Thermal Stability of Some Phosphorus-Containing Polyesters and Polyesterimides

TACHITA VLAD-BUBULAC1, CORNELIU HAMCIUC4*, OANA PETREUS1, GABRIELA LISA1
1 Institute of Macromolecular Chemistry "Petru Poni", 41A Gr. Ghica Voda, Iasi-700487, Romania
2 "Gh. Asachi" Technical University Iasi, Faculty of Industrial Chemistry, Bd. D. Mangeron 71, Iasi-700050, Romania

The thermal decomposition behaviour of some phosphorus-containing polyesters and a polyesterimide was studied using thermogravimetric analysis in air at several heating rates between 5°C/min and 20°C/min. The results of this study, realized for polyesters with phosphorus linkage as pendant group, were compared with the behaviour of some polyesters having the same backbone structure, with phosphorous in the main chain, respectively without phosphorous. A kinetic model of the reaction order was also proposed for thermal degradation of studied polymers by using Vyazovkin method.

Keywords: phosphorus-containing polymers, thermal degradation, flame retardant properties

Aromatic polyesters and polyesterimides are wholly well-known to show good physical properties [1, 2]. These polymers can be considered as advanced materials used in electronic devices and fibre composites due to their excellent mechanical properties, improved processability, good thermal, chemical, and dimensional stabilities. They have the disadvantage of poor melt-processibility because they possess high melting and isotropization temperatures. Several structural modifications of this class of polymers are essential for decreasing their thermal decomposition during processing, such as the incorporation of bulky substituents, the introduction of non-coplanar systems and the use of non-linear or kinked monomers.

An attractive synthetic approach to reduce melting temperatures and to improve the solubility of the polymers is the incorporation of pendant groups along the polymer backbone. The utilization of monomers containing 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. Moreover, incorporation of DOPO units into polymers also brought improved flame retardancy, thermal oxidative stability, good adhesion and low birefringence [3-10].

In a continuing effort to develop flame retardant polymers for practical applications, we have prepared phosphorus-containing copolymesters and polyesterimides [11-14]. In this article, we report the degradation behaviour of some aromatic copolymesters containing phosphorus linkages in the main chains and/or in the side chains. Also we present the degradation behaviour of an aromatic polyesterimide with phosphorus linkages in the side chains. For comparison phosphorus-free aromatic polyester and polyesterimide have been prepared and their thermal behaviour was also investigated. The thermal degradation of the polymers was studied by dynamic thermogravimetric analysis, in air, at different heating rates. A kinetic model of the reaction order was proposed for thermal degradation of studied polymers by using Vyazovkin method.

Experimental part
Phosphorus-containing polyesters 1a and 1b were prepared by melt polycondensation of hydroquinone or 2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)-1,4-benzenediol with phenyl phosphonic dichloride followed a method previously described [11]. Polyesters 1c and 1d were synthesized by polycondensation of hydroquinone or 2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)-1,4-benzenediol with terephthalic acid using SOCl2/pyridine condensing agent [12]. Polyesterimides 1e and 1f were prepared by poly-condensation in solution at high temperature of hydroquinone or 2-(6-oxido-6H-dibenz<c,e><1,2> oxaphosphorin-6-yl)-1,4-benzenediol with 4-chloroformyl-N(p-chloroformylphenyl)-phthalimide [13]. The structure of the polymers 1 is presented in scheme 1.

Infrared (IR) spectra were recorded with a Spectord M80 spectrometer by using KBr pellets.

Thermogravimetric analysis (TGA) was performed using a MOM Derivatograph (Hungary) in air, at different heating rates: 5°C/min, 10°C/min and 20°C/min.

Results and discussion
The synthesis of the polyesters and polyesterimides was presented elsewhere [11-13]. The structure of the polymers was identified by IR spectroscopy. All polyesters that contain phosphorus in the main or side chain showed characteristic absorption peaks at 3070 cm−1 (C-H), 1600 cm−1 and 1500 cm−1 (aromatic C=C), 1160 cm−1 and 925 cm−1 (P-O-Ar groups), 1470 cm−1 (P-Ar groups), 1205 cm−1 (P=O groups). Polyesters 1c and 1d showed also characteristic absorption peak at 1740 cm−1 due to carbonyl asymmetric stretching of ester group. Polyesterimides 1e and 1f showed also characteristic absorption peaks at 1740 cm−1 due to carbonyl asymmetric stretching of ester group. Polyesterimides 1e and 1f showed also characteristic absorption peaks at 1780 cm−1, 1720 cm−1, 1390 cm−1, 1100 cm−1 and 720 cm−1 characteristic to different stretching for imide carbonyl or imide ring.

The inherent viscosity of the polymers was in the range of 0.2-0.5 dL/g, determined with an Ubbelohde viscometer, by using polymer solutions in N-methylpyrrolidone, at 20°C, at a concentration of 0.5 g polymer/100 mL solvent.

The thermal stability of the polyesters was evaluated by dynamic thermogravimetric analysis in air, at three different heating rates 5°C/min, 10°C/min and 20°C/min. Figure 1 shows the TGA curves of polymers 1, with the heating rate of 10°C/min. The thermogravimetric data are also listed in table 1.

* email: hamciuc@yahoo.co.uk.
All phosphorus-containing polyesters \( \text{1a, 1b, 1d, and 1f} \), exhibited two stages of decomposition, while the degradation process of phosphorus free polymers \( \text{1c and 1e} \) presented only one step of decomposition. The thermogravimetric characteristics presented in table 1 could offer only a general comparison between two kinds of polyesters, with phosphorus and without it.

It is interesting to observe that all phosphorus containing polyesters as a pendant group exhibited higher thermostability. Polymer \( \text{1a} \) containing phosphorus only in the main chain had the lowest thermal stability. When phosphorus is present both in the main and side chain (\( \text{1b} \)), higher thermostability was observed. The unusual high thermal stability of 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 formed char acts as a protective layer for the polymer main chain. Even the phosphorus content for \( \text{1a and 1b} \) is nearly similar, the char residue for \( \text{1b} \) is higher. This is a conscience of enhanced aromaticity of the polymer that leads to a higher content of carbon in the

### Table 1

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Stage 1 ( T_i^a )</th>
<th>Stage 2 ( T_f^b )</th>
<th>( W^a )</th>
<th>( T_i^c )</th>
<th>( T_f^d )</th>
<th>( W^e )</th>
<th>( T_{max}^f )</th>
<th>( T_{max}^g )</th>
<th>Char yield at 700°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{1a} )</td>
<td>220</td>
<td>470</td>
<td>52.00</td>
<td>470</td>
<td>700</td>
<td>30.00</td>
<td>346</td>
<td>525</td>
<td>18.00</td>
</tr>
<tr>
<td>( \text{1b} )</td>
<td>320</td>
<td>520</td>
<td>52.00</td>
<td>520</td>
<td>700</td>
<td>15.40</td>
<td>475</td>
<td>631</td>
<td>32.60</td>
</tr>
<tr>
<td>( \text{1c} )</td>
<td>330</td>
<td>700</td>
<td>87.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>478</td>
<td>-</td>
<td>10.40</td>
</tr>
<tr>
<td>( \text{1d} )</td>
<td>345</td>
<td>470</td>
<td>30.60</td>
<td>470</td>
<td>700</td>
<td>32.40</td>
<td>441</td>
<td>549</td>
<td>35.00</td>
</tr>
<tr>
<td>( \text{1e} )</td>
<td>380</td>
<td>700</td>
<td>82.80</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>486</td>
<td>-</td>
<td>10.20</td>
</tr>
<tr>
<td>( \text{1f} )</td>
<td>360</td>
<td>490</td>
<td>39.40</td>
<td>490</td>
<td>700</td>
<td>37.80</td>
<td>453</td>
<td>552</td>
<td>20.80</td>
</tr>
</tbody>
</table>

\( ^a \) First process of polymer decomposition; \( ^b \) Second process of polymer decomposition; \( ^c \) First temperature corresponding to the maximal degradation rate; \( ^d \) Second temperature corresponding to the maximal degradation rate; \( ^e \) Initial temperature of a decomposition process; \( ^f \) Final temperature of a decomposition process; \( ^g \) Weight loss of the polymer after the end of a decomposition process.

\( \text{Scheme 1} \)

Chemical structure of polyesters and poly(ester-imide)s

\( \text{Table 1} \)

THERMOGRAVIMETRIC CHARACTERISTICS FOR THE HEATING RATE OF 10°C / min

\( \text{Fig. 1. TG curves of polymer 1} \)
residue. Also, polyester 1d exhibited higher thermal stability and higher char residue. The presence of phosphorus pendant group in the case of the polymer 1f, when higher thermostable imide ring is present in the structural unit, did not influence significantly the thermal resistance.

For establishing the influence of heating rate on thermal stability, thermograms at three heating rate of 5°C/min, 10°C/min and 20°C/min for the interested thermal domain have been recorded. The discussions presented previously are based on the kinetic model of the „reaction order”. A rigorous study includes the nucleation process. As a consequence, the Vyazovkin method has been used [15-17].

In solid-state kinetics, the concept of reaction model, as a representative of the mechanism, started to form in the 1920, when MacDonald and Hinshelwood [18] introduced the idea of the formation and growth of product nuclei in a decomposing solid. This idea spurred intensive development of mechanistic models. Galwey and Brown [19] give the most recent compendium of the reaction models. Table 2 collect together some of these models.

The mechanistic interpretations of solid-state kinetics are based on the concept of single-step reaction as given by equation:

$\frac{da}{dt} = k \cdot f(\alpha)$  \hspace{1cm} (1)

were f(\(\alpha\)) is the reaction model that represents a certain solid-state mechanism. The concept of the reaction model suggests that solid-state mechanisms give rise to the characteristic \(\alpha\) versus t or \(\frac{da}{dt}\) versus t plots or mathematical functions (i.e. f(\(\alpha\))). Then one can compare experimental data against a set of the model plots and choose the model that accurately reproduces data. This enables the data to be interpreted in terms of the mechanism represented by the chosen reaction model. To choose the model, one can use the reduced time plots of a against t or \(\frac{da}{dt}\) against \(\alpha\) (usually 0.5 to 0.9). According to the integral form of equation (1), that is

$$g(\alpha) = \int_0^\frac{a}{\alpha} \frac{da}{f(\alpha)} = k \cdot t \hspace{1cm} (2)$$

the reduced time plots are independent of the temperature, if the concept of a single-step reaction holds.

The results for the dependence of activation energy (E<sub>a</sub>) versus conversion degree in the first stage of thermal degradation for polymers 1a, 1b, 1d, 1f are presented in figure 2. All the polymers that contain phosphorus in a pendant group presented an approximate linear relation between E<sub>a</sub> and conversion degree. It is interesting that at higher conversion degree the activation energy tends to increase when phosphorus group is in the main chain and is lower for phosphorus linkage in side chain.

The second stage of decomposition is presented only for phosphorus containing polymers (Figure 3). An increase of E<sub>a</sub> versus conversion degree could be observed. We suppose that in this stage, especially at higher degree of conversion, thermostable structures were formed, which needs more energy for pyrolysis. The highest E<sub>a</sub> at higher conversion degree could be observed for polyesterimide 1f.

Analysing the thermal degradation of polymers 1c and 1e, taking place in one step, we can observe the same relation between E<sub>a</sub> and conversion degree: at higher conversion degree E<sub>a</sub> increases for polyesterimide 1e (fig. 4). We can conclude that the rigidity of the polymer backbone or the presence of stable imide groups in the main chain had also a great importance for the thermostability of the polymer.

The type of the reaction model used for the description of the thermal degradation process of each polymer has been established. The obtained results are presented in table 3.

The analysis of the obtained results lead to the conclusion that the model of the degradation process for polymers 1a, 1b, 1c, 1e and 1d is specific to the random
nucleation according to the kinetic laws specific for mononuclear reactions. For the polymer 1f, the model of the thermal decomposition in the first stage indicates that the reactions are controlled by diffusion and volume nuclei growth. The same conclusion arises from the analysis of the second stage of thermal degradation of polymer 1b, the other polymers, for the same second stage, being in concordance with the kinetic laws of the first or second order mononuclear reactions.

**Conclusions**

Thermal degradation of phosphorus containing polyesters and polyesterimide revealed two-weight loss
stages while similar polymers without phosphorus exhibited only one step of decomposition. The dependence of the activation energy on the conversion degree for the first and second step of decomposition was determined. In the case of phosphorus containing polymers, in the second step of decomposition, an increase of the activation energy with the increase of the conversion degree appeared.

Acknowledgements: We acknowledge with great pleasure the financial support provided by the Romanian Ministry of Education and Research through CNCSIS grant no. 158/2006.

Bibliography
7. WU, H.S., LIU Y.L., Polymer, 43, 2002, p. 1773
15. VYAZOVKIN, S., Int. Review in Physical Chemistry, 19, 2000, p. 45
MATERIALE PLASTICE ♦ 44 ♦ Nr. 4 ♦ 2007