



## SYNTHESIS AND CHARACTERIZATION OF NEW AROMATIC-ALIPHATIC POLY(ESTER-IMIDE)S CONTAINING PHOSPHORUS

Diana SERBEZEANU,\* Tăchiță VLAD-BUBULAC and Corneliu HAMCIUC

“Petru Poni” Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, Iasi-700487, Roumania

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Poly(ester-imide)s with phosphorus have been prepared by solution polycondensation of various aliphatic diamines with two dianhydrides, namely 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-benzene-bis(trimellitate)dianhydride and 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, respectively. The polymers were easily soluble in polar organic solvents, such as N-methyl-2-pyrrolidone, N,N-dimethylformamide and chloroform. They showed high thermal stability, the decomposition temperature being above 360 °C and the glass transition in the temperature range of 70-142 °C. Solutions of the phosphorus-containing poly(ester-imide)s in N,N-dimethylacetamide showed photoluminescence having maximum emission wavelengths in the blue region. Due to the presence of phosphorus in the macromolecular structure the polymers gave high char yields at 700 °C.

### INTRODUCTION

Aromatic polyimides are a class of polymers that have high temperature stability, excellent mechanical and electrical properties, and outstanding chemical resistance. Therefore, they are widely used in aerospace, transportation, electrical and microelectronic industries. However, because of their chain rigidity and strong interchain interaction, most polyimides are insoluble in common organic solvents and intractable in their imide forms.<sup>1-3</sup> An attractive synthetic approach to improve the solubility of the polymers is the incorporation of bulky substituents as pendent groups along the polymer backbone. The utilization of monomers containing bulky groups including phosphorus, such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO), resulted in polymers with good solubility. Also, the incorporation of DOPO groups into polymers improved thermal stability, flame retardant properties, adhesion and decreased

birefringence.<sup>4-15</sup> In this study we describe the synthesis of some new poly(ester-imide)s prepared by solution polycondensation reaction of equimolar amounts of various aliphatic diamines with two dianhydrides namely 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-benzene-bis(trimellitate)dianhydride and 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, respectively. Some properties of these polymers, such as solubility, thermal and optical behavior, have been evaluated with respect to their structure.

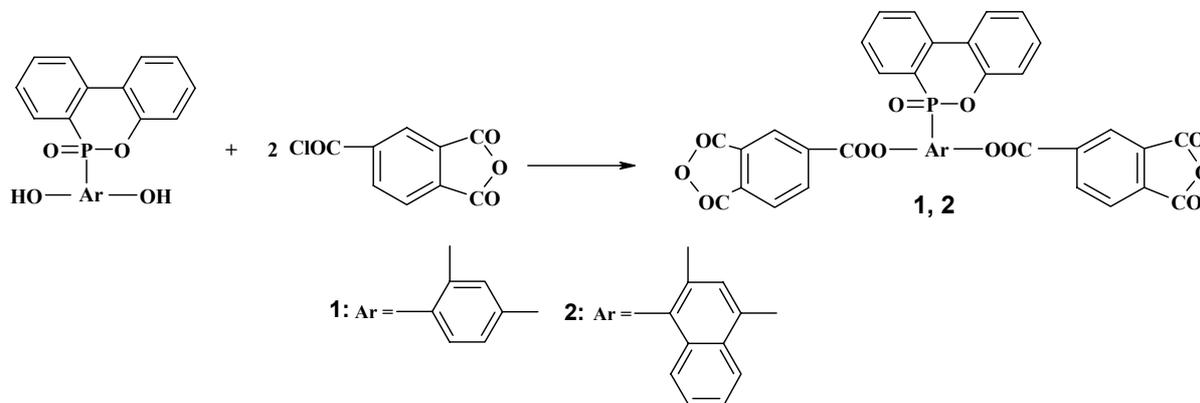
### RESULTS AND DISCUSSION

A new dianhydride monomer, 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-benzene-bis(trimellitate)dianhydride, **1**, was synthesized from trimellitic anhydride chloride and 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-benzenediol, **DOPO-BQ**, as shown in Scheme 1.

\* Corresponding author: [diana.serbezeanu@icmpp.ro](mailto:diana.serbezeanu@icmpp.ro)

1,4-[2-(6-Oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, **2**, was synthesized from trimellitic anhydride chloride and

2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalenediol, **DOPO-NQ**, as previously reported by us (Scheme 1).<sup>16</sup>



Scheme 1 – Preparation of dianhydrides **1** and **2**.

The polymers were prepared in two steps, in one pot. In the first step the poly(amic acid) **4'** or **5'** were synthesized by solution polycondensation reaction of dianhydrides **1** or **2** with aliphatic diamines **3**, at room temperature, in *N,N*-dimethylacetamide (DMAc) as solvent (Scheme 2). In the second step the resulting solutions of poly(amic-acid)s were heated, under a nitrogen stream, at 180–185 °C, for 4 h.

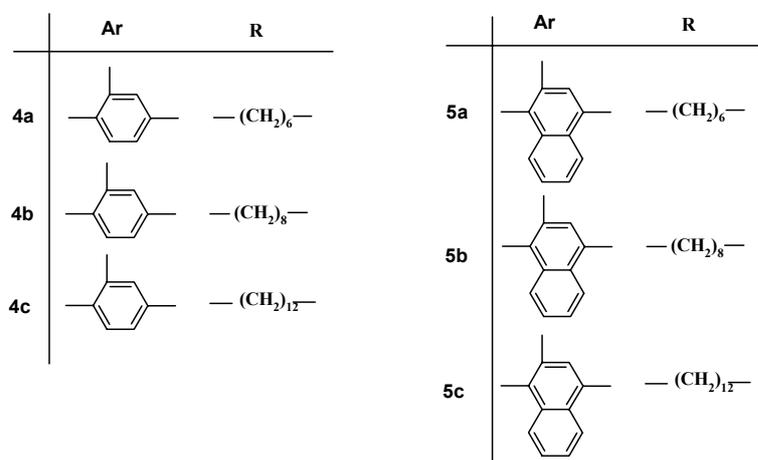
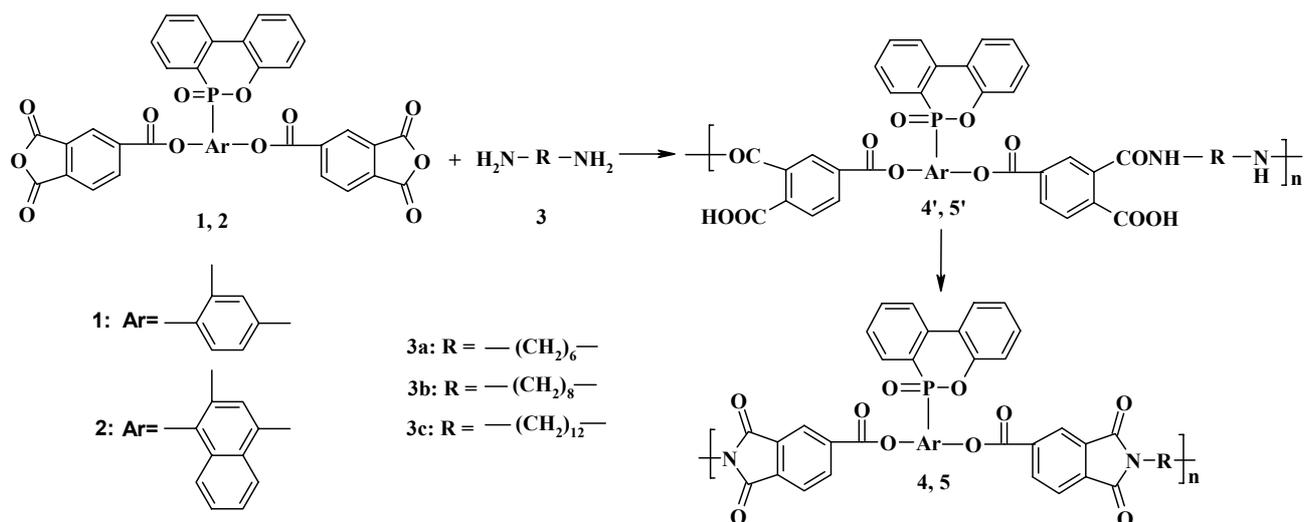
The structure of the polymers **4** and **5** was investigated by IR and <sup>1</sup>H NMR spectroscopy. The IR spectra of the polymer showed absorption peaks at 1774 cm<sup>-1</sup> (imide carbonyl asymmetric stretching), 1747 cm<sup>-1</sup> (ester carbonyl) and 1714 cm<sup>-1</sup> (imide carbonyl symmetric stretching). The absorption band at 1395 cm<sup>-1</sup> was due to C-N stretching of imide rings and the absorption at 723 cm<sup>-1</sup> was due to imide ring deformation. Characteristic bands at 3066 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> were due to aromatic C-H stretching and aromatic C=C stretching, respectively. Absorption peaks appeared at 920 cm<sup>-1</sup> and 1160 cm<sup>-1</sup> due to P-O-Ar groups, at 1205 cm<sup>-1</sup> due to P=O groups, and at 1477 cm<sup>-1</sup> due to Ar-P groups. The aromatic C-H deformation vibration band caused by the 1,2-disubstituted aromatic **DOPO** rings appeared at 758 cm<sup>-1</sup>. The IR spectra of polymers **4** and **5** exhibited absorption bands at 2934 cm<sup>-1</sup> and 2858 cm<sup>-1</sup> due to the presence of methylene groups. Figure 1 illustrates the IR spectrum of polymer **4a**, as an example.

The <sup>1</sup>H NMR spectrum of polymer **5b** is presented in figure 2 with the assignments for all the protons. The protons *H*<sub>6</sub>, *H*<sub>7</sub> and *H*<sub>8</sub>, closed to imide ring, appeared at the farthest downfield

region of the spectrum (8.85-8.2 ppm). The protons coming from the **DOPO-NQ** segments appeared in the range of 8.17-6.87 ppm. The spectrum showed a characteristic peak at 3.75 ppm corresponding to the protons *H*<sub>17</sub> of the methylene unit joined to the terminated imide rings. The characteristic peaks of the protons *H*<sub>18</sub> and *H*<sub>19</sub> appeared at 1.8 ppm and 1.47 ppm, respectively.

The solubility of the polymers **4** and **5** was tested in various solvents. All the polymers were soluble in polar solvents like *N*-methyl-2-pyrrolidone, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, dimethylsulfoxide, tetrahydrofuran (THF) and chloroform. The good solubility can be explained by the presence of bulky pendent **DOPO** groups which create a distance between the macromolecular chains preventing a strong packing of the chains and, consequently the diffusion of solvent molecules is facilitated.

The *T*<sub>g</sub> values of polymers, evaluated from differential scanning calorimetry (DSC) curves, were in the range of 70-142 °C (Figure 3a). As can be seen, the incorporation of aliphatic segments into the polymer backbone led to a decrease of *T*<sub>g</sub>, due to the increase in flexibility of polymer chain. It was observed that the *T*<sub>g</sub> decreased by increasing the number of the methylene groups coming from the aliphatic diamine. Thus, the polymers **4c** and **5c** derived from 1,12-diaminododecane exhibited the lowest *T*<sub>g</sub> (70 °C and 106 °C, respectively). In the case of the polymers **5** the values of the *T*<sub>g</sub> increased do to the presence of naphthalene-derived groups in the macromolecular structure.



Scheme 2 – Preparation of phosphorus containing poly(ester-imide)s 4 and 5.

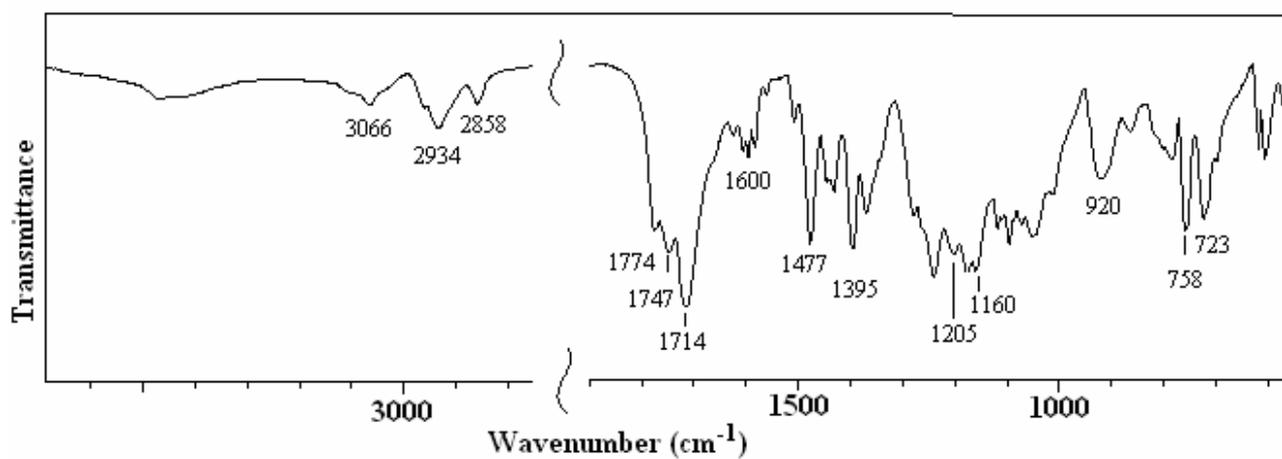


Fig. 1 – IR spectrum of polymer 4a.

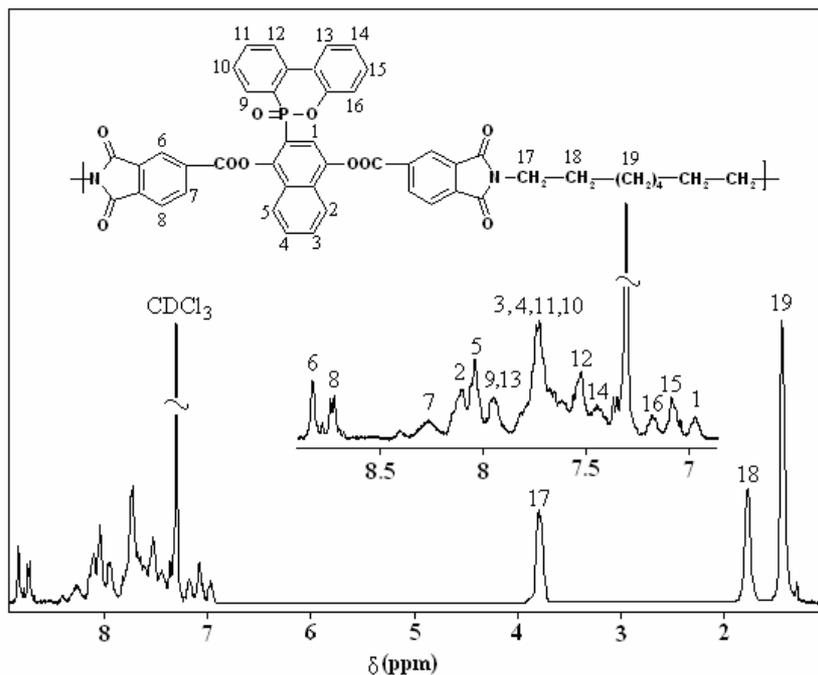


Fig. 2 –  $^1\text{H}$  NMR spectrum of polymer **5b**.

The thermo-oxidative stability was evaluated by thermogravimetric analysis (TGA) in air, at a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . Figure 3b shows the TG and DTG curves of polymers **4c** and **5b**. The polymers did not show significant weight loss below  $360\text{ }^\circ\text{C}$ . As can be seen in figure 3b phosphorus-containing poly(ester-imide)s decompose in a two-stage weight loss process. The first stage of decomposition was probably due to the destruction of aliphatic moieties, ester units and **DOPO** groups which were more sensitive to

degradation. The second stage of the decomposition was due to the degradation of polymer chain itself.<sup>15</sup> It is well known that phosphorus containing polymers are able to increase the char yield during burning thus decreasing the amount of flammable area and reducing the heat release from the flame to the materials. The char yield at  $700\text{ }^\circ\text{C}$  in the case of the polymer **4c** was 48 % and in the case of the polymer **5b** was 32.8 % being in agreement with the above statement.

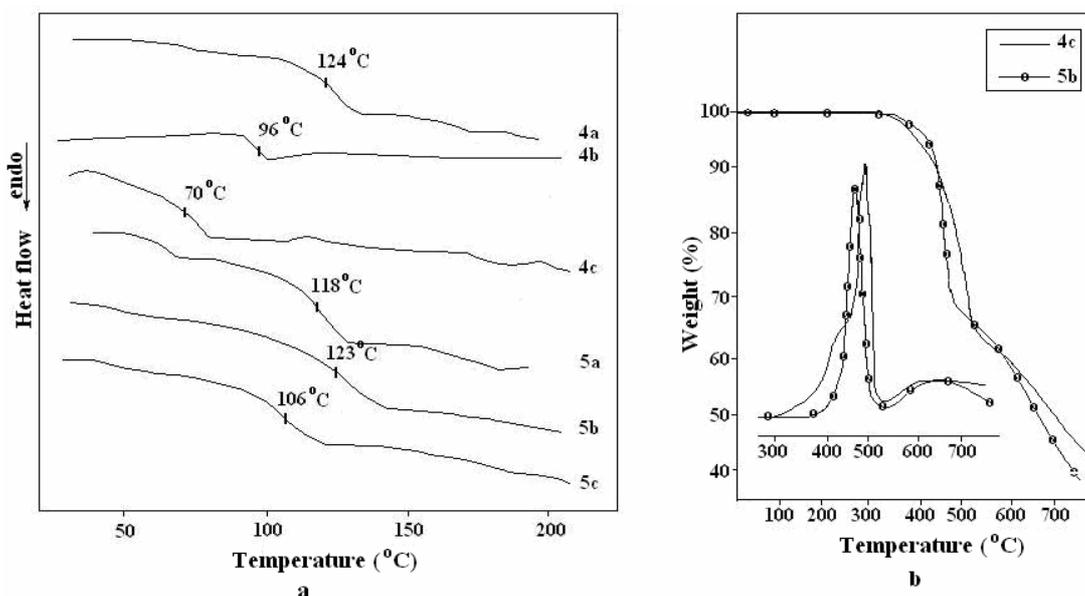


Fig. 3 – DSC curves of the polymers **4** and **5** (a) and TG curves of the polymers **4c** and **5b** (b).

The optical properties of the polymers were analyzed by UV-vis and Photoluminescence spectroscopy. Figure 4 illustrates the UV-vis spectra of polymers solution **4b** and **5b** in DMAc. It was found that polymer **5b** showed two UV absorption peaks ( $\lambda_{abs}$ ) at around 294 nm and 334 nm. The absorption of the polymer **4b** showed one maximum at 294 nm. The absorption properties were mainly determined by the segments coming from dianhydride units.

After being excited with UV light, the solution of polymer **4b** exhibited light emission with strong maxima of photoluminescence. To establish

conditions that produce the best photoluminescence spectrum, solutions of the polymer **4b** were excited with different wavelengths: 320 nm, 340 nm, 360 nm and 380 nm. In most cases, excited wavelength ( $\lambda_{ex}$ ) was equal to the maximum of absorption, which provides the best fluorescence spectrum<sup>17, 18</sup>. Figure 4b presents the emission spectra of the polymer **4b** under various excitation wavelengths. This polymer showed blue emission with maximum emission wavelength in the range of 457 – 463 nm when excited with  $\lambda_{ex}$  of 320-380 nm, being thus promising candidate for emissive materials in light-emitting devices.

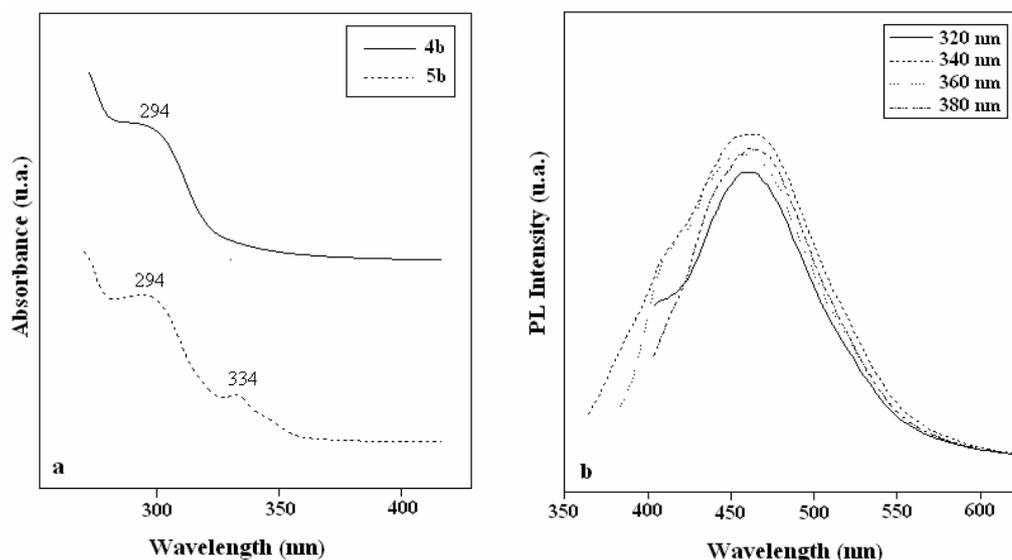


Fig. 4 – UV spectra of polymers **4b** and **5b** solutions in DMAc (a) and emission spectra of solutions of the polymer **4b**, under various excitation wavelengths (b).

## EXPERIMENTAL

### Materials

1,6-Diaminohexane, **3a**, 1,8-diaminooctane, **3b**, and 1,12-diaminododecane, **3c**, and other reagents were provided from commercial sources and were used as received. N,N-dimethylacetamide (DMAc), from Aldrich, was distilled over P<sub>2</sub>O<sub>5</sub>.

### Synthesis of the monomers

2-(6-Oxido-6H-dibenz<e><1,2>oxaphosphorin-6-yl)-1,4-benzenediol, **DOPO-BQ**, and 2-(6-oxido-6H-dibenz<e><1,2>oxaphosphorin-6-yl)-1,4-naphthalenediol, **DOPO-NQ**, were synthesized from **DOPO** and benzoquinone or naphthoquinone, respectively, as described in the literature.<sup>19,20</sup>

1,4-[2-(6-Oxido-6H-dibenz<e><1,2>oxaphosphorin-6-yl)]-benzene-bis(trimellitate)dianhydride, **1**, was synthesized as described below: to a solution of **DOPO-BQ** (40 mmol) in anhydrous THF (51.2 mL) and pyridine (15.4 mL) as an acid acceptor, was gradually added a solution of trimellitic anhydride chloride (80 mmol) in THF 96 mL, at 0 °C, with

continuous magnetic stirring for 2 h. Then the reaction was further continued at room temperature for 20 h, under stirring. The reaction mixture was filtered to collect the white precipitate consisting of crude product and pyridine hydrochloride salt as a by-product. The product was repeatedly washed with water to remove the salt. Since the product is partially hydrolyzed during this procedure, it was heated at 200 °C for 24 h in vacuum to ensure ring closure dehydration. The compound was purified by recrystallization from acetic anhydride. m.p.: 280-283 °C; IR (KBr, cm<sup>-1</sup>): 3070 (C-H aromatic), 1860 and 1782 (CO-O-CO), 1754 (ester C=O), 1600 (aromatic), 1479 (P-Ph), 1243 (ester C-O), 1222 (P=O), 1172 and 929 (P-O-Ph); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm):  $\delta$  = 8.89 (2H, s), 8.81 (2H, d), 8.10 (2H, m), 7.93 (1H, s), 7.86 (1H, d), 7.77 (1H, s), 7.62 (2H, d), 7.64 (3H, m), 7.34 (1H, m), 7.17 (2H, m).

1,4-[2-(6-Oxido-6H-dibenz<e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, **2**, was synthesized from trimellitic anhydride chloride and **DOPO-NQ**, as previously reported by us.<sup>16</sup> m.p.: 295-297 °C; IR (KBr, cm<sup>-1</sup>): 3067 (C-H aromatic), 1865 and 1791 (CO-O-CO), 1750 (ester C=O), 1600 (aromatic), 1478 (P-Ph), 1245 (ester C-O), 1220 (P=O), 1165 and 928 (P-O-Ph); <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, ppm):  $\delta$  = 9.05 (2H, s), 8.95 (2H, d), 8.28 (2H, m),

8.09 (1H, d), 8.01 (1H, s), 7.94 (2H, m), 7.73 (4H, m), 7.62 (2H, m), 7.49 (1H, m), 7.25 (1H, m), 7.07 (1H, d); UV-vis (DMF, nm):  $\lambda_{\text{abs}} = 296, 322$ ; PL (DMF, nm):  $\lambda_{\text{em}} = 401$  ( $\lambda_{\text{ex}} = 340$ ).

### Synthesis of the polymers

A typical polycondensation was run as shown in the following example: In a 100 mL three-necked flask equipped with mechanical stirrer and nitrogen-inlet and outlet were introduced dianhydride **1** (0.672 g, 1 mmol) and DMAc (11 ml). The mixture was stirred under nitrogen to complete dissolution. The diamine **3a** (0.116 g, 1 mmol) was added to the resulting solution and stirring was continued for 6 h. Then the flask was heated at 180–185 °C for 4 h, under a nitrogen stream, to perform the cyclization of the poly(amic acid) **4a'** to the corresponding polyimide **4a**. The water evolved during imidization was removed from the reaction mixture with a slow stream of nitrogen which was used as inert medium. The flask was cooled-down to room temperature and the resulting polymer solution was poured into methanol to precipitate the polymer. The solid product was filtered, washed three times with water under stirring, and dried at 120 °C for 6 h (Yield: 93%).

### Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. <sup>1</sup>H NMR spectra were recorded using a Bruker Avance DRX-400, at room temperature, by using solutions in deuterated dimethylsulfoxide (DMSO-d<sub>6</sub>) or deuterated chloroform (CDCl<sub>3</sub>). Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of 10 °C/min. The glass transition temperature ( $T_g$ ) of the precipitated polymers was determined with a Mettler-Toledo differential scanning calorimeter DSC 12E, at a heating rate of 15 °C/min, under nitrogen. Heat flow vs. temperature scans from the second heating run were plotted and used for reporting the glass transition temperature. The mid-point of the inflexion curve resulting from the typical second heating was assigned as the glass transition temperature of the respective polymers. UV spectra of polymer solutions were recorded on a Perkin Elmer Lambda 15 spectrometer. The photoluminescence spectra of polymer solutions were obtained with a Perkin Elmer LS 55 Spectrofluorimeter.

### CONCLUSIONS

New phosphorus-containing aromatic-aliphatic poly(ester-imide)s were prepared. They exhibited high thermal stability, with the decomposition temperature being above 360 °C, comparable with that of related poly(ester-imide)s without DOPO

pendent groups. The glass transition was in the range of 70–142 °C, allowing a large interval between the glass transition and decomposition temperature. Solutions of the polymers in N,N-dimethylacetamide showed photoluminescence in the blue region when excited with  $\lambda_{\text{ex}}$  of 320–380 nm.

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