

Flammability and Thermal Behavior of Phosphorus-Containing Polyamide-6

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SYNOPSIS

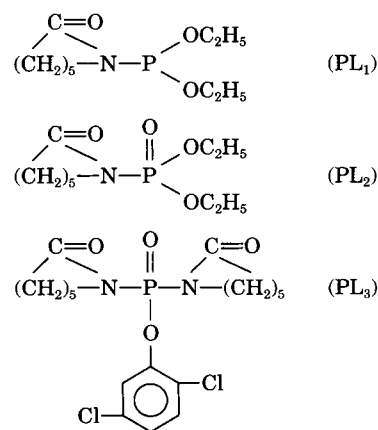
An investigation is reported on the flammability and thermal behavior of polyamide-6, obtained by anionic polymerization of ϵ -caprolactam, carried out in bulk, in the presence of the following *N*-substituted phosphorus-containing lactam derivatives: diethyl-(*N*-caprolactam)-phosphonite (PL₁), diethyl-(*N*-caprolactam)-phosphonate (PL₂), and 2,5-dichlorophenyl-bis(*N*-caprolactam)-phosphinate (PL₃). Phosphorus-containing lactam derivatives PL₁ and PL₃ are used as activators of the anionic polymerization of ϵ -caprolactam, and PL₂, as a modifying additive. The phosphorus-containing polyamide-6 possesses improved flame retardancy, as well as improved thermo- and thermooxidative resistance. Destruction kinetics were studied in nitrogen and air atmospheres, and the activation energy for thermal and thermooxidative destruction have been determined. The effect of PL₁, PL₂, and PL₃ on the melting temperature (T_m) and glass-transition temperature (T_g) of polyamide-6 was established. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

One of the methods used for stabilization of polyamides against flammability as well as for improving their thermo- and thermooxidative resistance is the chemical modification of the polymer.¹ Thus, by means of polymer-analogous reactions such as halogenation or phosphorilation, an improvement in the thermo- and flame retardancy of polyamide-6 (PA-6) has been realized.² However, there are certain problems with application of this method when the product has been prepared by polymerization in bulk.

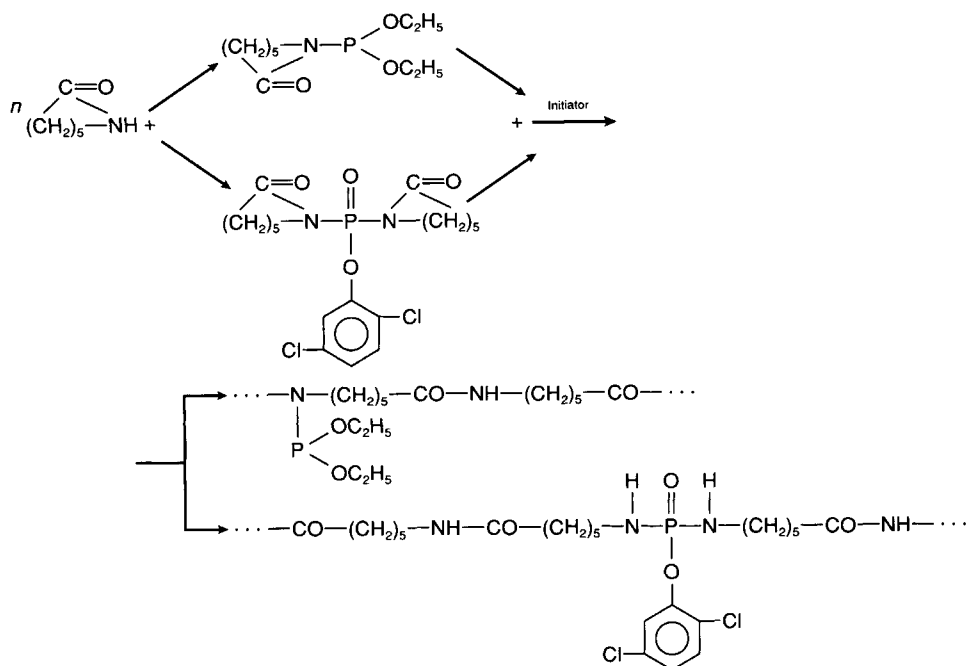
In the present work, the modification is made in the stage of polyamide production. This approach requires synthesis of monomers or polymerization-capable additives, containing groups similar to those of the efficient flame retarders and thermostabilizers.³

For this purpose the following *N*-substituted phosphorus-containing derivatives of ϵ -caprolactam have been synthesized:



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On the basis of their structures, the authors assumed that they would have an activating effect on the anionic polymerization of ϵ -caprolactam, i.e.,



Scheme I

they would act as activators and simultaneously would improve the thermo- and flame resistance of PA-6.

Some previous investigations of the authors showed that PL₁ and PL₃ had an activating effect on the anionic polymerization of ϵ -caprolactam (ϵ -CL) and that PL₂ might be introduced in PA-6 as a modifying additive.⁴

The objective of the present paper is to investigate the flammability and thermal behavior of polyamide-6, prepared by means of anionic polymerization of ϵ -CL in the presence of phosphorus-containing activators PL₁ and PL₃ and the modifying additive PL₂.

EXPERIMENTAL

Preparation of PL₁, PL₂, and PL₃

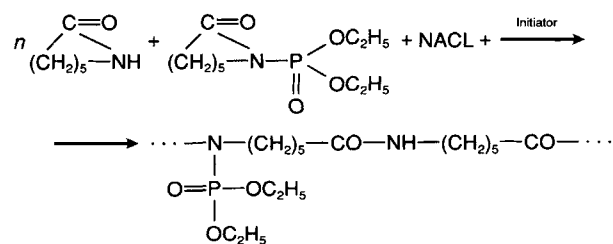
The *N*-substituted phosphorus-containing derivatives of ϵ -CL were synthesized by direct interaction of ϵ -CL with chloroanhydride (for PL₁ and PL₂) or dichloroanhydride (for PL₃) of the corresponding phosphoric acid in an organic solvent, under an inert atmosphere in the presence of triethylamine. More details about the techniques applied or about the molecular structure of these novel lactam derivatives were given in Refs. 5 and 6.

Preparation of Phosphorus-containing Polyamide-6

The phosphorus-containing polyamide-6 was produced by anionic polymerization of ϵ -CL, carried out in bulk at 180°C. Di-(methoxy-ethoxy)-di-(ϵ -CL)-sodium aluminate (DL) with concentrations of up to 2 mol % in respect to ϵ -CL was used as initiator. PL₁ and PL₃ were used as activators—up to 2 mol % calculated on the ϵ -CL used. In the case of modification by PL₂, the polymerization was activated by *N*-acetyl- ϵ -CL (NACL), with concentrations of up to 2 mol %, the amounts of PL₂ having been varied in the 1–5 mol % concentration range. In this case, the polymerization was performed at 160°C.

Analyses

Thermogravimetric analysis (TGA) in nitrogen and air atmospheres was carried out in a Mettler TA



Scheme II

Table I Some Properties of P-containing Polyamides as a Function of DL, NACL, and PL Content

	[DL] Content (mol %)	[NACL] Content (mol %)	[PL] Content (mol %)	P Content (wt %)		Yield of Polymer (%)	[η], (dL/g)	M_v ($\times 10^{-3}$)
				Theor.	Exp.			
PL ₁	2.0	2.0	—	—	—	91	1.59	34
	2.0	—	1.0	0.35	0.33	96	2.84	86
	2.0	—	2.0	0.70	0.66	92	2.65	78
	1.5	—	1.0	0.45	0.43	95	2.80	84
	1.5	—	1.5	0.50	0.45	97	2.95	90
	1.5	—	2.0	0.56	0.50	95	2.74	82
	4.0	—	2.0	0.70	0.66	92	— ^a	— ^a
	4.0	2.0	2.0	0.60	0.53	92	1.69	41
	10.0	—	10.0	1.66	1.60	88	1.05	21
PL ₂	2.0	2.0	1.0	0.25	0.23	91	1.21	25
	2.0	2.0	2.0	0.47	0.45	87	1.10	22
	2.0	2.0	3.0	0.60	0.52	80	0.91	17
	2.0	2.0	4.0	0.92	0.83	73	0.83	15
	2.0	2.0	5.0	1.10	0.99	65	0.72	12
	4.0	2.0	4.0	1.67	1.60	92	1.02	20
PL ₃	2.0	—	0.25	—	—	92	2.78	83
	2.0	—	0.50	—	—	94	2.00	52
	2.0	—	1.0	0.30	0.30	90	1.05	21
	2.0	—	2.0	0.62	0.60	91	1.00	20

The polymerization period with PL₁ and PL₃ was 3 h at 170°C; the polymerization with PL₂ was carried out for 5 h at 160°C.

^a This sample was insoluble in concentrated H₂SO₄ and *m*-cresol.

3000 apparatus, at a heating rate of 10°C/min. The TG analysis under static (isothermal) conditions was done in a Perkin-Elmer apparatus in an inert atmosphere at $T = 280^\circ\text{C}$ and a duration of heating of 3 h.

All the DSC traces were conducted at a heating rate of 10°/min in a Perkin-Elmer DSC-2C apparatus. The T_g values were determined in the same apparatus, operating at low temperatures ($-10 + 150^\circ\text{C}$) and 20°C/min heating rate.

The oxygen index was determined according to Bulgarian State Standard No. 12786/75. For determining the phosphorus content, colorimetric methods were used. The absorption at 400 nm was measured, the samples having been preliminary treated with perchloric acid. Intrinsic viscosity [η] was measured as indicated by Ivanova et al.⁷

RESULTS AND DISCUSSION

The phosphorus-containing polyamide-6 was obtained according to Scheme I where PL₁ and PL₃ were applied as activators, or in the presence of the additive PL₂, as shown in Scheme II.

Table II Influence of the Type and Concentration of the PL Additive upon the Oxygen Index of ϵ -CL-based Polyamides

	PL Content (mol %)	Phosphorus Content (wt %)	Oxygen Index (OI)
PL ₁	—	—	20.3
	1.0	0.42	22.2
	1.5	0.55	22.5
	2.0	0.90	22.5
	10.0	1.50	21.3
PL ₂	1.0	0.23	21.6
	2.0	0.45	21.9
	3.0	0.52	22.0
	4.0	1.60	23.7
PL ₃	1.0	0.32	22.1

For polymerization with PL₁ and PL₃, [DL] = 2 mol %, except the sample containing 10% PL₁, where [DL] = 10 mol %. For polymerization with additive PL₂, the ratio [DL]/[NACL] = 1, [DL] = 2 mol %, except for the last sample of this type, where [DL]/[NACL] = 2 and [DL] = 4 mol %.

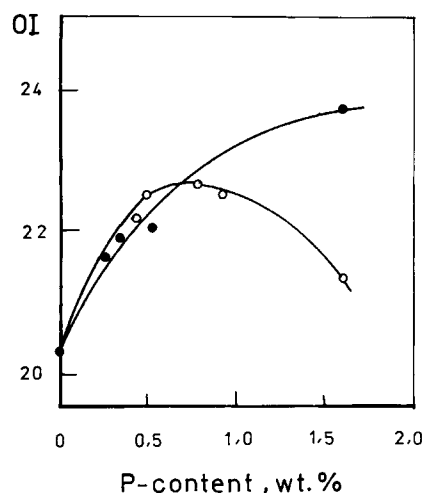


Figure 1 Oxygen index vs. phosphorus content of (○) PA-6/PL₁ and (●) PA-6/PL₂.

The phosphorus-containing polyamide-6 was characterized by P content, $[\eta]$, and M_v (Table I).

It was impossible to analyze the copolymers by NMR spectroscopy because they were difficult to dissolve in deuterated H₂SO₄, and the solutions, although diluted, had too high viscosities.

The data in Table I show that the polymerization of ϵ -CL in the presence of PL₁, PL₂, and PL₃ pro-

duces polymers with high yields and viscosities. The good correspondence between the theoretical and experimental phosphorus content was considered proof of the nearly complete consumption of the *N*-substituted derivatives of ϵ -CL during the polymerization.

Flame Retardancy

The flame retardancy of phosphorus-containing polyamide-6 was investigated through determination of the oxygen index of specimens obtained in a standard matrix. These data are shown in Table II.

The increase in the oxygen index (OI) by 1–3.5 units demonstrates that P-containing polyamides studied possess better flammability resistance than does polyamide-6 itself. The dependence of the OI on the phosphorus content for two batches of samples is given in Figure 1. With PA-6, containing PL₁, the curve passes through a maximum that is located in the concentration range of 0.55–0.90 wt % P. With increase of the phosphorus content up to 1.5 wt %, the oxygen index drops to 21.3. At the same time, the PL₂-modified polyamide-6 (i.e., PA-6 containing ethyl-phosphate groups) displays the highest OI value (23.7) at the same P-content—1.5 wt %. A conclusion can be made that the flame-retarding action of diethyl-phosphate groups (PL₂) is more ef-

Table III TG Data Comparison of Some Polyamides Containing Different Amounts and Types of Additives

	PL (mol %)	Phosphorus (%)	Nitrogen Atmosphere			Air Atmosphere		
			$T_{5\%}$ (°C)	IDT (°C)	Mass loss % (500°C)	$T_{5\%}$	IDT (°C)	Mass loss % (500°)
PL ₁	—	—	240	395	87.4	220	385	91.3
	1.0	0.43	360	410	80.0	370	415	86.0
	1.5	0.45	350	410	81.1	310	415	86.3
	2.0	0.50	370	415	78.5	350	418	86.0
	2.0	0.66	365	415	75.1	305	310 420	12 70.2
	10.0	1.60	250	390	72.0	205	290 415	15 55.4
PL ₂	1.0	0.23	260	385	78.0	300	395	77.3
	2.0	0.47	320	385	74.2	295	395	79.4
	3.0	0.60	310	380	87.4	260	340 395	14 55.9
	4.0	0.92	295	290 415	4.5 71.5	290	340 410	21 50.5
	5.0	1.10	320	330 415	9.5 67.2	300	340 410	15 59.3
	4.0	1.60	350	390	92.0	330	400	85.5
PL ₃	1.0	0.30	340	400	91.0	320	410	78.1
	2.0	0.6	360	400	94.0	325	400 515	77 10.0

With all the samples, the initiator concentration was 2 mol %. Exceptions: The last two samples containing PL₁ where [DL] was 4.0 mol % and in the last PL₂ modified sample in which [DL] = 5 mol %.

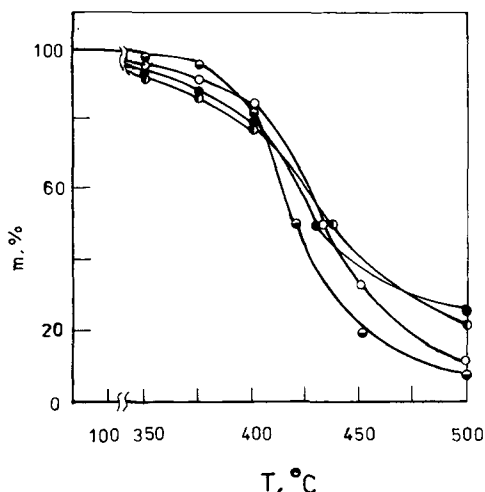


Figure 2 TG curves of PA-6 containing various amounts of PL₂ (nitrogen atmosphere): (○) no additive; (●) 2% PL₂; (●) 1% PL₂; (○) 4% PL₂.

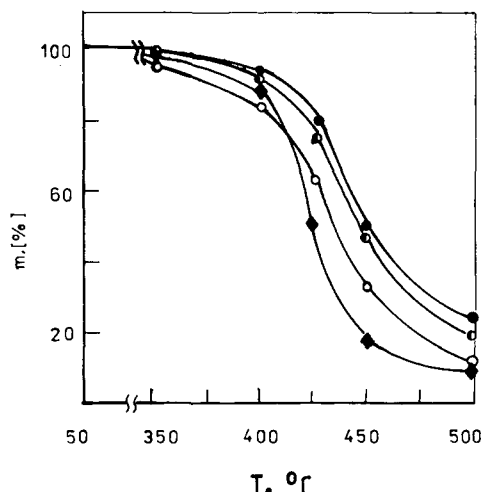


Figure 4 TG curves of PA-6 produced with PL₁ and PL₃ activators (nitrogen atmosphere): (○) PA-6/NACL; (●) 2% PL₁; (●) 1% PL₁; (◆) 2% PL₃.

ficient as compared to that of diethyl phosphate groups (PL₁).

Thermal Behavior of Phosphorus-containing Polyamide-6

The thermal characterization of the phosphorus-containing PA-6 was made by TGA in nitrogen and air atmospheres and by DSC, carried out under various conditions (Table 3 and Figs. 2-5).

In a nitrogen atmosphere, the initial decomposition temperature (IDT) of the PL₂ modified polyamide-6 (Fig. 2) was lower than the IDT of the non-modified PA-6. In the absence of oxygen, the destruction depends on the decomposition temperature of the chemical bonds and is limited by the energy of the weakest bonds.³ It is known that in the polyamides the weakest bond is —CH₂—N— (69 kcal/mol). Obviously, modification by PL₂ does not

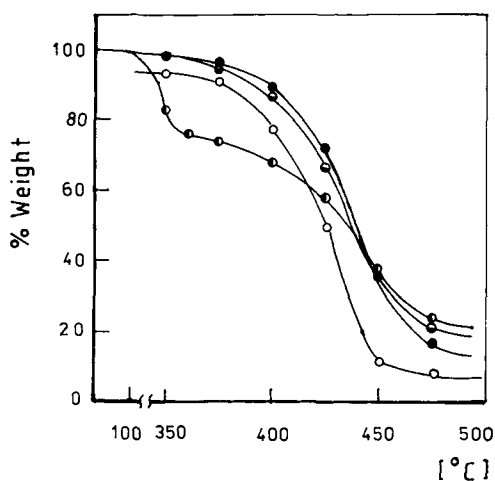


Figure 3 TG curves of PA-6 containing various amounts of PL₂ (air atmosphere): (○) no additive; (●) 2% PL₂; (●) 1% PL₂; (●) 3% PL₂.

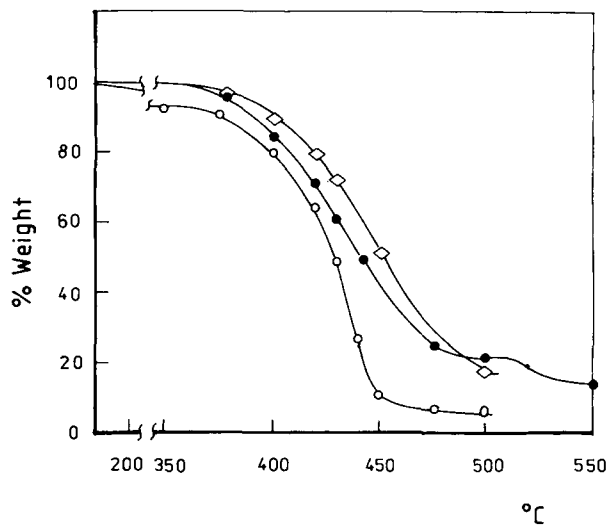


Figure 5 TG curves of PA-6 produced with PL₁ and PL₃ as activators (air atmosphere): (○) PA-6/NACL; (◇) PA-6/2% PL₁; (●) PA-6/2% PL₃.

Table IV Activation Parameters as a Function of the PL Type and Test Conditions for PL-modified PA-6

No.	[In]/[Ak] (mol %)	PL Type ^a	Nitrogen Atmosphere (kJ/mol)		Air Atmosphere (kJ/mol)	
			<i>n</i>	<i>E_a</i>	<i>n</i>	<i>E_a</i>
1	No modification	—	0.51	191.3	1.12	182.68
2	1/1	PL ₁	0.79	209.15	1.25	231.20
3	1/1	PL ₂	1.21	177.18	1.03	222.10
4	2/1	PL ₃	0.18	260.19	1.23	273.16

^a [PL_i] = 1.0 mol %.

affect these bonds, but the substitution of N—H groups partially by —N—P(O)—(OC₂H₅)₂ leads to a decrease of the resistance to thermooxidative degradation.

In an air atmosphere, the decomposition of the PL₂-modified polyamide-6 begins at a temperature that is 10–15°C higher than the IDT of the PA-6 that does not contain phosphorus (Fig. 3). The thermooxidative degradation of PA-6 begins with the formation of hydroperoxydes at the methylene group directly bonded to the N atom —CH—N—. ³ The introduction of a bulky diethyl phosphate substituent at the nitrogen atom probably impedes the oxygen attack upon this group that would have resulted as a delay of the thermooxidative degradation.

With increasing PL₂ concentration, the relationship between mass loss and temperature, in both air and nitrogen atmospheres, showed bimodal character (Table III and Fig. 3). As the temperature of the beginning of decomposition at the second step is higher by about 20–25°C than the IDT of PA-6 not containing phosphorus, it could be assumed that during the heating in the temperature range 300–350°C some products are formed that impede the thermo- and thermooxidative degradation reactions. In all PL₂-modified samples, the residue at 500°C increases with phosphorus content.

Unlike the PL₂ modifications, TG analyses of polyamides produced by using of PL₁ and PL₃ as activators showed that the IDT increased both in air (Fig. 5) and in a nitrogen atmosphere (Fig. 4) by 30–35°C and 15–20°C, respectively. With increasing concentrations of PL₁ (Table III) and PL₃ (Table III), the dependence of mass loss and temperature became bimodal only in the presence of oxygen. The first stage of decomposition of PA-6, containing diethyl phosphite groups (i.e., PL₁), be-

gins at a lower temperature than for the polymer containing diethyl phosphate groups (i.e., modifications with PL₂). A possible reason could be the increased inclination of the trivalent phosphorus to oxidative processes.

Whereas the increase in the IDT with all phosphorus-containing samples did not exceed 35°C, the increase in *T*_{5%} is much greater. This means that the influence of *N*-substituted phosphorus-containing derivatives of ε-CL is much stronger within the temperature range below the IDT, i.e., PL₁, PL₂, and PL₃ impede to a greater extent the initial degradation. That should be reflected in the values of the activating energy *E_a* for degradation. Therefore, an investigation was performed on the kinetics of thermo- and thermooxidative destruction by TG

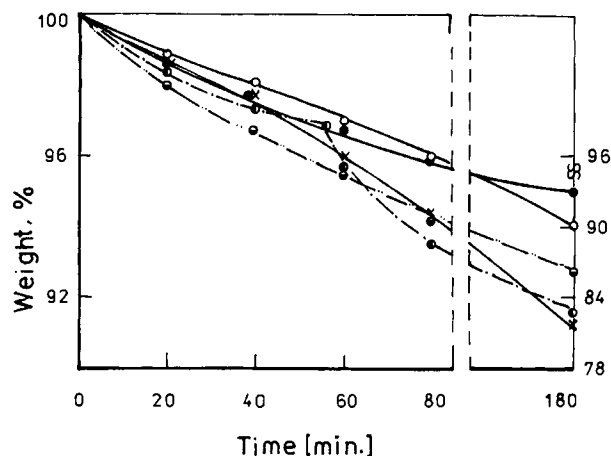


Figure 6 TG investigation of PA-6 containing various concentrations of phosphorus lactam derivatives: (○) PA-6/PL₁ (1.0%); (●) PA-6/PL₁ (1.5%); (⊙) PA-6/PL₂; (X) PA-6/PL₃; (◐) pure PA-6. Conditions: *t* = 300°C; duration of heating 3 h; nitrogen atmosphere.

Table V Kinetic Data Comparison for ϵ -CL-based Polyamides Containing Various Types and Amounts of PL Additives

PL Type	Additive Content (mol %)	Degradation Rate, W (%/min)	Mass Loss Δm after 60 min (%)	Mass Loss Δm_{180} after 180 min (%)
—	—	0.209	4.6	13.8
PL ₁	1.0	0.048	1.9	9.0
PL ₁	1.5	0.069	3.2	6.5
PL ₂	4.0	0.082	4.3	17.0
PL ₃	1.0	0.045	4.0	18.0

analysis, carried out under static conditions. The analysis was made at 10 various temperatures below IDT and the mass changes as a function of heating time were followed. The results obtained are shown in Table IV.

All samples revealed a higher activation energy for thermo- and thermooxidative destruction than did the pure PA-6. An exception was observed when PL₂ additive was employed. In that case, the E_a value for thermal degradation was slightly lower than for PA-6 without phosphorus. This result is in a good agreement with the decrease of the IDT, as seen from the TG analysis made under dynamic conditions in a nitrogen atmosphere (Table III and Fig. 2).

The kinetics investigations of thermal degradation in an inert atmosphere (Fig. 6 and Table V) led to the following conclusions:

Table VI Influence of DL and PL Content upon the T_m and ΔH_m Values of Various P-containing Polyamides

No.	[DL] Content (mol %)	PL Type	[PL] Content (mol %)	T_m (°C)	ΔH_m (J/g)
1	2.0	—	—	217	84.37
2	2.0	PL ₁	1.0	221	73.23
3	1.5	PL ₁	1.0	216	51.13
4	1.5	PL ₁	1.2	227	60.50
5	1.5	PL ₁	1.5	224	74.86
6	4.0	PL ₁	2.0	218	54.76
7	2.0	PL ₂	1.0	220	76.45
8	2.0	PL ₂	2.0	219	81.14
9	2.0	PL ₂	3.0	212	91.86
10	2.0	PL ₂	4.0	198	90.56
11	2.0	PL ₂	5.0	212	103.96
12	2.0	PL ₃	1.0	223	84.49
13	2.0	PL ₃	0.5	218	37.77
14	2.0	PL ₃	0.25	219	38.39
15	2.0	PL ₃	0.125	218	36.68

The degradation begins with the highest rate of 0.209%/min for PA that does not contain phosphorus and with the lowest rate—0.045%/min for PA-6 produced with PL₃ activator. In all cases, the phosphorus-containing PA-6 showed a decreased rate of degradation during the first hour. With PA-6 modified by 4 mol % PL₂, the dependence has a bimodal character. The polyamide produced by PL₁ activator has the best indices (Fig. 6, ●): The mass loss after 180 min (Δm_{180}) is one-half than that of polyamide-6 that does not contain phosphorus.

As degradation and combustion of a polymer material are usually preceded by softening or melting, the phosphorus-containing PA-6 were studied by DSC to determine the melting temperatures T_m (Table VI).

As is apparent from Table V, when the modifying additive PL₂ was below 2 mol %, the melting temperature, T_m , and the enthalpy of the transition, ΔH_m , did not change considerably. A decrease in T_m was observed that in sample 10 is lower by approximately 20°C than is the T_m of the unmodified polyamide-6.

The differential scanning analysis of phosphorus-containing PA-6 produced with the activators PL₁

Table VII T_g as a Function of PL Type and Concentration

No.	PL Content (mol %)	Additive	T_g (°C)	[DL]/[PL]
1	—	—	47.21	—
2	0.5	PL ₁	45.78	2
3	1.0	PL ₁	47.15	1
4	1.5	PL ₁	52.27	0.67
5	2.0	PL ₁	57.58	0.50
6	0.125	PL ₃	49.01	8
7	0.25	PL ₃	50.53	4
8	0.50	PL ₃	49.12	2

Initiator concentration [DL] = 1.0 mol %.

and PL₃ shows that T_m remains constant and, with some samples, even has a tendency to increase (up to 10°C with sample 4, Table VI). At the same time, the transition enthalpy ΔH_m decreases (see Table VI), whereas the glass transition temperature, T_g , as seen in Table VII, decreases.

When the concentration of phosphorus-containing activators PL₁ and PL₃ was lower than the concentration of DL, T_g increased slightly. At a twofold excess of PL₁ in respect to DL, T_g was 10°C higher than the T_g of PA-6 (Table VII, sample 5). It can be assumed that the use of these activators leads to substantial changes in the overall structure of polyamide-6.

As a result of our investigation, the conclusion can be made that when using phosphorus-containing lactam derivatives, PL₁, PL₂, and PL₃, as activators or modifying additives, the polyamide-6 produced possesses improved flame retardancy, as well as increased thermo- and thermooxidative resistance.

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