

New Phosphorus-containing Copoly(ester-amide-imide)

Synthesis and characterization

DIANA SERBEZEANU^{1*}, TACHITA VLAD-BUBULAC, CORNELIU HAMCIUC

¹"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda 41A, 700487, Iasi, Romania

A phosphorus-containing copoly(ester-amide-imide) 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 4,4'-oxydianiline and isophthaloyl chloride. The polymer was easily soluble in polar organic solvents, such as N-methyl-2-pyrrolidone, N,N-dimethylformamide, tetrahydrofuran and chloroform. The polymer shows high thermal stability, the decomposition temperature being above 410 °C. The value of the glass transition temperature was 231°C. Due to the presence of phosphorus, the polymer gave high char yield in thermogravimetric analysis.

Keywords: copoly(ester-amide-imide), phosphorus-containing polymer, thermal stability

Polyimides are a class of engineering plastics which possess many outstanding characteristics including high thermal and chemical resistance, good tensile strength and modulus, low dielectric constant and ease of processing into films or coatings. As a result, polyimides have been extensively used in particular in microelectronics, both in packaging and integrated circuit fabrication. However, the commercial use of these polymers is often limited because of their poor solubility and high softening or melting temperatures. To overcome these problems, much research effort has been focused on the synthesis of soluble polyimides in fully imidized form without deterioration of their own excellent properties. The introduction of ester, amide, ether or other flexible groups in the main chain of aromatic polyimides leads to enhanced solubility of these polymers, with a minimum sacrifice of their thermal stability [1–10].

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 phosphorous, such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (**DOPO**), resulted in polymers with good solubility. Also, the incorporation of **DOPO** units into polymers, improved thermal stability, flame retardant properties, adhesion and decreased birefringence [11–22].

In the present study we describe the synthesis of a copoly(ester-amide-imide) prepared by solution polycondensation reaction 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 4,4'-oxydianiline and isophthaloyl chloride. Some properties of this polymer, such as solubility, thermal stability, glass transition temperature and photoluminescence have been investigated. Due to the presence of phosphorus, the polymer gave high char yield in thermogravimetric analysis, hence good flame retardant properties.

Experimental part

Materials

4,4'-Oxydianiline, **2**, and other reagents were provided by commercial sources and used as received. N-methyl-2-pyrrolidone (NMP), from Aldrich, was distilled over P₂O₅.

* email: diana.serbezeanu@icmpp.ro

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). ¹H NMR (DMSO-d₆, 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**. The reaction took place in tetrahydrofuran as solvent and pyridine as an acid acceptor. The compound was purified by recrystallization from acetic anhydride [24]. 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); ¹H NMR (DMSO-d₆, 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 polymer

1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis(trimellitate)-dianhydride (2.888 g; 4 mmol) was added at 5–10 °C, under nitrogen atmosphere, to a solution of 4,4'-oxydianiline (1.6 g; 8 mmol) dissolved in NMP (33 mL), and the reaction mixture was stirred for 1 h at 20 °C. The obtained oligo-amic solution was cooled down to 5–10 °C and isophthaloyl chloride (0.812 g; 4 mmol) was added. The solution was stirred for 1 h at 20 °C, triethylamine (4 mmol) was added to the resulting solution and stirring was continued for 6 h. The solution was poured into methanol and the precipitated polymer was dried at 120 °C for 4 h. The solid product was heated slowly up to 250 °C for imidization. The resulting polymer **4** was dissolved in NMP, precipitated in methanol, filtered and dried in a vacuum oven at 120 °C for 8 h.

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.

^1H NMR (400 MHz) spectra were performed at room temperature on a Bruker Avance DRX 400 spectrometer, using DMSO-d_6 as solvent.

The molecular weight distribution was measured by Size Exclusion Chromatography with a PL-EMD 950 evaporative mass detector equipped with 2 x PLgel $5\mu\text{m}$ MIXED-C,D, 300 x 7.5 mm columns. Polystyrene standards of known molecular weight were used for calibration. The sample was eluted with *N,N*-dimethylformamide (DMF) and the flow rate was 1 mL/min.

The glass transition temperature (T_g) of the precipitated polymer was determined with a Mettler-Toledo differential scanning calorimeter DSC 12E, at a heating rate of $15\text{ }^\circ\text{C}/\text{min}$, under nitrogen. Heat flow vs. temperature scan from the second heating run was 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 polymer.

Thermogravimetric analysis (TGA) was performed on a MOM derivatograph (Hungary) in air, at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$. 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.

Scanning electron microscopy (SEM) was performed on a TESLA BS 301 instrument, at 25 kV, with a magnification of 380-3600. The images were recorded on film surfaces deposited on Al supports and coated by sputtering with Au thin films using an EK 3135 EMITECH device.

UV-vis spectrum of polymer solution in NMP was recorded on a Perkin Elmer Lambda 15 spectrometer. The photoluminescence (PL) spectrum of polymer solution in

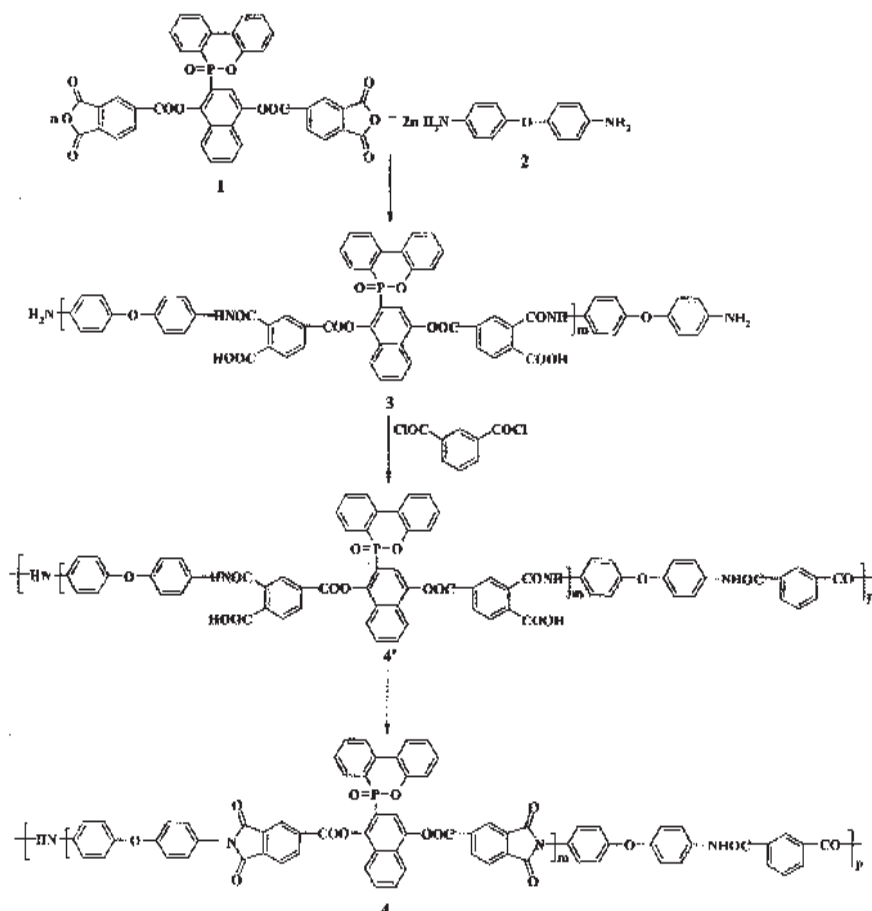
NMP was recorded on a Perkin Elmer LS 55 Spectrofluorimeter.

Results and discussions

The synthesis of the aromatic copoly(ester-amide-imide) **4** took place in three steps. In the first step an oligo-amic acid **3** was synthesized by the reaction of an aromatic diamine **2** with phosphorus-containing dianhydride **1**, in NMP as solvent (scheme 1). In the second step the solution of oligo-amic acid **3** was reacted with isophthaloyl chloride to obtain a poly(amic-acid) **4'**. In the last step copoly(ester-amide-imide) **4** was prepared by thermal imidization of poly(amic-acid) **4'**.

The structure of the polymer **4** was investigated by FTIR and ^1H NMR spectroscopy. The FTIR spectrum of the polymer showed absorption peaks at 1781 cm^{-1} (imide carbonyl asymmetric stretching) and 1723 cm^{-1} (ester carbonyl and imide carbonyl symmetric stretching). The FTIR spectrum showed also a characteristic absorption band at 1672 cm^{-1} due to the amide carbonyl group. 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. Aromatic C=C bands were found at 1600 cm^{-1} and 1499 cm^{-1} , while aromatic C-H absorption was found at 3065 cm^{-1} . Absorption peaks appeared at 921 cm^{-1} and 1160 cm^{-1} due to P-O-Ar group, at 1205 cm^{-1} due to P=O group, and at 1478 cm^{-1} due to Ar-P group. The aromatic C-H deformation vibration band caused by the 1,2-disubstituted aromatic DOPO rings appeared at 757 cm^{-1} . Figure 1a illustrates the FTIR spectrum of polymer **4**.

^1H NMR spectrum of the polymer showed characteristic peak of the protons of -NHOC- groups at 10.52 ppm. The peaks associated to aromatic protons appeared in the interval $\delta = 8.78\text{-}7.18$ ppm.



Scheme 1. Preparation of phosphorus containing copoly(ester-amide-imide) **4**.

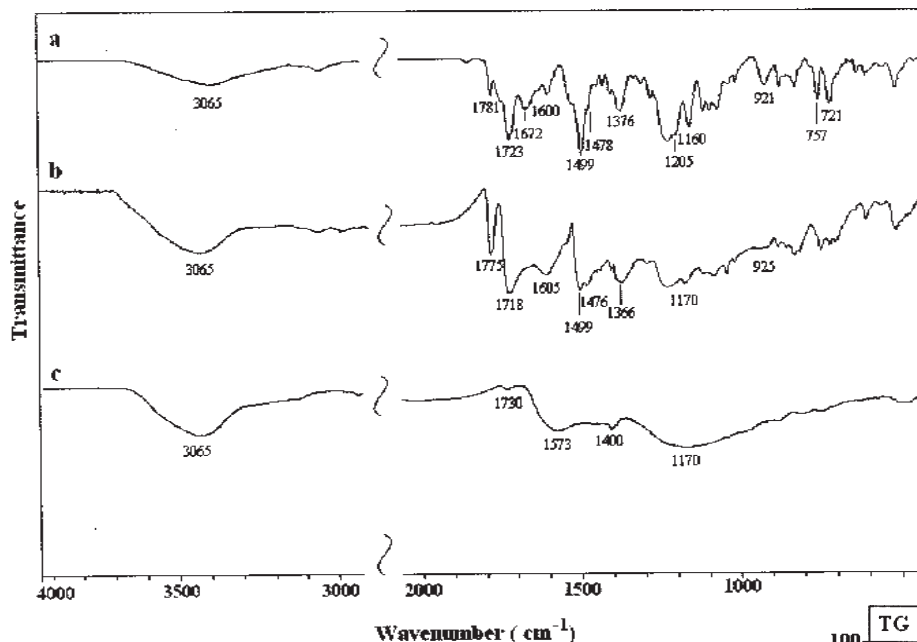


Fig. 1. FTIR spectra of polymer 4 as synthesized (a); polymer 4 after heating up to 480 °C (b); polymer 4 after heating up to 700°C (c), with 10 °C/min, in air

The solubility of the polymer 4 was tested in various solvents, by using 15 mg polymer/mL solvent, at room temperature. The polymer was easily soluble in polar solvents like NMP, DMF, N,N-dimethylacetamide, dimethylsulfoxide (DMSO), tetrahydrofuran and chloroform. The good solubility can be explained by the presence of bulky pendent **DOPO** groups which creates a distance between the macromolecular chains preventing a strong packing of the chains and, consequently, the diffusion of solvent molecules is facilitated.

The molecular weight of polymer 4 was determined by size exclusion chromatography. The values of weight-average molecular weight (M_w) and number average molecular weight (M_n) were 24500 g/mol and 15100 g/mol, respectively. The polydispersity index M_w/M_n was 1.6.

Thermal stability

The T_g value of polymer, evaluated from differential scanning calorimetry (DSC) curve, was 231 °C. The presence of **DOPO** pendent group in the macromolecular structure of the polymer 4 increased the rigidity of the chains causing an increase in the T_g value. The polymer exhibited no crystallization or melting transition in DSC measurements (fig. 2).

The thermo-oxidative stability was evaluated by thermogravimetric analysis (TGA) in air, at a heating rate of 10°C/min. Figure 3 shows the TG and DTG curves of polymer 4. The polymer did not show significant weight loss below 415°C and showed a 10% weight loss at 435 °C. The DTG curve shows two steps of decomposition. The first step, in the range of 420-480°C, was due to the destruction of amide, ester units and **DOPO** groups which were more sensitive to degradation. The second step,

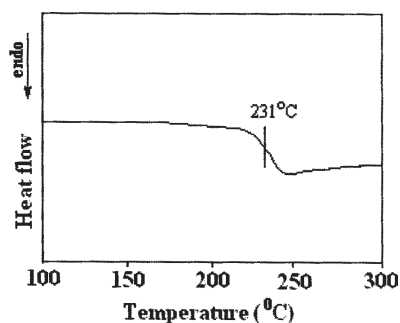


Fig. 2. DSC curve of polymer 4

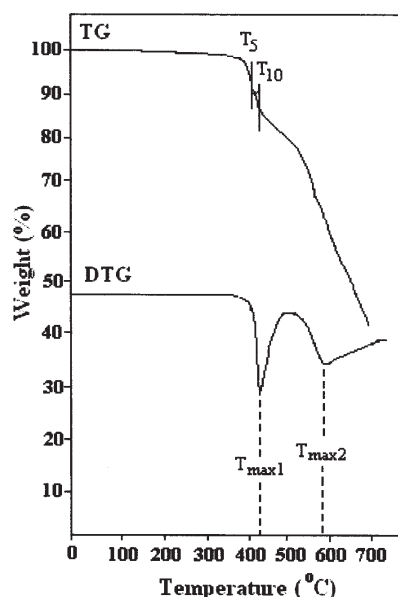


Fig. 3. TG and DTG curves of polymer 4

above 525 °C, was due to the degradation of polymer chain itself. The temperature corresponding to the maximum rate of the first step of degradation (T_{max1}) was 420 °C and temperature corresponding to the maximum rate of the second step of degradation (T_{max2}) was 580°C.

For a better understanding of fire retardancy, the thermal decomposition behavior of the polymer was studied through FTIR-TGA analysis. The FTIR spectra of polymer 4 and its solid residues, after heating the samples up to 480°C and 700°C, are presented in figures 1a, 1b and 1c. The value of 480°C represents the temperature of the end of the first decomposition process from DTG curve. As can be seen from figure 1b, after the thermal treatment, a high content of aromatic skeleton was detected. The absorption bands close to 1605 cm^{-1} and 1499 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. The decrease of the absorption band at 1718 cm^{-1} was observed, probably due to the decomposition of the ester groups. During the heating process, the disappearance of the absorption band at 1672 cm^{-1} was observed, suggesting the decomposition of amide groups. The organophosphorus P-O-P group incorporated in the solid residue is distinguishable by the absorption band at 925 cm^{-1} . The

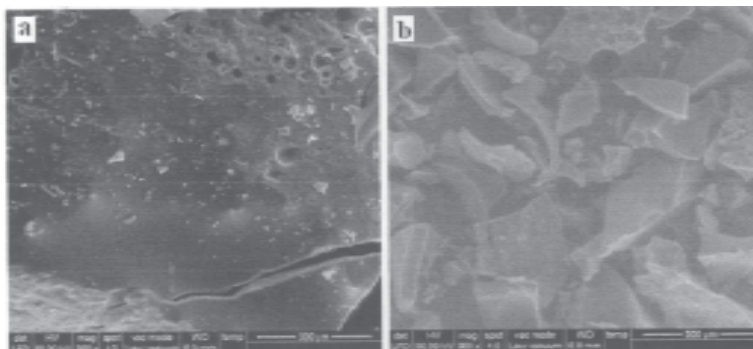


Fig. 4. SEM micrographs of residual chars obtained from polymer 4 at 480 °C (a) and polymer 4 at 700°C (b).

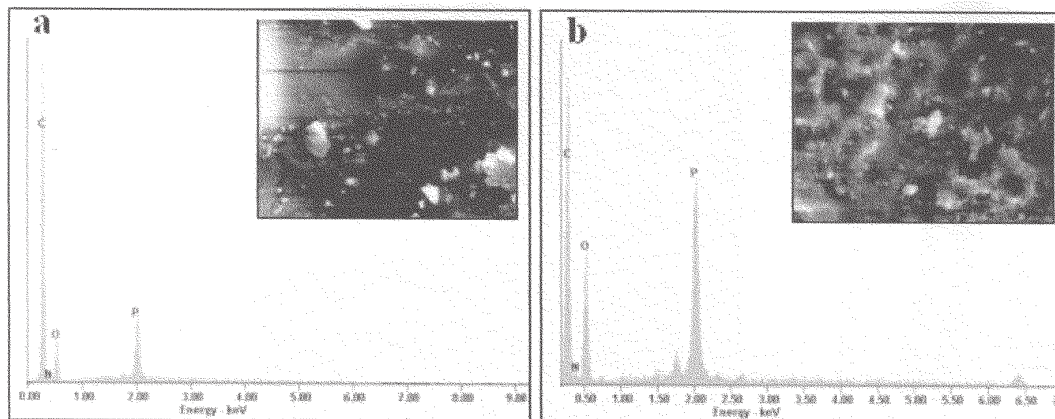


Fig. 5. EDX spectra of polymer 4 after heating up to 480 °C (a) and 700°C (b)

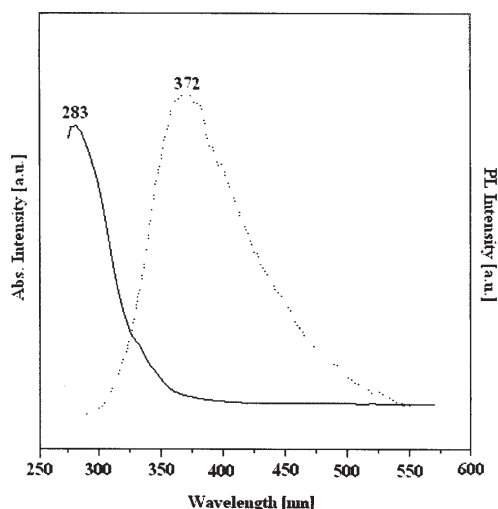


Fig. 6. UV-vis spectra along with the PL spectra ($\lambda_{ex} = 283$ nm) for polymer solution 4 in NMP.

characteristic bands 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 and amide carbonyl groups with an increase of phosphorus content took place, as the characteristic bands of P - C (1400 cm^{-1}) and P = O (1170 cm^{-1}) are still present in the solid residue at 700°C (fig.1c). This agreed with the high char yield at high temperature. The char yield at 700°C was 47.6%. The high char yield limits the production of combustible gases, decreases 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.

To explore how the structure of intumescent char determines fire-resistant properties, the residue chars left after heating coatings under air at 480 and 700°C are examined for char appearance by SEM analysis. In general,

the resistance of generated char to thermal oxidation depends on its structure: a more compact char structure led to a better resistance against heat and oxygen. Figure 4a and 4b presents the SEM micrographs of intumescent chars obtained from polymer 4 at different temperatures. Comparing figure 4a with figure 4b, it is found that the residual char of the polymer 4 at 700°C is more dense and compact than that of the residual char at 480°C , the results being in agreement with FTIR-TGA investigations, as the 480°C temperature is related to the volatilization of the amide groups.

The EDX spectra for polymer 4 after heating up to 480 and 700°C are presented in figure 5. As can be seen the content of the phosphorus is higher in the sample heated up to 700°C confirming the FTIR-TGA analysis. The EDX analysis confirmed the action of these flame retardant in condensed phase, due to the presences of the P in the char.

Optical properties

The optical properties of the studied polymer were analyzed by UV-vis and PL spectroscopy. The UV-vis and PL spectra of the polymer in NMP solution are illustrated in figure 6.

It was found that polymer 4 showed one UV absorption peak (λ_{abs}) at around 283 nm. The polymer exhibited light emission with strong maxima of photoluminescence of 372 nm which are determined by the presence of DOPO groups. The shape of the fluorescence spectra of the polymer is asymmetric. The broad tail toward longer wavelength suggests the presence of longer polymer chain [25]. The polymer exhibited Stokes shift value of 89 nm. The Stokes shift is generated by electronic or geometric structure relaxation of the photoexcited molecule [26], which is induced by the intramolecular charge transfer process. This information suggests a significant conformational difference between an absorbing ground state (S_0) and the emitting excited state (S_1) [27]. If the Stokes shift is too small, then the emitted light will be self-

absorbed and the luminescence efficiency will decrease in devices.

Conclusions

A novel copoly(ester-amide-imide) with phosphorus has been prepared. The solubility of the polymer was significantly improved by the incorporation of bulky, noncoplanar, and polar **DOPO** groups. The polymer exhibited high thermal stability, having the initial decomposition temperature above 415°C. The 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 polymer, the char yield at 700°C being 47.6%.

Acknowledgements: This research was financially supported by European Social Fund - "Cristofor I. Simionescu" Postdoctoral Fellowship Programme (ID POSDRU/89/1.5/S/55216) and Sectoral Operational Programme Human Resources Development 2007-2013".

References

- HUANG, S. J., HOYT, A. E., Trends Polymer Sci., **3**, 1995, p. 262
- de ABAJO, J., de la CAMPA, J. G., Adv. Polym. Sci., **140**, 1999, p. 23
- HSIAO, S. H., CHEN, W. T., J. Polym. Res., **10**, 2003, p. 95
- YANG, C. P., HSIAO, F. Z., J. Polym. Res., **10**, 2003, p. 181
- BRUMA, M., FITCH, J. W., CASSIDY, P. E., J. Macromol. Sci., Rev. Macromol. Chem. Phys., **36**, 1996, p. 119
- HAMCIUC, C., HAMCIUC, E., BRUMA, M., Polymer, **46**, 2005, p. 5851
- VLAD-BUBULAC, T., HAMCIUC, C., PETREUS, O., BRUMA, M., Polym. Adv. Tech., **17**, 2006, p. 647
- HAMCIUC, C., HAMCIUC, E., Polimeri heterociclici termostabili, Ed. PIM, Iasi, 2007
- HAMCIUC, E., HAMCIUC, C., in Advances in Functional Heterochain Polymers, Cazacu, M., Ed., Nova Science Publishers, Inc., New York, 2008, p. 187
- HAMCIUC, C., HAMCIUC E., Poliamide heterociclice termostabile, Ed. Tehnopress, Iasi, 2008
- WANG, C. S., LIN, C. H., CHEN, C. Y., J. Polym. Sci., Part A: Polym. Chem., **36**, 1998, p. 3051
- WU, C. S., LIU, Y. L., CHIU, Y. S., Polymer, **43**, 2002, p. 1773
- HOFFMANN, T., POSPIECH, D., HAUSSLER, L., KOMBER, H., VOIGT, D., HARNISCH, C., KOLLANN, C., CIESIELSKI, M., DORING, M., PEREZ-GRATEROL, R., SANDLER, J., ALTSTADT, V., Makromol. Chem. Phys., **206**, 2005, p. 423
- VLAD-BUBULAC, T., HAMCIUC, C., PETREUS, O., High Perform. Polym., **18**, 2006, p. 255
- VLAD-BUBULAC, T., HAMCIUC, C., PETREUS, O., LISA, G., Mat. Plast., **44**, no. 4, 2007, p. 284
- VLAD-BUBULAC, T., HAMCIUC, C., PETREUS, O., Mat. Plast., **44**, no.3, 2007, p. 199
- HAMCIUC, C., VLAD-BUBULAC, T., PETREUS, O., LISA, G., Eur. Polym. J., **43**, 2007, p. 980
- YANG, S. C., KIM, J. P., J. Appl. Polym. Sci., **106**, 2007, p. 1274
- PETREUS, O., VLAD-BUBULAC, T., HAMCIUC, C., High Perform. Polym., **20**, 2008, 588
- ZHAO, C. S., CHEN, L., WANG, Y. Z., J. Polym. Sci.: Part A: Polym. Chem., **46**, 2008, p. 5752
- HAMCIUC, C., VLAD-BUBULAC, T., PETREUS, O., LISA, G., Polym. Bull., **60**, 2008, p. 657
- VLAD-BUBULAC, T., HAMCIUC, C., Polymer, **50**, 2009, p. 2220
- SUN, Y. S., WANG, C. S., Polymer, **42**, 2001, p. 1035
- HAMCIUC, C., HAMCIUC, E., SERBEZEANU, D., VLAD-BUBULAC, T., Polym. Adv. Technol, DOI: 10.1002/pat. 1784, 2010
- WANG, C., SHIEH, S., LE GOFF E., KANATZIDIS, M. G., Macromolecules, **29**, 1996, p. 3147
- THOMAS, I. S. W., SWAGER, T. M., Macromolecules, **38**, 2005, p. 2716
- WANG, B. C., LIAO, H. R., YEH, H. C., WU, W. C., CHEN, C. T., J Lumin, **113**, 2005, p. 321

Manuscript received: 8.07.2010