), and 4,4'-methylenedianiline (DDM) and 1,6 hexamethylenediamine (HMDA), respectively. The effects of various compositions on the soluble, thermal, and transparent properties of the resulting polyimides were studied.

### Results and discussions

A well known approach to increase the solubility and processability of a polymer is to introduce into the main chain flexible bonds like amides and ether groups, aliphatic segments<sup>7</sup> or bulky and asymmetrical groups, large pendent or polar substituents.<sup>8-11</sup> The introduction of alicyclic structure using alicyclic dianhydride is also studied.<sup>12-16</sup>

From the tetracarboxylic dianhydrides, Epiclon is a cycloaliphatic,

asymmetrical and flexible chemical structure. Two polyimides, a semi-aliphatic one (**PI1**) and an aliphatic one (**PI2**) were obtained by solution polycondensation reaction. Imidization was initiated at 70 °C and it was performed at 195 °C. The properties of these polymers with respect to their chemical stability and glass transition temperature, solubility and film forming ability have been evaluated. A general reaction scheme for the synthesis of the polyimides **PI1**, **PI2** is presented Scheme 1.

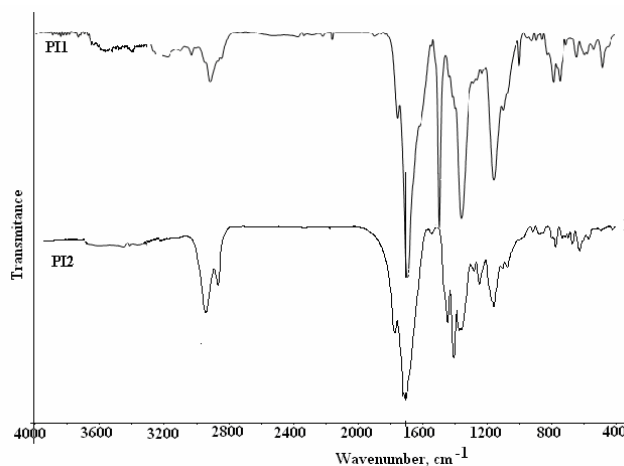


**Scheme 1** Synthesis of the polyimides PI1, PI2

The polymers were prepared by conventional two-step polycondensation reaction, via polyamic acid precursor. It was found that a considerable gelation occurred during the addition of 1,6-hexamethylene diamine (HMDA) to a solution of Epiclon (polyimide **PI2**). The solution became clear on stirring. This phenomenon is probably due to the formation of salt complex between highly basic aliphatic diamine and carboxylic acid groups of polyamic acid, which prevented the chain growth of polymer, and thus explains the low molecular weight of the resulting polyimide **PI2**.

*Spectral characterization.* The structures of polyimides were characterized by FT-IR and  $^1\text{H-NMR}$  spectroscopy. Figure 1 shows the FT-IR spectra of the polyimides **PI1**, **PI2**.

FT-IR spectra confirm the chemical structures of the polymers by the presence of the characteristic peaks attributable to the imide structure at:  $1770\text{ cm}^{-1}$  and  $1709\text{ cm}^{-1}$  (assigned to the symmetrical and asymmetrical stretching vibrations of the carbonyl in imide rings),  $1380\text{ cm}^{-1}$  (due to C–N stretching in imide ring) and at  $775\text{--}760\text{ cm}^{-1}$  (possibly associated to imide ring deformation). Polyimides **PI1** presented strong infrared absorptions at  $1510\text{ cm}^{-1}$  attributable to the =CH in aromatic rings, while the polymer **PI2** showed characteristic peaks at  $2930\text{--}2920\text{ cm}^{-1}$  associated with the aliphatic sequences in the monomers.



**Figure 1.** FT-IR spectra of the polyimide PI1, PI2

$^1\text{H-NMR}$  spectroscopy also confirms the polymer structures. The  $^1\text{H-NMR}$  spectra contains the signals characteristic to the monomers. The peaks between  $1.20\text{--}4.30\text{ ppm}$  were associated with the resonance values of the aliphatic protons in the polymer unit structure: methylene and methine

protons in the succinimide ring, the cycloaliphatic ring and HMDA moiety. The aromatic protons can be observed in the 7.20-7.96 ppm region.

*Solution properties.* Both obtained polymers have excellent solubility in polar solvents such as DMF, NMP, DMAc, DMSO, and *m*-cresol. In addition, polyimide **PI2** dissolve easily in chloroform (Table 1).

**Table 1.** Molecular weight and Solubility data

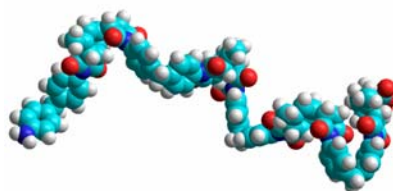
Sample	Mn	Solubility				
	g/mol	NMP	DMAc	DMSO	<i>m</i> -cresol	CHCl <sub>3</sub>
<b>PI1</b>	50000	++	+ -	++	++	-
<b>PI2</b>	27100	++	++	++	++	++

<sup>a</sup> - Insoluble, +- slightly soluble at r.t., ++ soluble at r.t.

There are some explanations that facilitate an easier diffusion of the solvent among macromolecules, increasing the solubility:

- the polymer chain flexibility promoted by the aliphatic and cycloaliphatic moieties with greater rotational freedom;
- the introduction of the bulky and asymmetric structure (Epiclon unit) which decreases close packing by decreasing of the entropy energy of internal rotation.<sup>17</sup>

Figure 3 presents a model molecule for a fragment of the polymer **PI1**, obtained by means of the Hyperchem program, version 8.07 Evaluation copy.<sup>6</sup>



**Figure 2.** Model molecule for a fragment of the polymer PI1

Molecular modeling showed that the shapes of these macromolecular chains are very flexible in comparison with the wholly aromatic polyimides, usually rigid linear polymers.

*Thermal behavior.* The thermal stability of the polymers (Table 2) was evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperature  $T_g$ , as a second order endothermic transition, could be considered as the temperature at which a polymer undergoes extensive cooperative segmental motion along the backbone. The flexible linkages decrease the energy of internal rotation, lowering the  $T_g$ .<sup>18</sup> The  $T_g$ s of the polyimides, depending on the structure of diamine component, decreased with the decreasing of rigidity of the polymer backbone and were observed in the range of 122- 255 °C.

**Table 2.** Thermal stability of the polyimides PI1, PI2

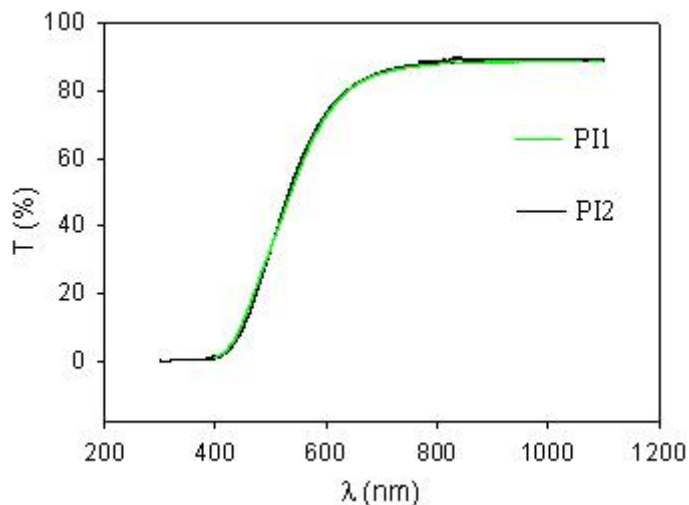
Polymer code	$T_g$ (°C) <sup>a</sup>	Thermal stability				
		$T_0$ (°C) <sup>b</sup>	$T_{10}$ (°C) <sup>c</sup>	$T_{d1}$ (°C) <sup>d</sup>	$T_{d2}$ (°C) <sup>e</sup>	$R_{700}$ (%) <sup>f</sup>
PI1	255	440	465	570	-	24.4
PI2	122	345	380	480	565	14.2

<sup>a</sup> Determined by 2<sup>nd</sup> heating at rate of 20 °C / min in air ; <sup>b</sup> onset temperature of degradation; <sup>c</sup> temperature at 10% weight loss; <sup>d, e</sup> 1st, 2<sup>nd</sup> Max. decomposition temperature; <sup>f</sup> Residue at 700°C.

The resulted polyimides show 10% wt loss in the range of 380 - 465 °C, with a two-step weight loss behavior (due to the thermally labile methylene segments in the aliphatic diamine moiety). The low char residue for these polymers may be associated with their low aromatic ring density.

*Optical properties.* Polyimides containing alicyclic structures are expected to have better transparency than aromatic polyimide, due to the prohibition of electron conjugation by the introduction of alicyclic moiety.<sup>19</sup>

Transmission UV-visible spectra of polyimide films are shown in Figure 3.



**Figure 3.** The UV-Vis spectrum of the polyimide films PI1, PI2

Transparency in the visible region was evaluated by averaging the transmittances in the range from 400 to 780 nm in the UV-VIS spectrum. Both polyimides films exhibited characteristic signal as from 400 nm, as a results of their chemical structure.

## Experimental

### Materials

5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon B-4400) 4,4'-methylenedianiline and 1,6-hexamethylenediamine were provided by different commercial sources and were used as received, since they were of a highly purified grade for polymer synthesis. N-methyl-2-pyrrolidinone (NMP) were dried before using, by standard methods.

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## Measurements

Infrared spectra were recorded with a Bruker Vertex 70 spectrometer in transmission mode, at  $24\text{ cm}^{-1}$  resolution, by using precipitated polymers ground in potassium bromide pellets.

Transmittance of polyimide films was recorded in 300–1000 nm wavelengths on a SPECORD 200 Analytik-Jena spectrophotometer.

The  $^1\text{H-NMR}$  spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer for polymer solution in dimethylsulfoxide- $d_6$  (DMSO- $d_6$ ) using tetramethylsilane (TMS) as internal standard.

Polymer solubility was determined at room temperature at a concentration of 1% (w/v).

The molecular weight were determined by gel permeation chromatography (GPC) using a PL-EMD 950 evaporative mass detector instrument. Polystyrene standards of known molecular weight were used for calibration and dimethylformamide as mobile phase.

Thermogravimetric analyses (TGA) were performed on a MOM derivatograph (Hungary) in air, at a heating rate of  $10^\circ\text{C}/\text{min}$ . The initial decomposition temperature (IDT) is characterized as the temperature at which the sample achieves a 5% weight loss. The temperature of 10% weight loss ( $T_{10}$ ), was also recorded.

The glass transition temperatures ( $T_g$ ) of the precipitated polymers were determined with a Mettler differential scanning calorimeter DSC 12E. The samples were heated from ambient temperature to above  $300^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflection curve resulting from the typical second heating was assigned as the glass transition



temperature of the respective polymers.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, version 8.07 Evaluation copy.<sup>6</sup>

### **Synthesis of polyimides**

The polymers were synthesized by reacting an alicyclic dianhydride with two diamine types: aromatic and aliphatic. The combination in one molecule of cycloaliphatic groups with aromatic or aliphatic diamine moieties produced a systematic variation in the properties of these polyimides. The polymers were prepared by polycondensation of equimolar amounts of Epiclon and diamine (4,4'-methylenedianiline and 1,6-hexamethylenediamine), in NMP, under anhydrous conditions, in a nitrogen atmosphere. As a general procedure, the reactor was purged with dry nitrogen for 10 min. As an example 4,4'-methylenedianiline was charged into the reactor. Until complete dissolution of diamine, epiclon was added to the reactor in two portions, within one half hour (solid content 15% in NMP). The reaction mixture was stirred 24 h at room temperature in N<sub>2</sub> atmosphere, resulting in a polyamic acid (PAA) after that, by thermally imidization was transformed in the corresponding polyimide (PI).

### **Polyimide films**

Polyimide films were prepared through imidization of polyamic acid films cast on a glass substrate, which was placed overnight in an 80 °C oven to remove most of the solvent. The semidried polyamic acid films were further dried and transformed into polyimides, by the following heating program: 120 °C, 160 °C, 180 °C, 210 °C and 250 °C for 1h at each

temperature. After stripping the films in hot water, the resulting samples were dried at 65 °C in a vacuum oven for 24 h.

### Conclusions

Two polyimides based on Epiclone with aromatic and aliphatic diamine moieties were obtained. Both polyimides were thermally stable up to 380 °C with glass transition in the range of 255 – 122 °C. The polyimides formed flexible films and showed high transmission above 80% in the wavelength of 400-700 nm. The introduction of aliphatic and cycloaliphatic moieties with greater rotational freedom in the polymer main chain, promoted an improved solubility and high transparency, by the decreasing of the close molecular packing. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

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