# Synthesis and Properties of Novel Phosphorus-Containing Thermotropic Liquid Crystalline Copoly(ester imide)s

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Received 14 July 2010; accepted 23 August 2010 DOI: 10.1002/pola.24344 Published online 5 October 2010 in Wiley Opline Library (wiley opline library op

Published online 5 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of novel phosphorus-containing polyesterimides were prepared from diols-a mixture of a new aromatic phosphorus-containing bisphenol, namely 1,4-bis[N-(4-hydroxyphenyl)phthalimidyl-5-carboxylate]-2-(6-oxido-6H-dibenz<c,e> <1,2>oxaphosphorin-6-yl)-naphtalene, with aliphatic diols such as 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 1,12-dodecanediol-and an aromatic diacid chloride containing two preformed ester groups, namely terephthaloylbis-(4-oxibenzoyl-chloride), via high-temperature polycondensation in o-dichlorobenzene. The structures of monomers and polymers were verified by means of Fourier transform infrared (FTIR) spectroscopy and <sup>1</sup>H NMR spectroscopy. The molar ratio of aromatic bisphenol to aliphatic diol was varied to generate a series of copolyesterimides with tailored physicochemical properties, structure-properties relationships being established. The effect of the phosphorus content on the thermal properties and the flame retardancy was evaluated by means

**INTRODUCTION** Aromatic polyimides are well known as high-performance polymers because of their high thermal and thermooxidative stabilities, high transition temperatures, and outstanding mechanical, insulating, and chemical resistance properties. Therefore, polyimides have been widely used in many applications such as aerospace, microelectronics, optoelectronics, and information industries.<sup>1-4</sup> However, wholly aromatic polyimides have usually deficiencies in solubility, processability, melting or softening behavior, transparency, and dielectric constant. Significant improvements in the performances of polyimides have been made: fluorination,<sup>2,5</sup> bulky substituents,<sup>6,7</sup> incorporation of asymmetric, noncoplanar, or alicyclic units,<sup>8–10</sup> flexible bridging,<sup>11,12</sup> copolymerization,<sup>13,14</sup> and so forth. From a practical point of view, the most important copolyimides are poly(ester imide)s (PEIs), poly(amide imide)s, and poly(ether imide)s, but other linear copolyimides have also been investigated, such as poly(anhydride imide)s.<sup>15</sup>

Thermotropic liquid crystalline poly(ester imide)s (TLC PEIs) have been developed to achieve both good processability and good mechanical properties. One of the main objecof thermogravimetric analysis (TGA), TGA–FTIR, and scanning electron microscopy. The polymers were stable up to 340 °C showing a 5% weight loss in the range of 340–395 °C and a 10% weight loss in the range of 370–415 °C. The char yields at 700 °C were in the range of 13.6–38% increasing with the content of phosphorus-containing bisphenol. The effect of the aliphatic content on the liquid crystalline behavior was investigated by polarized light microscopy, differential scanning calorimetry, and X-ray diffraction. The transition temperatures from crystal to liquid crystalline melt were in the range of 209–308 °C. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 48: 5391–5403, 2010

**KEYWORDS**: flame retardancy; liquid crystalline polymers (LCPs); phosphaphenanthrene; structure–property relations; thermal properties; thermal stability; thermotropic liquid crystalline poly(ester imide)s

tives in TLC PEIs research has been to reduce the transition temperature to a temperature range that is suitable for conventional processing facilities, equal to or less than about 300 °C. Random copolymerization is an effective approach, which has been used to design TLC PEIs by disturbing the regular molecular structure of the polymer chain. The lack of periodicity along the chain inhibits crystallization and, thus, reduces the crystal size and perfection and depresses the melting transitions  $T_{\rm m}$ . The introduction of kinked linkages into the polymer backbone effectively reduces the regularity of the molecule and lowers the melting temperature. However, the incorporation of kinked units has an unfavorable influence on the liquid crystallinity because the kinks disrupt the molecular linearity. Modification of the p-aromatic backbone with flexible segments is another important way to improve the melt processability. By inserting flexible segments to separate the mesogenic units along the polymer chain, the chemical periodicity of the mesogenic molecule is preserved. The most typical spacer segments used are polymethylene units  $(CH_2)_n$  of varying length *n*. Introducing lateral substituent groups to p-oriented monomers has also been applied to lower the melting points of LCPs. Grafting

Journal of Polymer Science: Part A: Polymer Chemistry, Vol. 48, 5391-5403 (2010) © 2010 Wiley Periodicals, Inc.

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bulky side groups onto the polymer main chain influences the melting temperature in several ways: it effectively increases the interchain distance and reduces the interchain forces so that the efficiency of the chain packing is reduced and the effect is much enhanced by randomly distributing the side chain along the polymer backbone. Kricheldorf, Chung or Lenz have reported investigations on PEIs synthesis, ordered structures, phase transition behavior, morphology, rheology, and crystallization behavior.<sup>16–20</sup>

Actually, the development of new polymeric structures having excellent combined properties required to meet increasing demands and reduce production costs is an important topic in the field of polymer science. There is a great deal of effort in developing less flammable polymer materials. To protect the environment and human health, researchers are focused on exploiting environmental friendly halogen-free fire retardants for plastic materials used in various industries. Phosphorus-containing compounds have received significant attention for many years because they are considered to be the most effective flame retardants, as demonstrated in recent studies.<sup>21-26</sup> Phosphorus-containing polymers tend to char rather than burn; thus, charring provides a diffusion barrier of gaseous products to the flame, shields the polymer surface from heat and oxygen, and reduces the production of combustible gas during polymer degradation.<sup>27</sup>

In the light of these facts, we decided to perform a comprehensive study on the relationship between the aliphatic/aromatic ratio, polymer liquid crystalline phase structure, flame retardancy, and thermooxidative stability of novel synthesized TLC aromatic-aliphatic copoly(ester imide)s based on a new phosphorus-containing monomer, namely, 1,4-bis[N-(4-hydroxyphenyl)phthalimidyl-5-carboxylate]-2-(6-oxido-6Hdibenz<c,e><1,2>oxaphosphorin-6-yl)-naphthalene, a series of aliphatic diols (1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 1,12-dodecanediol), and terephthaloyl bis-(4-oxybenzoyl-chloride).

### **EXPERIMENTAL**

#### Materials

9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (**DOPO**) was purchased from Chemos GmbH, Germany. Naphthoquinone (**NQ**), trimellitic anhydride chloride (**TMAC**), *p*-aminophenol, terephthalic acid, 4-hydroxybenzoic acid, and monomers **1** (1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 1,12-dodecanediol) were provided from Aldrich and used as received. All other reagents were used as received from commercial sources or were purified by standard methods.

# Measurements

Melting points of the monomers and intermediates were measured on a Melt-Temp II (Laboratory Devices). The inherent viscosities of the polymers,  $\eta_{inh}$ , were measured using an Ubbelohde viscometer, at 20 °C by using 0.5 g/dL solutions in *N*-methyl-2-pyrrolidone. Fourier transform infrared (FTIR) spectroscopy was performed on a Bruker Vertex 70 at frequencies ranging from 400 to 4000 cm<sup>-1</sup>. Samples were mixed with KBr and pressed into pellets. <sup>1</sup>H NMR (400 MHz) spectra were obtained on a Bruker Avance DRX 400 spectrometer. The polymer samples were dissolved in DMSO- $d_6$ upon heating and then measured at room temperature or were dissolved in a mixture of solvents (CDCl<sub>3</sub>:  $CF_3COOD =$ 9/1, v/v) at room temperature. Elemental analysis was carried out with a CHNS 2400 II Perkin Elmer instrument. Elemental analysis for phosphorus was performed with molybdenum blue method.<sup>28</sup> Thermogravimetric analysis (TGA) was performed on 15 mg samples under air atmosphere at a heating rate of 10 °C/min using a Mettler Toledo model TGA/SDTA 851 instrument. Pyrolysis residues were collected at various weight losses in the thermogravimetric experiments and were subsequently analyzed by FTIR spectroscopy. In these experiments, samples of about 15 mg were heated to a defined temperature, cooled to room temperature, transferred to Bruker Vertex 70 instrument, and FTIR spectrum was recorded for each sample. The differential scanning calorimetry (DSC) analysis was carried out using a Perkin-Elmer Pyris Diamond instrument using nitrogen as a carrier gas at a flow rate of about 10 mL/min. The samples were first heated from room temperature to 350 °C using a heating rate of 10  $^{\circ}$ C/min and then cooled to 20  $^{\circ}$ C at a cooling rate of 10 °C/min. A second heating and a subsequent cooling were performed in the same conditions. The melting temperatures and the liquid crystalline phase transition temperatures of copoly(ester imide)s 4 were taken as maximum of endothermic peaks. Polarized light microscopy (PLM) was carried out with an Olympus BH-2 polarized light microscope fitted with a THMS 600/HSF9I hot stage, at a magnification of  $200 \times$  or  $400 \times$ . The mesomorphic transition temperature and disappearance of birefringence, that is, the crystal-to-nematic and nematic-to-isotropic transition, were noted. The wide-angle X-ray diffraction (WAXD) experiments at room temperature and variable temperature XRD were performed on a D8 Advance Bruker AXS diffractometer using a  $CuK\alpha$  source with an emission current of 36 mA and a voltage of 30 kV. Scans were collected over the  $2\theta$  = 2–40 range using a step size of  $0.01^{\circ}$  and a count time of 0.5 s per step. 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 deposed on Al supports and coated by sputtering with Au thin films using an EK 3135 EMITECH device.

# Synthesis of the Monomers and Intermediates

Terephthaloyl-bis-(4-oxybenzoylchloride), **2**, was synthesized by treating the corresponding dicarboxylic acid that resulted from the reaction between 4-hydroxybenzoic acid (2 mol) and terephthaloyl chloride (1 mol), with excess thionyl chloride, at reflux temperature, according to a method presented in the literature.<sup>29</sup> m.p.: 223–226 °C.

FTIR (KBr, cm<sup>-1</sup>): 1780 (COCl), 1730 (COO), 1600 (C-C aromatic), and 1210 (Ph-O-OC).

2-(6-0xido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-1,4-naphthalene diol (**DOPO-NQ**) was synthesized from **DOPO** and **NQ** according to the method previously reported





SCHEME 1 Synthetic route of bisphenol 3.

(Scheme 1).<sup>29</sup> It was recrystallized from ethoxyethanol; m.p. (DSC): 279–280 °C.

FTIR (KBr, cm<sup>-1</sup>): 3430 (-OH), 1582 (P-Ph), 1190 (P=O), and 1165 and 925 (P-O-Ph). <sup>1</sup>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), and 6.6 (1H, d).

1,4-[2-(6-Oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]naphthalene-bis(trimellitate)dianhydride was synthesized from **DOPO-NQ** and **TMAC** according to our recently reported procedure (Scheme 1).<sup>30</sup> The crude product was finally recrystallized from anhydrous acetic anhydride.

Yield: 71.8%; m.p.: 295–297 °C; ELEM. ANAL.: Calcd.  $C_{40}H_{19}O_{12}P$  (722 g/mol) (%): C, 66.48; H, 2.63. Found: C, 65.74; H, 2.39; FTIR (KBr, cm<sup>-1</sup>): 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), and 1165 and 928 (P—O—Ph); <sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta$  = 9.05 (2H, s), 8.95 (2H, d), 8.28 (2H, m), 8.09 (1H, d), 8.01

(1H, s), 7.94 (2H, m), 7.73 (4H, m), 7.62 (2H, m), 7.49 (1H, m), 7.25 (1H, m), and 7.07 (1H, d). <sup>31</sup>P NMR (DMSO- $d_6$ , ppm):  $\delta$  = 27.72. UV-vis (DMF, nm):  $\lambda_{abs}$  = 296, 322; PL (DMF, nm):  $\lambda_{em}$  = 401 ( $\lambda_{ex}$  = 340 nm).

1,4-Bis[*N*-(4-hydroxyphenyl)phthalimidyl-5-carboxylate]-2-(6oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)-naphtalene, **3**, was synthesized according to the following synthetic procedure: 4-aminophenol (0.219 g, 0.002 mol), 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis (trimellitate)dianhydride (0.722 g, 0.001 mol), and acetic acid (7 mL) were loaded into a 100-mL three-necked flask, which was equipped with mechanical stirrer. The mixture was heated to reflux and stirred for 8 h. After the completion of the reaction, the mixture was allowed to cool down, filtered off, and washed several times with water. The resulted product was filtered off and dried at 100 °C for 8 h in a vacuum oven. The entire synthetic route of **3** is depicted in Scheme 1.

Yield = 80%. FTIR (KBr, cm<sup>-1</sup>): 3450 (-OH), 3065 (C-H aromatic), 1780 (C=O, imide carbonyl asymmetric stretching), 1730 (C=O, ester carbonyl and imide carbonyl symmetric stretching), 1600 (C-C aromatic), 1478 (P-Ph), 1368 (C-N-C), 1245 (ester C-O), 1205 (P=O), and 1160, 925 (P-O-Ph). <sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta$  = 9.8 (2H, d), 8.69 (2H, d), 8.45 (2H, m), 8.23 (2H, m), 7.95 (6H, m), 7.62 (4H, m), 7.49 (1H, m), 7.29 (5H, m), 7.09 (1H, d), and 6.97 (4H, d). <sup>31</sup>P NMR (DMSO- $d_6$ , ppm):  $\delta$  = 18.7-16.9.

# Synthesis of the Copoly(ester imide)s 4

The polymers **4** were prepared by solution polycondensation reaction of equimolar amounts of aliphatic diols **1**/aromatic bisphenol **3** with aromatic diacid chloride **2** (Scheme 2). A typical polycondensation was run as shown in the following example for the synthesis of homopolymer **4a**: In a 100-mL three-necked flask, which was equipped with nitrogen inlet and nitrogen outlet and a magnetic stirrer, bisphenol **3** (2.712 g, 0.003 mol), diacid chloride **2** (1.329 g, 0.003 mol), and *o*-dichlorobenzene (9.4 mL) were introduced. The reaction mixture was heated to reflux (180 °C) and stirred 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 in a vacuum oven.

Yield: 89%. <sup>1</sup>H NMR (DMSO- $d_6$ , ppm):  $\delta = 8.73$  (d, 2H, aromatic), 8.5–8.16 (m, 8H, aromatic), 8.09–7.85 (m, 6H, aromatic), 7.8–7.5 (m, 11H, aromatic), 7.4–7.11 (m, 8H, aromatic), and 6.94 (m, 4H, aromatic). The same procedure was used to synthesize the copoly(ester imide)s **4b–4f** by reacting 0.114 g (0.0015 mol) 1,3-propanediol, 0.135 g (0.0015 mol) 1,4-butanediol, 0.156 g (0.0015 mol) 1,5-pentanediol, 0.177 g (0.0015 mol) 1,6-hexanediol, and 0.303 g (0.0015 mol) 1,12-dodecanediol, respectively, 1.329 g (0.003 mol) compound **2** and 1.356 g (0.0015 mol) aromatic bisphenol **3**. Copoly(ester imide)s **4g**, **4h**, and **4i** were synthesized by using 0.1515 g (0.00255 mol), 0.4545 g (0.00225 mol), and 0.5757 g (0.00285 mol) of 1,12-dodecanediol and 2.034 g (0.00225 mol), 0.678 g (0.00075 mol), and 0.1356 g



SCHEME 2 Synthesis of the polymers 4.

(0.00015 mol) of diol **3**, based on the above procedure; 1.329 g (0.003 mol) of compound **2** was added for each polymer (Scheme 2). The FTIR and <sup>1</sup>H NMR spectra of copoly(ester imide)s **4b**-**4i** are almost identical differing only in relative signal intensities. For example, copolymer **4e**: FTIR (KBr, cm<sup>-1</sup>): 3066 (=C-H); 2938 and 2856 (-CH<sub>2</sub>--); 1779 (C=0, imide carbonyl asymmetric stretching); 1734 (C=0, ester carbonyl and imide carbonyl symmetric stretching); 1604 and 1501 (C=C, aromatic); 1472 (Ar-P); 1369 (C-N-C); 1267 and 1015 (C-O-C, ester); 1202 (P=0); 1162 and 929 (P-O-C); and 760 and 718 (C-H, aromatic).

### **RESULTS AND DISCUSSION**

The concept of achieving thermal stability, flame retardancy, and liquid crystalline behavior through combination of phosphorus-containing monomers and aliphatic moieties into aromatic mesogenic moieties was successfully applied for the control of thermal stability, phase transitions, and crystallinity degree of aromatic-aliphatic phosphorus-containing copolyesters.<sup>29,31-33</sup> Recently, Wang and coworkers have paid attention to the use of phosphorus-containing TLC polymers for flame retardation on other thermoplastic polymers.<sup>34-36</sup> Thermal stability and flame retardancy of these polymers were excellent, but the mesophase and melting temperatures need to be more decreased. Thus, our aim here was to synthesize a new phosphorus-containing bisphenol, which has preformed imide rings. In terms of flame retardant proper-

ties, phosphorus–nitrogen synergism was expected to induce a high level of fire resistance, providing a dual mechanism of degradation associated with the condensed and gas phases.<sup>27,37</sup>

# Synthesis, Chemical Structure Confirmation, and Mesomorphic Behavior of Monomer 3

The phosphorus-containing bisphenol **3** was synthesized in three steps starting from **DOPO** and **NQ**. In the second step, the obtained aromatic diol, **DOPO-NQ**, was treated with **TMAC** to form a new dianhydride, namely, 1,4-[2-(6-oxido-6H-dibenz<c,e><1,2>oxaphosphorin-6-yl)]-naphthalene-bis (trimellitate)dianhydride. In the last step, the phosphoruscontaining dianhydride was reacted with *p*-aminophenol to form a new bisphenol containing phosphorus and preformed imide rings. The entire synthetic route of **3** is illustrated in Scheme 1. Complete procedures for the synthesis of all intermediates and monomers are described in the "Experimental" section.

The chemical structure of the monomer **3** was confirmed by FTIR, <sup>1</sup>H NMR, and <sup>31</sup>P NMR spectroscopies. The spectra were in good agreement with the proposed molecular structure. Figure 1 shows the FTIR spectrum of bisphenol **3**. The characteristic absorption bands appeared at 3450 cm<sup>-1</sup> due to functional —OH groups and at 1780 and 1730 due to C=O imide carbonyl asymmetric stretching and C=O ester carbonyl and imide carbonyl symmetric stretching. Absorption peaks appeared at 1478 cm<sup>-1</sup> due to P—Ar, at 925 and



1160  $\text{cm}^{-1}$  due to P–O–Ar groups, and at 1205  $\text{cm}^{-1}$  due to P=0 groups. Aromatic C=C bands were found at 1600 and 1500 cm<sup>-1</sup>, whereas aromatic C–H stretching band was found at 3065  $\text{cm}^{-1}$ . The representative <sup>1</sup>H NMR of the monomer 3 is illustrated in Figure 2, with the assignments for all the protons. The monomer **3** shows the characteristic resonances of the phosphaphenanthrene bulky group at 7.62 and 7.29 ppm and of the naphthalene unit at 7.95-7.62 ppm and 7.09 ppm, respectively.<sup>30</sup> The protons  $H_1$ ,  $H_2$ , and  $H_3$ , which are characteristic for the TMAC segment, appeared at higher ppm values (8.69, 8.45, and 8.23 ppm, respectively), whereas the protons  $H_{18}$ , which are closed to the terminal hydroxyl groups, appeared at the farthest up field region of the spectrum. The <sup>31</sup>P NMR spectrum (Fig. 3) provides further information regarding the expected structure of the monomer 3. The single  ${}^{31}P$  signal can be observed for 3 at around 18.7-16.9 ppm, as a split signal (Fig. 3, detailed view) probably because of the presence of different chiral centers in the molecule of  $\mathbf{3}^{26}$ 

Phase characterization of the monomer **3** was performed by DSC, TGA, and PLM. A typical thermogram obtained by DSC of phase transitions of the monomer **3** during the first heating (15 °C/min) is presented in Figure 4(a). An endothermic peak centered at 327.5 °C starts at high temperature (above 300 °C) when heating, which correspond to crystal-liquid crystal transition, due to the fact that the naphthalene ring



FIGURE 2 <sup>1</sup>H NMR spectrum of bisphenol 3.

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can effectively increase the melting points.<sup>38</sup> PLM confirmed that the bisphenol **3** exhibited liquid crystalline phase after melting. Under visual observation, the sample melts around 347 °C exhibiting a fine liquid crystalline texture [Fig. 4(c)], difficult to ascribe but, generally, typical for a nematic phase, whereas the clearing point was not observed up to 430 °C. The 430 °C value, according to the TGA, represents the temperature at which the sample reaches 5% of weight loss [Fig. 4(b)]. Because of the partial decomposition at high temperature, only data from the first heating scan were available.

# Synthesis, Chemical Structure Confirmation, and General Characterization of the Poly(ester imide)s 4

Aromatic–aliphatic copoly(ester imide)s **4** were synthesized from various ratios of 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or 1,12-dodecanediol, **1**, terephthaloyl bis-(4-oxybenzoyl-chloride), **2** (**TBOC**) and **DOPO**containing bisphenol **3**, namely 1,4-bis[*N*-(4-hydroxyphenyl)phthalimidyl-5-carboxylate]-2-(6-oxido-6H-dibenz<c,e> <1,2>oxaphosphorin-6-yl)-naphtalene, by heating the reaction mixture for 20 h at reflux temperature (180 °C) using



FIGURE 3 <sup>31</sup>P NMR spectrum of bisphenol 3.



FIGURE 4 Mesomorphic behavior of monomer **3** [DSC curve, heating scan (a), thermogravimetric analysis (b), and polarized light microscopy micrograph (c)]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

*o*-dichlorobenzene as reaction medium. The reaction system got temporarly homogeneous, and then the polymers precipitated during the polycondensation process. The inherent viscosities of the polymers, measured in *N*-methyl-2-pyrrolidone, were in the range of 0.17-0.27 dL/g (Table 1) suggesting moderate molecular weights for this type of PEIs. Bisphenol **3** contains polar side-chain **DOPO** groups responsible for the enhanced rigidity and polarity of the polymeric chains, which can subsequently reduce the reactivity of functional end groups and hindrance further propagation of the polycondensation process.

The structure of the resulting polymers was investigated by FTIR and <sup>1</sup>H NMR spectroscopies. Figure 5 shows the FTIR spectrum of polymer **4a**, as an example. As can be seen from FTIR, the most important absorbtion bands are associated with aromatic C—H (3066 cm<sup>-1</sup>, stretching vibration), C=O groups of imide rings and ester linkages (1780 and 1734/1705 cm<sup>-1</sup>, asymmetrical and symmetrical stretching vibrations), ester C—O—C (1244 and 1015 cm<sup>-1</sup>, asymmetric and symmetric stretching vibrations), P—O—Ar (925 and 1160 cm<sup>-1</sup>, stretching vibrations), P—Ar (1470 cm<sup>-1</sup>), P=O (1203 cm<sup>-1</sup>), aromatic C—H (756 cm<sup>-1</sup>, deformation vibration caused by the 1,2-disubsituted aromatic **DOPO** rings), and

thaloyl ring<sup>39,40</sup>) together with imide ring deformation (725  $cm^{-1}$ ). Aromatic C=C bands were found at 1601 and 1501  $\mathrm{cm}^{-1}\!.$  The FTIR spectra also showed a broad weak absorbtion peak centered at 3454 cm<sup>-1</sup>, which is characteristic of the stretching vibration of unreacted OH groups. A longer reaction time did not lead to the disappearance of such weak absorbtion bands. The <sup>1</sup>H NMR spectrum of the polymer 4f (recorded in  $CDCl_3$ :  $CF_3COOD = 9:1$ , v/v) is presented in Figure 6 with the assignments for all the protons. The protons  $H_{9}$ ,  $H_{10}$ , and  $H_{11}$  closed to imide ring appeared at higher ppm in the <sup>1</sup>H NMR spectrum (8.95-8.35 ppm). The protons coming from **DOPO-NQ** unit appeared in the range of 7.90-7.25 ppm. The polymers 4b-4i showed characteristic peaks of the aliphatic protons, one singlet which corresponds to the methylene groups located in the  $\alpha$ -position of the ester linkages (0– $CH_2$ ,  $4H_1$ ,  $\delta \simeq 4.35$  ppm) and one singlet which corresponds to the methylene groups located in the  $\beta$ -position of the ester linkages, respectively  $(O-CH_2-CH_2, 2H_2)$  for polymer **4b**, or  $4H_2$  for the others,  $\delta~\cong~$  1.73 ppm). In the case of polymers **4f-4i**, the peak characterizing the other methylene groups of the structural unit (*CH*<sub>2</sub>, 16*H*<sub>3</sub>) appeared at  $\delta \cong 1.47$ –1.24 ppm. From the <sup>1</sup>H NMR spectra of the copolymers, it was found that the

aromatic C-H (deformation vibration from aromatic tereph-

TABLE 1 The Visco	sity and Thermo	ogravimetric Data	of Polymers 4
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Polymer	$\eta_{\rm inh}$ (dL/g)	IDT <sup>a</sup> (°C)	<i>T</i> <sub>10</sub> <sup>b</sup> (°C)	T <sub>max1</sub> <sup>c</sup> (°C)	T <sub>max2</sub> <sup>d</sup> (°C)	Char Yield at 700 $^\circ\text{C}$ (%)
4a	0.17	355	390	425	615	33.6
4b	0.20	340	370	410	645	30
4c	0.21	365	385	400	615	38
4d	0.22	365	375	400	590	30
4e	0.19	360	370	385	595	28.8
4f	0.23	375	400	420	620	27.6
4g	0.27	395	415	445	595	36.4
4h	0.25	375	385	400	585	18.4
4i	0.22	385	400	410	600	13.6

<sup>a</sup> Initial decomposition temperature = the temperature of 5% weight loss.

<sup>b</sup> Temperature of 10% weight loss.

<sup>c</sup> First maximum polymer decomposition temperature.

<sup>d</sup> Second maximum polymer decomposition temperature.



composition of the polymer is similar with the composition of the reactants used in the synthesis.

The solubility of the polymers **4** was tested in various solvents, by using 15 mg polymer/mL solvent, at room temperature. All the polymers **4** were easy soluble in DMAc, in NMP and DMSO they were soluble after heating the solutions, whereas in solvents such as DMF or CHCl<sub>3</sub> they were only partially soluble. The lower solubility of the polymers **4** 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.

# Thermal Analysis of the Poly(ester imide)s 4

The thermooxidative stability of the polymers was evaluated by TGA in air at a heating rate of 10  $^\circ$ C/min; the traces of

polymers **4a**, **4f**, **4h**, and **4i** are shown in Figure 7. The most important TGA data (the initial decomposition temperature, temperature of DTG peaks, and the yields of char residue at 700 °C) are presented in Table 1. TGA revealed that the polymers were stable up to 340 °C showing a 5% weight loss in the range of 340–395 °C and a 10% weight loss in the range of 370–415 °C.

As can be seen from the differential thermogravimetric curves (DTG), phosphorus-containing PEIs decomposed in two-stage weight loss process. The first maximum of decomposition ( $T_{max1}$ ) was in the range of 385–445 °C and was due to the decomposition of ester units and aliphatic moieties, which were more sensitive to degradation. The second maximum of the decomposition ( $T_{max2}$ ) was in the range of 585–645 °C and was due to the degradation of aromatic polymer chain itself (Table 1). For a better understanding of the degradation mechanism and fire retardancy, the thermal



FIGURE 6 <sup>1</sup>H NMR spectrum of polymer 4f.



FIGURE 7 TG and DTG curves of the polymers 4a, 4f, 4h, and 4i.

decomposition behavior of the polymers was studied through FTIR-TGA and SEM-TGA analysis. The FTIR spectra of the polymer **4e** and the solid residue of the polymer **4e**, after heating the sample up to 500 °C, are presented in Figure 8. The value of 500 °C represents the temperature of the end of the first decomposition process from DTG curve, which corresponds to a 44% weight loss. At this stage, a decrease in intensity of the aliphatic C—H (2938 and 2856 cm<sup>-1</sup>) and the disappearance of C—O—C ester absorption bands (1244 and 1015 cm<sup>-1</sup>), associated with the decomposition of the

ester units followed by the volatilization of the aliphatic moieties from the macromolecule, can be observed (Fig. 8). After heating the sample up to 500  $^{\circ}$ C, the 1734–1717 cm<sup>-1</sup> region, which represents two carbonyl peaks [Fig. 8(a)], transformed into one band with the overall absorption at 1720 cm<sup>-1</sup>, whereas the imide C=O appeared at 1776 cm<sup>-1</sup> in one more intense absorption band, suggesting the destruction of the ester groups from the macromolecular chains with an increase of the aromatic (1600 and 1503  $\text{cm}^{-1}$ ) and heteroaromatic content. The organophosphorus P-O-C group incorporated in the solid residue is distinguishable by the absorption band at 939  $\text{cm}^{-1}$ . The characteristic bands of P-C and P=0 were observed at 1467 and 1194  $cm^{-1}$ , respectively, indicating the presence of phosphorus in the solid residue. It can be concluded that in the first step of degradation, the destruction of aliphatic moieties and ester groups with an increase of phosphorus content took place, as the characteristic bands of P-C and P=O are still present in the solid residue at 500 °C. It has been demonstrated that the inherent flammability of many synthetic polymers can be decreased by increasing their char-forming tendency.41-43 The residual char reduces the rates at which the formation of volatile fuels are generated from pyrolysis and subsequent combustion, acts as a barrier to heat spread and flame penetration, and consequently reduces the flame propagation rates. Furthermore, the chars of polymers are easily oxidized in air when they are heated above 500 °C; therefore, the resistance of polymeric char to thermal oxidation strongly affects polymer flammability. A more compact structure of the generated char led to a better resistance against heat and oxygen admission to the polymeric substrate.<sup>44</sup> The SEM images of the residues of the polymers 4a and 4e obtained after heating the samples up to 510 and 500 °C, respectively, are shown in Figure 9. The char from 4a displayed a more compact structure [Fig. 9(a)] when compared with the char from **4e**, supporting the results obtained by FTIR-TGA, which indicated that the aliphatic content of the polymers 4 was released after the first step of decomposition process, penetrating through the char and, thus, giving a less compact



FIGURE 8 FTIR spectra of polymer 4e, sample at room temperature (a) and sample heated up to 500 °C (b).



FIGURE 9 SEM micrographs of solid residue obtained from polymers 4a at 510 °C (a) and 4e at 500 °C (b).

structure of the char [Fig. 9(b)]. This agreed with the high char yield at high temperature. The char yields at 700  $^{\circ}$ C were in the range of 13.6–38% (Table 1) increasing with the content of phosphorus-containing bisphenol **3**. Therefore, the efficiency against heat transfer and air access from the surface to the inner substrates of the polymeric residue and the better inhibition of the effectively flame spread can be controlled by increasing the content of the phosphorus-containing monomer into the final polymeric matrix.

### **Thermal Transitions Behavior**

The thermal properties and the phase transition temperatures of the polymers **4**, obtained during the first heatingcooling cycle, are determined by DSC, and the data for **4a**, **4f-4i** are summarized in Table 2. The data listed in Table 2 revealed a considerable effect of molecular structure on the melting temperatures and mesomorphic properties as will be discussed in this section. Figure 10 shows the DSC heating-cooling curves of the polymer **4i** at a heating rate of 10 °C/min. The DSC curves showed multiple melting endotherms. The phenomenon of multiple melting was reported in many articles as a feature in common for liquid crystalline polymers.<sup>45-48</sup> Multiple melting behavior has previously attributed to reasons including the presence of different crystal structures<sup>49,50</sup> to crystal reorganization<sup>51,52</sup> or to dif-

ferent components of the morphology formed in multiple stages of crystallization.<sup>53</sup> The as-synthesized copolymer 4i (Fig. 10, H-1 curve) exhibited multiple melting endotherms ( $T\sim$ 167, 178, 196, and 204 °C), a very tiny endotherm (indicated by arrow, 238 °C) corresponding to a smectic-to-nematic transition and finally a broad endothermic peak at 304 °C corresponding to the nematic-to-isotropic transition. Upon cooling from isotropic state (310 °C) to room temperature, the copolymer **4i** showed a tiny broad peak ( $T \sim 183$  °C) corresponding to a liquid crystal-to-liquid crystal transition and a sharp crystallization exotherm ( $T \sim 138$  °C) with a shoulder at 146 °C, whereas the isotropic-to-nematic transition was not observable (Fig. 10, C-1 curve). Second heating scan of the copolyester 4i after cooling from the mesomorphic state transformed the multiple melting peaks into one major endotherm ( $T \sim 157$ ), whereas the mesomorphic transition and isotropization transition were not observable. The first heating run for the copolymer 4h exhibited similar behavior with multiple melting endotherms and relevant mesomorphic smectic-to-nematic transition, but the isotropization transition was not detected and the first cooling scan did not show the expected exotherms (Table 2). The disappearance of the endotherms and exotherms in the second heating-first cooling scans can be explained by the fact that the different crystalline structures induced by the solvent used in the

<b>TABLE 2</b> Phase Transitior	Temperatures o	of Synthesized	Polymers 4
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	Transition Temperatu	Transition Temperature in °C <sup>a</sup>		
Polymer	First Heating	First Cooling	in °C, from PLM <sup>b</sup>	
4a	K293N(–)I	I(–)N(–)K	K308LC > 400I	
4f	K <sub>1</sub> 177K <sub>2</sub> 186(189)N(-)I	I(-)N165K	K259LC > 400I	
4g	K172N(–)I	I(-)N(-)K	K291LC > 400I	
4h	K <sub>1</sub> 180K <sub>2</sub> 200(207)Sm239N(–)I	I(-)N(-)Sm145K	K213LC369I	
4i	K <sub>1</sub> 167(178)K <sub>2</sub> 196(204)Sm(238)N304I	I(-)N183Sm146(138)K	K209LC312I	

K, K<sub>1</sub>, K<sub>2</sub>, solids; Sm, smectic phase; N, nematic phase; I, isotropic phase; LC, liquid crystalline phase; (–), peak temperature not observed by DSC.

<sup>a</sup> Peak temperatures from DSC were taken as the phase transition temperature.

 $^{\rm b}$  Phase transition temperature taken from PLM observation, first heating cycle at a heating rate of 10  $^\circ \rm C/min.$ 



FIGURE 10 DSC thermogram of polymer 4i, H-1, first heating and C-1, first cooling.

synthesis stage can be influenced by thermal treatment.<sup>45</sup> The DSC trace of the polymer **4a** did not show a multiple melting behavior, but a melting endotherm appeared at about 293 °C, and the liquid crystalline to isotropic state transition did not appeared up to 350 °C. The polymers **4a**-**4e** and **4g** that have no or small aliphatic content (n = 3-6, Scheme 2) exhibited enantiotropic mesophases and revealed

nematic phases (N, fine textures and schlieren textures), whereas the copolyesters **4f**, **4h**, and **4d** with a higher content of long methylene segment as spacer lengths exhibited enantiotropic mesophase and revealed smectic phases (SmA, fan-shape texture) because of the increasing of molecular interaction of the macromolecules. As shown in Table 2, introduction of laterally attached **DOPO** bulky groups does not affect the LC properties in small amounts, but increasing the content of aromatic diol decreased the ability of the polymers **4a** and **4g** to form more ordered liquid crystalline phases. The result suggests that the sterically hindered **DOPO** group might decrease the molecular interaction between macromolecules leading to the appearance of the less ordered liquid crystalline mesophases.<sup>33</sup>

# **Texture Analysis**

Polarizing light microscopy was used to identify the liquid crystalline phases and to complement the phase transitions observed by DSC. Optical micrographs of different textures are shown in Figure 11. The data of the mesomorphic transition temperatures ( $K \rightarrow LC \rightarrow I$ ) are given in Table 2. A suitable amount of sample for each polymer was charged between two clean glass plates. The samples were heated up to clearing point, which is considered as the liquid crystalline to isotropic state transition. The transition temperatures from crystal to liquid crystalline melt were in the range of



**FIGURE 11** Optical micrographs of polymers **4**: (a) polymer **4a** heating cycle at 365 °C, fine texture; (b) polymer **4i** cooling cycle at 288 °C showing fine droplets appearance from the isotropic state; (c) polymer **4i** second cooling cycle at 238 °C showing a fanshaped texture (SmA phase); and (d) polymer **4i** second cooling cycle at 221 °C showing a fingerprint texture.

TABLE 3 X-Ray Diffraction Data for Some of the Polymers 4

Polymer	Peak (2θ) (°)	<i>d</i> -Spacing (Å)	Intensity (%)	Crystallinity (%)
4a	3.6	24	67	39
	19.9	4.4	100	
	23.0	3.9	68	
4e	3.6	24.3	69	36
	19.4	4.6	100	
	23.3	3.8	61	
4f	3.5	24.9	65	28
	19.6	4.5	61	
	23.3	3.8	39	
4g	3.6	24.7	66	32
	19.3	4.6	90	
	20.9	4.2	63	
	23.4	3.8	60	
4i	2.2	39.8	64	43
	2.8	31.5	79	
	5.2	16.9	17	
	19.4	4.6	100	
	21.4	4.2	37	
	23.4	3.8	75	

209-308 °C and depended on the aliphatic content, polymer **4a** having the highest value for the transition  $K \rightarrow LC$  (308) °C). The LC  $\rightarrow$  I transition temperatures for **4i** and **4h** were 312 and 369 °C, respectively. For the polymers 4a-4g, this transition cannot be found in PLM investigation because these PEIs had too high  $T_i$  to match the limiting temperature of the hot stage of PLM (400 °C).  $T_i$  greatly depends on the content of phosphorus-containing bisphenol 3, which has preformed imide rings. As seen in Table 2, the broad mesophase temperature range makes these polymers interesting from practical point of view.<sup>54</sup> The transition temperatures of the polymers 4 obtained by PLM were compared with those measured by DSC measurements. These two methods gave comparable results as seen in Table 2. The observed differences could be explained by the variation of heatingcooling rate, amounts of the sample used for the measurements, or the presence of the different atmosphere (nitrogen, in the case of DSC, and air, in the case of the PLM investigation).

Upon heating all as-synthesized polymers **4** formed fine textures [Fig. 11(a)], difficult to ascribe to a smectic or nematic phase, but similar to those reported for thermotropic polymers based on terephthaloyl-bis(4-oxyphenylene carbonyl) units.<sup>20,55,56</sup> Upon cooling from the isotropic state, the polymers **4** behave different as a function of the aliphatic content. The flexible methylene spacer groups separate the mesogenic alignment, thereby reducing the overall rigidity. Thus, the polymers **4i** and **4h** containing a higher ratio of 1,12-dodecanediol seem to form textures typical of smectic phases, whereas the polymers with a smaller content of methylene groups in the structural unit (4b-4g) loose the ability to organize into more ordered phases and displayed only fine threaded textures, typical of nematic phases. For example, in the case of the polymer **4i**, upon cooling at a rate of 5 °C/min, some tiny birefringent droplets start to appear from the isotropic state [Fig. 11(b)]. On continued cooling, these tiny droplets organize in some Schlieren droplets [Fig. 11(b), down left corner] or they grow and populate the whole microscopic view developing interesting fingerprint textures [Fig. 11(b), down right corner]. On the second cooling run, when the temperature approaches 238 °C (the temperature corresponding to smectic-to-nematic transition from DSC, first heating), under shearing the nematic disclination structures transforms into more ordered phase showing a fan-shaped texture, suggestive of a smectic A phase [Fig. 11(c)] or a fingerprint texture [Fig. 11(d)]. The polymer 4h features similarly, whereas the polymers 4a-4g displayed only threaded nematic textures over the melting temperatures.

### **X-Ray Measurements**

The mesophase of the polymers was also characterized through X-ray diffraction measurements. The XRD data (percentage crystallinity, peaks intensity, d-spacing values, and Bragg angles) of the polymers 4a, 4e, 4f, 4g, and 4i, respectively, obtained at room temperature are summarized in Table 3. Representative XRD curve for **4i** at room temperature is shown in Figure 12. The sample 4i showed sharp and strong peaks at low angle ( $2\theta \approx 2.2^{\circ}$ ,  $2.8^{\circ}$ , and  $5.2^{\circ}$ , respectively) suggesting d-spacing near 39.8, 31.5, and 16.9 Å, respectively, and strong sharp peaks in wide angle (2heta pprox19.4° and 23.4°) indicating *d*-spacing near 4.6 and 3.8 Å, respectively, confirming the results obtained from DSC and PLM investigations. Other studied polymers showed relatively broad reflections at wide angles (associated with the lateral packing) and only one weak sharp reflection at small angles (associated with weak smectic layers),<sup>57</sup> which evidenced the inability to identify smectic organizations under DSC and PLM observations. Furthermore, the intensity of sharp reflection at low angle increased with the number of  $-CH_2$  and with increasing the molar ratio of the aliphatic monomer indicating strengthening smectic layer structure. It can be concluded that the intermolecular distance of the polymer chains became smaller by decreasing the content of



FIGURE 12 Wide-angle X-ray diffractogram of polymer 4i.

bulky phosphorus-containing groups laterally attached to the macromolecular chains.<sup>33</sup> The percent crystallinity of the polymers was determined by bisecting the experimental plot into crystalline domain and amorphous domain by curve fitting. The areas under the crystalline and amorphous domain are determined computationally, and the percentage crystallinity was calculated. The percentage crystallinity varies from 28 to 43%, for the studied polymers, depending slightly upon aliphatic segment content in the polymer (Table 3). The percentage crystallinity decreased by introducing equimolecular amounts of 3 and 1,6-hexanediol or 1,12-dodecanediol, respectively, when compared with polymer 4a. Decreasing the molar ratio of 1,12-dodecanediol in 4g slightly increased the percentage crystallinity from 28 to 32% (4f vs. 4g, Table 3), illustrating that the molecular packing is disrupted by difference in the size of comonomer units and also by random comonomer sequences.<sup>58</sup> The polymer 4i that contains the smallest quantity of aromatic bisphenol 3 in the structural unit of the macromolecular chain exhibited the highest value for the percentage crystallinity.

### **CONCLUSIONS**

A series of main-chain LC PEIs bearing bulky phosphoruscontaining groups were synthesized by using various aliphatic diols, the mesogenic terephthaloyl-bis-(4-oxibenzoylchloride), and a new LC phosphorus-containing monomer. The chemical structures of the monomers and polymers were characterized with FTIR and <sup>1</sup>H NMR spectroscopies. The liquid crystalline phases were confirmed by DSC and Xray diffraction experiments and were also compared with the PLM observations. The samples 4a-4g exhibited nematic phases upon heating and cooling, whereas the samples 4h and 4i displayed both smectic and nematic phases. The mesomorphic transition temperatures of the synthesized polymers decreased by increasing the number of methylene units in the macromolecular chain (polymers 4b-4f). Also, the mesomorphic transition temperatures decreased with the increase of the aliphatic molar ratio in the polymer backbone (polymers 4f-4i). Broad mesophase temperature ranges were observed for these polymers, making them interesting from practical point of view. The thermal properties and the flame retardancy of the polymers were evaluated by means of TGA, TGA-FTIR, and SEM. The TGA results showed that 5% weight loss temperatures were greater than 340 °C for all the polymers, and the residue at 700 °C increased with the increase of phosphorus-containing units in the macromolecular system.

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.

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