New Phosphorus-Containing Polyesterimides. Synthesis and Characterization

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A series of phosphorus-containing polyesterimides has been synthesized by solution polycondensation reaction of an aromatic dianhydride, namely 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, with various aromatic diamines. The polymers were easily soluble in polar organic solvents, such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, tetrahydrofuran and chloroform. They showed high thermal stability, the decomposition temperature being above 400°C and the glass transition in the temperature range of 174-194°C. Due to the presence of phosphorus the polymers gave high char yield in thermogravimetric analysis. Solutions of the polymers in N,N-dimethylacetamide showed photoluminescence in the blue region.

Keywords: polyesterimides, phosphorus-containing polymers, good solubility, thermal properties, photoluminescence.

Aromatic polyimides are a class of polymers that have excellent mechanical and electrical properties, unique high temperature stability and outstanding chemical resistance. They are widely used in the transportation, aerospace, electrical and microelectronic industries. However, most of the aromatic polyimides are insoluble in common organic solvents and intractable in their imide form because of their strong interchain interaction and chain rigidity [1-3]. To overcome these limitations, many efforts have been made to improve the processability of polyimides while maintaining their excellent properties. Different structural modifications of the polymer backbone, such as the addition of bulky substituents or flexible groups to the main chains, and the introduction of geometrically asymmetric units, have been studied to reduce the chain interaction [4, 5]. Thus, the presence of ether, amide or ester groups in the main chain of aromatic polyimides enhanced solubility of these polymers [6-10].

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 voluminous 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 [11–22].

In this study we describe the synthesis of some new polyesterimides prepared by solution polycondensation reaction of equimolar amounts of a phosphorus-containing dianhydride, namely 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride with different aromatic diamines. Some properties of these polymers, such as solubility, thermal and optical behaviour, have been evaluated with respect to their structure.

Experimental part

Materials

4,4'-Oxydianiline, **2a**, 4-(4{[4-(4-aminophenoxy)phenyl]sulfonyl}phenoxy)aniline, **2b** 4,4-(4,4'-isopropylidenediphenyl-1,1'-diyldioxy)dianiline, **2c**, and 4,4'-(1,4-phenylenediisopropylidene)dianiline, **2d**, and other reagents were provided from commercial sources and uses as received. N-methyl-2-pyrrolidone (NMP), from Aldrich, was distilled over P_2O_5.

Synthesis of the monomers

2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalenediol, **DOPO-NQ**, was synthesized from **DOPO** and naphthoquinone [23]. It was recrystallized from ethoxyethanol; m.p. (DSC): 279-280°C. IR (KBr, cm^{-1}): 3430 (OH), 1480 (P-Ph), 1190 (P=O), 1165 and 925 (P-O-Ph). ^{1}H NMR (DMSO-d_6, ppm): δ = 7.9 (2H, m), 7.8 (1H, m), 7.7 (1H, m), 7.5 (4H, m), 7.4 (1H, m), 7.3 (1H, m). 7.2 (1H, t), 7.1 (1H, t), 6.6 (1H, d).

1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)-dianhydride, **1**, was synthesized from trimellitic anhydride chloride and **DOPO-NQ**, as shown in scheme 1 [24]. The reaction took place in tetrahydrofuran as solvent and pyridine as an acid acceptor. The compound was purified by recrystallization from acetic anhydride. m.p.: 295-297°C; IR (KBr, cm^{-1}): 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); ^{1}H NMR (DMSO-d_6, ppm): δ = 9.05 (2H, s), 8.95 (2H, d), 8.28 (2H, m), 8.19 (1H, t), 8.09 (1H, d), 8.01 (1H, s), 7.94 (2H, m), 7.84 (1H, t), 7.73 (4H, m), 7.62 (2H, m), 7.49 (1H, m), 7.25 (1H, m), 7.07 (1H, d); UV-vis (DMF, nm): λ_{abs} = 296, 322; PL (DMF, nm): λ_{em} = 401 (λ_{ex} = 340 nm).

Synthesis of the polymers

The polymers were prepared by solution polycondensation reaction of equimolar amounts of dianhydride **1** with the aromatic diamines **2** (Scheme 2). 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 diamine **2a** (0.200 g, 1 mmol) and NMP (11 ml). The mixture was stirred under nitrogen to complete dissolution. The dianhydride **1** (0.722 g, 1 mmol) was added to the resulting solution and stirring was

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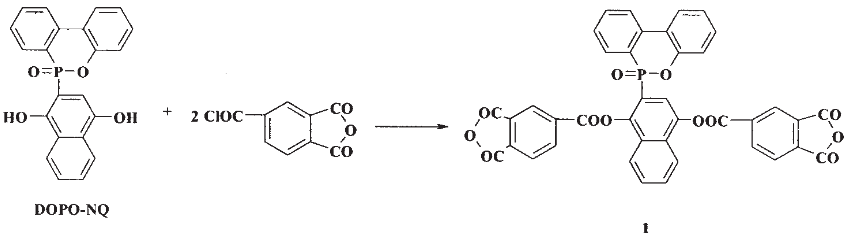
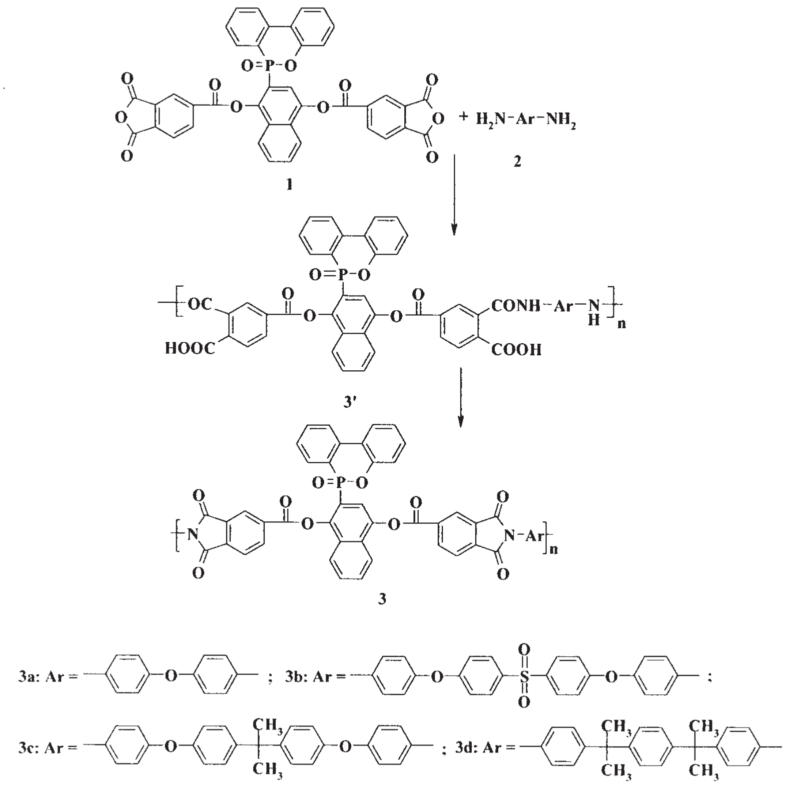


Scheme 1. Preparation of dianhydride **1**



Scheme 2. Preparation of phosphorus containing polyesterimides **3**

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) to the corresponding polyimide structure **3a**. 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.

^{1}H NMR spectra were recorded using a Bruker Avance DRX-400, at room temperature, by using solutions in deuterated dimethylsulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$).

The molecular weight distributions were measured by Size Exclusion Chromatography with a PL-EMD 950 evaporative mass detector equipped with 2 x PLgel 5μm MIXED-C,D, 300 x 7.5 mm columns. Polystyrene standards of known molecular weight were used for calibration. The samples were eluted with DMF and the flow rate was 1 mL/min.

Thermogravimetric analysis (TGA) was 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 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 (PL) spectra of polymer solutions were obtained with a Perkin Elmer LS 55 Spectrofluorimeter.

Results and discussion

Synthesis of the polymers and general characterization

Polyesterimides **3** were synthesized in two steps, in one pot. In the first step a poly(amic acid) was prepared by the reaction of aromatic diamines **2** with phosphorus-containing dianhydride **1**, at room temperature, in NMP as solvent (scheme 2). In the second step the resulting solution of poly(amic acid) was heated, under a nitrogen stream, at 180–185 °C, for 4 h. The imidization water was evacuated by a slow stream of nitrogen which was used as inert medium, at the same time.

The structure of the polymers **3** was investigated by IR and ^{1}H NMR spectroscopy. The IR spectra of the polymers showed absorption peaks at 1781 cm^{-1} (imide carbonyl symmetric stretching) and 1723 cm^{-1} (ester carbonyl and imide carbonyl asymmetric stretching). The absorption band at 1376 cm^{-1} was due to C-N stretching of imide rings and the absorption at 721 cm^{-1} was due to imide ring deformation. Characteristic bands at 3065 cm^{-1} and 1600 cm^{-1} were due to aromatic C-H stretching and aromatic C=C stretching, respectively. Absorption peaks appeared at 921 cm^{-1} and 1160 cm^{-1} due to P-O-Ar groups, at 1205 cm^{-1} due to P=O groups, and at 1499 cm^{-1} due to Ar-P groups. The IR spectra of polymers **3c** and **3d** exhibited absorption bands at 2966 cm^{-1} and 2870 cm^{-1} due to the presence of isopropylidene groups. Figure 1a illustrates the IR spectrum of polymer **3a**, as an example. The ^{1}H NMR spectrum of polymer **3d** is presented in figure 2 with the assignments for all the protons. The protons H_6, H_7 and H_8, close to imide ring, appeared at the farthest downfield region of the spectrum (8.85-7.86 ppm). The proton H_9 appeared at higher ppm values (7.69 ppm), when compared with the protons characteristic for **DOPO-NQ**, due to the electron withdrawing characteristic of imide rings. The protons coming from the bisphenol (**DOPO-NQ**) segment appeared in the range of 7.68-6.87 ppm. The protons of CH$_3$ groups can be observed as a singlet at 1.63 ppm.

The solubility of the polymers **3** was tested in various solvents, and the results are summarized in table 1. All the polymers were soluble in polar solvents like NMP, N,N-dimethylacetamide (DMAc) N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), tetrahydrofuran 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 polymers **3c** and **3d** showed higher solubility due to the presence in their structure of flexible isopropylidene groups.

The molecular weight of polymers **3** was determined by size exclusion chromatography. The values of weight-average molecular weight (*Mw*) and number average molecular weight (*Mn*) were in the range of 31800-57900

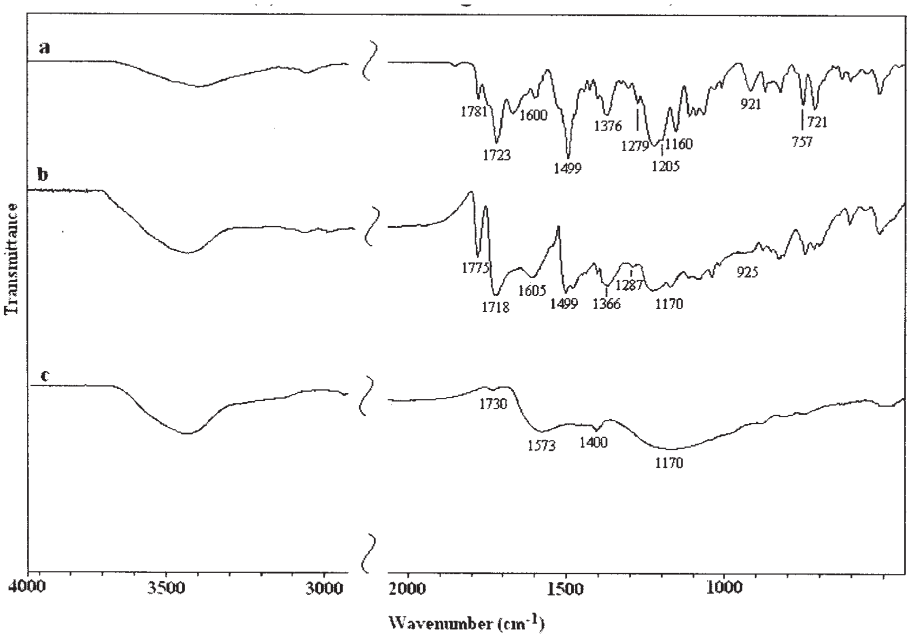


Fig. 1. IR spectra of polymers: **3a** (a), **3a** after heating up to 480°C (b), and **3a** after heating up to 700°C (c), with the heating rate of 10°C/min, in air

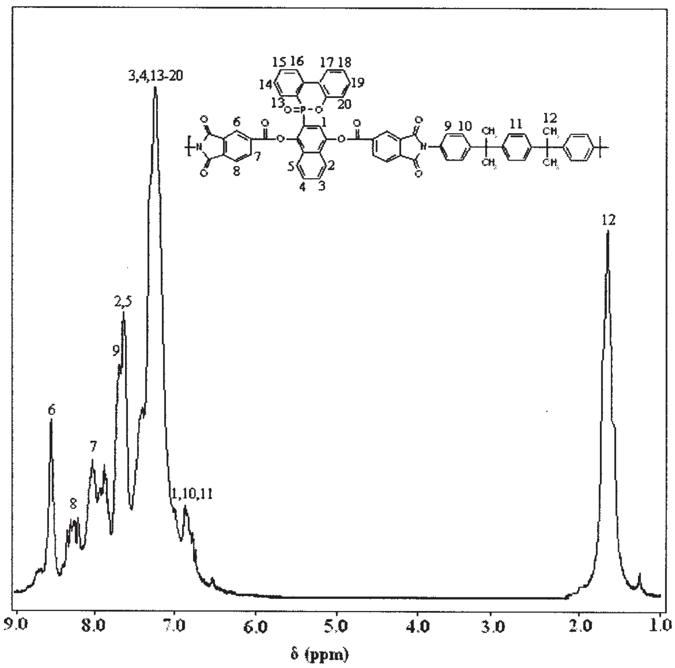


Fig. 2. ^{1}H NMR spectrum of polymer **3d**

Table 1
SOLUBILITY OF POLYMERS **3**

Polymer	DMF	DMAc	DMSO	NMP	THF	$CHCl_3$
3a	+	+	+	+*	+	±
3b	±	+	+	+*	±	±
3c	+	+	+	+*	+	+
3d	+	+	+	+*	+	+

NMP = N-methyl-2-pyrrolidone; DMF = N,N-dimethylformamide; DMAc = N, N-dimethylacetamide; DMSO = dimethyl sulfoxide, THF = tetrahydrofuran; + = soluble; +* = soluble after heating; ± = partial soluble.

Table 2
GPC DATA FOR POLYMERS **3**

Polymer	Mn (g/mol)	Mw (g/mol)	Mw/Mn
3a	9600	31800	3.31
3b	-	-	-
3c	11600	48800	4.20
3d	11900	57900	4.87

g/mol and 9600-11900 g/mol, respectively. The polydispersity *Mw*/*Mn* was in the domain of 3.31-4.87 (table 2).

Thermal stability

The T_g values of polymers, evaluated from differential scanning calorimetry (DSC) curves, were in the range of 174-194°C (table 3). The presence of **DOPO** pendent groups in the macromolecular structure of the polymers **3** increases the rigidity of the chains causing an increase in the T_g value. The polymers exhibited no crystallization or melting transition in DSC measurements (fig. 3).

The thermo-oxidative stability was evaluated by termogravimetric analysis (TGA) in air, at a heating rate of 10°C/min. Figure 4 shows the TG and DTG curves of polymer **3b**. The most important TGA data (the initial decomposition temperature, temperature of DTG peaks, the yield of char residue at 700°C) are also summarized in Table 3. The polymers did not show significant weight loss below 400°C. They began to decompose in the range of 400-425°C, and showed a 10% weight loss in the range of 420-445°C. Phosphorus-containing polyesterimides decompose in a two-stage weight loss process. The first maximum of decomposition (T_{max1}) was in range of 420-435°C and was due to the destruction of ester units and **DOPO** groups which were more sensitive to degradation. The second maximum of the decomposition (T_{max2}) was in the range of 585-605°C and was due to the degradation of polymer chain itself (table 3).

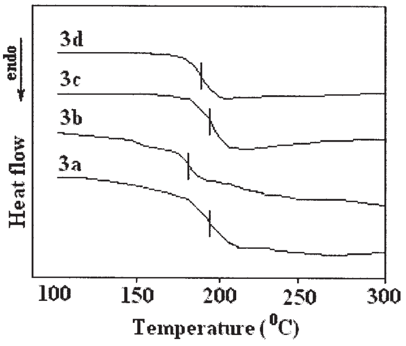


Fig.3. DSC curves of the polymers **3**

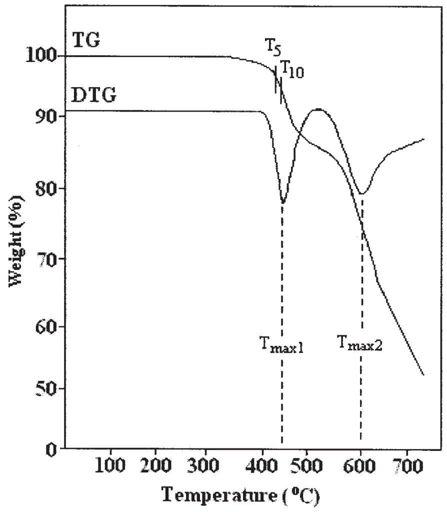


Fig.4. TG curves of the polymers **3b**

For a better understanding of fire retardancy, the thermal decomposition behavior of the polymers was studied through IR-TGA analysis. The IR spectra of polymer **3a** and its solid residues, after heating the samples up to 480°C and 700°C, are presented in figure 1b and 1c, respectively. The value of 480°C represents the temperature of the end of the first decomposition process from DTG curve. As it can be seen from figure 1b, after the thermal treatment, a

Table 3
THERMAL PROPERTIES OF POLYMERS **3**

Polymer	T_g [a] (°C)	IDT [b] (°C)	T_{10} [c] (°C)	T_{max1} [d] (°C)	T_{max2} [e] (°C)	Char Yield at 700°C (%)
3a	192	400	420	430	585	47.6
3b	174	420	440	430	600	56.8
3c	194	425	445	435	605	50.0
3d	187	410	420	420	590	50.8

[a] Glass transition temperature; [b] Initial decomposition temperature = the temperature of 5% weight loss; [c] Temperature of 10% weight loss; [d] First maximum polymer decomposition temperature; [e] Second maximum polymer decomposition temperature.

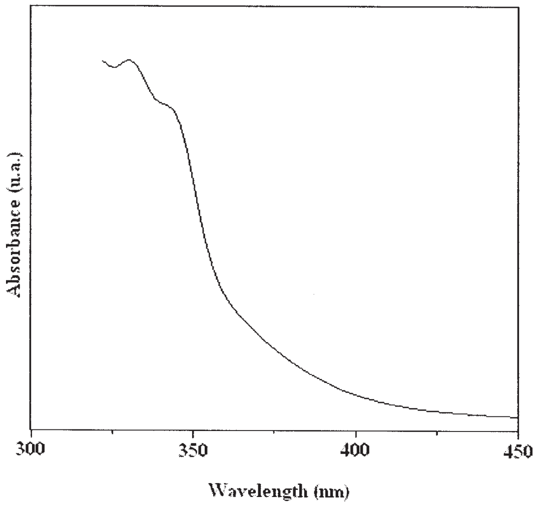


Fig. 5. UV spectrum of polymer solution **3c** in DMAc

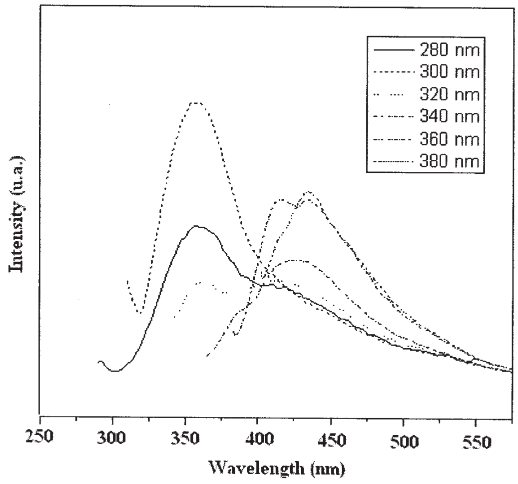


Fig. 6. Emission spectra of the polymer solution **3c** under various excitation wavelengths, in DMAc

high content of aromatic skeleton was detected. The absorption bands close to 1600 cm^{-1} and 1500 cm^{-1} due to aromatic rings were found in the IR spectrum. The characteristic absorption bands for carbonyl groups of imide ring at 1775 cm^{-1} and 1718 cm^{-1} were still present in the spectrum. A decrease of the absorption band at 1718 cm^{-1} suggesting the decomposition of ester groups was observed. The organophosphorus P-O-P group incorporated in the solid residue is distinguishable by the absorption band at 925 cm^{-1} [25]. The characteristic band of P-C and P=O were observed at 1476 cm^{-1} and 1170 cm^{-1}, respectively, indicating the presence of phosphorus in the solid residue. It can be concluded that in the first step of degradation, the destruction of ester groups with an increase of phosphorus content took place, as the characteristic bands of P-C and P=O are still present in the solid residue at 700°C. This agreed with the high char yield at high temperature. The char yields at 700°C were in the range of 47.6-56.8 % (Table 3). The high char yields limits the production of combustible gases, decrease the exothermicity of the pyrolysis reactions of the polymers and inhibits the thermal conductivity of the burning materials, thus increasing the flame retardancy of the polymers.

Optical properties of the polymers

The optical properties of the polymers were analyzed by UV-Vis and PL spectroscopy. Figure 5 illustrates the UV-Vis spectrum of polymer solution **3c** in DMAc. It was found that this polymer showed two UV absorption peaks (λ_{abs}) at around 330 nm and 340 nm, respectively.

After being excited with UV light, the polymer solution **3c** exhibited light emission with strong maxima of photoluminescence which are determined by the presence of **DOPO** groups. To establish conditions that produce the best photoluminescence spectrum, the polymer solution **3c** was excited with different wavelengths: 280 nm, 300 nm, 320 nm, 340 nm, 360 nm, and 380 nm. Figure 6 presents the emission spectra of the polymer solution **3c** under various excitation wavelengths (λ_{ex}). By increasing λ_{ex} an increase of the wavelength of the maximum photoluminescence peak (λ_{em}) appeared. This polymer showed blue emission (λ_{em} in the range 414-434 nm) when excited with λ_{ex} of 320-380 nm, being thus promising candidate for emissive materials in light-emitting devices.

Conclusions

New polyesterimides were synthesized by polycondensation of a dianhydride containing phosphorus and ester units with different aromatic diamines having ether, SO_2 or isopropylidene groups. The solubility of the polymers was significantly improved by the incorporation of bulky, noncoplanar, and polar **DOPO** groups. The polymers exhibited high thermal stability, having the initial decomposition temperature above 400°C. Their thermal decomposition was investigated on the basis of thermogravimetric and IR measurements. It has been found that properties like flame retardancy can be achieved by using phosphorus monomers in the synthesis of the polymers, the char yield at 700°C being in the range of 47.6-56.8%. Solutions of the polymers in N,N-dimethylacetamide showed photoluminescence in the blue region when excited with λ_{ex} of 320-380 nm.

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