ACADEMIA ROMÂNĂ
Revue Roumaine de Chimie
http://web.icf.ro/rrch/

Rev. Roum. Chim.,
2011, *56*(3), 209-215

NOVEL POLYIMIDES CONTAINING ALICYCLIC UNITS. SYNTHESIS AND CHARACTERIZATION

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Received March 30, 2010

A series of novel polyimides containing alicyclic moieties have been synthesized. These polyimides were prepared by high-temperature polycondensation of an alicyclic dianhydride, 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon) with two diamines, 4,4'-methylenedianiline (DDM) and 1,6-hexamethylenediamine (HMDA). Polycondensation reactions proceeded at 185 °C and produced imide type polymers with high thermal stability. All the polymers had good solubility toward polar solvents, were stable up to 345 °C with 5% weight loss and had glass transition temperatures in the range of 122-235°C. The polyimides formed flexible films and showed high transmission above 80% in the wavelength of 400 - 700nm. The correlation between the polymers structure and their properties has been discussed.

INTRODUCTION

Polyimides (PI) are one of the most important classes of polymers and are useful in a variety of applications in the microelectronics (flexible printed circuit boards for electronic devices) and photoelectronics industries (as photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays) due to their excellent high thermal stability, chemical resistance and good mechanical and electric properties.[1] Other applications include, adhesives and matrix resins for composites. 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. The investigations into polyimides have also concentrated on fully or semi - aliphatic systems. As a consequence, because of their higher transparencies and lower dielectric constants derived from their low molecular density and polarity and low probability of undergoing interior intramolecular CT, these polymers, fully aliphatic and alicyclic polyimides (API) are being considered for the applications in optoelectronics and interlayer dielectric materials. [2-5]

The paper presents the synthesis and characterization of three polyimides from 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohexene-1,2-dicarboxylic anhydride (Epiclon) and two diamine: 4,4'-methylenedianiline (DDM) and 1,6 hexamethylenediamine (HMDA). The diamine (aromatic or aliphatic) has been used alone or in combination with one another. The effects of various compositions on the soluble, thermal, and transparent properties of the resulting polyimides were studied.

RESULTS AND DISCUSSION

Much effort has been focused on the synthesis of soluble and colorless polyimides without sacrificing their excellent properties. One approach to increase the solubility and processability is to introduce into the polymer chain flexible bonds like amides and ether groups, or aliphatic segments.[6]

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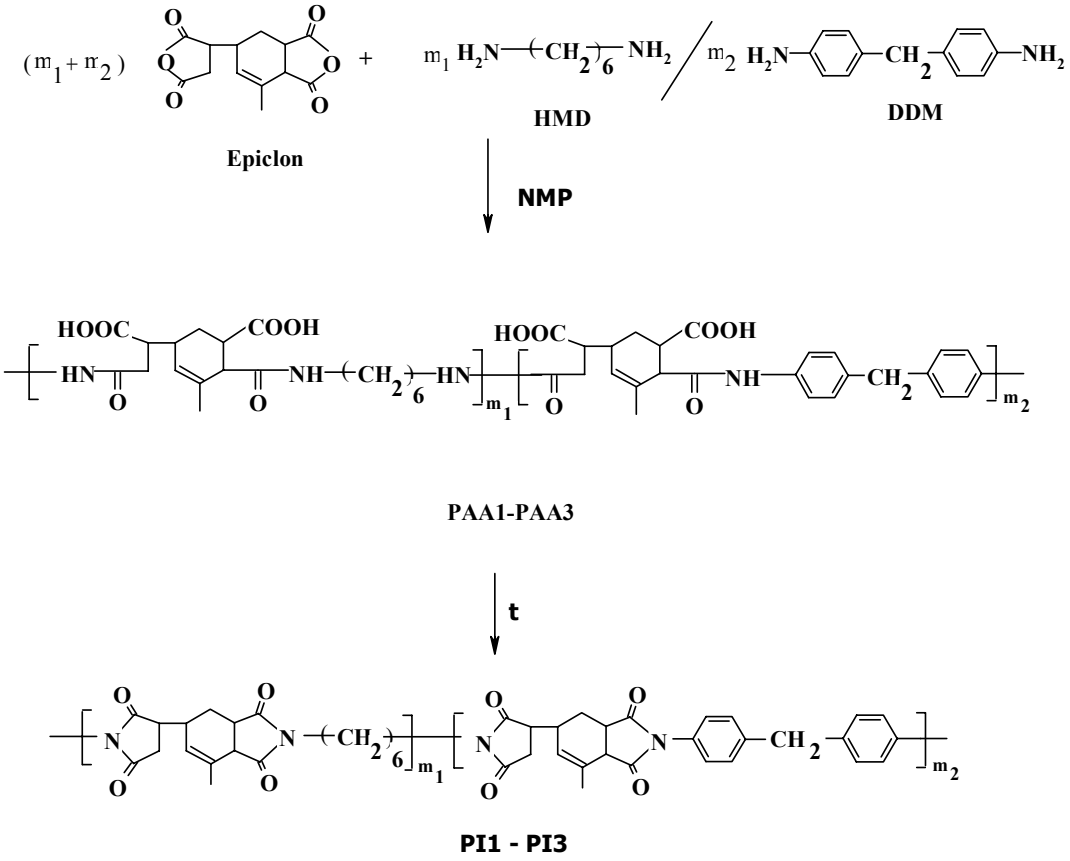
Another approach is the incorporation of bulky and asymmetrical groups, large pendent or polar substituents.[7-10] The introduction of alicyclic structure using alicyclic dianhydride is also studied .[11-15]

It is expected that the combination in the polymer backbone of epiclon moieties together with aromatic rings and flexible aliphatic sequences, would develop new synthetic polymers, offering a favorable balance structure-properties. From the tetracarboxylic dianhydrides, Epiclon is a cycloaliphatic, asymmetrical and flexible chemical structure. Three polymers, semi-aliphatic (**PI1**, **PI2**) and aliphatic (**PI3**) polyimides were prepared by using classical solution polycondensation. Imidization was initiated at 70 ºC and it was performed at 195 ºC. 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-PI3** is presented in Scheme 1.



Polymer	PI1	PI2	PI3
Diamine molar ratio (DDM : HMDA)	100 : 0	50 : 50	0 : 100

Scheme 1 – Synthesis of the polyimides **PI1**-**PI3**.

The polymers were obtained by conventional two-step polycondensation reaction, via polyamic acid precursor. The reactions proceeded homogeneously (polyimides **PI1** and **PI2)** without gelation or precipitation of the resultant polymers. It was found that a considerable gelation occurred during the addition of 1,6 hexamethylenediamine (HMDA) to a solution of Epiclon (polyimide **PI3**). 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 the polyamic acid, which prevented the chain growth of polymer, and thus explains the low molecular weight of the resulting polyimide **PI3** (Table 1).

Spectral characterization. The structures of polyimides were characterized by FT-IR and ^{1}H-NMR spectroscopy. Figure 1 shows the FT-IR spectra of the polyimides **PI1-PI3.**

In FT-IR spectra measured in transmission mode, three characteristic peaks attributable to the imide structure can be observed at about: 1770 cm^{-1} and 1709 cm^{-1} (assigned to the symmetrical and asymmetrical stretching vibrations of the carbonyl in imide rings), 1380 -1370 cm^{-1} (due to C–N stretching in imide ring) and at 775–760 cm^{-1} (possibly associated to imide ring deformation). Polyimides **PI1** and **PI2** presented strong infrared absorptions at 1510 cm^{-1} attributable to the =CH in aromatic rings. All polymers showed characteristic peaks at 2930–2920 cm^{-1} associated with the aliphatic sequences in the monomers. The broad absorption band at 3350–3450 cm^{-1} characteristic of NH amidic and the narrow absorption peak at 1650–1660 cm^{-1} due to C=O group in amide linkage disappeared entirely, indicating the completion of thermal imidization of the intermediate polyamidic acid into final polyimide structure and confirms the successful synthesis of polymers by polycondensation in solution.

^{1}H-NMR spectroscopy confirms the polymer structures. The ^{1}H-NMR spectra contains the signals characteristic to the monomers (Table 1). The peacks between 1.80 – 4.15 ppm were associated with the resonance values of the aliphatic protons in the polymer unit structure: methyl, methylene and methine protons in the cycloaliphatic and aliphatic moieties. The aromatic protons can be observed in the 7.10 - 7.86 ppm region.

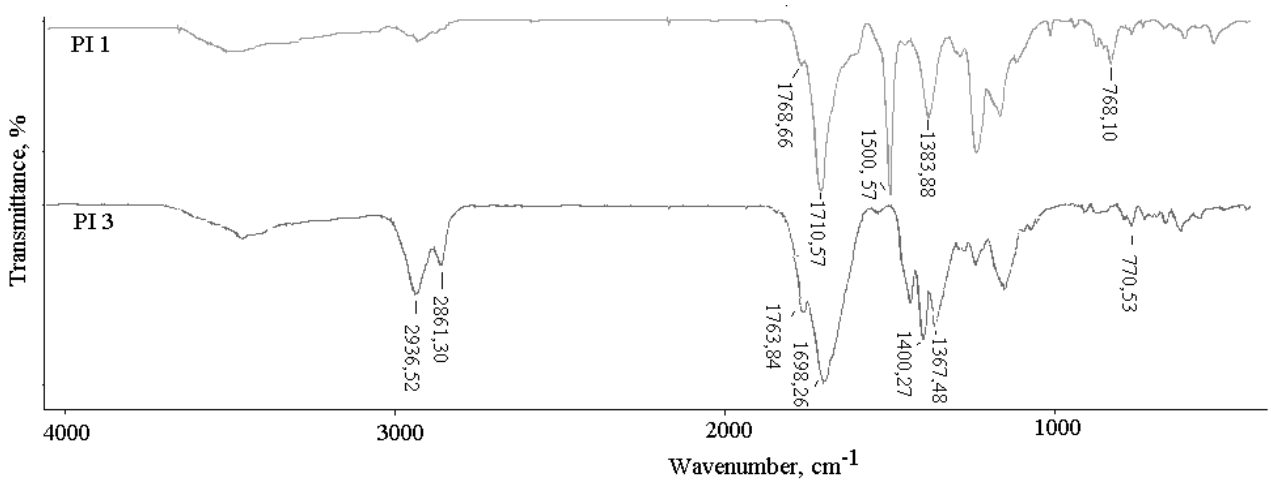


Fig. 1 – FT-IR spectra of the polyimides **PI1** and **PI3**.

Table 1

^{1}H-NMR data of the polymers **PI1-PI3**

Polymer	**^{1}H-NMR spectral data** [a] **δ (ppm)**
PI1	7.10-7.57 (m, 8H, aromatic); 4.15 (s, 2H, CH_2); 3.35-3.84 (m, 3H, CH, CH_2, succinimide, imide); 2.55-3.01 (m, 5H, CH, CH_2, cycloaliphatic, succinimide, imide); 1.85 (s, 3H, CH_3).
PI2	7.20 - 7.86 (m, 8H, aromatic); 4.10 (s, 2H, CH_2); 3.20-3.65 (m, 10H, CH, succinimide, imide, aliphatic); 2.45-2.80 (m, 10H, CH, CH_2, cycloaliphatic, succinimide); 1.80 (s, 6H, CH_3); 1.30-1.55 (m, 8H, CH_2, aliphatic)

Table 1 (continued)

PI3	3.10-3.75 (m, 7H, CH, CH_2, succinimide, imide, aliphatic); 2.35-2.85 (m, 5H, CH, CH_2, cycloaliphatic, succinimide, imide); 1.80 (s, 3H, CH_3); 1.30-1.68 (m, 8H, CH_2, aliphatic.)

[a] Multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet.
Solvent DMSO-d_6; internal reference TMS.

Solution properties. The solubilities of the polymers toward various kinds of organic solvents were tested. All the polyimides obtained have excellent solubility in polar solvents such as DMF, NMP, DMAc, DMSO, and *m*-cresol. In addition, polyimide **PI3** dissolve easily in chloroform (Table 2).

Table 2

Molecular weight and Solubility data

Sample	Diamine molar ratio DDM: HMDA	Mn g/mol	Mw /Mn	Solubility NMP	DMAc	DMSO	*m*-cresol	$CHCl_3$
PI1	100:0	50000	2.3	++	+-	++	++	-
PI2	50:50	27000	1.9	++	++	++	++	+-
PI3	0:100	17100	1.7	++	++	++	++	++

[a] - Insoluble, +- slightly soluble at r.t., ++ soluble at r.t.

Improvement in polymer solubility is due to chain flexibility promoted by the aliphatic and cycloaliphatic moieties with greater rotational freedom. The introduction of the Epiclon unit which is also a bulky and asymmetric structure, decreases close packing, by decreasing of the entropy energy of internal rotation.[17] Thus, it is facilitated an easier diffusion of the solvent among macromolecules, increasing the solubility.

Thermal behaviour. The thermal stability of the polymers (Table 3) 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 Tg.[17] Different intra- and intermolecular interactions including hydrogen bonding, electrostatic and ionic forces, chain packing efficiency and chain stiffness, affect the T_g. The T_gs of the polyimides **PI1**-**PI3** were observed in the range of 122 – 255 °C, depending on the structure of diamine component and, decreased with the decreasing of rigidity of the polymer backbone.

Table 3

Thermal stability of the polyimides **PI1-PI3**

Polymer code	Tg (°C) [a]	Thermal stability T_0(°C) [b]	T_{10}(°C) [c]	T_{d1}(°C) [d]	T_{d2}(°C) [e]	R_{700}(%) [f]
PI1	255	440	465	570	-	24.4
PI2	190	370	440	495	575	18.8
PI3	122	345	380	480	565	14.2

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

The obtained polyimides begin to decompose between 345 - 440 °C and show 10% wt loss in the range of 380- 465 °C. The polyimides **PI2** and **PI3** showed two-step weight loss behavior (due to the

thermally labile methylene segments in the aliphatic diamine moiety). The prepared polyimides were thermally stable up to about 440 °C according to T_{10}, and drastic degradation (T_{d1}) occurred in the range of 480-495 °C, which was followed by the second degradation (T_{d2}) above 560°C. The low char residue for these polymers may be associated with their low aromatic ring density.

Surface properties. In order to examine the surface morphology of **PI 3** film, atomic force microscopy measurements were made. Figure 2 plots the bi- and three-dimensional structure, observing that the film surface is covered with nanometers-scaled granules (mean diameter of the grains was 80 nm).

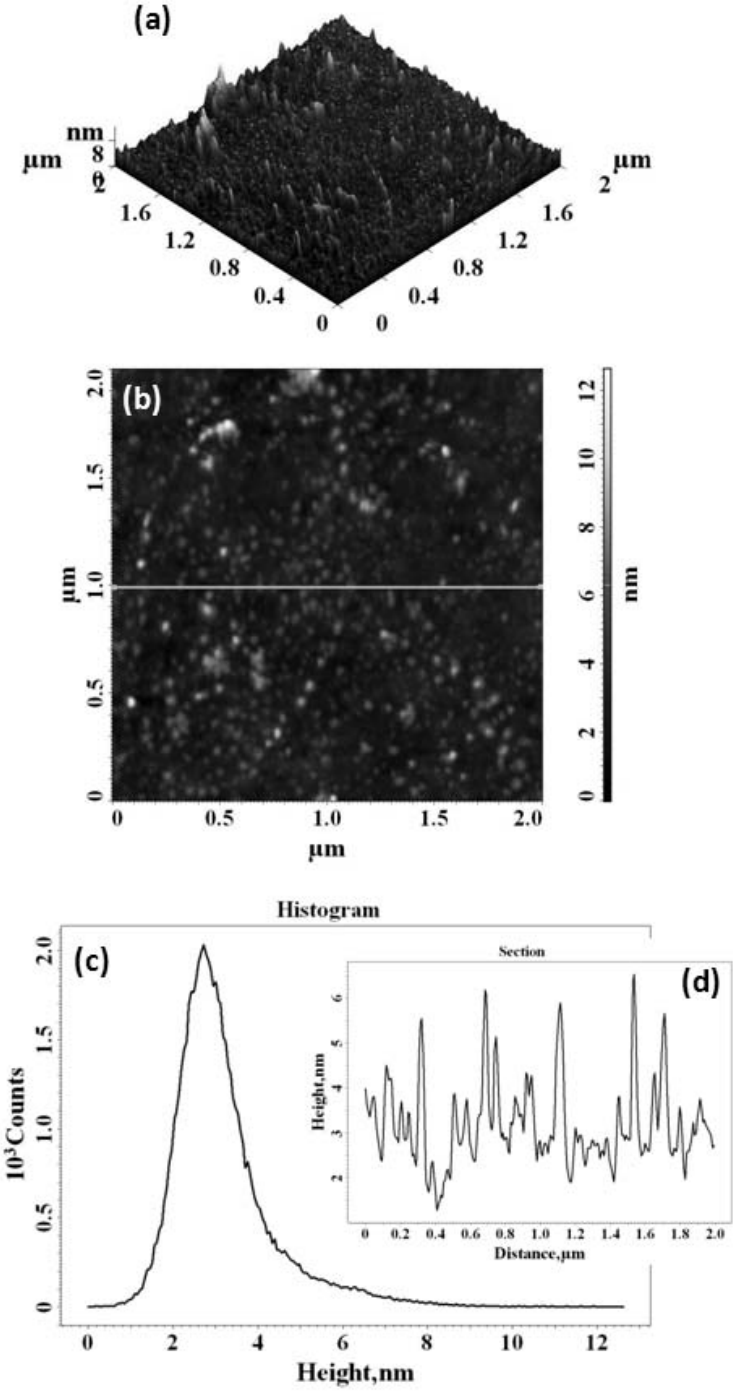


Fig. 2 – AFM characterization of **PI 3** – film: (a.) 3D AFM image; (b) 2D tapping mode AFM image; (c) height profile taken along the line from 2D AFM image; (d) surface height histogram. Scan area: 2 µm x 2 µm.

The AFM analysis showed a smooth topography of the surface, with root-mean-square (Sq) roughness of the 1.19 nm order and average roughness (Sa) of 0.84 nm order over an 2 μm x 2 μm area. From height profile (figure 2c) and height histogram analysis (figure 2d) it can be obtained the average height of 3.18 nm. The surface morphology and roughness of the polyimide film could be mainly the result of polymer chains characteristics that govern aggregation and molecular ordering during drying and thermal imidization processes.

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.[18] The films obtained from the resulting polyimides were pale-yellow. Their optical transparency was experimentally measured by UV-visible spectroscopy and the results are shown in Table 4.

Table 4

Optical transparency of films derived from polyimides **PI1**-**PI3**

PI	T_{500} [a] %	$\lambda_{80\%}$ [b]	λ_{cutoff} [c]
PI1 (semiaromatic polyimide)	43	636	400
PI2 (partial aromatic copolyimide)	31	606	302
PI3 (nonaromatic polyimide)	36	617	301

[a] Transmittance at 500 nm.
[b] Wavelength of 80% transmittance.
[c] Wavelength of UV cutoff.

From the transmission spectra the transmittance at 500 nm wavelength decreased from 43% to 31% and exhibited a shift in the cutoff wavelength ($\lambda_{cuttoff}$) from 400 to 300 nm. These films showed transparency higher than 80% above 606 nm.

EXPERIMENTAL PART

Materials

5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-3-cyclohex-ene-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) was dried before using, by standard methods.

Measurements

Infrared spectra were recorded with a Bruker Vertex 70 spectrometer in transmission mode, at 24 cm^{-1} resolution, by using precipitated polymers ground in potassium bromide pellets. UV-Visible spectra were recorded on a SPECORD 200 Analytik Jena UV-visible spectrophotometer.

The ^{1}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 solubilities were 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°C/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°C at a heating rate of 10°C/min under nitrogen. Heat flow versus temperature scans from the second heating run were plotted and used for reporting the glass transiton 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.

The atomic force microscopy (AFM) measurements were made on a Scanning Probe Microscope Solver Pro-M platform (NT-MDT, Russia), in air, at room temperature (23°C), in tapping mode. A rectangular "golden" silicon cantilever NSG10 (NT-MDT, Russia), with a typical force constant K_N = 11.8 N m^{-1} and 209 kHz oscillation frequency was used. The tip curvature radius and height was 10 nm and 14-16 μm, respectively. The scan area was 2 μm x 2 μm, 256 x 256 scan point size images being thus obtained. For image acquisition and image analysis, the last version of the NT-MDT NOVA software was used.

Synthesis of polyimides

Polyimides were synthesized by reacting Epiclon (EPI) with 4,4'-methylenedianiline (DDM) and /or 1,6 hexamethylene diamine (HMDA). An equimolar ratio of both diamines has been applied for preparation of the copolyimide. The combination of the cycloaliphatic groups with both flexible

aromatic and / or aliphatic diamines, produced a systematic variation in the properties of these polyimides. The polymers were prepared by polycondensation of equimolar amounts of Epiclon and diamine in NMP, under anhydrous conditions, in a nitrogen atmosphere. As a general procedure, the reactor was purged with dry nitrogen for 10 min. The diamine, (DDM and/or HMDA) in different mole ratios, was charged into the reactor through an addition funnel (the amount used is listed in the Table 1). NMP (solid content 30%) was then charged. Until complete dissolution of diamines, epiclon was added to the reactor in two portions, within one half hour. To dilute the reaction mixture (solid content 15%) after epiclon was charged, residual NMP was added into the reactor. The reaction mixture was stirred 24 h at room temperature in N_2 atmosphere, resulting in a polyamic acid (PAA) after that, by thermally imidization was transformed in the polyimide (PI).

Polyimide films

Polyimide films were prepared through imidization of poly(amic acid) films cast on a glass substrate, which was placed overnight in an 80 °C oven to remove most of the solvent. The semidried poly(amic acid) films were further dried in an oven 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.

CONCLUSION

The incorporation of cycloaliphatic Epiclon units together with methylene sequences into the main chain of polyimides gave products with an improved solubility in polar solvents, and high transparency. These polymers maintained high thermal stability, the decomposition temperature being above 380ºC and the glass transition in the range of 255 – 122 ºC. The polyimides formed flexible films and showed high transmission above 80 % in the wavelength of 400 -700 nm. The AFM analysis revealed a smooth topography of these surfaces, with root-mean-square (Sq) roughness between 2.32 - 1.19 nm and average roughness (Sa) in the range of 1.91 - 0.84 nm over an 2 μm x 2 μm area. The good solubility makes the present polymers potential candidates for practical applications in spin coating and casting processes.

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