





# Thermal Stability of Some Phosphorus-Containing Polyesters and Polyesterimides

TACHITA VLAD-BUBULAC<sup>1</sup>, CORNELIU HAMCIUC<sup>1\*</sup>, OANA PETREUS<sup>1</sup>, GABRIELA LISA<sup>2</sup>

<sup>1</sup> Institute of Macromolecular Chemistry "Petru Poni", 41A Gr. Ghica Voda, Iasi-700487, Romania

<sup>2</sup>, „Gh. Asachi” Technical University Iasi, Faculty of Industrial Chemistry, Blvd. 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 behavior 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-processability because they possess high melting and isotropization temperatures. Several structural modifications of this class of polymers are essential for decreasing their melting temperature, in order to prevent 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 temperature and to improve the solubility of the polymers is the incorporation of pendent 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 copolyesters and polyesterimides [11-14]. In this article, we report the degradation behaviour of some aromatic copolyesters 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 SOCl<sub>2</sub>/pyridine condensing agent [12]. Polyesterimides **1e** and **1f** were prepared by polycondensation 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 Specord 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.

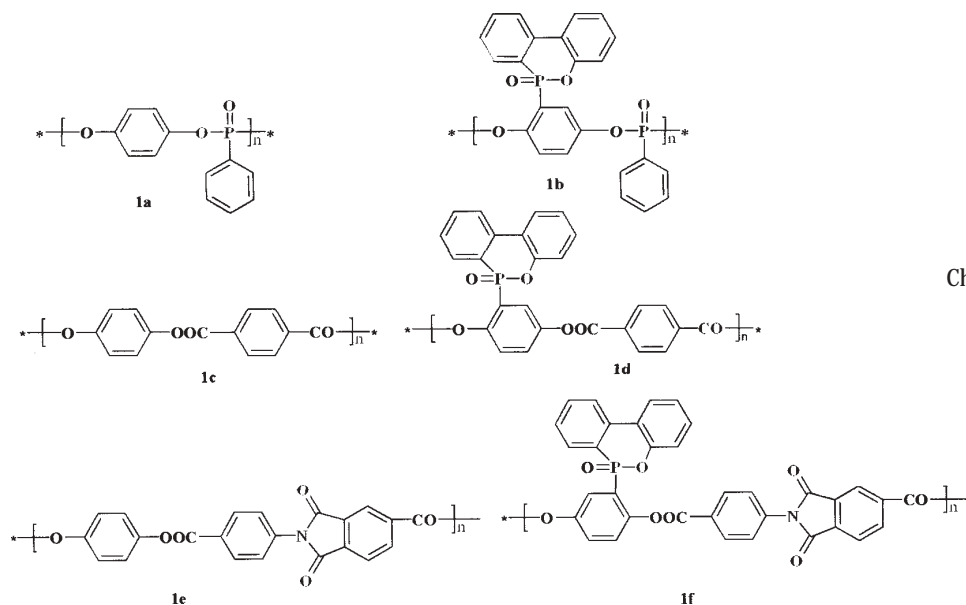
## Results and discussion

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<sup>-1</sup> (C-H), 1600 cm<sup>-1</sup> and 1500 cm<sup>-1</sup> (aromatic C=C), 1160 cm<sup>-1</sup> and 925 cm<sup>-1</sup> (P-O-Ar groups), 1470 cm<sup>-1</sup> (P-Ar groups), 1205 cm<sup>-1</sup> (P=O groups). Polyesters **1c** and **1d** showed also characteristic absorption peak at 1740 cm<sup>-1</sup> due to carbonyl asymmetric stretching of ester group. Polyesterimides **1e** and **1f** showed absorption peaks at 1780 cm<sup>-1</sup>, 1720 cm<sup>-1</sup>, 1390 cm<sup>-1</sup>, 1100 cm<sup>-1</sup> and 720 cm<sup>-1</sup> 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 polymers 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.



Scheme 1  
Chemical structure of polyesters and poly(ester-imide)s

Polymer	Stage 1 <sup>a</sup>			Stage 2 <sup>b</sup>			T <sub>max 1</sub> <sup>c</sup> (°C)	T <sub>max 2</sub> <sup>d</sup> (°C)	Char yield at 700°C (%)
	T <sub>i</sub> <sup>e</sup> (°C)	T <sub>f</sub> <sup>f</sup> (°C)	W <sup>g</sup> (%)	T <sub>i</sub> <sup>e</sup> (°C)	T <sub>f</sub> <sup>f</sup> (°C)	W <sup>g</sup> (%)			
<b>1a</b>	220	470	52.00	470	700	30.00	346	525	18.00
<b>1b</b>	320	520	52.00	520	700	15.40	475	631	32.60
<b>1c</b>	330	700	87.60	-	-	-	478	-	10.40
<b>1d</b>	345	470	30.60	470	700	32.40	441	549	35.00
<b>1e</b>	380	700	82.80	-	-	-	486	-	10.20
<b>1f</b>	360	490	39.40	490	700	37.80	453	552	20.80

**Table 1**  
THERMOGRAVIMETRIC  
CHARACTERISTICS FOR THE  
HEATING RATE OF 10°C / min

<sup>a</sup> First process of polymer decomposition; <sup>b</sup> Second process of polymer decomposition; <sup>c</sup> First temperature corresponding to the maximal degradation rate; <sup>d</sup> Second temperature corresponding to the maximal degradation rate; <sup>e</sup> Initial temperature of a decomposition process; <sup>f</sup> Final temperature of a decomposition process; <sup>g</sup> Weight loss of the polymer after the end of a decomposition process.

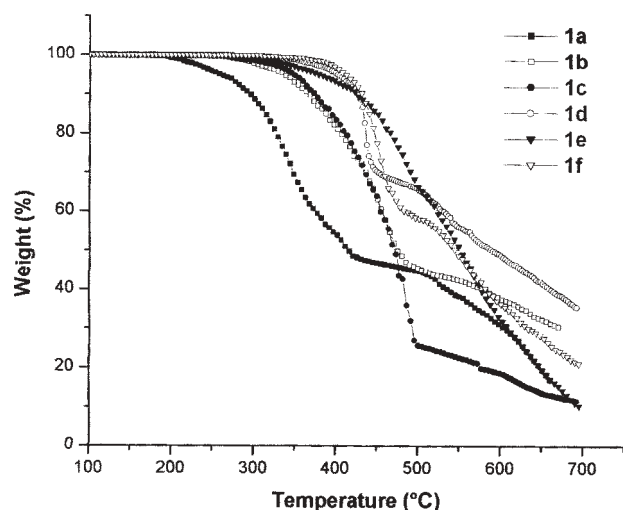


Fig. 1. TG curves of polymer 1

All phosphorus-containing polyesters **1a**, **1b**, **1d** and **1f**, exhibited two stages of decomposition, while the degradation process of phosphorus free polymers **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 **1a** containing phosphorus only in the main chain had the lowest thermal stability. When phosphorus is present both in the main and side chain (**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 **1a** and **1b** is nearly similar, the char residue for **1b** is higher. This is a consequence of enhanced aromaticity of the polymer that leads to a higher content of carbon in the

**Table 2**  
SET OF REACTION MODELS APPLIED TO DESCRIBE THERMAL  
DECOMPOSITION IN SOLIDS

Reaction model	f(α)	g(α)
1 Power law	4α <sup>3/4</sup>	α <sup>1/4</sup>
2 Power law	3α <sup>2/3</sup>	α <sup>1/3</sup>
3 Power law	2α <sup>1/2</sup>	α <sup>1/2</sup>
4 Power law	2/3α <sup>-1/2</sup>	α <sup>3/2</sup>
5 One-dimensional diffusion	1/2α <sup>-1</sup>	α <sup>2</sup>
6 Mampel (first order)	1-α	-ln(1-α)
7 Avrami - Erofeev	4(1-α)[-ln(1-α)] <sup>3/4</sup>	[-ln(1-α)] <sup>1/4</sup>
8 Avrami - Erofeev	3(1-α)[-ln(1-α)] <sup>2/3</sup>	[-ln(1-α)] <sup>1/3</sup>
9 Avrami - Erofeev	2(1-α)[-ln(1-α)] <sup>1/2</sup>	[-ln(1-α)] <sup>1/2</sup>
10 Three-dimensional diffusion	2(1-α) <sup>2/3</sup> [1-(1-α) <sup>1/3</sup> ] <sup>-1</sup>	[1-(1-α) <sup>1/3</sup> ] <sup>2</sup>
11 Contracting sphere	3(1-α) <sup>2/3</sup>	1-(1-α) <sup>1/3</sup>
12 Contracting cylinder	2(1-α) <sup>1/2</sup>	1-(1-α) <sup>1/2</sup>

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:

$$\frac{d\alpha}{dt} = k \cdot f(\alpha) \quad (1)$$

where f(α) 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 α versus t or dα / dt versus t plots or mathematical functions (i.e f(α)). 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/t<sub>α</sub>, where t<sub>α</sub> is the time to reach a certain values of α (usually 0.5 to 0.9). According to the integral form of equation (1), that is

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = k \cdot t \quad (2)$$

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 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

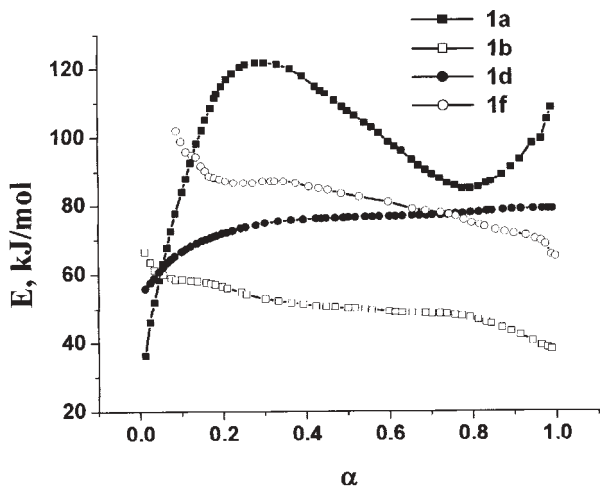


Fig. 2. The dependence of activation energy versus conversion degree of the first process of decomposition for polymers 1a, 1b, 1d, 1f

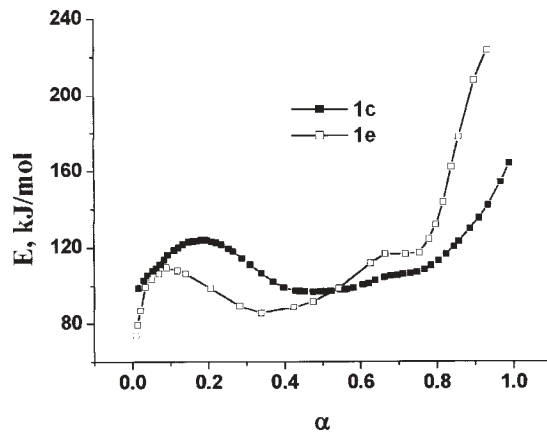


Fig. 4. The dependence of activation energy versus conversion degree of the first process of decomposition for polymers 1c, 1e

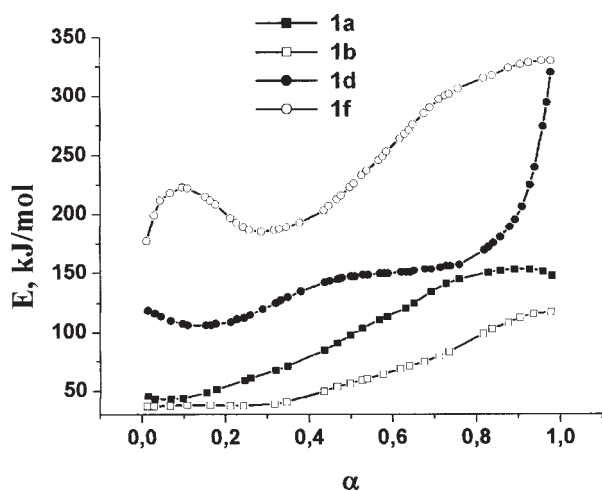


Fig. 3. The dependence of activation energy versus conversion degree of the second process decomposition for polymers 1a, 1b, 1d, 1f

**Table 3**  
THE MODEL OF THERMAL DEGRADATION OF POLYMER

Polymer	Stage 1 <sup>a</sup>		Stage 2 <sup>b</sup>	
	Model <sup>c</sup>	$g(\alpha)$ <sup>d</sup>	Model <sup>c</sup>	$g(\alpha)$ <sup>d</sup>
<b>1a</b>	First order	$-\ln(1-\alpha)$	First order	$-\ln(1-\alpha)$
<b>1b</b>	Power law	$\alpha^{1/2}$	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$
<b>1c</b>	First order	$-\ln(1-\alpha)$	-	-
<b>1d</b>	Power law	$\alpha^{1/3}$	Second order	$(1-\alpha)^{-1}-1$
<b>1e</b>	Second order	$(1-\alpha)^{-1}-1$	-	-
<b>1f</b>	Avrami-Erofeev	$[-\ln(1-\alpha)]^{1/4}$	First order	$-\ln(1-\alpha)$

<sup>a</sup> First process of polymer decomposition; <sup>b</sup> Second process of polymer decomposition; <sup>c</sup> The model of thermal degradation; <sup>d</sup> Function of the conversion rate.

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.

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