Aromatic-Aliphatic Phosphorous-containing Copolyesters

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*A series of phosphorous-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 equimolecular amount of **1** and different aliphatic diols **2**, such as: ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,12-dodecanediol with an aromatic diacid chloride containing two preformed ester groups **3**, namely terephthaloyl-bis-(4-oxybenzoyl-chloride). The copolyesters exhibited good thermal stability having the decomposition temperature above 360°C and char yield at 700°C in the range of 8.4-41%. The glass transition temperature was in the range of 83-160°C. The polymers exhibited thermotropic liquid crystalline behaviour.*

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

Aromatic polyesters are well known as high performance engineering thermoplastics because of their good thermal stability, chemical resistance and excellent mechanical properties [1]. However, they have the disadvantage of poor melt-processability because they possess high melting and isotropization temperatures [2]. 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. The utilization of monomers containing phosphorous 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 [3-10].

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 [11-14].

Here, we describe the results of the polycondensation of an aromatic bisphenol incorporating **DOPO**, **1**, or equimolecular amount of **1** and different aliphatic diols **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 part

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 [15]. 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): δ = 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 ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,12-, dodecanediol were provided from different commercial sources 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 [16]. 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 equimolecular amount of **1** and diols **2** with the diacid chloride **3**. A typical polycondensation was run as shown in the following example for the synthesis of polymer **4b**: In a 50 mL flask equipped with magnetic stirrer and nitrogen-inlet and outlet were introduced bisphenol **1** (0.6645 g, 0.0015 mol), ethylene glycol (0,093 g, 0.0015 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 (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.

^{1}H-NMR spectra were recorded using an Avance DRXx400, at room temperature.

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% weight loss. The temperature of 10% weight loss (T_{10}) was also recorded.

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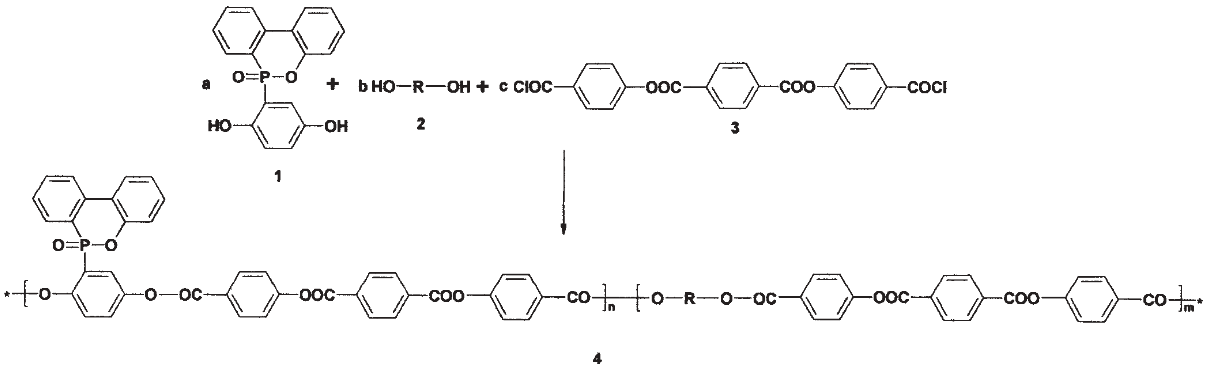


4a: $a = 1$; $b = 0$; $c = 1$;
4b: $a = 0{,}5$ $b = 0{,}5$ $c = 1$ $R = (CH_2)_2$
4c: $a = 0{,}5$ $b = 0{,}5$ $c = 1$ $R = (CH_2)_3$
4d: $a = 0{,}5$ $b = 0{,}5$ $c = 1$ $R = (CH_2)_4$
4e: $a = 0{,}5$ $b = 0{,}5$ $c = 1$ $R = (CH_2)_6$
4f: $a = 0{,}5$ $b = 0{,}5$ $c = 1$ $R = (CH_2)_{12}$

Scheme 1. Preperation of coplyesters **4**

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 [17]. 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 equimolecular amount of **1** and different diols **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 copolyesters were obtained in high yields. Their inherent viscosities could not be measured, because they were only partial soluble in organic solvents.

The structure of the resulting polymers was confirmed by IR spectroscopy. Figure 1 (a) shows the IR spectrum of polymer **4f** 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 band. 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

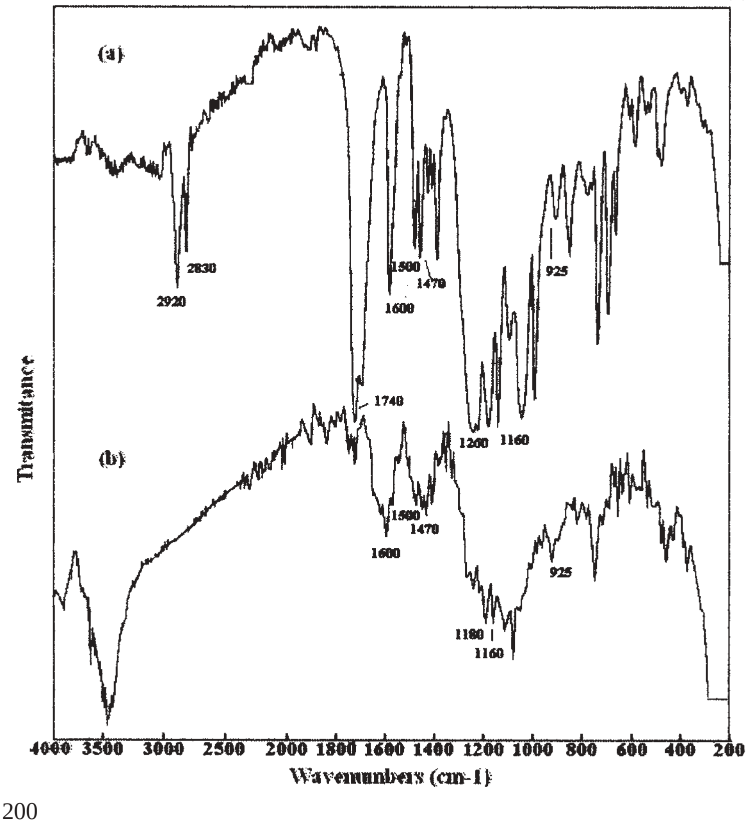


Fig. 1. IR spectra of polymer 4f (a) initial and (b) after heating up to 475°C with the heating rate of 10°C/min

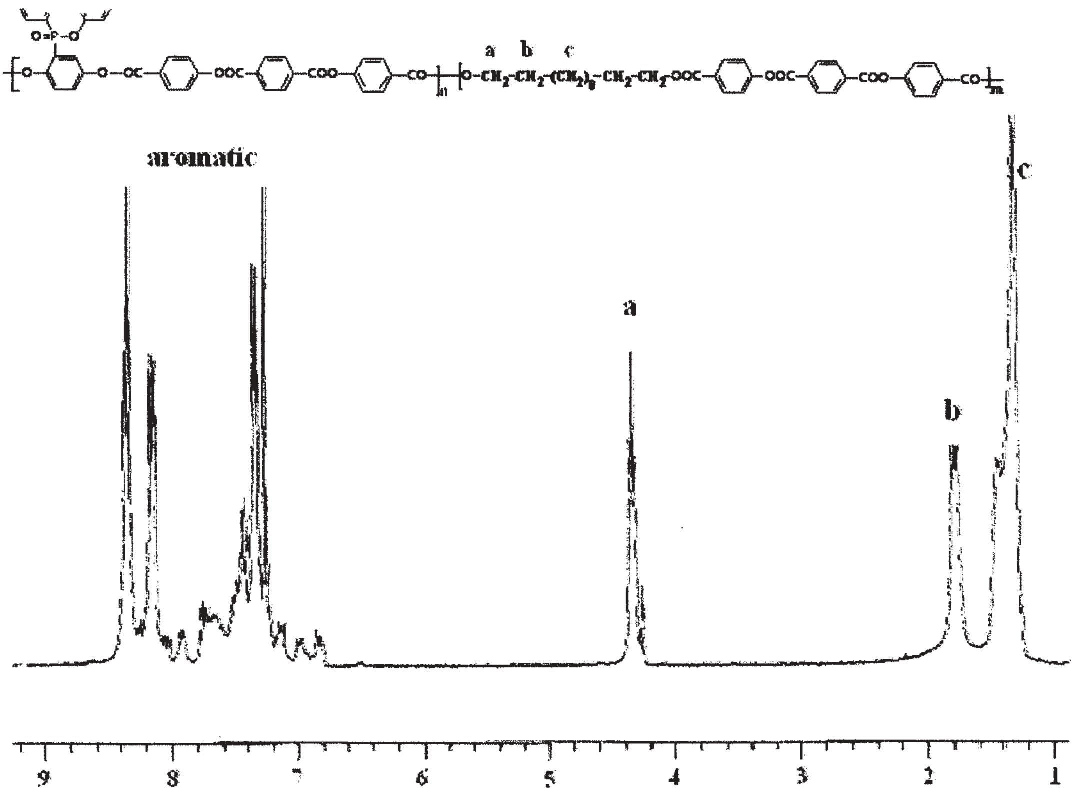


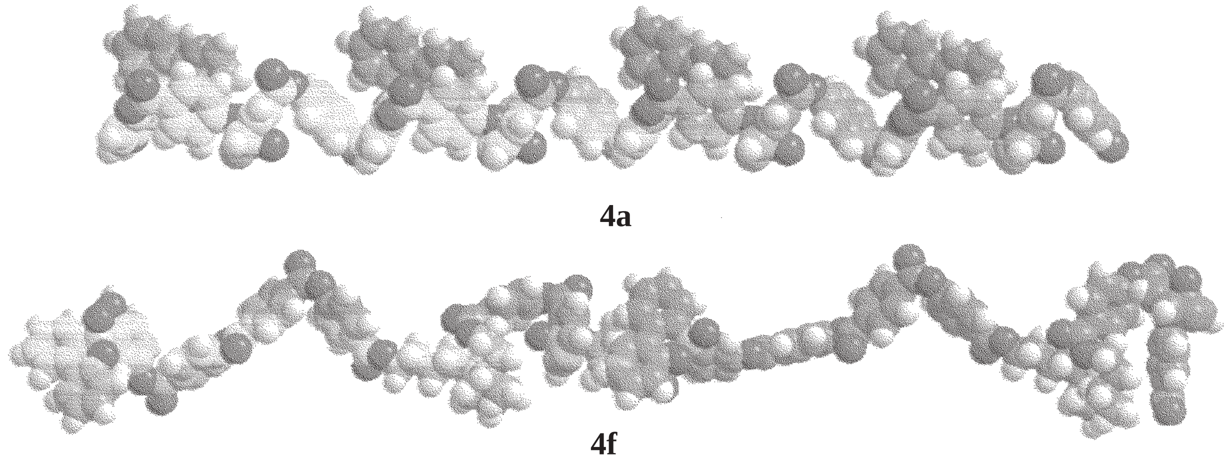
Fig. 2. ^{1}H-NMR spectrum of polymer 4f, in deuterated chloroform

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} In the case of the IR spectra of polymers **4b-f** characteristic absorption bands appeared at 2920 cm^{-1} and 2830 cm^{-1} due to the presence of methylene groups.

The ^{1}H-NMR spectrum of the polymer **4f** exhibited characteristic peaks in the range of 8.36-6.81 due to the presence of the aromatic protons. The peaks that characterize the methylene groups of the unit structure appeared at 4.34 ppm (O-CH$_{2;}$ 4 H), 1.8 ppm (O-CH$_2$-$\underline{CH_2}$, 4H) and 1,31 (CH$_2$, 16 H) (fig. 2). It was found a good correlation between the chemical structure of the resulted copolymer and the molar ration of bisphenol **1** and aliphatic diol **2** used for synthesis.

Except polymer **4f**, all the other polymers were only partial soluble in polar aprotic solvents like N,N-dimethylformamide or N-methylpyrrolidone. 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 rigid conformation that reduces the solubility. The shape of a fragment of polymer **4a**, as evidenced by molecular modeling, is presented in figure 3. In the case of polymers **4b-f** appeared an increase of the flexibility of the macromolecular chains due to the presence of the segments coming from aliphatic diols. The shape of a fragment of polymer **4f**, as evidenced by molecular modeling, is presented in figure 3. As it can be seen from figure 3 the shape of the macromolecular chain is far from one linear, rigid. Due to the higher flexibility of the macromolecular chains polymer **4f** was soluble in polar aprotic solvents like N-methylpyrrolidone and even in low polar solvents like chloroform.

The thermal stability was evaluated by thermogravimetric analysis. The polymers did not show significant weight loss below 360°C. They began to decompose in the range of 370-408°C; they showed 10% weight loss in the range of 382-432°C (table 1). Figure 4 presents typical TGA and differential thermogravimetric (DTG) curves of polymers **4a** and **4f**.


4a

4f

Fig. 3. Model molecules of polymers **4a** (four repeating units) and **4f** (two repeating units)

Table 1
PROPERTIES OF POLYMERS **4**

Polymer	T_g[a] (°C)	T_m[b] (°C)	T_i[c] (°C)	IDT[d] (°C)	T_{10}[e] (°C)	T_{max1}[f] (°C)	T_{max2}[g] (°C)	Char yield at 700°C (%)
4a	160	385.0	-	408	432	479	628	41.0
4b	147	370.5	-	380	400	430	575	16.8
4c	127	369.1	384.9	387	405	450	614	21.2
4d	110	290.3	307.5	375	385	413	568	13.0
4e	94	256.6	275.9	370	382	405	590	11.2
4f	83	233.6	281.4	387	401	421	601	8.4

[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% weight loss; [e] Temperature of 10% weight loss; [f] First maximum polymer decomposition temperature; [g] Second maximum polymer decomposition temperature.

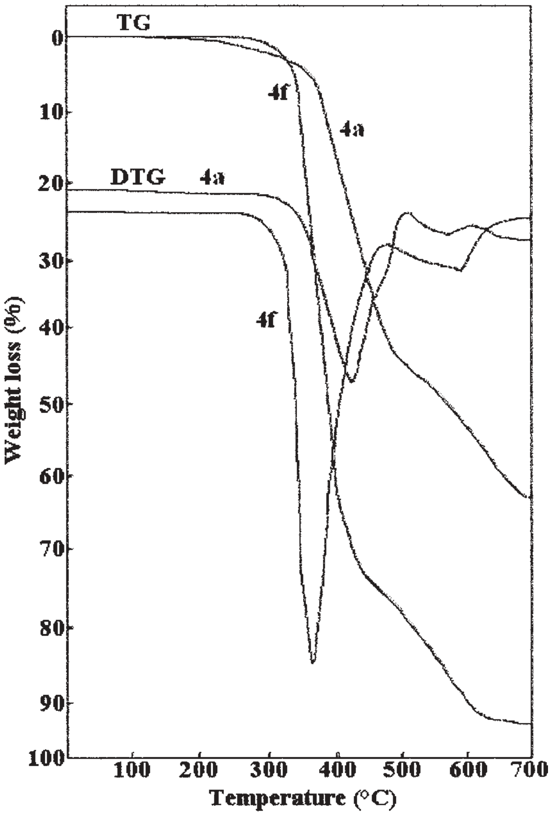


Fig. 4. TG and DTG curves of polymers **4a** and **4f**

As it can be seen from DTG curves, the degradation process exhibited two maxima of decomposition. The first one (T_{max1}) was in the range of 405-479°C and the second maximum of the decomposition (T_{max2}) was in the range of 568-628°C (Table 1). The char yields at 700°C were in the range of 8.4-41%. High char yield was obtained due to the presence of P atom in the unit structures of the polymers. A decrease of char yield at 700°C was observed by introduction aliphatic diols with a higher number of methylene groups. IR spectrum of the solid residue of the polymer **4f**, after heating up to 475°C with the heating rate of 10°C/min, was examined (fig. 1 (b)). The value of 475°C represents the temperature of the end of the first decomposition process, from DTG curve (fig. 4). As it 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. Also, it was observed the disappearance of absorption bands at 2920 cm^{-1} and 2830 cm^{-1} which characterize the methylene groups of the aliphatic segments. The absorption bands at 1600 cm^{-1} and 1500 cm^{-1} which characterize aromatic rings were still presented 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 phosphorous 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 and methylene units with an increase of phosphorous 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, increasing thus the flame retardancy of the polyesters.

The glass transition temperature (T_g) of polymers **4**, evaluated from DSC curves, was in the range of 83-160°C (table 1) being dependent on the nature of the diol **2**. Thus, the fully aromatic polyester **4a** exhibited the highest T_g. The introduction of an aliphatic diol decreased the T_g. It

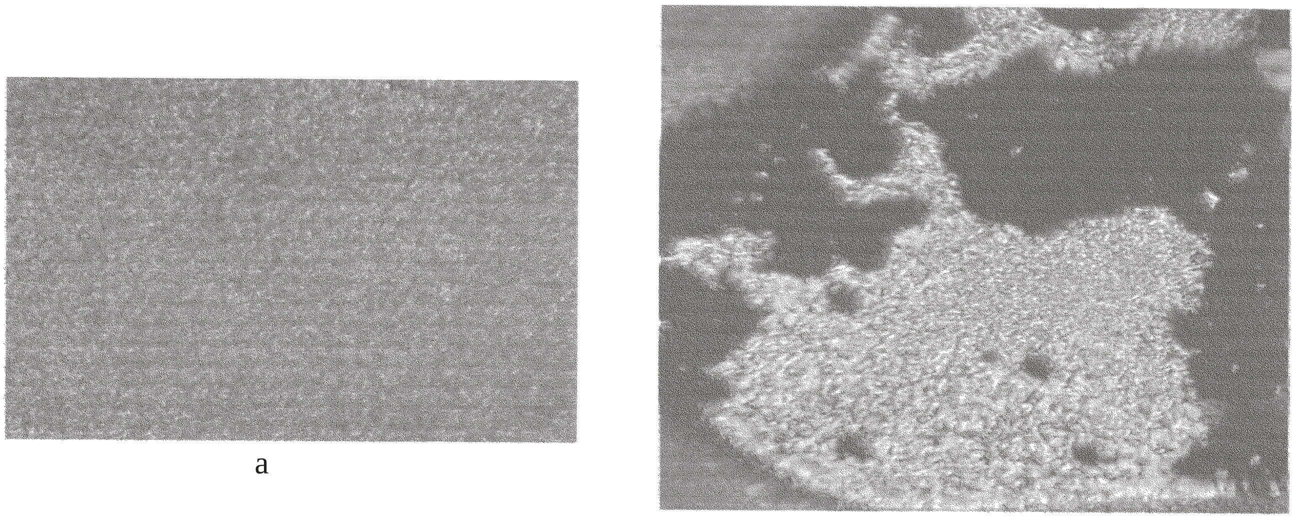


Fig. 5. Optical polarization micrographs (heating cycle, 400x) of polimer 4e at 256.6 °C (a) and 275.8 °C (b)

was observed that the T_g decreased by increasing the number of the methylene groups of the structure of the aliphatic diol. Polymer **4f** derived from dodecanediol exhibited the lowest T_g (83°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 **4** 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 5 presents the nematic phase, as well as the nematic to isotropic phase transition of polymer **4e**.

In general the liquid crystalline behaviour of the copolyesters **4** depends on the nature of the segments coming from the diols **2**. The T_m of the polymers **4a-c** was relatively high, in the range of 369-385°C due to a high rigidity of the macromolecular chains. The isotropic phase for polymers **4a** and **4b** was not clearly detected due to some degradation processes that took place. A decrease of the T_m and T_i was observed for the copolyesters **4c-f** due to the copolymerization effect and the introduction into the macromolelcular chains of aliphatic segments with higher number of methylene groups.

Conclusions

The polycondensation of 2-(6-oxido-6H-dibenzo<c,e><1,2>oxaphosphorin-6-yl)1,4-benzenediol, **1**, or of an equimolecular amount of **1** and different other aliphatic diols with an aromatic diacid chloride containing two preformed ester groups, in *o*-dichlorbenzene, at high temperature, gave aromatic-aliphatic copolyesters. They exhibited good thermal stability, with decomposition temperatures above 360°C and glass transition temperatures in the range of 83-160°C. The presence of P atom in the unit structure of the polymers increased the char yield at 700°C, improving the flame retardancy. The polymers exhibited nematic melt according to observations of their texture on a cross-polarizing microscope.

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