



PHOSPHORUS-CONTAINING POLY(ESTER IMIDE) WITH PENDANT PHTHALONITRILE GROUPS

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A new phosphorus-containing poly(ester imide) was prepared by polycondensation reaction of a diamine containing a phthalonitrile unit, namely 4,4'-diamino-4''-(3,4-dicyanophenoxy)triphenylmethane, with an aromatic dianhydride having preformed ester groups, namely 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride. This polymer was easily soluble in polar aprotic solvents such as N-methyl-2-pyrrolidinone, N,N-dimethylacetamide, N,N-dimethylformamide or dimethyl sulfoxide. The poly(ester imide) showed high thermal oxidative stability, the decomposition temperature being above 360°C, and high transition temperature, around 252°C. The thermal decomposition behavior was studied using thermogravimetric analysis in air, at several heating rates between 4 and 19°C/min. The kinetic processing of the data was carried out using ASTM-E1641 method.

INTRODUCTION

Aromatic polyimides are well-known as high performance polymers due to their high thermal and thermooxidative stabilities, high transition temperatures, outstanding mechanical, insulating and chemical resistance properties. They have been widely used in many applications such as aerospace, microelectronics, optoelectronics and information industries.¹⁻³ However, wholly aromatic polyimides have usually deficiencies in solubility, processability, melting or softening behavior. Therefore, much amount of research has been directed towards the search for new soluble polyimides in fully imidized form. Several approaches to soluble polyimides including the incorporation of flexible linkages, bulky substituents or asymmetric non-coplanar units have been developed.^{4,5} The introduction of ester groups into the macromolecular chains of a polyimide improves the solubility. Thus, poly(ester imide)s

represent a class of polymers which combines the advantage of high temperature stability with ease of processability.

The utilization of monomers having phosphorus units such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (**DOPO**), which possesses a polar P=O group and a bulky structure, results in polymers with good solubility. Also, the incorporation of **DOPO** units into polymers improves thermal oxidative stability and generates good adhesion and low birefringence. In addition, phosphorus-containing polymers meet the requirements of low toxicity and amounts of smoke emitted during combustion for environmental and health consideration.⁶⁻¹⁴

Polymerization of phthalonitrile monomers or oligomers occurs through nitrile groups by an addition cure mechanism, resulting in high temperature resistant resins. During this reaction little or no volatiles are evolved leading to void-free crosslinked products such as triazine, phthalocyanine and isoindoline.¹⁵⁻¹⁷

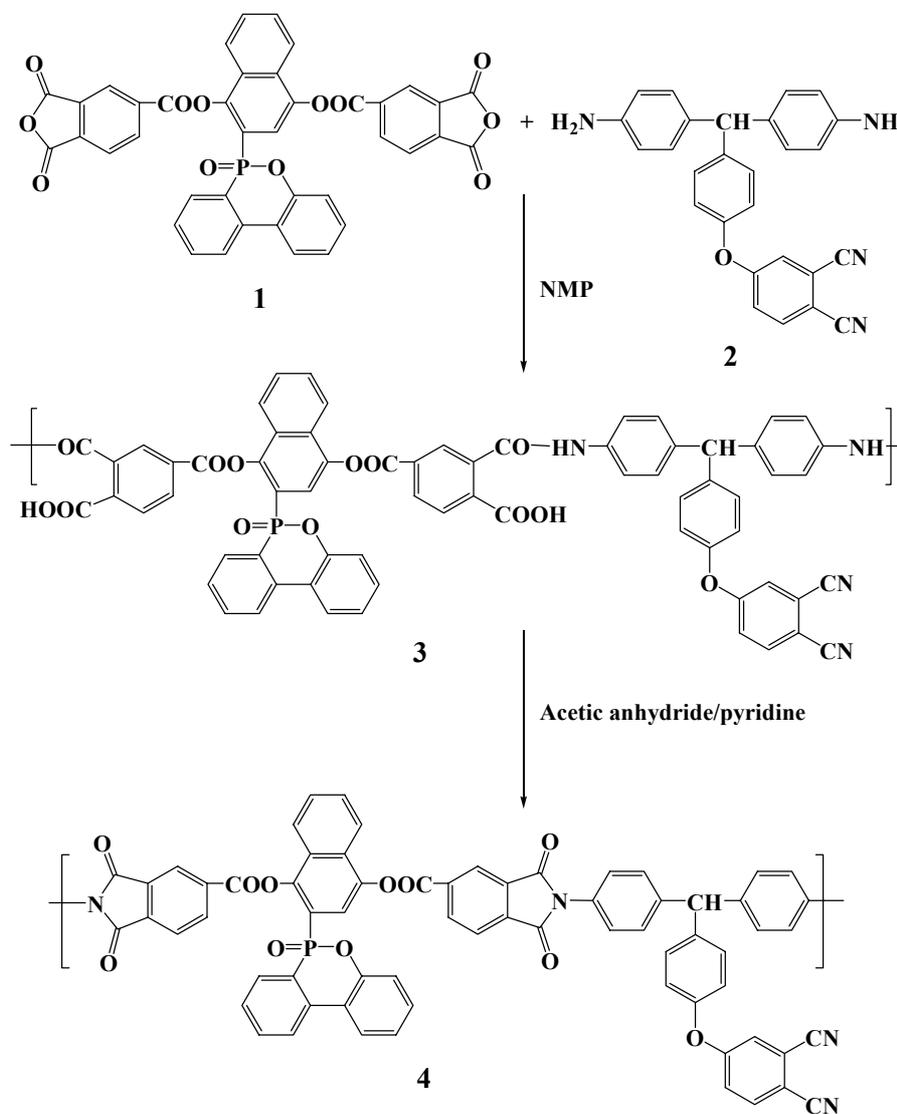
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The introduction of **DOPO** and phthalonitrile groups into poly(ester imide) macromolecular chains is expected to provide polymers with high performance characteristics, good solubility and high thermal stability. Therefore, this study is connected with the synthesis of a poly(ester imide) containing pendant **DOPO** and phthalonitrile groups. The polymer was obtained by solution polycondensation reaction of an aromatic diamine having a phthalonitrile group with a dianhydride containing two ester units and a **DOPO** group. The properties of the polymer, such as solubility, glass transition temperature and thermal stability were investigated. The thermal degradation was studied by dynamic thermogravimetric analysis, in air, at different heating rates. The kinetic data processing was performed by applying integral (ASTM-E1641)¹⁸ method, and the influence of the heating

rate and the dependence of the activation energy on conversion degree were examined.

RESULTS AND DISCUSSION

A new poly(ester imide) **4** was synthesized in two steps. In the first step the poly(amic acid) **3** was prepared by the reaction of the aromatic diamine **2** which has a phthalonitrile group with phosphorus-containing dianhydride **1**, at room temperature, in N-methyl-2-pyrrolidinone (NMP) as solvent (Scheme 1). In the second step the resulting poly(amic acid) **3** was cyclodehydrated to the corresponding imide structure **4** in the presence of a mixture acetic anhydride/pyridine.



Scheme 1 – Preparation of poly(ester imide) **4**.

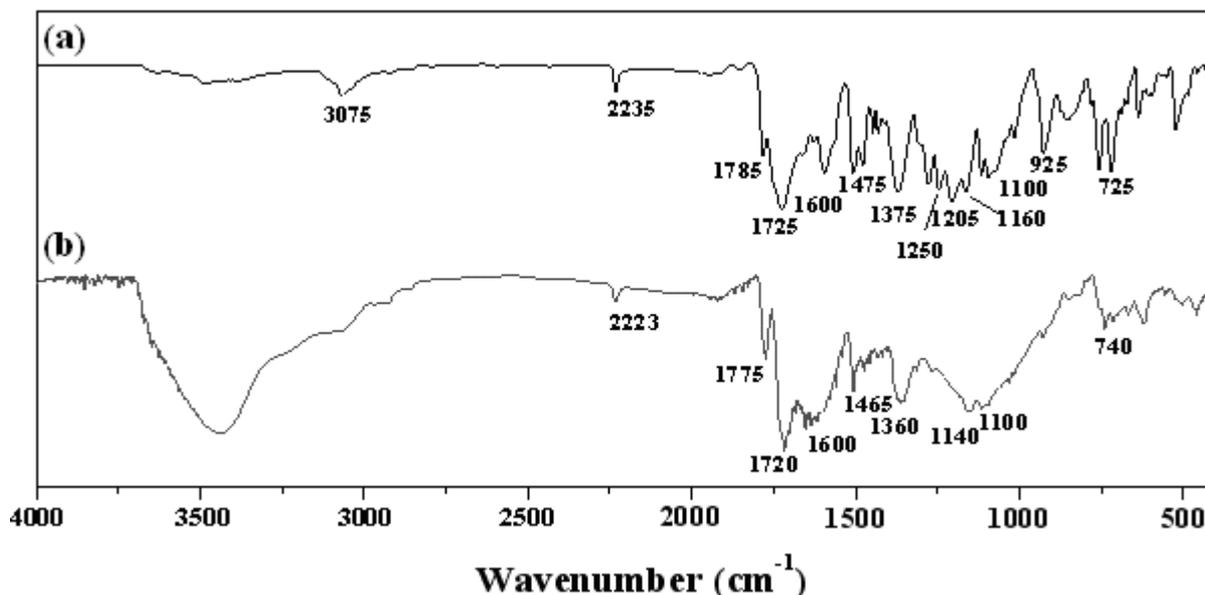


Fig. 1 – FTIR spectra of polymer 4 at room temperature (a) and polymer 4 heated up to 480°C, with the heating rate of 10°C/min (b).

The structure of the polymer 4 was investigated by FTIR and ^1H NMR spectroscopy. The FTIR spectrum (Fig. 1a) showed absorption peaks at 1785, 1725, 1375, 1100 and 725 cm^{-1} , characteristic to different stretching for imide carbonyl or imide ring. Absorption peaks appeared at 3070 cm^{-1} aromatic (C-H), 1600 and 1510 cm^{-1} (aromatic C=C), 1160 and 925 cm^{-1} (P-O-Ar groups), 1475 cm^{-1} (P-Ar groups) and 1205 cm^{-1} (P=O groups). The polymer 4 showed also a broad IR absorption band at 1725 cm^{-1} characteristic to the carbonyl bonds of the imide ring and ester unit. The bands appearing at 2235 and 1250 cm^{-1} were typically for nitrile groups and aromatic ether units, respectively, belonging to the polymer segments coming from the diamine 2. In the ^1H NMR spectrum of the polymer 4 the signal corresponding to the aliphatic protons appeared at 5.93 ppm. The peaks associated to aromatic protons were observed in the interval $\delta = 7.10\text{--}8.78$ ppm.

The molecular weight of poly(ester imide) 4 was determined by gel permeation chromatography (GPC). The values of weight-average molecular weight (M_w) and number-average molecular weight (M_n) were 21500 g mol^{-1} and 55900 g mol^{-1} , respectively. The polydispersity M_w/M_n was 2.6. Inherent viscosity of the polymer, measured in NMP, was 0.16 dL/g.

The polymer was soluble in aprotic polar solvents such as NMP, N,N-dimethylacetamide (DMAc) and N,N-dimethylformamide (DMF). The

good solubility of the polymer can be explained by the presence of pendant DOPO and phthalonitrile units which disorder the chains and hinder dense chain stacking, thereby reducing the interchain interactions lowering the density of cohesive energy and thus improving solubility.

The glass transition temperature (T_g) of polymer 4, evaluated from DSC curve, was situated around 252°C. This high T_g value is due to the increase in rigidity of polymer backbone determined by the presence of pendant DOPO and phthalonitrile groups. The DSC measurements showed no evidence of crystallization or melting which proves an amorphous morphology.

The thermal stability of the polymer 4 was studied by thermogravimetric analysis (TGA) in air, at several heating rates. The polymer did not show significant weight loss below 360°C and it began to decompose in the range of 367–408°C. Fig. 2a shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves recorded using the Mettler Toledo derivatograph at the six heating rates (4, 7, 10, 13, 16 and 19°C/min). As it can be seen from DTG curve, the degradation process of polymer 4 in air exhibited two stage of decomposition. The first one was due to the destruction of ester units and DOPO groups which were more sensitive to degradation. The second stage of decomposition was due to the degradation of polymer chain itself.¹⁹ The FTIR spectrum of the solid residue of the polymer 4,

after heating the sample up to 480°C with the heating rate of 10°C/min, was examined (Fig. 1b). 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 Fig. 1b, after the thermal treatment, a high content of aromatic skeleton was detected. The absorption bands at 1600 cm⁻¹ and 1500 cm⁻¹ due to aromatic rings were found in the FTIR spectrum. The characteristic absorption bands for carbonyl groups of imide ring at 1775 cm⁻¹ and 1720 cm⁻¹ were still present in the spectrum. It was observed a decrease of the absorption band at 1720 cm⁻¹ suggesting the decomposition of ester groups. The FTIR spectrum showed characteristic bands of P–C at 1465 cm⁻¹ indicating the presence of phosphorus in the solid residue. It can be concluded that in the first step of

degradation, the destruction of ester and **DOPO** groups with an increase of phosphorus content took place.

Table 1 shows the values of characteristic temperatures (T_{onset} – the initial temperature thermal degradation, T_{peak} – the temperature corresponding to the maximum degradation rate, T_{endset} – the final temperature) and weight ($W\%$) for each stage of thermal degradation. Regardless of the rate of heating, the thermal decomposition in the air of the analyzed sample is not complete, as there is about 9% residue.

Research has been extended to the kinetic processing of the thermogravimetric data. Non-isothermal integral (ASTM-E1641) method was utilized to obtain variation of activation energy with conversion degree from TG and DTG curves.

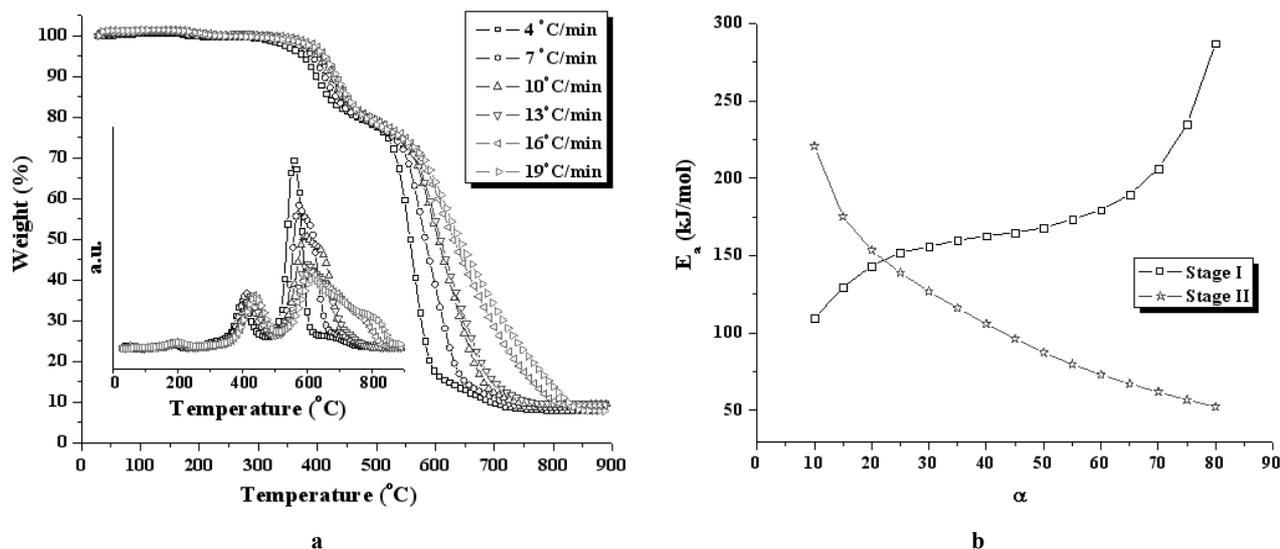


Fig. 2 – TG and DTG curves of polymer 4, at different heating rates (a), activation energy variation with the conversion degree for polymer 4 (b).

Table 1

Thermogravimetric properties at various rates of heating for polymer 4

a^1 (°C/min)	Stage I				Stage II				Char yield at 900°C (%)
	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	T_{onset} (°C)	T_{peak} (°C)	T_{endset} (°C)	W (%)	
4	367	399	424	20.35	533	555	595	71.40	8.25
7	378	413	441	21.14	548	572	645	70.01	8.85
10	388	422	462	20.88	560	592	699	69.73	9.39
13	397	430	464	22.14	559	597	726	68.23	9.63
16	402	434	471	21.78	570	598	807	69.11	9.11
19	408	438	475	22.60	579	615	837	68.06	9.34

¹ heating rate

The ASTM–E1641¹⁸ standardized method was used to obtain the activation energy (E_a) at various

conversion degrees, according to the equation (1):

$$\log a = \log \frac{A \cdot E_a}{R} - \log F(\alpha) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (1)$$

where $F(\alpha)$ is the conversion function. E_a results from the slope of the line in the graphic representation $\log a = f(1/T)$ when $\alpha = \text{constant}$. The results recorded for polymer **4** are shown in Fig. 2b. Their analysis supports the assumption according to which the thermal degradation process undergone by this polymer is complex, as the activation energy varies with the conversion degree. In the first degradation stage, the activation energy increases with the conversion degree up to 290 kJ/mol, whereas the second stage witnesses an almost linear decrease of the activation energy values, when α is within the 20 to 70% range. The activation energy values of the first thermal degradation stage are similar to those achieved by other researchers, who employed the same kinetic evaluation method for various phosphorus-containing polymers.^{19,20} In the first stage of thermal oxidative degradation, the decomposition of the **DOPO** groups induced the formation of a heat-resistant char, which, therefore, exhibited high activation energies of thermal degradation.

EXPERIMENTAL

Materials. 4-Nitrophthalonitrile, 4-hydroxybenzaldehyde, aniline, trimellitic anhydride chloride, naphthoquinone were provided from Aldrich and used as received. **DOPO** was purchased from Chemos GmbH, Germany. All other reagents were used as received from commercial sources or were purified by standard methods. 4,4'-Diamino-4''-hydroxy-triphenylmethane (**DHTM**) was obtained by the reaction of 4-hydroxybenzaldehyde and aniline, as was previously reported.²¹ Diamine **2** was prepared by nucleophilic displacement reaction of 4-nitrophthalonitrile with **DHTM**, in the presence of anhydrous potassium carbonate.²² M.p.: 78.4°C (DSC, 10°C/min). 1,4-[2-(6-Oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)dianhydride, **1**, was synthesized to our recently reported procedure.¹⁰ The crude product was finally recrystallized from anhydrous acetic anhydride. M.p.: 295–297°C.

Preparation of polymer 4. The synthetic route of the polymer **4** is depicted in Scheme 1. The poly(amic acid) solution **3** was prepared by polycondensation of dianhydride **1** with diamine **2**. A typical polycondensation reaction 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 **2** (0.416 g, 1 mmol) and NMP (6.5 mL). The mixture was stirred under nitrogen to complete dissolution. Further, **1** (0.722 g, 1 mmol) was added to the resulting solution and stirring was continued at room

temperature for 12 h. Then, a mixture of acetic anhydride/pyridine (0.48 mL/0.24 mL) was added and the solution was stirred overnight at room temperature, and 1.5 h at 80°C. The solution was poured into water and the precipitate that formed was washed several times with water and ethanol. The final poly(ester imide) was dried in a vacuum oven at 120 °C for 12 h.

Measurements. Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). FTIR spectra were recorded on a Bruker Vertex 70 at frequencies ranging from 400 to 4000 cm^{-1} by using KBr pellets. ¹H NMR (400 MHz) spectrum was performed at room temperature on a Bruker Avance DRX 400 spectrometer, using DMSO-*d*₆ as solvent. The molecular weights and their distributions were determined by Gel Permeation Chromatography with a PL-EMD 950 evaporative light scattering detector instrument. Two poly(styrene-co-divinylbenzene) gel columns (PLgel 5 μm Mixed-D and PLgel 5 μm Mixed-C) were used as stationary phase, while DMF was the mobile phase. The eluent flow rate was 1.0 mL min^{-1} . Polystyrene standards of known molecular weight were used for calibration. The inherent viscosity of the polymer, η_{inh} , was determined at 20 °C, for solution of polymer (0.5 g/dL) in NMP, using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) analysis was performed using a Mettler Toledo DSC 1 (Mettler Toledo, Switzerland) operating with version 9.1 of Stare software. The samples were encapsulated in aluminium pans having pierced lids to allow escape of volatiles. Thermogravimetric analysis (TGA) was carried out under constant air flow (20 mL/min) at six different heating rates: 4°C/min, 7°C/min, 10°C/min, 13°C/min, 16°C/min and 19°C/min, using a Mettler Toledo TGA/SDTA 851° balance. The heating scans were performed on 2 to 5 mg of sample in the temperature range 25–900°C. Alumina crucible (70 μl) is used as sample holder. The experiments were repeated for three times at heating rate of 10°C/min for each sample to test the repeatability of the experiments, which showed the almost similar behaviors. In order to obtain the thermal and kinetic properties, the data were processed using the STAR software and the “Kinetics nth order” module from Mettler Toledo.

CONCLUSIONS

The incorporation of **DOPO** and phthalonitrile pendant groups into the structure of a poly(ester imide) produced a polymer with good solubility in organic solvents while retaining high thermal stability. The non-isothermal kinetic survey led to the conclusion that the polymer exhibits good thermal stability, as the thermal degradation onset temperature is higher than 360°C, regardless of the rate of heating. The rate of heating does not influence the thermal behavior of

the analyzed polymer, the degradation mechanism is not altered by the increase of the rate of degradation, as the appearance of the TG and DTG curves is similar. Also, the activation energy values calculated by the standardized ASTM-E1641 method are higher in the first than in the second stage.

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