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# Thermal and optical behaviour of some aliphatic-aromatic polyimide films

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By the polycondensation reaction of 3,3'-dimethyl-4,4'-diaminodiphenylmethane and a mixture of an aliphatic dianhydride, bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA), and an aromatic one, benzophenonetetracarboxylic dianhydride (BTDA), taken in various molar ratio, have been synthesized aliphatic-aromatic polyimides. All the obtained compounds have been characterized in terms of solubility, inherent viscosity, and film forming ability, thermal stability, optical and mechanical properties.

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*Keywords:* Polyimides, Polycondensation, Thermal properties, Transparency, Fluorescence

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## 1. Introduction

In the last few decades the interest in polyimides have been growing steadily due to their excellent characteristics like thermo-oxidative stability, unique electrical properties, high radiation, mechanical and solvent resistance. These characteristics made polyimides useful in many applications including photoresists, passivation and dielectric films, soft print circuit boards, and alignment films within displays and many others [1-5].

Nevertheless, these polymers often have low solubility in common solvents and have high softening temperatures, thus making their workability very difficult or too expensive. The most common technique used to obtain polyimides is the processing their soluble intermediate, the polyamidic acid. Films are cast in thin layers and then are thermally dehydrated at high temperatures to produce the final imide form. This process can have other difficulties, such as inefficient cyclizations or appearance of microvoids in the final product due to the water removing.

Fully aromatic polyimides have poor solubility and non-melting features due to their rigid chain and strong interchain interactions. These strong interactions arise from intra- and interchain charge transfer complex (CTC) formation and electronic polarization which are supported by the strong acceptor and the electron donor characteristics of imides and amine segments, respectively [4]. The extended applications in optoelectronic materials are hindered by insolubility in common solvents in fully imidized form and the dark-yellow colour of polyimide films.

Many studies have been performed to modify the molecular interactions of polyimides to enable processing by conventional techniques, such as melt processing or solvent casting, while keeping the thermo-oxidative stability of the polymer. The replacement of the aromatic units with alicyclic groups or using of fluorinated monomers is the most used way to reduce the tendency of the formation of charge transfer complexes and can contribute to the destroying the conjugated structure [4]. A promising method of modifying the properties of the polyimide is the introduction into the polymer backbone of aromatic and non-aromatic structures, thermally stable, such as cardo, spiro, fluorine-containing structures or multicyclic structures (such as adamantane) [6,7].

Optical transparency of a polyimide is of special importance when it is applied in optical devices. Polyimides that contain adamantane, produce light-colored films with high transmittance in the visible region and good thermal stability [4,7]. The introduction of bulky $CF_3$ groups into macromolecular chain of polyimides is another approach to obtain light-colour polyimide films. On the other hand, polyimide backbone containing $CF_3$ units maintained high thermal stability, increased solubility and optical transparency, in addition lower dielectric constants [4,8-10].

The solubility and the optical transparency at visible light wavelength were increased by introducing pendant groups in the 2 and 2'-positions of dianhydrides or diamines. These improvements in the solubility and colour of polyimides result from the twisting of the conformation caused by the existence of 2, 2'-position substitutions, which inhibits chain packing and crystallization and breaks up the conjugation along the backbone [11]. Other authors obtained fully aromatic polyimides with good solubility, high thermal stability and good transparency by replacing the 4,4'-diaminodiphenylmethane with 4,4'-diamino-3, 3'dimethyldiphenylmethane (MMDA) [12].

By using of an alicyclic, bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) and aromatic one, benzophenonetetracarboxylic dianhydride (BTDA), in combination with an aromatic methyl substituted diamine (4,4’-diamino-3,3’dimethyldiphenylmethane) we attend to obtain aliphatic-aromatic copolyimides with good optical transparency, high thermal stability and a good solubility. First, we synthesized the neat polyimide from BOCA and MMDA and then copolyimides based on the same diamine (MMDA) and a mixture of BOCA and BTDA taken in different ratio. Aromatic polyimide from BTDA and MMDA was previously reported [12,13] and it will be compared with compounds reported in this paper.

## 2. Experimental

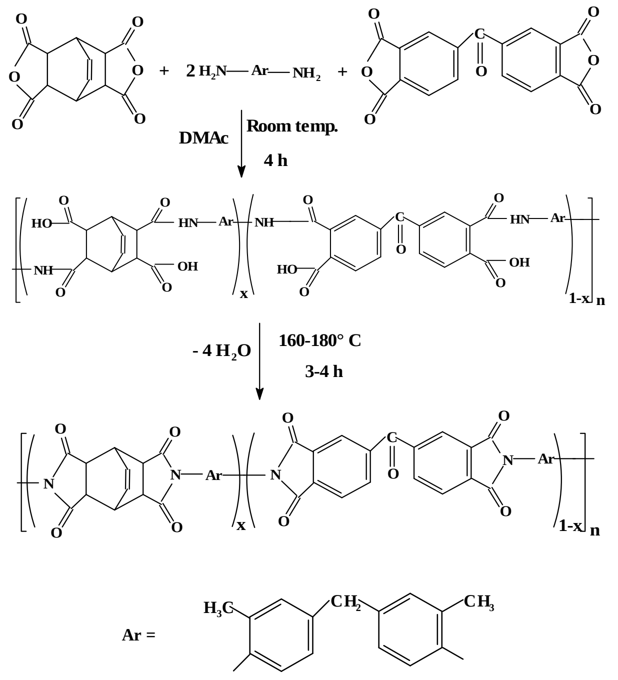
### 2.1. Starting materials

3, 3’-Dimethyl-4, 4’-diaminodiphenylmethane (MMDA) used in this study was synthesized in our laboratory by a previously reported method [13]. Benzophenonetetracarboxylic dianhydride (BTDA), bicyclo [2.2.2]-oct-7-ene-2, 3, 5, 6-tetracarboxylic dianhydride (BOCA), and N, N’-dimethylacetamide (DMAc) were acquire from Sigma-Aldrich and used as received.

### 2.2. Synthesis of polymers

The polymer precursor, polyamidic acid, was synthesized by the reaction of equimolar amounts of bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BOCA) (or a mixture of BOCA and BTDA, taken in different ratio) and 4,4’-diamino-3,3’-dimethyldiphenylmethane in N, N’dimethylacetamide (DMAc), in 14-15% solids concentration, by a method previously described [13]. This step of polycondensation was performed in inert atmosphere at room temperature, for 4-5 h. The second step of the reaction consisted in the thermal imidization of the polyamidic acid solution in the same reaction flask, by heating at reflux temperature (170 - 180 ºC) for another 4-5 h, under a slow stream of nitrogen to remove the water of imidization (Scheme 1). The final product was precipitated in water, washed with water and ethanol, and dried in at 105 ºC under vacuum.

The ratio between the aliphatic and aromatic dianhydride decreased from 3:1 to 1:3 and was used to abbreviate the obtained compounds as presented in Table 1.



Scheme 1. Synthesis of the polyimides

Polymeric films were obtained by casting polyimide solutions (after imidization) in DMAc onto glass plates and heating at 60 ºC over 4 h and at 100 ºC, 150 ºC, 200 ºC, and 250 ºC consecutively (1 h at each temperature). All polymers gave free standing flexible films, except homopolyimide PI-1, which gave only brittle film.

Table 1. Abbreviation of the polymers

| Abbreviation | Ratio of dianhydrides | |
|---|---|---|
| | BOCA[a] [mol%] | BTDA[b] [mol%] |
| **PI-1** | 1 | - |
| **PI-11** | 1 | 1 |
| **PI-13** | 1 | 3 |
| **PI-31** | 3 | 1 |

[a] BOCA= bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride,
[b] BTDA= benzophenonetetracarboxylic dianhydride

### 2.3. Measurements

*FTIR spectra* were recorded with a FT-IR VERTEX 70 (Bruker Optics Company), at a resolution of 0.5 $cm^{-1}$ in reflexion mode, by using free-standing films.

*UV-Vis absorption spectra* were recorded with a Specord M42 apparatus in the range of 250-800 nm, by using free-standing films.

*The molecular weights* were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with 0.2% polymer solutions in DMF. Polystyrene standards of known molecular weight were used for calibration.

*Inherent viscosities* were determined at 20°C for solutions of polymers (0.5 g/dL) in DMF, using an Ubbelohde viscometer.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5 [14]. The same program was used to visualise the structures obtained after energy minimisation. The calculations were carried out with full geometry optimisation (bond lengths, bond angles and dihedral angles).

*Thermogravimetric analysis (TGA)* was performed on a Mettler Toledo model TGA/SDTA 851 under nitrogen flow (20 $cm^3min^{-1}$), at a heating rate of 10°C/min, from 25 to 800°C. The initial mass of the samples was 6-9 mg.

*Differential scanning calorimetry (DSC)* analysis was performed on a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland), with 9.1 $STAR^e$ software. The samples (6–9 mg) were encapsulated in aluminium pans with pierced lids for volatiles evacuation. A heating rate of 10 °C $min^{-1}$ and a nitrogen flow of 100 mL $min^{-1}$ were employed. Heating-cooling-heating cycles were performed in the temperature range of 25-300°C for all polyimides in order To obtain the glass transition temperature of the analyzed materials. Heat flow vs. temperature scans from the second heating run were plotted and used for reporting the glass transition temperature.

*The mechanical properties* of the polymer films were determined by stress-strain measurements at room temperature on an Instron Single Column Systems tensile testing machine (model 3345) equipped with a 5 kN load cell and activate grips, which prevented the slippage of the sample before break. The cross head speed was 50 mm $min^{-1}$.

## 3. Results and discussions

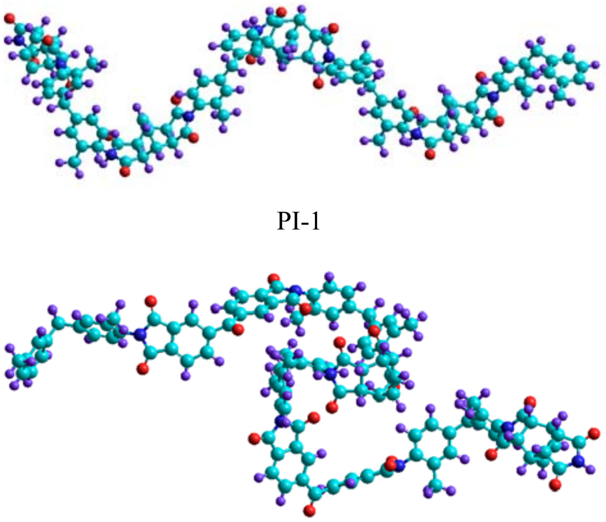
### 3.1. Structural characterization

The structure of final polymers was identified by FTIR spectra. Thus, the characteristic imide ring absorption bands appeared in the FTIR spectra of polyimide and copolyimides in the range of 1774 $cm^{-1}$ (symmetrical C=O imide stretching), 1707 $cm^{-1}$ (asymmetrical C=O imide stretching), 1384 $cm^{-1}$ (C-N stretching) and 717 $cm^{-1}$ (imide ring deformation), demonstrating the conversion of the intermediate polyamidic acid to final copolyimide [11-13]. By increasing the quantity of BOCA, the intensity of the band characteristic for the imide cycle remained unmodified. In addition, the intensities of the IR bands characteristic for aliphatic CH units increased when a higher content of BOCA was used, this can be attributed to the incorporation of this dianhydride. All the copolymers showed the characteristic absorption bands for the methyl groups at about 2923 $cm^{-1}$, and for the methylene groups at about 2850 $cm^{-1}$. The absorption band at 1630 $cm^{-1}$ (C=O stretching) is present in the copolyimides due to the carbonyl band from BTDA.

The introduction of alicyclic dianhydride units in the macromolecular chain breaks down the internal order in the polyimides matrices which is responsible for increased solubility in polar organic solvents. Thus, all polymers are easy soluble in N-methylpyrolidone (NMP) and other amidic polar solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), dimethylsulfoxide (DMSO).

As can be seen in Fig. 1, the molecular models of polymers show that the shape of the polymer chain is far from that of linear rigid rod which is characteristic to completely insoluble aromatic polyamides or polyimides (Fig. 1). Due to such a shape, the dense packing of the chains is disturbed, the diffusion of small molecules of solvents between the polymer chains is facilitated and that leads to better solubility [15].

Inherent viscosity values of these polymers are in the range of 0.27 – 0.56 dL/g (Table 2). The molecular weight of the polymers was determined by gel permeation chromatography (GPC), by using polymer solutions in DMF. The weight average molecular weight values Mw of the measured polymers are in the range of 21000 – 44000 g/mol and the dispersity Mw/Mn in the range of 1.98-2.2 (Table 2). These values indicate that these polymers have moderate molecular weight and a narrow dispersity. Seeing calibration with polystyrene may give questionable results when the polarity and backbone stiffness of the studied polymers deviate strongly from those of polystyrene, these values have to be taken as indicative only.



PI-1

PI-11

*Fig. 1. Molecular models of polyimide **PI-1** and copolyimide **PI-11***

*Table 2. The characterization of the polymer samples*

| PI samples | $^{a}\eta_{inh}$ dL/g | $^{b}$Mw g/mol | $^{c}$D | $^{d}T_5$ (°C) | $^{e}T_{10}$ (°C) | $^{f}T_{max}$ (°C) | $^{g}$Tg (°C) | Residual weight, % |
|---|---|---|---|---|---|---|---|---|
| **PI-1** | 0.27 | 21000 | 2.2 | 385 | 440 | 470 | $N_d$ | 32.7 |
| **PI-11** | 0.47 | 44000 | 2.08 | 479 | 510 | 538 | 270 | 57.0 |
| **PI-13** | 0.56 | 43000 | 1.98 | 464 | 503 | 603 | $N_d$ | 57.3 |
| **PI-31** | 0.44 | 42500 | 2.0 | 432 | 455 | 469 | $N_d$ | 43.0 |

$^{a}\eta_{inh}$ –determined at 5% concentration in DMF at 20°C; $^{b}$Mw- weight molecular weight; $^{c}$D– dispersity index; $^{d}$ $T_5$ –temperature at which the polymer lost 5%; ; $^{e}$ $T_{10}$–temperature at which the polymer lost 10%; $^{f}$ $T_{max}$– temperature of maximum rate of decomposition; $^{g}$Tg – glass transition temperature; $N_d$ – not detected until 300°C.

### 3.2. Thermal behaviour of polymers

The thermal stability of pristine polyimide (PI-1) and copolyimides (PI-11, PI-13 and PI-31) was carried out by TGA and DTG as shown in Fig. 2 and Table 2. From Fig. 2, it was shown that the initial decomposition temperature for the neat polyimide (PI-1) was lower than those of copolyimides reported in the present paper. As shown in Table 2 the initial decomposition temperature ($T_5$) of neat polyimide was 385 °C and in the range of 432-479°C for copolyimides. The similar thermal stability was reported for other polymers which contain BOCA units [16]. By comparing with the plain polyimide obtained from BTDA and MMDA reported earlier by us [17], which showed an initial decomposition temperature of 498°C, it can be seen that by introduction of BOCA units in the macromolecular chain of an aromatic polyimide, the thermal stability gradually decreased by increasing the quantity of alicyclic content. The reduction of thermal stability is probably related to the degradation of alicyclic units which influence the decomposition of copolyimides. DTG curves show that the temperatures of maximum rate of decomposition $T_{max}$ increase from 470°C for neat polyimide to 603°C for PI-13 (the copolyimide with the highest content of aromatic units). However, it was also observed that with the incorporation of aromatic dianhydride in the polyimide, the residual char yields increased from 32.7% for neat polyimide, PI-1, to 57.3% for a high content of aromatic dianhydride (PI-13) at 800°C and denotes that these compounds possess excellent thermal stability.

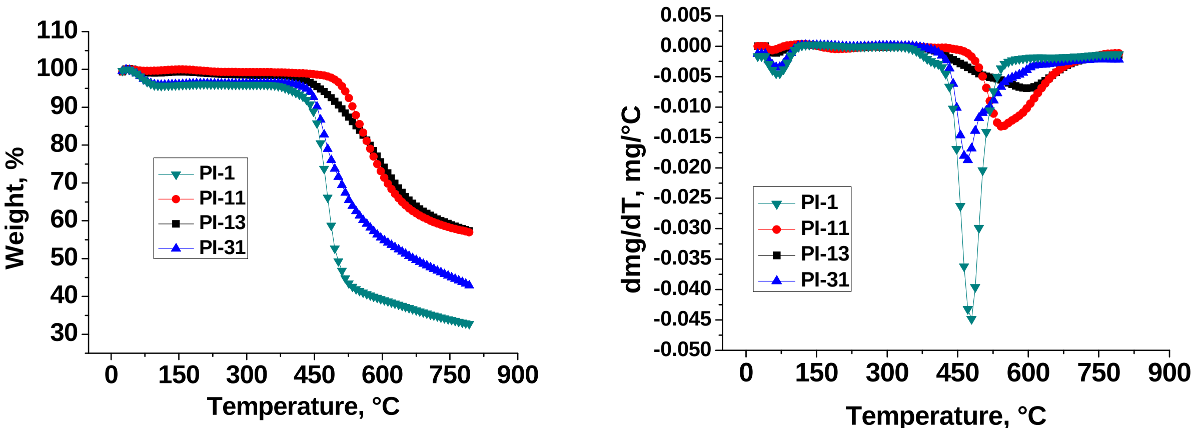


*Fig. 2. ATG (up) and DTG (down) curves of polymers*

### 3.3. Optical properties

UV-visible spectra of thin films of copolyimides were recorded and the obtained results are presented in Fig. 3. All copolyimide films exhibit cut-off wavelengths in UV region shorter than 300 nm. As can be seen from Fig. 3 the transmittance of all copolyimide films are higher than 90 % at 450 nm. The higher transparency and shorter cut-off of these copolyimide films can be attributed for the less chain packing and less intermolecular interaction of the polyimide chain compared to the other polyimides.

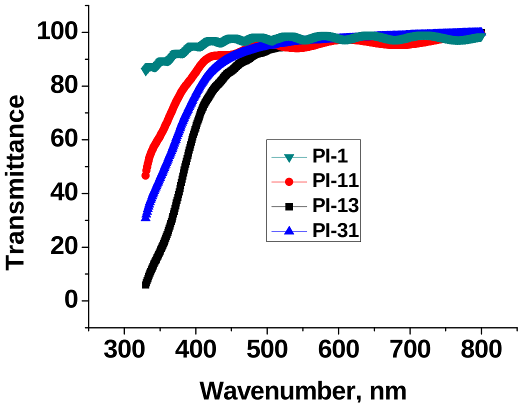


*Fig. 3. The UV-visible transmission spectra of polyimide films*

Fig. 4 shows the UV-Vis absorption spectra of the BOCA polyimide films, and their first significant feature is that all the spectra do not display any absorption bands above 400 nm. The use of both alicyclic dianhydride and slightly aliphatic MMDA segments in the same macromolecular structure prevents a tight molecular packing in the polyimide backbone and leads to weak intermolecular interactions. The absorption intensity of the homopolymer PI-1 is weaker as compared to the copolyimides, all intensities slightly diminishing with the increase of the alicyclic segments content. This is ascribed to a loose intermolecular charge transfer in the copolymers containing alicyclic units as compared to the ones with fewer or no BOCA segments.

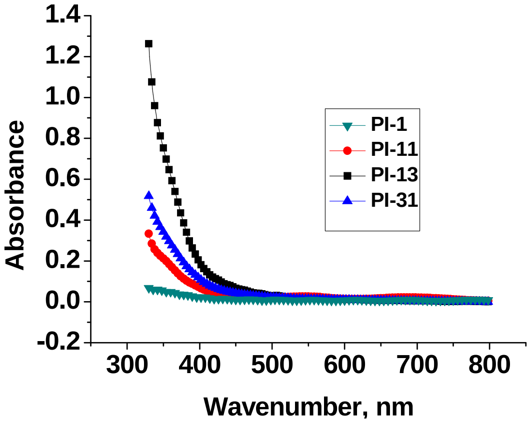


*Fig. 4. The UV-Vis absorption spectra of polyimide films*

The fluorescence spectra of copolyimide films excited at 300 nm are shown in Fig. 5. The emission peaks were found at 483 nm and the other one is shifted to 527 nm. The intensity of the emission increased with increasing the quantity of BOCA component and at **PI-31** is present a supplementary peak at around 460 nm and a shoulder at 420 nm. This behaviour can be explained by the intramolecular band excitation and the excitation of intermolecular ground state charge transfer complex, respectively [18-23]. It can be concluded that by increasing the quantity of alicyclic units together with a methyl substituted aromatic diamine to the macromolecular chain of copolyimide, the aggregation of the polyimide chain and the charge transfer formation are hindered to some degree. In this mode it is explain the obtained transparent copolyimide films in the visible region.

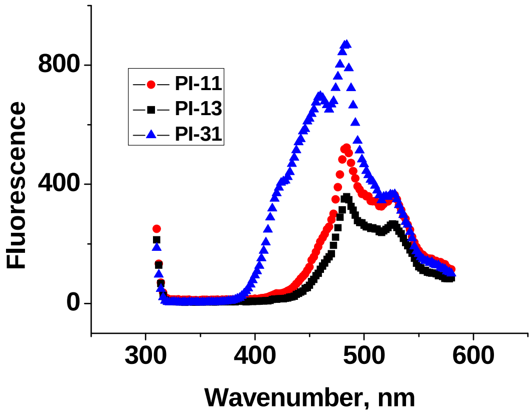


*Fig. 5. The fluorescence spectra of copolyimide films*

### 3.4. Mechanical properties

All copolyimides gave free-standing flexible films. These free-standing films were prepared by casting copolymer solution in DMAc and were subjected to tensile tests and the results are shown in Fig. 6. These polyimides substantiate satisfying mechanical properties, with tensile strength values between 37.7 and 46.6 MPa and elongation at break in the range of 1.85 – 3.7%. These values are similar to those of the earlier reported for plain polyimide from BTDA and MMDA [17] and with other polyimide-type macromolecular architectures employing the same dianhydride [24]. As can be seen in Fig. 6, by increasing the quantity of alicyclic dianhydride the elongation at break was increased maintaining at the same value the tensile strength.

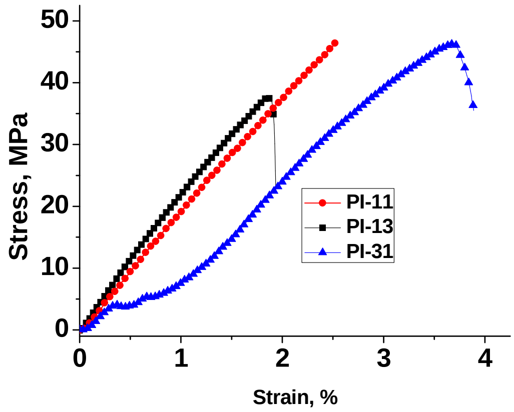


*Fig. 6. Stress-strain curves of the copolyimide films*

## 4. Conclusions

Aliphatic-aromatic polyimides based on 4,4′-diamino-3’3’-dimethyldiphenyl methane and a mixture between an aliphatic and an aromatic dianhydride taken in various molar ratio, have been obtained and characterized. The presence of aromatic units from BTDA into macromolecular chain of the synthesized copolyimides increase thermal stability and improve film forming ability. The obtained films from copolyimides showed high transparency and good mechanical properties.

All copolymer films display absorption bands only below 400 nm and emission peaks at 483 and 527 nm when excited at 300 nm. In spite of their high glass temperature (above 350°C), these compounds prove good solubility and a wide range of optical transparency, which generate many fruitful opportunities for applications as photopolymeric materials in optoelectronic devices.

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