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THERMAL ANALYSIS OF OLIGO-AMIDOPHOSPHATES

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Differential thermal analysis and thermogravimetry have been carried out on oligoamidophosphates with established plastifying and anti-ignition effects, which contained various amounts or bound phosphorus, had different molecular masses, and were obtained on the basis of epsilon-caprolactam, oligo- or polycaproamide. The ranges of thermal stability were determined and some differences between the combustion mechanisms of the starting polycaproamide and the oligoamidophosphates were shown. A probable mechanism of the anti-ignition action of the latter is proposed.

It was established previously [1, 2] that the reactions of epsilon-caprolactam and polycaproamide (PCA) with orthophosphoric acid lead to the same oligomeric products, containing an appreciable amount of bound phosphorus (up to 14.5%) and having well-established plastifying [3] and anti-ignition effects [4].

The study of the thermal properties of these products, which we named oligoamidophosphates (OAPh), is of great interest, both in connection with finding the conditions of their application in polymer blends and for elucidating the mechanism of their anti-ignition action.

The purpose of the present work was to investigate the influence of the type of starting material, the molecular mass and the content of phosphorus in the OAPh upon their thermal properties, with the help of differential thermal analysis (DTA) and thermogravimetry (TG).

Experimental

The following materials were employed: epsilon-caprolactam (SChC-Stara Zagora), m.p. 69°; polycaproamide (SChC-Vidin), purified by reprecipitation from a solution of *m*-cresol, molecular mass 23,000 (viscosimetrically), m.p. 220°; orthophosphoric acid, concentrated (86.5%), analytically pure; oligo-amidophosphates with molecular mass 360 to 2000 (by the isopiestic method [5] and a phosphorus content by the Lieb and Wintersteiner method [6] of 5.84 to 14.44%, obtained on the basis of epsilon-caprolactam, oligo- or polycaproamide, as described in the previous papers [1, 2].

Thermal analysis of the starting materials and the OAPh was carried out on a Paulik–Paulik–Erdey derivatograph (Hungary). The thermal curves were taken in the temperature region 25 to 800° at a heating rate of 5°/min. All samples were dried previously to a constant weight of about 200 mg.

Results and discussion

The following characteristics were used to establish the thermal properties of the oligo-amidophosphates: m.p., temperature of recording of first loss in weight (T_0), temperature range of basic mass alteration ($T_1 - T_2$), mass loss in % (ΔM) as referred to temperature.

The thermal curves of all the OAPh, irrespective of the basis of preparation, the molecular mass or the phosphorus content, proved similar, so that only one of them is shown here (Fig. 1, curves 2 and 4).

The same Figure illustrates the manner of determining T_0, T_1 and T_2, while the temperatures obtained in our studies are shown in Table 1.

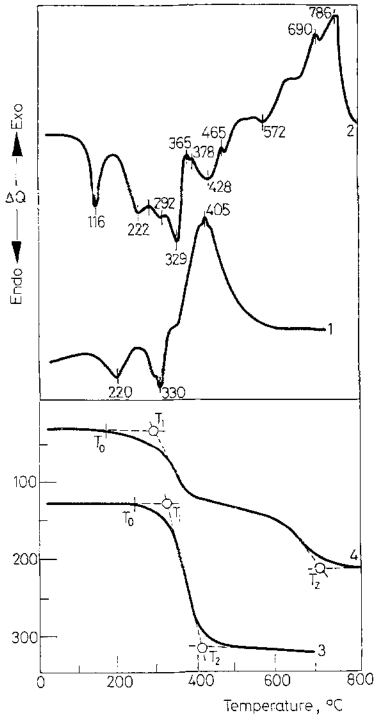

Fig. 1. DTA and TG curves of polycaproamide (curves 1 and 3) and oligo-amidophosphate (curves 2 and 4) containing approximately one molecule of phosphoric acid per elementary unit

Table 1

Thermal properties of OAPh, investigated in air

Characteristics	Polycaproamide	OAPh-1	OAPh-2	OAPh-3	OAPh-4	OAPh-5
Phosphorus content, %	—	14.33	14.09	14.12	10.64	5.84
Ratio: Mol. phosph. acid/elem. units	—	1 : 1	1 : 1	1 : 1	1 : 2	1 : 3
Molecular mass	23,000	360	930	1300	1105	1420
M.p., °C	220	103	116	120	115	145
T_0, °C	290	170	180	188	183	190
$T_1 - T_2$, °C	340–405	290–764	292–740	300–735	305–742	312–760
Mass loss, % at given temperature:						
180°	0	1.5	0	0	0	0
190°	0	4.6	2.5	1.2	1.5	0
290°	0	21.3	22.4	10.3	9.6	9.9
400°	98.6	49.7	50.2	48.3	61.3	56.1
807°	—	97.5	89.9	91.3	99.4	98.8

It is evident from Fig. 1 that, in comparison to the starting polycaproamide, the OAPh display substantially different DTA and TG curves. The differences relate to both the number and the situation of the endo- and exothermic peaks and the respective losses in weight. Table 1 shows that the molecular mass has only a slight influence upon the corresponding m.p., whereas the phosphorus content appreciably affects T_0.

In the DTA curve of polycaproamide (Fig. 1, curve 1) one observes an endothermic peak at about 220° (without loss in weight), corresponding to the temperature range of melting of that polymer. A further endothermic peak (at about 350°) and an exothermic one (at about 395°) are also evident. Their corresponding endo- and exothermic effects are accompanied by sharp alterations in the weight of the sample (Fig. 1, curve 3). The thermal effects observed with polycaproamide, as well as the loss in mass upon heating, are in agreement with the mechanism of burning of polymers proposed by some authors [7], according to which burning starts with an endothermic stage of destruction, leading to the formation of a solid residue and combustible gases. This stage is called "primary pyrolysis" [8]. There follows the exothermic combustion of the gases, i.e. "secondary pyrolysis in flame" [8]. Part of the liberated heat is transferred into the surrounding space, whereas the other part provokes thermal destruction of new portions of the polymer. The endothermic peak in the region about 330° (Fig. 1, curve 1) in the DTA curve of polycaproamide corresponds to intensive thermal destruction, while the exothermic one at about 395° is associated with intensive thermal oxidation processes. As a result, with polycaproamide one observes complete combustion too, characteristic of polymers with a saturated chain [9]. This is due to the predomination of the destructional over the structurizing processes, and to the low rate of self-stabilization: at about 400° the loss in mass of polycaproamide is almost 100 per cent (Fig. 1, curve 3).

Both curve 4 in Fig. 1 and also Table 1 show that at 400° the OAPh display a loss in mass of only about 50%. This difference could be explained unambiguously only by the presence in the OAPh of phosphoric acid which is very slightly volatile (b.p. 869° at 753 mm Hg [10]). A certain stabilization of the OAPh results, which hinders their combustion. A proof of this is the fact that, when introduced into a flame, they do not ignite and do not burn.

The shift in T_0 for the OAPh toward lower temperatures, as compared with polycaproamide (Table 1), shows that the association of phosphoric acid to the amide-containing polymers does not increase their stability against thermal destruction; on the contrary, thermal destruction starts at lower temperatures, which is presumably associated with hydrolytic processes, catalyzed by the phosphoric acid present. The latter hampers the thermal oxidation processes in the main, which hinders ignition and the development of higher temperatures. As a result, the OAPh start to undergo destruction at lower temperatures than does polycaproamide, but they do not ignite and do not burn. Complete loss of mass takes place as high as at about 800°.

On the basis of the above considerations, one could assume that the anti-ignition effect of the OAPh is due precisely to the suppression of the oxidizing processes by the phosphoric acid present, by the small quantity of combustible volatile products liberated, and by the introduction of a non-combustible solid residue from the thermal destruction of the compositions blended with them.

In conclusion, as a result of the DTA and TG of oligo-amidophosphates and the starting materials used for their preparation it was possible to establish the domain of thermal stability, and to show some differences between the combustion mechanisms of the starting polycaproamide and the oligo-amidophosphates obtained by us; we have proposed a presumable mechanism for their anti-ignition effect.

References

1. Bulg. Auth. Gert. No 24 005 (12. 02. 77).
2. I. Mladenov, T. Vladkova, B. Tsenkova and S. Fakirov, Vysokomolekul. Soedin. A22, (1980) — in print.
3. Bulg. Auth. Cert. No 45 786/3. 12. 79.
4. Bulg. Auth. Cert. No 45 447/9. 11. 79.
5. A. Shatenshtein, Pract. Manual in Determn. Mol. Wt. and Mol. Wt. Distrib. of Polymers, Khimia-M (USSR), 1974.
6. B. Stoyanova-Ivanova, A Brief Course in Org. Anal., Nauka i Izkustvo–Sofia, 1967.
7. J. E. Bastik, K. K. Yen and R. H. Barker, J. Polym. Sci., 17 (1973) 471.
8. H. Herlinger, Textilveredlung, 12 (1977) 13.
9. A. B. Blumenfeld, Vysokomolekul. Soedin. B14 (1972) 403.
10. E. Tilo and R. Sauer, J. Prakt. Chem., 4 (1957) 324.

RÉSUMÉ — On a effectué l'analyse thermique différentielle et la thermogravimétrie d'oligo-amidophosphates à effets plastifiants et ignifuges bien établis contenant diverses quantités de phosphore lié, de masses molaires différentes et obtenus à partir d'epsilon-caprolactame, d'oligo et poly-caproamides. Les domaines de stabilité thermique ont été déterminés et quelques différences dans le mécanisme de combustion du polycaproamide initial et des oligo-amidophosphates ont été mises en évidence. On propose un mécanisme probable de l'action ignifuge de ces derniers.

ZUSAMMENFASSUNG — Differentialthermoanalyse und Thermogravimetrie wurden an Oligo-Amidophosphaten bekannter Plastifizier- und Entzündungshemmwirkung durchgeführt, welche verschiedene Mengen gebundenen Phosphors enthielten, verschiedene Molekularmassen hatten und auf der Basis von Epsilon-Caprolactam, Oligo- und Poly-Caproamiden erhalten wurden. Die Bereiche der Thermostabilität wurden bestimmt und einige Unterschiede im Verbrennungsmechanismus des Ausgangs-Polycaproamids und der Oligoamidophosphate gezeigt. Ein wahrscheinlicher Mechanismus der Zündungshemmwirkung der Letzteren wird vorgeschlagen.

Резюме — Диференциально-термический анализ и термогравиметрия были использованы для исследования олигоамидофосфатов, обладающих пластифицирующим и антивоспламеняющим свойствами. Эти соединения содержали различные количества связанного фосфора, имели различный молекулярных вес и были получены на основе ε-капролактама, олиго- или поликапроамида. Определены области термоустойчивости и показаны некоторые различия в механизме горения исходных поликапроамида и олигоамидофосфатов. Для последних соединений предложен механизм их антивоспламеняющего действия.