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Synthesis and characterization of new aromatic polyesters and poly(ester-imide)s containing phosphorous cyclic bulky groups

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Summary

New phosphorous-containing polyesters were prepared by polycondensation of 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalene diol, **1**, with different aromatic dicarboxylic acids using a $SOCl_2$/pyridine condensing agent. Two poly(ester-imide)s were prepared by polycondensation in solution at high temperature of the same aromatic bisphenol **1**, with diacid chlorides containing preformed imide rings. The most of the polymers were easily soluble in polar organic solvents such as N-methylpyrrolidone, N,N-dimethylformamide and chloroform. They showed high thermal stability, the decomposition temperature being in the range of 330-442°C and glass transition in the temperature range of 193-226°C. One of these polymers exhibited thermotropic liquid crystalline behavior. Due to the presence of phosphorus the polymers gave high char yield in termogravimetric analysis, hence good flame retardant properties.

Keywords

polyesters; poly(ester-imide)s; phosphorous-containing polymers; thermal stability; flame retardant properties

Introduction

Natural and synthetic polymer materials are widely used in modern industries, such as constructions, electrical and electronic components and transport. Fire hazard of these materials due to their high flammability represents an important problem. Phosphorous-containing polymers are the most effective flame retardant materials [1–3]. Their products of decomposition are less toxic and corrosive and produce little damage to the environment during fire.

Wholly aromatic polyesters and poly(ester-imide)s have received considerable attention for their excellent mechanical properties, thermal stability, chemical resistance and low melting viscosity. However these polymers exhibit low solubility in organic solvents and high melting temperatures which make them difficult to be processed [4-6]. An attractive synthetic approach to improve the solubility is the incorporation of bulky substituents as pendent groups along the polymer backbone. If the pendent groups are carefully chosen, it is possible to promote the solubility without affecting thermal and mechanical properties to any great extent. Thus, utilization of monomers containing phosphorous group, such as 9,10-dihydro-oxa-10-phosphaphenanthrene-10-oxide (**DOPO**), which possess a polar P=O group and a bulky structure, resulted in polymers with good solubility. Moreover, incorporation of **DOPO** units into polymers also brought improved flame retardancy, thermal oxidative stability, good adhesion and low birefringence [7-15].

Aromatic polyesters containing **DOPO** pendent units have been prepared by the reaction of 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)1,4-benzenediol (**DOPO-BQ**) with different aromatic diacid chlorides in *o*-dichlorobenzene, at high temperature [16] or by the reaction of the same **DOPO**-containing diol with aromatic dicarboxylic acids using a $SOCl_2$/pyridine condensing agent [17]. Also, phosphorous-containing poly(ester-imide)s were prepared by polycondensation in solution at high temperature of **DOPO-BQ** with various aromatic diacid chlorides containing preformed imide rings [18]. All the polymers exhibited good solubility in organic solvents, high glass transition and good thermal stability. Some of the polymers exhibited thermotropic behavior.

Here, we describe the synthesis and characterization of some aromatic polyesters prepared from 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalene diol, **1**, and different aromatic diacids using $SOCl_2$/pyridine condensing agent. Also, we present two poly(ester-imide)s obtained by high temperature solution polycondensation of the same compound **1** and different diacid chlorides containing preformed imide rings. These polymers have bulky lateral phosphorus containing groups and exhibit high aromatic contents and symmetrical 1,4-naphthalene structure simultaneously in the main chain. The properties of the polymers such as solubility, glass transition temperature and thermal stability have been investigated. Mesogenic phases were observed with hot stage polarizing microscope.

Experimental

Instrumental

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). The inherent viscosities (η_{inh}) of the polymers were determined with an Ubbelohde viscometer, by using polymer solutions in N-methylpyrrolidone (NMP), at 20°C, at a concentration of 0.5 g/dL. Infrared spectra were recorded with a Specord M80 spectrometer by using KBr pellets. ^{1}H-NMR spectra were recorded on a Brucker Avance DRX 400 instrument, using solution in deuterated dimethylsulfoxide (DMSO-d_6). 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. Thermogravimetric analysis (TGA) was performed under nitrogen flow

(15 cm^3/min) at a heating rate of 10°C/min from 25°C to 900°C with a Mettler Toledo model TGA/SDTA 851. The initial mass of the samples was 4-6 mg.

Synthesis of the monomers

2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalene diol, **1**, was synthesized from **DOPO** and naphthoquinone [19]. It was recrystalised from ethoxyethanol; mp (DSC): 279-280°C. IR (KBr, cm^{-1}): 3430 (-OH), 1582 (P-Ph), 1190 (P=O), 1165 and 925 (P-O-Ph). ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 7.9$ (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).

4-Chloroformyl-N(p-chloroformylphenyl)-phthalimide, **3a**, was obtained by treating with excess thionyl chloride, at reflux temperature, the corresponding dicarboxylic acid resulting from the condensation of trimellitic anhydride with *p*-aminobenzoic acid [20]; mp: 194-195°C. IR (KBr, cm^{-1}): 1780 (C=O of imide ring and COCl), 1720 (C=O of imide ring), 1600 (aromatic), 1390 (C-N), 1100 and 720 (imide ring). ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 8.38$ (1H, d), 8.29 (1H, s), 8.12 (1H, s), 8.05 (2H, s), 7.65 (2H, d).

2,2-Bis[N-(4-chloroformylphenyl)phthalimidyl]hexafluoropropane, **3b**, was obtained by treating with thionyl chloride the corresponding dicarboxylic acid resulting from the condensation reaction of hexafluoroisopropylidene di(phthalic-anhydride) with *p*-aminobenzoic acid, in glacial acetic acid as a solvent and dehydrating reagent, at reflux [21]; mp: 311-313°C. IR (KBr, cm^{-1}): 1780 (C=O of imide ring and COCl), 1720 (C=O of imide ring), 1600 (aromatic), 1390 (C-N), 1210 and 1180 (CF_3), 1100 and 720 (imide ring). ^{1}H-NMR (DMSO-d_6, ppm): $\delta = 8.22$ (2H, d), 8.11 (4H, d), 7.91 (2H, d), 7.73 (2H, s), 7.61 (4H, d).

The monomers **2,** such as terephthalic acid, **2a**, 2-nitroterephthalic acid, **2b**, isophthalic acid **2c**, 5-*tert*-butyl-isophthalic acid, **2d**, and 4,4'-oxybis(benzoic acid), **2e**, were provide from Aldrich and used as received.

Synthesis of the aromatic polyesters 4

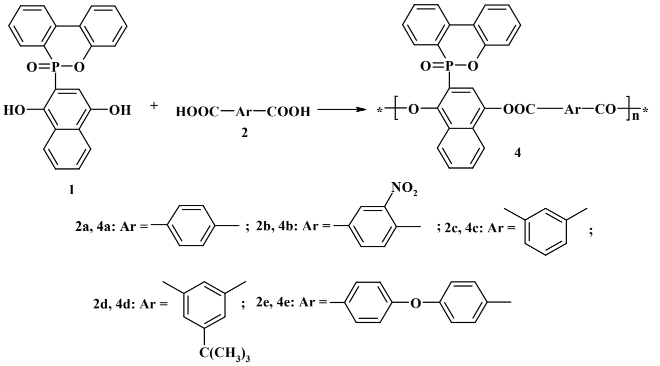
The polyesters **4** were obtained as described in the literature [22-25], by polycondensation reaction of bisphenol **1** with aromatic diacids **2**, such as terephthalic acid, 2-nitroterephthalic acid, isophthalic acid**,** 5-*tert-butyl*-isophthalic acid and 4,4'-oxybis(benzoic acid). A typical polycondensation was run as shown in the following example: to cold $SOCl_2$ (0.2 mL) in an ice-water bath, pyridine (2.5 mL) was added slowly over a period of 10 min to keep the reaction temperature low. A solution of terephthalic acid (0.208 g, 1.25 mmol) in pyridine (2.5 mL) was added over a period of 20 min to control the reaction temperature. The cooling bath was removed, and the reaction mixture was stirred at room temperature for an additional 20 min. Bisphenol **1** (0.467 g, 1.25 mmol) in pyridine (2.5 mL) was added all at once to the mixture and the solution was heated at 80°C for 4 h. The resulting mixture was diluted with pyridine and poured into methanol, and the isolated polymer was washed in boiling methanol and dried at 60°C in a vacuum oven for 10 h.

Synthesis of poly(ester-imide)s **5**

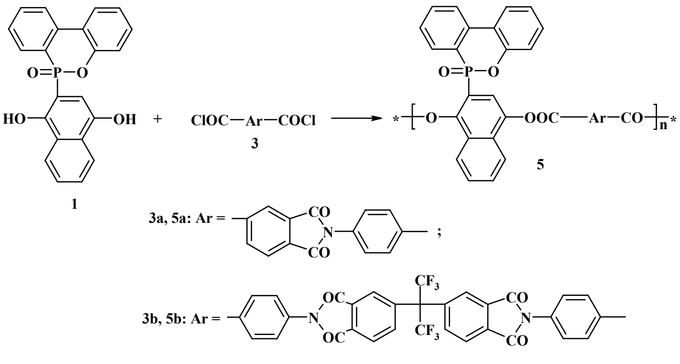
The poly(ester-imide)s **5** were obtained by solution polycondensation reaction of aromatic bisphenols **1** with diacid chlorides **3** [18]. A typical polycondensation was run as shown in the following example: In a 50 mL flask equipped with magnetic stirrer and nitrogen-inlet and outlet were introduced bisphenol **1** (0.374 g, 1 mmol), diacid chloride **3a** (0.348g, 1 mmol) and *o*-dichlorobenzene (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.

Results and discussion

The aromatic polyesters **4** were synthesized from aromatic diol **1** and different aromatic diacids **2** using $SOCl_2$/pyridine as condensing agent. (Scheme 1). The yield of the reactions was in the range of 70-80%. The aromatic poly(ester-imide)s **5** were synthesized by solution polycondensation in *o*-dichlorobenzene at high temperature of equimolar amount of aromatic compound **1** with two diacid chlorides **3**, as shown in scheme 2.



Scheme 1. Preparation of phosphorous containing polyesters **4**.



Scheme 2. Preparation of phosphorous containing poly(ester-imide)s **5**.

The structure of the polymers was confirmed by IR spectroscopy. In the IR spectra of polymers **4** the characteristic absorption band at 1750 cm^{-1} was due to carbonyl asymmetric stretching of ester groups. The spectrum of polymer **4b** showed characteristic absorption bands at 1540 cm^{-1} and 1370 cm^{-1} due to the asymmetric and symmetric stretching of NO_2 groups. In the IR spectrum of polyester **4d** characteristic absorption bands appeared at 2964 cm^{-1} and 2870 cm^{-1} due to the asymmetric and symmetric stretching of CH_3 groups of *tert*-butyl units. The IR spectra of poly(ester-imide)s **5** showed absorption peaks at 1780 cm^{-1} (imide carbonyl symmetric stretching) and 1730 cm^{-1} (ester carbonyl and imide carbonyl asymmetric stretching). The absorbtion band at 1390 cm^{-1} was due to C-N stretching of imide rings and the absorptions at 1100 cm^{-1} and 720 cm^{-1} were due to the imide ring deformation. In the IR spectrum of polymer **5b** appeared two absorption bands at 1170 cm^{-1} and 1210 cm^{-1} due to the presence of hexafluoroisopropylidene groups. The spectra of the polymers **4** and **5** showed a week peak between 3600 cm^{-1} and 3200 cm^{-1} characteristic of the stretching vibration of the unreacted OH groups. All the spectra showed characteristic peaks at 1470 cm^{-1} due to the P-C groups and 924 cm^{-1} due to O=P-C groups. An absorption band at 1240 cm^{-1} appeared due to P=O groups and C-O groups of ester units.

The solubility of the polymers **4** and **5** was tested in various solvents, by using 15 mg polymer/1 mL solvent, at room temperature, and the results are summarized in table 1. Except polymers **4a** and **4c**, all the other polymers were easily soluble in polar aprotic solvents like N-methylpyrrolidone, N,N-dimethylformamide or N,N-dimethylacetamide. The polymers **4a** and **4c** exhibited lower solubility in organic solvents probably due to a higher rigidity of their macromolecular chains. Polymer **4b** was soluble in polar solvents due to the presence of nitro groups situated on the phenylene groups coming from the diacid segments. Some of the polymers were also soluble in less polar solvents like chloroform, tetrahydrofuran or pyridine. The good solubility of the polymers can be explained by the presence of bulky pendent **DOPO** groups which create a distance between the macromolecular chains and, consequently the diffusion of solvents is facilitated. The poly(ester-imide) **5a** exhibited limited solubility in chloroform, while the poly(ester-imide) **5b** was easily soluble. The higher solubility of the polymer **5b** can be explained by the presence of hexafluoroisopropylidene groups which increase the flexibility of the macromolecular chains and the free volume of the polymer thus increasing the solubility.

Table 1. The solubility of polymers **4** and **5**.

Polymer	NMP	DMF	DMAc	Py	THF	$CHCl_3$	Acetone
4a	-	-	-	-	-	-	-
4b	+	+	+	+	-	-	-
4c	-	-	-	-	-	-	-
4d	+	+	+	+	+	+	-
4e	+	+	+	+	+	+	-
5a	+	+	+	-	-	+-	-
5b	+	+	+	+-	+-	+	-

NMP = *N*-methylpyrrolidone; DMF = *N,N*-dimethylformamide; DMAc = *N,N*-dimethylacetamide; Py = pyridine; THF = tetrahydrofuran; + = soluble; +- = partial soluble; - = insoluble.

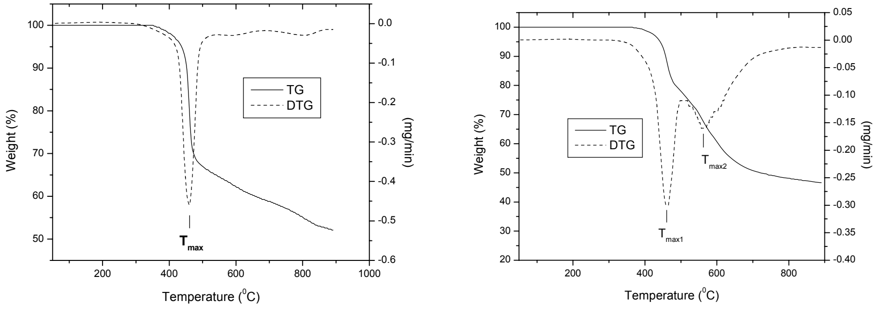
The inherent viscosity of the polymers was in the range of 0.21-0.46 dL/g (Table 2). The glass transition temperature (T_g), evaluated from DSC curves, was in the range of 193-226°C for the polyesters **4** and 195-216°C for poly(ester-imide)s **5** (Table 2). The DSC curves showed no melting points revealing that these polymers were amorphous. The presence of **DOPO** pendent units in the macromolecular chains of the polyesters increased the rigidity of the backbone resulting in higher values of the T_g. The introduction of *meta*-phenylene rings or bulky *tert*-butyl groups, in the case of polymers **4c** and **4d**, decreased the T_g values (206°C and 193°C, respectively) when compared with that of polymer **3a** (226°C). The presence of nitro pendent groups, in the case of polymer **4b**, slightly decreased the T_g. An increase of the T_g was observed in the case of the polymer **5b** containing hexafluorizopropylidene groups (T_g = 216°C) when compared with the T_g value of polymer **5a** (**T_g** = 195°C).

Table 2. The properties of polymers **4** and **5**.

Polymer	η_{inh}[a] (dL/g)	T_g[b] (°C)	IDT [c] (°C)	T_{10}[d] (°C)	T_{max1}[e] (°C)	T_{max2}[f] (°C)	% Char yield at 700°C
4a	-	226	437	452	459	-	59
4b	0.21	217	330	351	396	-	56
4c	-	206	404	434	453	-	52
4d	0.28	193	403	440	448	-	32
4e	0.46	219	442	449	452	-	60
5a	0.26	195	408	423	447	593	48
5b	0.32	216	440	458	459	564	50

[a] Measured at a concentration of 0.5 g polymer in 100 ml of NMP, at 20°C; [b] Glass transition temperature; [c] Initial decomposition temperature = the temperature of 5% weight loss; [d] Temperature of 10% weight loss; [e] First maximum polymer decomposition temperature; [f] Second maximum polymer decomposition temperature.

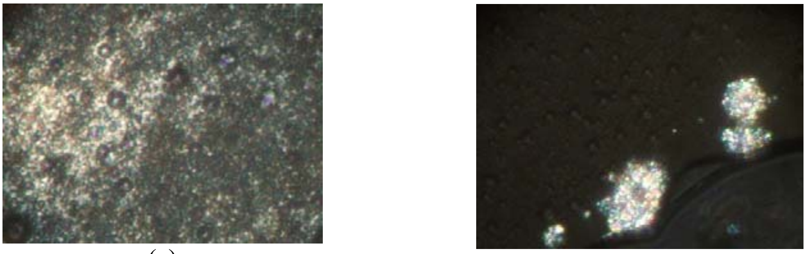
The thermal stability was evaluated by TGA. Figure 1 shows the TG and DTG curves of polymers **4a** and **5b**. Except polymer **4b**, all the other polymers did not show significant weight loss below 400°C; they began to decompose in the range of 403-442°C (Table 2). The aromatic polyesters exhibited one step of degradation having the maximum polymer decomposition temperature in the range of 396-459°C. The poly(ester-imide)s exhibited two steps of degradation having the maximum polymer decomposition temperature in the range of 447-459°C and 564-593°C, respectively. The polymer **4b** exhibited lower thermal stability due to the presence of nitro groups more sensitive to thermal degradation. The char yields of 700°C were in the range of 32-60%. The polymer **4d** exhibited the lower char yields at 700°C probably due to the presence of aliphatic *tert*-butyl groups. The char yields of the polyesters were closed with those of poly(ester-imide)s **5**. High char yield was obtained due to the presence of a P atom in the structure of the polymers. When a phosphorous-containing polymer is heated crosslinking carbonization occurs during the decomposition process. The high char yield limits the production of combustible gases, decreases the exotermicity of the pyrolysis reactions of the polymers, inhibits the thermal conductivity of the burning materials thus increasing the flame retarding of the polymers [19].



(a) (b)

Figure 1. TG and DTG curves of polymers **4a** (a) and **5b** (b).

The melt morphology of the polymers **4** and **5** was evaluated by visual observation on a hot stage polarizing microscope. The poly(ester-imide) **5a** formed nematic phase according to the observation of their optical texture on a cross-polarizing microscope. Figure 2 presents the nematic phase, as well as the nematic to isotropic phase transition of polymer **5a**. The polymer **4a** did not reveal any mesophase due to very high rigidity of the macromolecular chains introduced by the *p*-phenylene units. T_m was probably higher then the decomposition temperature. Also, the other polymers **4** did not exhibit a T_m up to the decomposition temperature.



(a) (b)

Figure 2. Optical polarization micrographs (heating cycle, 400x) of polymer **5a** at 335°C (a) and at 385°C (b).

Conclusions

The polycondensation of 2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalene diol with aromatic dicarboxylic acids in the presence of $SOCl_2$/pyridine condensing agent gave phosphorous containing aromatic polyesters. The poly-condensation of the same aromatic diol with diacid chlorides containing preformed imide rings gave aromatic poly(ester-imide)s. The polymers exhibited solubility in organic solvents, good thermal stability and high glass transition temperatures. The presence of P atom in the unit structure of the polymers increased the char yield at

700°C, improving the flame retardancy. A poly(ester-imide) exhibited nematic melt according to observations of their texture on a cross-polarizing microscope.

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