

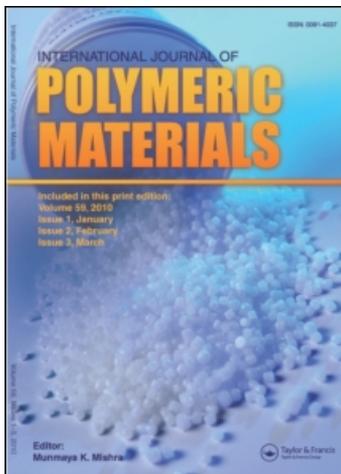
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### “Transfer” Stabilization of Thermally Stable Polymers

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## “Transfer” Stabilization of Thermally Stable Polymers

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A new concept of stabilization, the “transfer” stabilization is presented and evaluated for the case of thermally stable polymers.

**KEY WORDS** Polymer stabilization, aromatic and heterocyclic polymers

### RESULTS AND DISCUSSION

Considerable experience has been accumulated concerning the synthesis of various heterocyclic high molecular weight compounds belonging to the class of thermally stable polymers. Some of these polymers, such as polyimides, polybenzimidazoles, polybenzoxazoles, and other compounds based on nitrogen-containing rings have been manufactured on an industrial scale and have been widely used in the advanced fields of modern technology. At first, these polymers appeared in the form of various products that retained their service characteristics at much higher temperatures than the previous generation of thermally stable polymers and met the technical requirements of specialists. However, as the requirements imposed on products working under extreme thermal conditions began to increase, the question was raised about achieving a higher thermal stability limit. The attempts to synthesize new organic polynuclear heterocyclic structures did not lead to any considerable success. Therefore, the necessity for polymer stabilization appeared again but now in the range of cyclic chain polymers with aromatic and heterocyclic structures. Moreover, the requirements for stabilizers which should work effectively in a much higher temperature range than previously became more stringent. This condition drastically decreased the quantity of potential stabilizers, in particular, those with an organic structure suitable for using in polymer products operating at 300–500°C and higher.

The search for new stabilizers has led to a conceptual determination of the main requirements for stabilizers of thermally stable polymers. These requirements contain both the classical features of polymer stabilizers and certain new conditions induced by the new temperature limits for effective polymer stabilization. In our

opinion, the main feature of a stabilizer for thermally stable polymers should be its polyfunctionality. We mean by this term that certain properties of the stabilizer result from its chemical structure. These properties permit the stabilizer to suppress various degradation processes of polymers under thermally extreme conditions and favor the processes that improve the required service characteristics of a polymer's product under the same conditions. These new types of stabilizers should retain and even improve these properties under both dynamic and isothermic conditions of polymer heating over the required temperature ranges.

These new qualitative requirements have naturally resulted from a marked increase in the temperature limit of polymer use. The temperature limit of 500°C is characterized by drastic changes in all thermochemical reactions taking place in a polymer: both in the kinetics and in the qualitative structure of these reactions. The reaction rates of oxidation, hydrolysis, thermolysis, and other degradation processes increase tremendously, the role of diffusion processes becomes much more important, and all possible reactions of rearrangement, restructuring, and secondary synthesis take place. The competition among these reactions, induced to a great extent by an increase in temperature and service time at high temperatures, leads to such a superposition of all thermochemical reactions that in some cases one cannot speak about retention of the stable structure of the initial polymer. In this case it is more correct to state that a certain transition structure exists at the present time or in a given temperature range and it is stable under these conditions. Hence, it is clear that a new type of stabilizer should exhibit universal properties and its polyfunctionality should cover, as far as possible, the entire temperature range of serviceability of a thermally stable polymer.

If we single out the main qualities of this stabilizer on the basis of the polyfunctionality requirement, one of the most important criteria for this compound should be the "active viability" of its structure in the polymer over the entire temperature range. What do I mean by this strange term? This is the ability of a compound used as a stabilizer for thermally stable polymers to remain in a polymer in a given temperature-time range with an invariable or variable structure. These compounds should suppress in any possible way the chemical reactions that lead to deterioration of the product based on the stabilized polymer.

In my opinion, this pragmatic formulation makes it possible to use any thermochemical reactions proceeding in the polymer-stabilizer pair regardless of their individual character as the mechanism controlling the stabilization of these polymers. This formulation leads to the concept of "transfer stabilization" of thermally stable polymers. According to this concept, the stabilizer (introduced either into the finished polymer or in a certain stage of its synthesis, e.g., processing occurs more easily taking into account the peculiar features of the synthesis of heterocyclic compounds), as the service temperature or time increases, undergoes a number of successive transformations. During these transformations either the stabilizer or the products of its transformation suppress undesirable reactions in the polymer.

This stabilizer can play the role of a catalyst in the synthesis stage of thermally stable polymers and their intermediates, catalyzing formation of the polymer structure in the desired direction. During prepolymer transformation into polyheterocyclic compounds, it ensures protection of intermediates and oligomers against

reversible reactions (hydrolysis, acidolysis, etc.) and controls the molecular weight of the polymer. When the temperature increases, it also suppresses oxidative and secondary oxidative and thermohydrolytic reactions that are characteristic of the intramolecular cyclization of heterochain polymers. This stabilizer is converted into intermediate products of thermal oxidation and thermal hydrolysis and, hence, prevents the attack of oxygen and hydroxyl ions on the polymer. As a result of the deactivation of these degrading processes, the polymers in the thermolysis state acquire favorable conditions for the directed structuring of the main polymer backbone with increasing temperature. This subsequently leads to a considerable energy gain in the development of the turbo structure of the precarbonized state of polyheterocyclic polymers having a changed structure.

Consequently, this "transfer stabilization" of the polymer by transferring the stabilizer during the course of a change in its properties and the continuously varying nature of its effect on the polymer makes it possible to utilize the unique features of many thermally stable polymers for a longer time and at higher temperatures.

The following example is a proof of "transfer stabilization" of thermally stable polymers. It is known that many organic compounds of phosphorus, antimony, boron, and vanadium have been used as stabilizers of various polymers. One of the first heterocyclic compounds for which these stabilizers were used, was a well known thermally stable polyimide PM and the most outstanding example of "transfer stabilization" was the polyimide PM-triphenylphosphate (TPP) pair.

TPP has long been known as a plasticizer used in the manufacture of many polymer products. A question may be raised about the extent to which TPP exhibits its plasticizing action in the synthesis of polyimides (PI) and its effect on the thermal stability of the end product. TPP is usually introduced into a solution of already prepared polyamic acid (PAA), and the cyclodehydration of a film cast from this solution proceeds in the presence of TPP. It is known that without TPP, as a result of PAA degradation and incomplete cyclodehydration, "defective" structures are accumulated in polyimide molecules. They are end groups and remaining amic acid which essentially decrease the thermal stability of the final product. It is possible to follow the effect of TPP on the process of PAA transformation into a polyimide with the aid of MTA and TGA. Figure 1 shows the MTA curves for PAA based on a pyromellitic anhydride and diaminodiphenyl ether (PAA PM): a) without and b) with the addition of 10% of TPP. It is clear that TPP remains in the film until cyclodehydration is virtually completed, and only after that does it begin to escape from the polyimide.

In case b) the temperature range of PAA cyclodehydration is about 50° narrower than in case a). The activation energy of this process calculated from the curve of water elimination changes on approaching the curve maximum from 113 to 76 kJ/mole for a sample with TPP and from 80 to 58 kJ/mole for pure PAA. Because of the acceleration of cyclodehydration as a result of the plasticizing effect of TPP, the degree of intramolecular degradation of PAA and the incomplete character of imidization become less pronounced than those for non-plasticized PAA. This fact is indicated by an increase in thermal stability and an improvement in the mechanical properties of polyimide.

It should be noted, however, that the effect of TPP on cyclodehydration probably

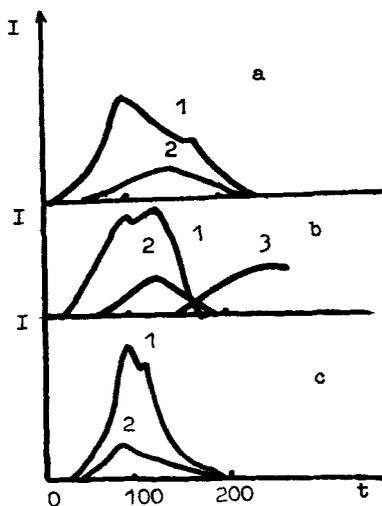


FIGURE 1 MTA curves for PM PAA prepared in DMF. I) Ion intensity; t) temperature ( $^{\circ}\text{C}$ ); the same in Figure 3. a) Without additions; additions of: b) 10 TPP c) 15%  $\text{H}_3\text{PO}_4$ . *m/e*: 1) 73, DMF; 2) 17,  $\text{H}_2\text{O}$ ; 3) 326, TPP.

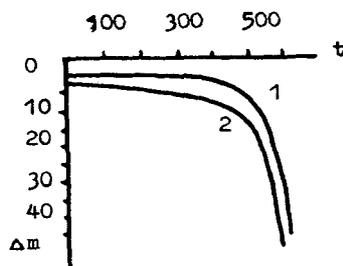
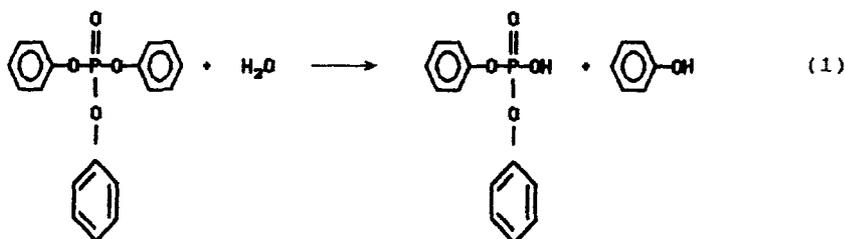


FIGURE 2 TGA curves for PM film without additive (1) and with addition of 10% TPP (2).  $\Delta m$ ) Weight loss; t) temperature ( $^{\circ}\text{C}$ ).

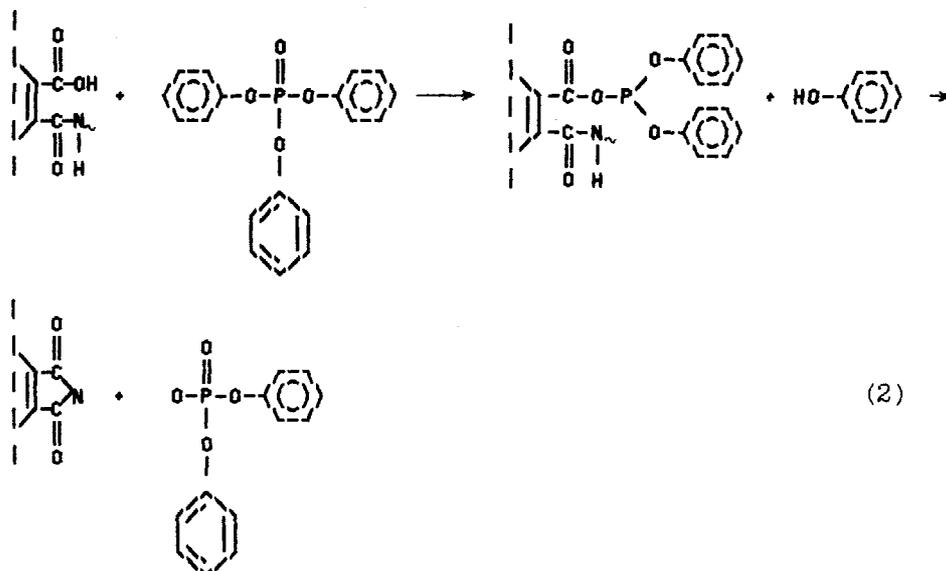
cannot be explained by the plasticizing action alone. It may be assumed that when TPP is present in PAA partial saponification of TPP is possible due to the influence of water eliminated during imidization.



In this reaction an acid ether is formed. It exhibits approximately the same catalytic effect as phosphoric acid.

Another possible mechanism of interaction between TPP and PAA, which ac-

celerates imidization may be the reaction of ring closure via intermediate formation of a mixed anhydride.



The thermal cyclodehydration of PAA is usually accompanied by intramolecular degradation. Water present in the system can hydrolyze anhydride end groups formed as a result of degradation and this yields carboxylic acids inactive in acylation. TPP reacting with these acids by a mechanism similar to reaction (2) facilitates the resynthesis of PAA, which leads to an increase in the molecular weight of the final PI and, hence, to a smaller number of structural defects.

The question of whether phosphorus containing compounds remain in the final polyimide is of a fundamental nature. A mass spectrometric analysis of gas products evolved from polyimide upon heating can provide an unambiguous answer to this question. Figure 2 shows the curve of the TPP evolution obtained with the aid of MTA for a polyimide film prepared from a PAA solution in the presence of a 10% addition of TPP. It should be noted that TPP is the only product isolated from the

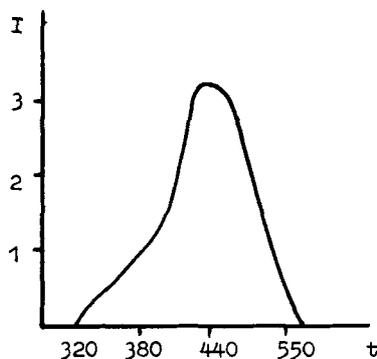


FIGURE 3 MTA curves for PM film with addition of 10% TPP ( $m/e = 326$ ).

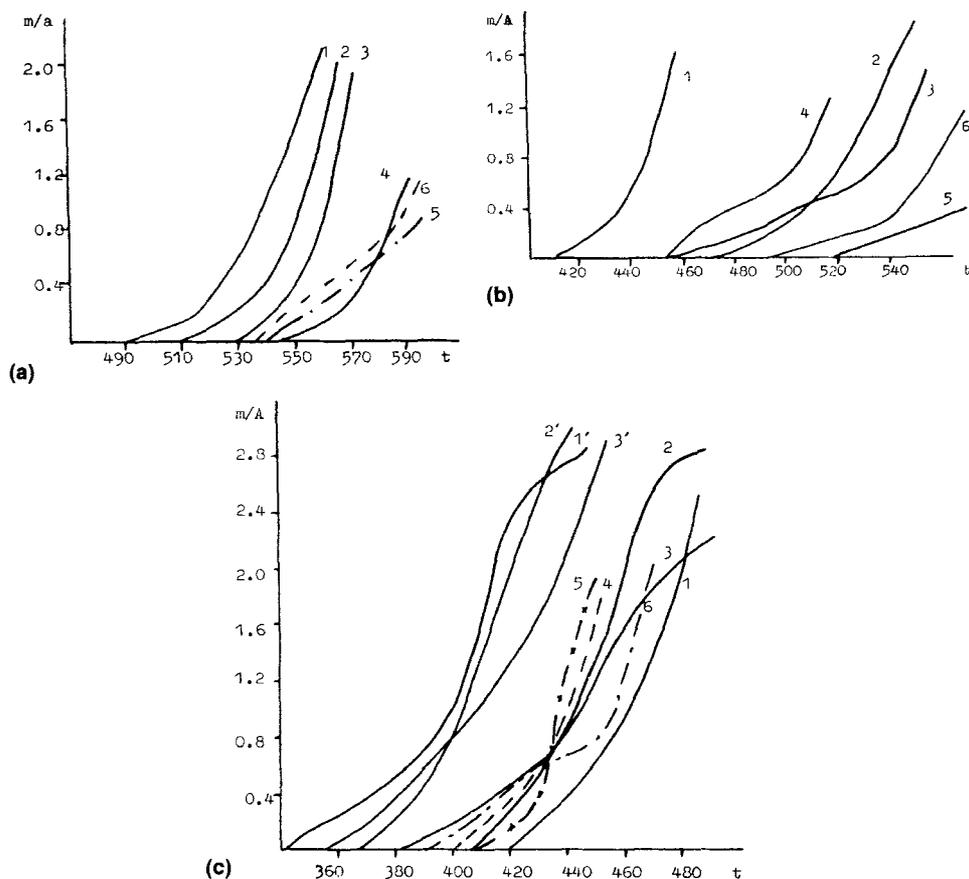


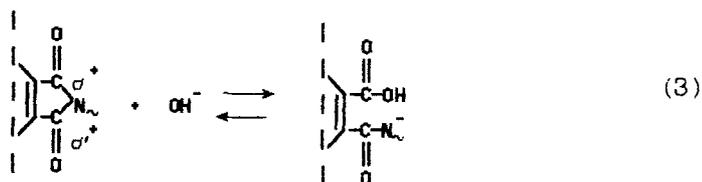
FIGURE 3 (a) Dependence of evolution  $\text{CO} + \text{CO}_2$  during thermal degradation in vacuum on temperature of PM (1-3) and N-PhI (4-6) films without additions (1,4) and with additions of 5%  $\text{B}_2\text{O}_3$  (2,5) and 5% of TPP (3,6).  $\text{m/A}$  Number of moles of oxides evolved per structural unit of the polymer;  $t$ ) temperature ( $^\circ\text{C}$ ). (b) Dependence of evolution  $\text{CO} + \text{CO}_2$  during thermal hydrolysis on temperature of PM (1-3) and N-PhI (4-6) films without additions (1,4) and with additions of 5%  $\text{B}_2\text{O}_3$  (2,5) and 5% of TPP (3,6). (c) Dependence of evolution of  $\text{CO} + \text{CO}_2$  during thermal oxidation on temperature of PM (1-3) and N-PhI (4-6) films without additions (1,4) and with additions of 5%  $\text{B}_2\text{O}_3$  (2,5) and 5% of TPP (3,6), (1'-3') in presence of moisture.

film on heating to  $500^\circ$ , which enables us to estimate its amount by the weight method. It is evident that even under high vacuum the polyimide film retains a certain amount (1-3%) of TPP up to  $500^\circ$  and higher when the degradation processes start. It is natural that under service conditions (presence of moisture and  $\text{O}_2$ , atmospheric pressure, etc.) the temperature for the initiation of degradation can be lower and the amount of TPP remaining in the film at this moment can be greater than in the above example. Hence, the influence of TPP on degradation processes cannot raise doubts. In order to elucidate the mechanisms by which TPP affects the processes of polyimide degradation, we used data obtained for polyimides and model compounds by the CTA method. This method is essentially the quantitative determination of carbon oxides formed upon sample heating in sealed ampoules under isothermal conditions.

Figure 3a shows the cumulative curves of gas evolution for PM films and N-phenylphthalimide (N-PhI) during thermal degradation under vacuum without any additive and with the addition of 5% wt of TPP or boric anhydride. It is clear that in the N-PhI case the effect of additives is slight, whereas polyimide is stabilized by them. It is noteworthy that in spite of their different natures both additives have the same effect. The defective structures present in polyimide are naturally destroyed earlier than imide fragments with a regular structure. The products resulting from this destruction, in particular water, can have a degrading effect on the main structure.

However, this water can also react with TPP and  $B_2O_3$ , and in both cases a relatively strong acid is formed. Probably, it is the acid character of the additives modified in this way that plays the stabilizing role. In this connection, several possible mechanisms for the stabilization of the imide structure may be considered. First, it has been repeatedly reported that TPP and  $B_2O_3$  exert the greatest stabilizing effect in the thermal hydrolysis of polyimides and model imides. Gas evolution curves during the thermal hydrolysis of PI-PM and N-PhI can serve as an example (Figure 3b). In both cases additives have a considerable stabilizing effect which is approximately the same for TPP and  $B_2O_3$ .

It is usually assumed that imide hydrolysis starts from a nucleophilic attack on the carbonyl carbon by either a water molecule or by a stronger nucleophilic agent, a hydroxyl ion:

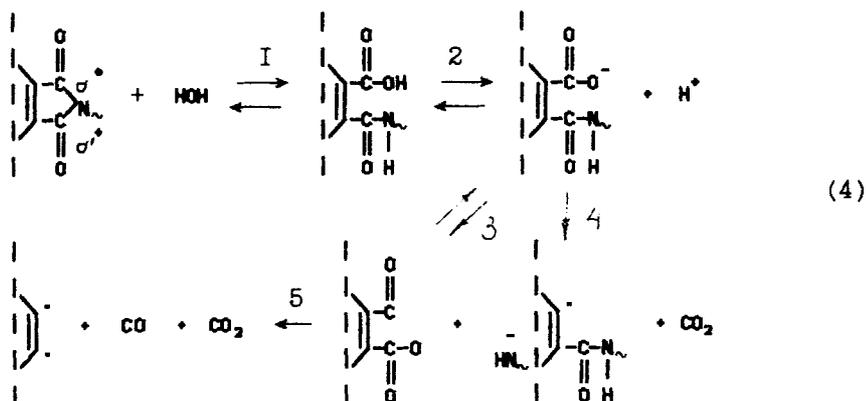


The concentration of hydroxyl ions and, hence, the hydrolysis rate of imides increase with temperature (although it should be noted that the ionic behavior of water depends on temperature in rather a complex way). The appearance of strong acids in the system leads to a considerable increase in the concentration of protons and a decrease in that of hydroxyl ions, which is one of the reasons for a decrease in the hydrolysis rate of the imides.

However, the stabilizing effect of TPP is not limited to this mechanism. Since at the temperatures considered here the imide ring should also undergo considerable hydrolysis by a non-dissociated water molecule, amic acid fragments will appear in the system. These further transformations can proceed by a different pathway.

The undissociated forms of o-amic acid are known to have a tendency to close into an imide ring, whereas dissociation of the acid group favors an intramolecular decomposition of the amic acid group with formation of an anhydride and an amine (Reaction 3). In the temperature range considered here (above  $400^\circ$ ), the anhydride groups intensively decompose with the evolution of gaseous products (reaction 5). Moreover, dissociation leads to decarboxylation of the acid itself (reaction 4).

Consequently, the stabilizing effect due to the acidic nature of the TPP derivatives (as well as other additives of the acid type) is the suppression of the dissociation



of the carboxyl of the amic acid group. On the basis of scheme (4) one can establish the following positive effects of this suppression:

- 1) The stabilization of the imide ring as a result of shifting the equilibrium (1) towards cyclodehydration.
- 2) The stabilization of amic acid fragments by decreasing the contribution of depolycondensation according to reaction (3).
- 3) The stabilization of carboxylic groups proper.

The two first effects have been discussed above, and the third effect may be illustrated by the CTA data for benzoic acid (Figure 4). In this case also a considerable thermostabilizing effect is observed (moreover, quite identical) upon the introduction of TPP or  $B_2O_3$ . This fact is another confirmation of our conclusion that the mechanism of the stabilizing action of these additives is the same.

It may be shown that a synergistic effect of thermal oxidation exists for PI and model imides (Figure 3c). Since in thermal oxidation water is eliminated (and in a closed system it is accumulated) at some stage, two processes are superposed: thermal oxidation and hydrolysis. It is natural to assume that just at this moment the mechanism of stabilization to thermal hydrolysis of the imide structure should occur due to the effect of TPP. The consideration of Figures 3b and 3c shows that actually in the beginning of thermal oxidation TPP does not exhibit a stabilizing effect, and only at temperatures about  $450^\circ$  does this effect begin to be observed. Hence, it may be assumed that in the case of thermo-oxidation the effect of TPP is also related to the stabilization of the imide structure to thermal hydrolysis. Another confirmation of this assumption is provided by the data on the thermal oxidation of PI when water is added (Figure 3c). As was to be expected, in this case the thermostabilizing effect is already observed in the early stages of thermal oxidation.

If we compare the thermo-oxidative stability of PI films stabilized by various phosphorus compounds (Figure 5), the effect is most pronounced when TPP and or hexametapol is used. The organic compounds of trivalent phosphorus do not exert a stabilizing effect on the thermal oxidation of polyimides. There are reasons to assume that some antimony or vanadium take part in the "transfer stabilization" of both polyimides and polybenzimidazoles. However, the first experiments with

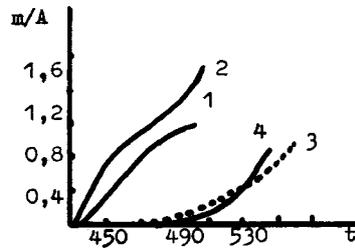


FIGURE 4 Dependence of evolution of CO + CO<sub>2</sub> on temperature during thermal degradation in vacuum (1) and thermal hydrolysis (2-4) of benzoic acid without additions (1,2) and with additions of 5% B<sub>2</sub>O<sub>3</sub> and 5% TPP (4).

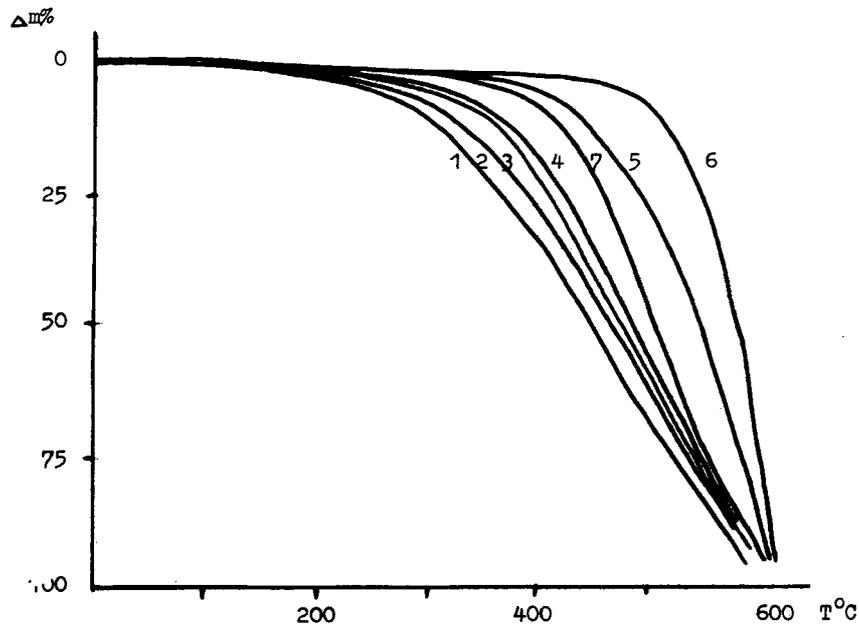


FIGURE 5 TG curves of polyimide film stabilized by acid ester of trivalent phosphor (1-4) curves, by TPP (6) and (5) by hexamethylpol; 7-curve is anstabilized polyimide PM.

such compounds as so far give only single stabilization effects which need further detailed investigation.