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New Phosphorus-Containing Copolyesters

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A series of phosphorus-containing copolyesters was prepared by polycondensation of 2-(6-oxido-6H-dibenzo<c,e><1,2>oxaphosphorin-6-yl)1,4-benzenediol, ***1****, or of an equimoleculare amount of* ***1*** *and different bisphenols* ***2****, such as: hydroquinone, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-isopropylidenediphenol, 4,4′-(1,4-phenylene-diisopropylidene)bisphenol, 2,7-dihydroxynaphthalene, 4,4′-dihydroxybiphenyl, 9,9-bis-(p-hydroxyphenyl)fluorene, with an aromatic diacid chloride containing two preformed ester groups* ***3****, namely terephthaloyl-bis-(4-oxybenzoylchloride). The copolyesters exhibited thermal stability having the decomposition temperature above 350°C and char yield at 700°C in the range of 19–41%. The glass transition temperature was in the range of 131–164°C. Some of the polymers exhibited thermotropic liquid crystalline behavior.*

Keywords aromatic polyesters, solution polycondensation, phosphorus-containing polymers, thermal properties

Introduction

Wholly aromatic polyesters are well-known to show not only thermotropic liquid crystalline mesophases but also good physical properties (1). However, they have the disadvantage of poor melt-processability because they possess high melting and isotropization temperatures (2–4). There are some modification methods to control the phase transition temperatures and to improve the processability. An attractive synthetic approach to reduce melting temperature and to improve the solubility of the polymers is the incorporation of pendent groups along the polymer backbone (5). 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, resulted in polymers with good solubility. The incorporation of DOPO units into polymers also gave improved thermal oxidative stability, good adhesion and low birefringence. In addition, phosphorus-containing polymers meet the requirements of low toxicity and low smoke during combustion for environmental and health consideration (6–13). The unusually high thermal stability of the P—O—C bond in this compound may be attributed to the O=P—O group being protected by phenylene groups. After the cleavage of the O=P—O pendant group, the char formed acts as a protective layer for the polymer main chain (14).

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Another useful approach for reducing the melting temperature of the polymers and increasing the solubility is the copolymerization of monomers by which the symmetry of the structure is lowered and the lateral packing is disrupted. In addition, the introduction of flexible spacers between rigid-rod mesogens can also be used to lower melting temperature and to improve the solubility (3, 15–17).

Aromatic polyesters containing DOPO pendent units have been prepared by the reaction of 2-(6-oxido-6H-dibenzo<c,e><1,2>oxaphosphorin-6-yl)1,4-benzenediol, **1**, with different aromatic diacid chlorides, in *o*-dichlorobenzene, at high temperature (18). Aromatic copolyesters containing DOPO were synthesized by melt polycondensation of acetylated compound **1** with *p*-acetoxybenzoic acid, terephthalic acid and isophthalic acid (16). Also, such polymers were prepared by polycondensation of the same compound **1**, with aromatic dicarboxylic acids using $SOCl_2$/pyridine condensing acid (19). The copolyesters exhibited high glass transition temperature and good thermal stability. Some of them exhibited thermotropic behavior.

Here, we describe the results of the polycondensation of an aromatic bisphenol incorporating DOPO, **1**, or equimoleculare amount of **1** and different bisphenols **2**, with a diacid chloride containing two preformed ester groups **3**. The properties of the polymers such as solubility, thermal stability or glass transition temperature have been investigated. Mesogenic phases were observed with a hot-stage polarizing microscope.

Experimental

Synthesis of the Monomers

2-(6-Oxido-6H-dibenzo<c,e><1,2>oxaphosphorin-6-yl)1,4-benzenediol, **1**, was synthesized from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and *p*-benzoquinone (20). It was recrystallized from toluene/ethanol 1 : 1. Mp.: 255–256°C. IR (KBr, cm^{-1}): 3240 (—OH), 1582 (P—Ph), 1190 (P═O), 1168 and 925 (P—O—Ph). ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 8.24$ (2H, m), 7.74 (2H, m), 7.52 (2H, m), 7.31 (3H, m), 6.91 (1H, s), 6.67 (1H, s).

The monomers **2**, such as hydroquinone, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-isopropylidenediphenol, 4,4′-(1,4-phenylene-diisopropylidene)bisphenol, 2,7-dihydroxynaphthalene, 4,4′-dihydroxybiphenyl and 9,9-bis-(*p*-hydroxyphenyl)fluorene were provided from Aldrich and used as received.

Terephthaloyl-bis-(4-oxybenzoylchloride), **3**, was synthesized by treating with excess thionyl chloride, at reflux temperature, of the corresponding dicarboxylic acid that resulted from the reaction of 4-hydroxybenzoic acid (2 mol) with terephthaloyl chloride (1 mol), according to a method presented in the literature (21). Mp.: 223–226°C. IR (KBr, cm^{-1}): 1780 (COCl), 1730 (COO), 1600 (aromatic), 1210 (Ph—O—OC).

Synthesis of the Copolyesters 4

The copolyesters **4** were obtained by solution polycondensation reaction of **1**, or of an equimoleculare amount of **1** and bisphenols **2** with the diacid chloride **3**. A typical polycondensation was run as shown in the following example for the synthesis of polymer **4a**: In a 50 mL flask equipped with magnetic stirrer and nitrogen-inlet and outlet were introduced bisphenol **1** (1.329 g, 0.003 mol), diacide chloride **3** (1.044 g, 0.003 mol) and *o*-dichlorobenzene (7.5 mL). The reaction mixture was refluxed for 20 h, it was cooled to room temperature and poured into methanol (20 mL), under stirring, to obtain a precipitate which was filtered, washed with methanol, and dried at 100°C for 10 h. For the synthesis of copolyesters **4b–h**, the same method was used, equimolecular amount of bisphenols **1** and **2** being added (Scheme 1).

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.

Thermogravimetric analysis (TGA) was performed using 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 achieved a 5 wt % loss. The temperature of 10 wt % loss (T_{10}) was also recorded.

The glass transition temperature (T_g) of the precipitated polymers was determined with a Mettler differential scanning calorimeter (DSC 12E), at a heating rate of 10°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.

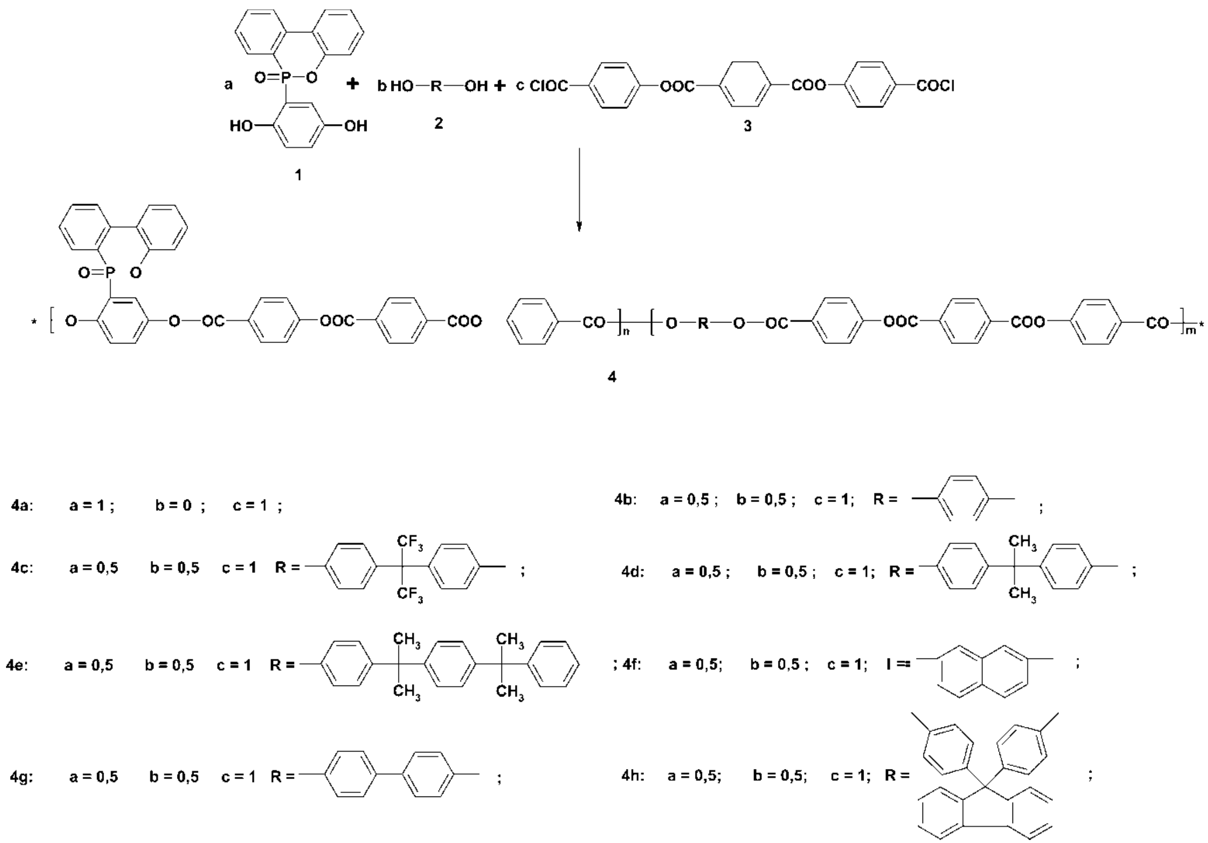
Polarized light microscopy investigations were performed with an Olympus BH-2 polarized light microscope fitted with a THMS 600/HSF9I hot stage, at a magnification of 400×. The mesomorphic transition temperature and disappearance of birefringence, that is, the crystal-to-nematic (T_m) and nematic-to-isotropic (T_i) transition were noted.

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 4 (22). The same program was used to visualize the structures obtained after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

Results and Discussion

Aromatic copolyesters **4** were synthesized from a DOPO-containing bisphenol **1** or an equimoleculare amounts of **1** and different bisphenols **2** with a diacid chloride having two ester groups **3** (Scheme 1). The process was performed by heating the reaction mixture for 20 h at reflux temperature. The reaction system got temporarily homogeneous, then the polymers precipitated during the polycondensation process. The aromatic copolyesters were obtained in high yields. Their inherent viscosities could not be measured, because they were insoluble in organic solvents.

The structure of the resulting polymers was confirmed by IR spectroscopy. Figure 1 a shows the IR spectrum of polymer **4a**, as an example. The characteristic absorption peak at 1740 cm^{-1} was due to carbonyl asymmetric stretching of ester groups. The IR spectra showed also a broad weak absorption peak between 3600 cm^{-1} and 3200 cm^{-1} which is characteristic of the stretching vibration of unreacted OH groups. A longer reaction time did not lead to the disappearance of such weak absorption bands. Characteristic absorption peaks appeared at 925 cm^{-1} and 1160 cm^{-1} due to P—O—Ar groups, at 1470 cm^{-1} due to Ar—P groups and at 1205 cm^{-1} due to P═O groups. Aromatic C═C bands were found at 1600 cm^{-1} and 1500 cm^{-1}, while C—H absorption was found at 3070 cm^{-1}. The IR spectrum of polymer **4c** exhibited absorption bands at 1180 cm^{-1} and 1210 cm^{-1} due to hexafluoroisopropylidene groups, while the IR spectra of



Scheme 1. Preparation of copolyesters **4**.

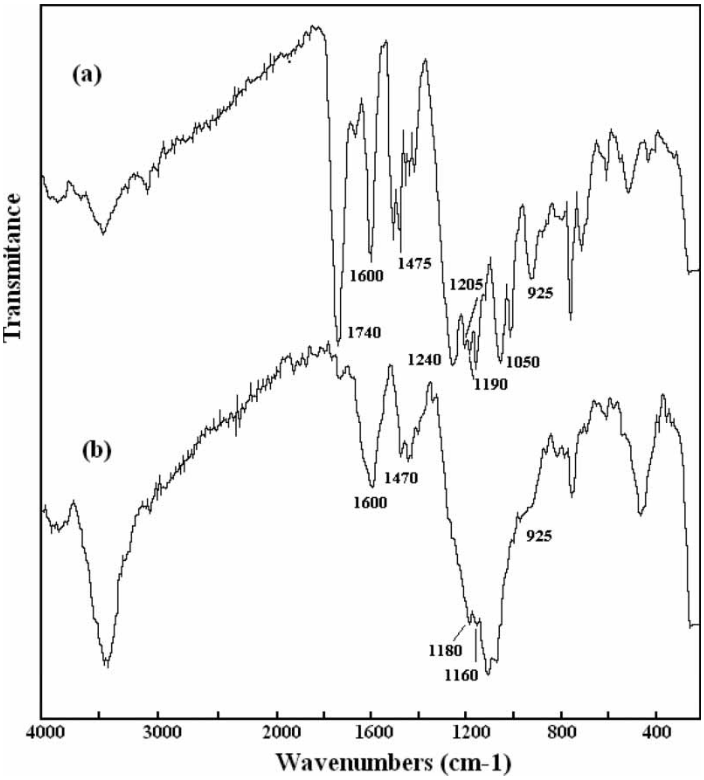


Figure 1. IR spectra of polymer **4a** (a) initial and (b) after heating up to 535°C with the heating rate of 10°C/min.

polymers **4d** and **4e** exhibited characteristic absorption bands at 2970 cm^{-1} due to isopropylidene groups.

Polymers **4** were only partially soluble in organic solvents like N,N-dimethylformamide, N-methylpyrrolidone or dimethylsulfoxide. They were partially soluble even in a 40/60 (w/w) mixture of 1,2-dicloroethane/phenol. The low solubility of the polymers can be explained by the high rigidity of the segment coming from the diacid chloride which contains three *p*-phenylene groups connected by ester units. The macromolecular chains can have a linear conformation and allowed a strong packing that reduced the solubility. The shape of a fragment of polymer **4a**, as evidenced by molecular modeling, is presented in Figure 2.

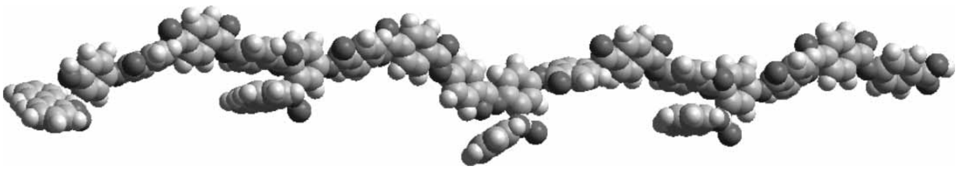


Figure 2. Model molecule (four repeating units) of polymer **4a**.

Table 1
Properties of polymers **4**

Polymer	P content (%)	T_g[a] (°C)	T_m[b] (°C)	T_i[c] (°C)	IDT[d] (°C)	T_{10}[e] (°C)	$T_{\max 1}$[f] (°C)	$T_{\max 2}$[g] (°C)	Char yield at 700°C (%)
4a	4.46	160	385	—	408	432	479	628	41
4b	2.64	154	—[h]	—[h]	362	398	479	629	19
4c	2.21	146	257	297	417	438	498	660	23
4d	2.39	139	220	251	358	376	412	610	28
4e	2.20	131	—[h]	—[h]	352	369	405	601	22
4f	2.53	135	318	320	417	439	474	669	39
4 g	2.48	134	—[h]	—[h]	380	414	478	641	24
4 h	2.19	164	280	334	411	424	481	669	26

[a] Glass transition temperature.
[b] The mesomorphic transition temperature (determined by hot-stage polarized light microscope).
[c] Isotropization temperature (determined by hot-stage polarized light microscope).
[d] Initial decomposition temperature = the temperature of 5 wt % loss.
[e] Temperature of 10 wt % loss.
[f] First maximum polymer decomposition temperature.
[g] Second maximum polymer decomposition temperature.
[h] Liquid crystalline behavior was not observed.

The glass transition temperature (T_g) of polymers **4**, evaluated from DSC curves, was in the range of 131–164°C (Table 1) being dependent on the nature of bisphenols **2.** Polymers **4** showed a glass transition temperature and no significant endothermic peaks. The presence of DOPO pendent units in the macromolecular chains increased the rigidity of the backbone resulting in higher values of the T_g. Figure 3 presents the DSC curves of polymers **4**. The polymer **4a** derived from monomers **1** and **3** exhibited a high T_g (160°C). A decrease of the T_g was obtained in the case of copolyesters **4b–g**. The polymer **4c** containing hexafluoroisopropylidene groups exhibited higher T_g (146°C) when compared with the polymer **4d** having isopropylidene units. The polymer **4e** incorporating two isopropylidene groups per unit structure had the lowest T_g (131°C) from this series of the polymers. The polymer **4h** contained in the unit structure two bulky pendent groups (DOPO and fluorene units) exhibited the highest T_g (164°C).

For the characterization of the melt morphology of the copolyesters, polymers **4** were evaluated by visual observation on a hot-stage polarizing microscope. The aromatic copolyesters **4a**, **4c**, **4d**, **4f** and **4 h** formed nematic phases according to observation of their optical texture on a cross-polarizing microscope. The data of the mesophasic transition temperature T_m and isotropization temperature T_i are given in Table 1. Figure 4 presents the nematic phase, as well as the nematic to isotropic phase transition of polymers **4a** and **4c**.

In general the liquid crystalline behavior of the copolyesters **4** depends on the nature of the segment coming from the bisphenol **2**. The T_m of the polymer **4a** was relatively high (385°C) due to the rigidity of the macromolecular chains (Figure 4a). The isotropic phase, appearing at a temperature higher than 430°C, was not clear detected due to some degradation processes that took place (Figure 4b). A decrease of the T_m and T_i was observed for the copolyesters **4c**, **4d**, **4f** and **4h** due to the copolymerization effect. Thus, the polymer **4c**

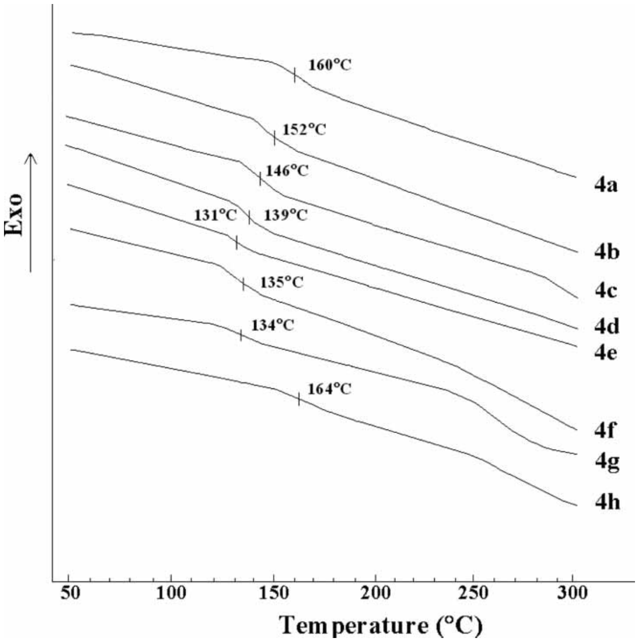


Figure 3. DSC curves of polymers **4**.

containing units coming from 4,4′-(hexafluoroisopropylidene)diphenol exhibited lower T_m and T_i (Fig. 4c, d). A decrease of the T_m and T_i was observed in the case of polymer **4d** containing units coming from 4,4′-isopropylidenediphenol. The introduction of naphthalene units or 9,9-bis(phenyl)fluorene groups increased the T_m and T_i of polymers **4f** and **4h**.

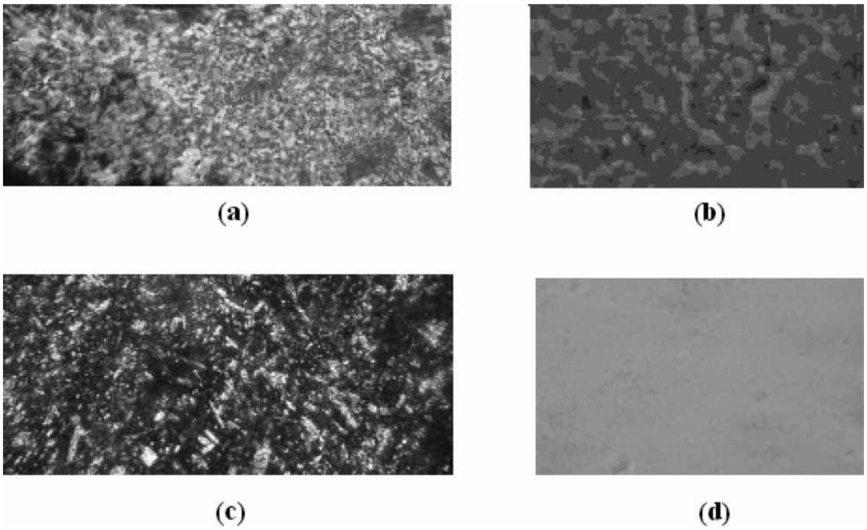


Figure 4. Optical polarization micrographs (heating cycle, 400×) of polymers **4a** and **4c**: (a) **4a** at 380°C, (b) **4a** at 435°C; (c) **4c** at 260°C and (d) **4c** at 300°C.

The polymers **4b** and **4g** did not exhibit liquid crystalline mesophase due to very high rigidity of the macromolecular chains introduced by the *p*-phenylene and diphenylene units, respectively. T_m was probably higher then the decomposition temperature. Also, the polymer **4e**, with two isopropylidene groups in the segment coming from bisphenol **2**, did not exhibit liquid crystalline mesophase.

The thermal stability was evaluated by thermogravimetric analysis (TGA). The polymers did not show significant weight loss below 350°C. They began to decompose in the range of 352–417°C; they showed 10 wt % loss in the range of 369–439°C. Figure 5 presents the TGA curves of polymer **4a.**

As can be seen from differential thermogravimetric (DTG) curves of DOPO-containing polymers **4**, the degradation process exhibited two maxima of decomposition. The first (T_{max1}) was in the range of 405–498°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 601–669°C and was due to the degradation of polymer chain itself (Table 1). IR spectrum of the solid residue of the polymer **4a**, after heating up to 535°C with the heating rate of 10°C/min, was examined (Figure 1b). The value of 535°C represents the temperature of the end of the first decomposition process, from DTG curve (Figure 5). As can be seen from Figure 1, after the thermal treatment, the absorption of the ester groups almost completely disappeared, whereas a high content of aromatic skeleton was detected. Thus, the disappearance of the absorption band at 1740 cm^{-1}, which is characteristic to ester groups, was observed. The absorption band at 1600 cm^{-1} which characterizes aromatic rings was still presented

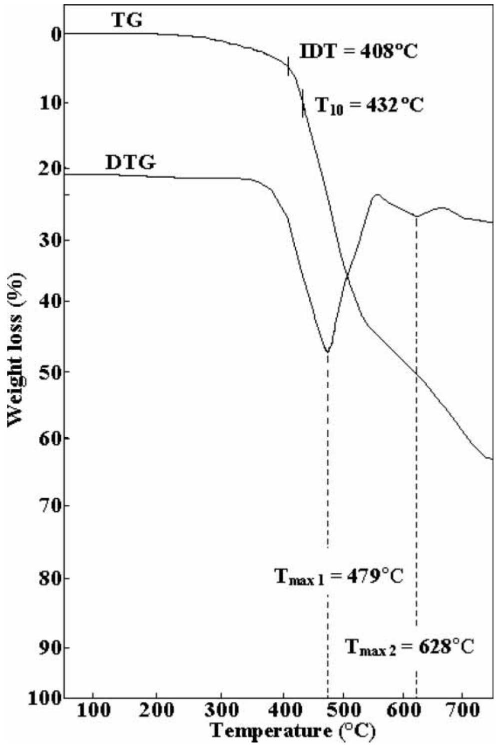


Figure 5. TGA curves of polymer **4a**.

in the IR spectrum. The characteristic bands of P—C and P═O, were observed at 1470 cm^{-1} and 1180 cm^{-1}, respectively. Also, the characteristic P—O—Ar stretching was observed at 1160 cm^{-1} and 925 cm^{-1} indicating the presence of phosphorus in the solid residue. We presume that a crosslinked structure containing P—C, C—O—Ar and C—P═O units was formed. It can be concluded that in the first step of degradation, the destruction of ester groups with an increase of phosphorus content took place. This agreed with the high chair yield at high temperature. The high char yield limits the production of combustible gases, decreases the exothermicity of the pyrolysis reactions of the polymers, inhibits the thermal conductivity of the burning materials, thus increasing the flame retardancy of the polyesters (23).

The amount of carbonized residue (char yield) of these polymers in air was 19–41% at 700°C. The residual char increased with the phosphorus content, indicating the flame retardancy is improved. Thus, polymer **4a** having the highest phosphorous content (4.46%), exhibited the highest chair yield at 700°C (41%).

Conclusions

The polycondensation of 2-(6-oxido-6H-dibenzo<c,e><1,2>oxaphosphorin-6-yl) 1,4-benzenediol, **1**, or of an equimoleculare amount of **1** and different other bisphenols with an aromatic diacid chloride containing two preformed ester groups, in *o*-dichlorbenzene, at high temperature, gave aromatic copolyesters. They exhibited good thermal stability, with decomposition temperatures above 350°C and glass transition temperatures in the range of 131–164°C. The presence of P atom in the unit structure of the polymers increased the char yield at 700°C, improving the flame retardancy. Some of the polymers exhibited nematic melt according to observations of their texture on a cross-polarizing microscope.

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