

HIGH TEMPERATURE DEGRADATION OF COMPOUNDS MODELLING POLYIMIDE FRAGMENTS

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ABSTRACT

Chromatography and mass spectrometry were used to investigate products and kinetics of thermal, thermo-oxidative and thermo-hydrolytic degradation of compounds modelling fragments of polypyromellitdiphenyloxidediimide. Data on the degradation of benzoic and pyromellitic acids, diphenyl and diaminodiphenyl ethers, N-phenyl benzamide and N-phenyl phthalimide made it possible to draw conclusions concerning the effect of the chemical structure of polyimides on their thermal stability.

INTRODUCTION

Problems of thermal stability of polymers, in particular, of polyimides, have recently been extensively and thoroughly investigated^{1–6}. However, most papers dealing with these questions investigated thermal stability of polyimides as a whole without a detailed study of the effect of single factors, such as the structure of macromolecules, their crystallinity, molecularweight, solvents, etc. The effect of the chemical nature of initial components used for the synthesis of polyimides on their thermal stability is of particular importance. Several papers have been published reporting valuable data on polyimide behaviour at high temperatures when the chemical structure of diamine or dianhydride is changed^{7–10}. Nevertheless, in these papers the problem of the relationship between the chemical structure of the initial products and the thermal stability of polyimide has been mainly considered for polymers themselves. From our standpoint the determination of thermal stability and main dependences of thermal degradation under different conditions both for compounds used in the synthesis of polyimides and for compounds modelling single elementary units of the polyimide chain will be of use for the selection of initial compounds for the synthesis of high temperature resistant polymers. Unfortunately, very few papers dealing with these problems have been published^{11–13} and they mainly consider some physico-chemical characteristics of model compounds related in their structure to some fragments of polyimides. One of our previous works¹⁴ dealt with a possibility of correlation between the thermal stability of model compounds and of polyimides containing elementary units similar to model compounds. Nevertheless, a pronounced

difference between the thermal stability of imide model compounds and polyimides shows that from the standpoint of chemical structure the thermal stability of polyimides depends not only on the structure of an "ideal" elementary unit but also on the chemical structure of all the fragments of the polyimide macromolecule. In fact, a common polyimide such as polypyromellitimide based on diaminodiphenyl ether can contain not only "ideal" elementary units which may be modelled by N-phenylphthalimide^{1,4} and diphenyl ether but also fragments with anhydride, carboxyl, amide and amine groups. These groups could be formed or could remain in the processes of synthesis of polyimide or of the preparation of articles from it. In the opinion of most investigators these groups are responsible for the thermal structure of polyimides and evidently cause the difference between the thermal structure of "ideal" models and common polymers.

In this work thermal stability of some model compounds was evaluated. In their structure they are close both to weak fragments of the polyimide chain: benzoic acid, pyromellitic dianhydride, diaminodiphenyl ether, N-phenylbenzamide and to compounds modelling the "ideal" polyimide structure—N-phenylphthalimide and diphenyl ether with this purpose the behavior of these compounds was investigated in the course of thermal degradation in vacuum, in thermooxidative degradation in the presence of oxygen and under the action of water vapors.

EXPERIMENTAL

Model compounds

Benzoic acid (BA), pyromellitic acid (PA), pyromellitic dianhydride (PD), diphenyl ether (DE) and diaminodiphenyl ether (DADE) were of commercial grade. N-phenylbenzamide (PhBA) and N-phenylphthalimide (PhI) were synthesized by the method described previously^{1,4}. All these compounds were purified by vacuum sublimation, their identity and purity were tested by using elemental analysis, infrared spectra and differential scanning calorimetry.

Pyrolysis

Pyrolysis of model compounds was carried out in double chamber pyrex ampoules with a breakable partition. A feed of the compound (20 mg) was placed in a chamber of the ampoule 20 ml in volume: the ampoule was evacuated to 10^{-2} torr and sealed. The initial oxygen pressure in thermooxidative degradation was 0.25 atm. The amount of water in experiments on thermohydrolytic degradation of samples was $(0.3-0.5) \cdot 10^{-3}$ g mol. The ampoules were placed in a furnace in which the temperature was maintained to within $\pm 0.5\%$. The pyrolysis was carried out under isothermal conditions.

Analysis of gaseous products

The volume of gaseous pyrolysis products was determined as follows. In order to avoid the penetration of air into the ampoule the partition was broken under a

layer of a saturated NaCl solution. Gaseous products were introduced into the measuring burette with a syringe. The amount of gaseous products evolved in the course of degradation was measured with a Tsvet-4 gas chromatograph¹⁵ or a chromato-mass spectrometer ("Chromass-2") which is a combination of a chromatographic column and a relatively simple mass spectrometer; it is intended for qualitative and quantitative analysis of mixtures of CO and CO₂ which are the main gaseous products of pyrolysis of model compounds. After the degradation of the sample the gas mixture was introduced into the "Chromass-2" by portions of 0.2 ml and the peaks corresponding to masses 44 and 28 were recorded successively. The volumes of CO₂ and CO were calculated by using the equation:

$$V_{\text{CO}_2} = \frac{V}{\frac{S_1 - 0.25S_2}{nS_2} \cdot \sqrt{\frac{M_2}{M_1}} + 1} \quad V_{\text{CO}} = V - V_{\text{CO}_2}$$

where V = the volume of gaseous pyrolysis products;

S_1 = the area of the chromatographic peak m/e 28;

S_2 = the area of the chromatographic peak m/e 44;

n = the ratio of intensities of molecular peaks of CO and CO₂;

0.25 = the coefficient for the contribution of CO₂ to the area of peak m/e 28;

$\frac{M_2}{M_1}$ = the factor for the change in the composition of the mixture in the ionic source as compared to the initial mixture.

The amounts of CO and CO₂ were measured by using the ratios of intensities of two lines in mass spectra (see equation) with a relative error of not more than 2%.

Calculation of kinetic characteristics

The rate constants of evolution of CO₂ and CO were calculated by using the equations for simultaneous irreversible reactions of first order¹⁶.

$$K = K_{\text{CO}_2} + K_{\text{CO}} \quad K = \frac{2.3}{t} \log \frac{C_0}{C}; \quad K_{\text{CO}_2} = \frac{V_{\text{CO}_2}}{V} \cdot \frac{2.3}{t} \log \frac{C_0}{C}$$

where V = the total volume of gas evolved by the moment t ;

V_{CO_2} = the volume of CO₂ evolved by the moment t ;

C_0 = the initial concentration of the starting substance;

C = the concentration of the starting substance at the moment t .

The activation energy and pre-exponential factors were calculated using the Arrhenius equation.

DISCUSSION OF RESULTS

Thermal degradation of acids

It is known that in the course of pyrolysis of polyimides at a temperature of the order of 400–450°C a certain amount of CO₂ is formed. Its appearance is usually ascribed to decomposition of acid groups in incompletely cyclized units. Nevertheless, the analysis of literature data shows^{17,18} that only relatively few monomolecular reactions of degradation of organic compounds have been investigated. In particular, no evidence is available concerning both the composition of degradation products and the kinetic characteristics of the process of degradation of benzoic and pyromellitic acids. Usually it is assumed that CO₂ is the main gaseous product of the pyrolysis of aromatic acids. Qualitative analysis of gaseous products of BA and PA degradation made in this work showed that in the course of this degradation in vacuum under isothermal conditions, not only CO₂ but also considerable amounts of CO are formed. The ratio CO/CO₂ for both acids is within the range 0.26–0.42 over the temperature range 460–520°C.

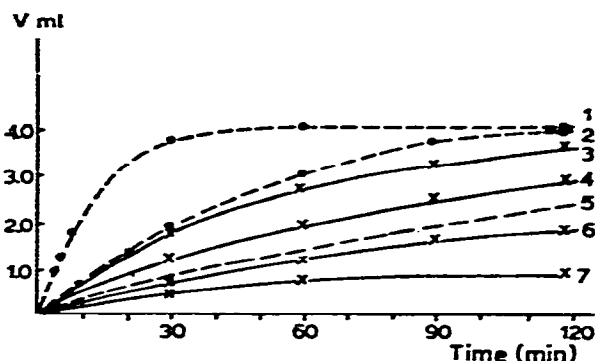


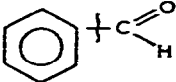
Fig. 1. Curves to gas evolution in pyrolysis of BA (dotted line) and PA (full line) at temperatures: 1,3 = 520°C; 2,4 = 500°C; 5,6 = 480°C; 7 = 460°C. The ordinate V represents the volume of gas evolved in ml.

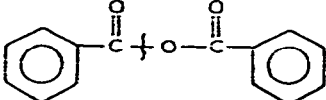
Analysis of curves of gas evolution (Fig. 1) showed that under experimental conditions at temperatures of 500 and 520°C BA decomposes almost completely over the period of 90 and 30 min, respectively (when BA is completely decomposed, the calculated volume of CO + CO₂ is 3.7 ml). In this case the ampoules do not contain solid residue. The analysis of the solid product remaining after incomplete degradation of BA showed that it contains benzoic anhydride which is presumably formed in the course of the establishment of thermal equilibrium at a temperature of about 400°C. Kinetic calculations of gas evolution during the pyrolysis of BA indicate that in the initial stage of its degradation which proceeds homogeneously, the reaction is close to first order in the initial BA. It may be suggested that CO can evolve as a result of three processes: (1) monomolecular degradation of BA molecules, (2) their bimolecular reaction, (3) monomolecular degradation of molecules of benzoic

TABLE I
KINETICS OF CO AND CO₂ EVOLUTION IN PYROLYSIS OF BA AND PA

Reactions	Benzole acid			Pyromellitic acid				E kcal mol ⁻¹	A sec ⁻¹	
	K (sec ⁻¹)		E kcal mol ⁻¹	K (sec ⁻¹)		E kcal mol ⁻¹	A sec ⁻¹			
	480°C	500°C		520°C	460°C					480°C
CO+CO ₂	1.3·10 ⁻⁴	5.0·10 ⁻⁴	1.6·10 ⁻³	3.3·10 ⁻³	7.3·10 ⁻³	1.3·10 ⁻³	1.3·10 ⁻⁴	2.2·10 ⁻⁴	33	10 ⁶
CO	3.8·10 ⁻⁵	1.0·10 ⁻⁴	3.6·10 ⁻⁴	1.1·10 ⁻⁵	2.1·10 ⁻⁵	3.8·10 ⁻⁵	—	—	32	10 ⁶
CO ₂	9.0·10 ⁻⁵	4.0·10 ⁻⁴	1.2·10 ⁻³	—	5.1·10 ⁻⁵	9.7·10 ⁻⁵	1.7·10 ⁻⁴	—	34	10 ⁶

anhydride. First order of reaction in BA in the early stage of CO evolution is in favor of reactions (1) and (3). The values of activation energy and pre-exponential factor for CO and CO₂ suggest that these products are formed as a result of simple monomolecular degradation with the breaking of one bond. The activation energy of CO formation also shows that CO is probably a product of degradation of benzoic

anhydride. In fact, the energy of the  bond in benzoic aldehyde has been

estimated to be 85 kcal mol⁻¹ and although the energy of the  bond in benzoic anhydride has not been established experimentally, it may be

estimated to be approximately 70 kcal mol⁻¹ (ref. 20).

Even in the initial degradation stages over the temperature range 460–500 °C the PA pyrolysis proceeds heterogeneously with the formation of the polymer film. By analogy with BA the formation of pyromellitic polyanhydride may be assumed. Moreover, it is possible that a polymer film of undetermined composition is formed as a result of the degradation of PA and polyanhydride. In the early degradation stages the reaction order is close to unity. The rate constants of CO₂ and CO evolution were calculated for the corresponding portions of kinetic curves proceeding from the assumption that they are formed as a result of two simultaneous processes. The activation energy and the pre-exponential factor for CO₂ and CO were approximately equal: E was 33 kcal mol⁻¹ and A was 10⁶. Previously, we have obtained the same values for the activation energy of the CO and CO₂ evolution in degradation of terephthalic acid under analogous conditions. Similar values of activation energies have been obtained by several authors in the degradation of polymers comparatively close to polyanhydrides in their structure²¹ and also in the early stages of polyimide degradation²².

The pronounced difference in the structure of these polymers and identical values of activation energy determined in the process of their degradation with the formation of CO₂ and CO appear to indicate that the heterogeneous character of these processes and the diffusion factors appreciably affect the kinetics of the evolution of gaseous pyrolysis products. The same factors may account for a considerable difference in the kinetics of BA and PA degradation.

Thus, data on chemical degradation of models imitating fragments of the polyimide chain containing acid groups, show a pronounced dependence of thermal stability of polyimide on the quantity of carboxyl groups in the macromolecule and the impossibility of improving this stability without elimination or stabilization of these "weak" places.

Thermal degradation of models containing amide and amine groups

Other vulnerable places in the polyimide macromolecule are its terminal NH₂

groups and amide bonds remaining in the polyimide structure as a result of incomplete imidization. Data on thermal degradation of DADE and PhBA modelling these polyimide fragments permit comparisons to be made between the thermal stability of these compounds and that of polyimides. DADE begins to decompose in vacuum at a temperature below 500°C . The main gaseous degradation product is hydrogen. However, this does not explain all negative effects of amine groups on the thermal stability of polyimide. It was observed that at temperatures of about 500°C amine end-groups react with carbonyl groups of imide rings; this causes a whole series of degradation processes in the polyimide structure including hydrolytic processes. Figure 2 shows curves of CO_2 evolution in the degradation of DADE and PhI (curves 2 and 3) and of their blend (curve 1). It can be seen that curve 1 is characterized by a certain induction period after which the rate of CO_2 evolution increases sharply. This is presumably due to the fact that, at first, water molecules are accumulated and then the rate of PhI degradation increases rapidly owing to hydrolytic processes according to the reaction shown below. The observed effect of free amine groups on the stability of the main polyimide structure enables us to determine the

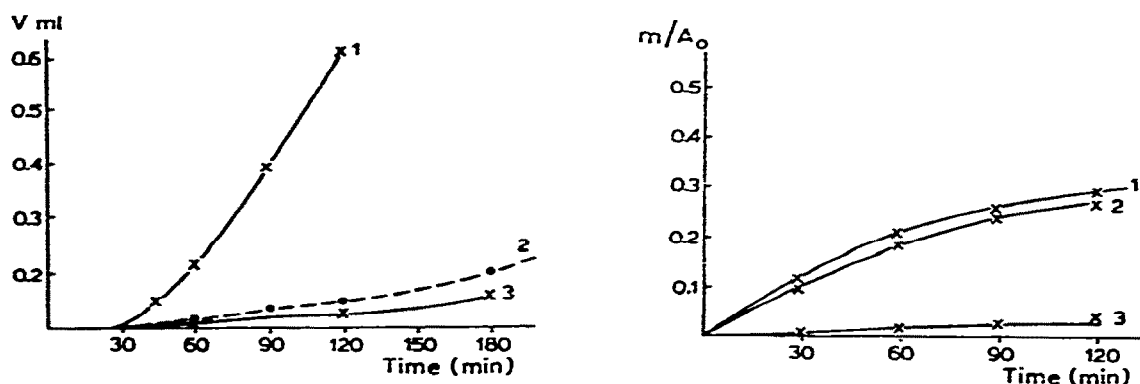


Fig. 2. Kinetics of CO_2 evolution in thermal degradation of PhI (curve 2), DADE (curve 3) and a blend of these products (curve 1) in a 1:1 molar ratio at 540°C .

Fig. 3. Kinetics of evolution of CO (curve 1), CO_2 (curve 2) and H_2 (curve 3) in thermal degradation of PhBA at 510°C . The ordinate represents m/A_0 where m is the quantity of g.mol of gas evolved, A_0 is the quantity of g.mol of the initial compound.

part played by amine ends of macromolecules while the behavior of PhBA at high temperatures makes it possible to follow the significance of the amine bond which may exist in common polyimides. Analysis of gaseous products of PhBA degradation in vacuum at 490 , 510 and 530°C shows that it starts at a temperature above 480°C and the main gaseous degradation products are CO , CO_2 and H_2 (Fig. 3). In the initial period the reaction is second order in PhBA. The composition of the products formed indicates that the degradation process is very complex. Thus, the quantity of CO_2 evolved is comparable to that of CO and the quantity of H_2 is lower by approximately an order of magnitude. This result would be difficult to interpret if we assume

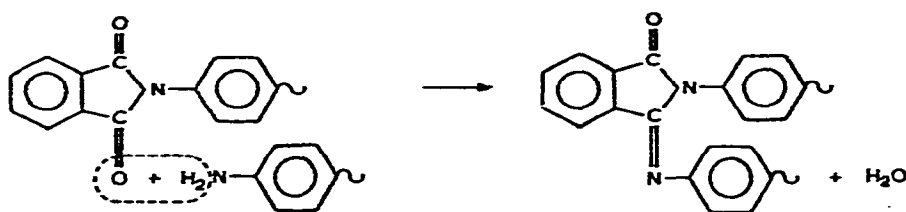
monomolecular degradation of PhBA. Considerable amounts of water are known to be formed in the thermal degradation of polyamides²⁸. Evidently, in this case also degradation proceeds with the formation of water molecules owing to a reaction between a labile hydrogen atom of the imine group with the amide carbonyl group with subsequent abstraction of hydroxyl ion and the formation of benzonitrile derivatives.

The activation energy of the overall degradation reaction is 46 kcal mol^{-1} and the pre-exponential factor is $10^{11} \text{ mol}^{-1} \text{ l}^{-1} \text{ sec}$. The activation energies of CO and CO₂ formation calculated for simultaneous irreversible reactions of second order in PhBA are 54 and 38 kcal mol^{-1} , respectively. The corresponding pre-exponential factors are 10^{13} and $10^8 \text{ mol}^{-1} \text{ l}^{-1} \text{ sec}$. This is an evidence in favor of either bimolecular PhBA degradation or a series of successive reactions leading to H₂O formation and to a hydrolytic stage of the degradation of model.

Hence, the presence of the amide bond in polyimide may cause high temperature hydrolysis of the main polymer structure even in vacuum. Moreover, it should be borne in mind that as a rule the amide bond in the chain in the presence of the carbonyl group increases the risk of thermohydrolytic degradation.

Thermohydrolytic degradation of model compounds

As we have shown previously¹⁴, compounds modelling the main structure of the polymer investigated (PhI and DE) begin to degrade in vacuum at temperatures in excess of 520°C. Nevertheless, when common polyimides are investigated, in the analysis of their thermal stability, it is necessary first of all to take into account a possibility of hydrolytic processes occurring at high temperatures. Water may be formed in reactions of thermal degradation of the compounds considered above and in reactions of interaction of free amine groups with carbonyl oxygen, such as:



The occurrence of high temperature hydrolytic processes is indicated by the presence in degradation products of a considerable amount of CO₂ at 570°C. The maximum of its mass spectrometric peak coincides with peaks for CO and H₂O and although the author reporting these data²⁴ is inclined to explain this phenomenon by intermolecular rearrangement of imide rings, in our opinion this is caused by their high temperature hydrolysis. The analysis of products of PhI degradation in vacuum and in the presence of water shows that at temperatures of about 500°C high-temperature hydrolysis of imide rings occurs. Figure 4 shows kinetics of evolution of gaseous products in pyrolysis of PhI in vacuum (curves 4, 5,6) and in the presence of water

(curves 1,2,3) at 540°C. The main gaseous degradation products are CO and CO₂. In thermal degradation of PhI in vacuum the ratio CO/CO₂ changes in the course of the experiment approximately from 50 to 20. In hydrolytic degradation this ratio is 0.5–0.45 and is very close to the value obtained by us in the pyrolysis of aromatic acids. The rate of pyrolytic degradation of PhI at 540°C is about 15 times greater than that of its thermal degradation. The activation energy of the overall reaction of thermal degradation of PhI changes from 105 kcal mol⁻¹ at 540°C to 62 kcal mol⁻¹

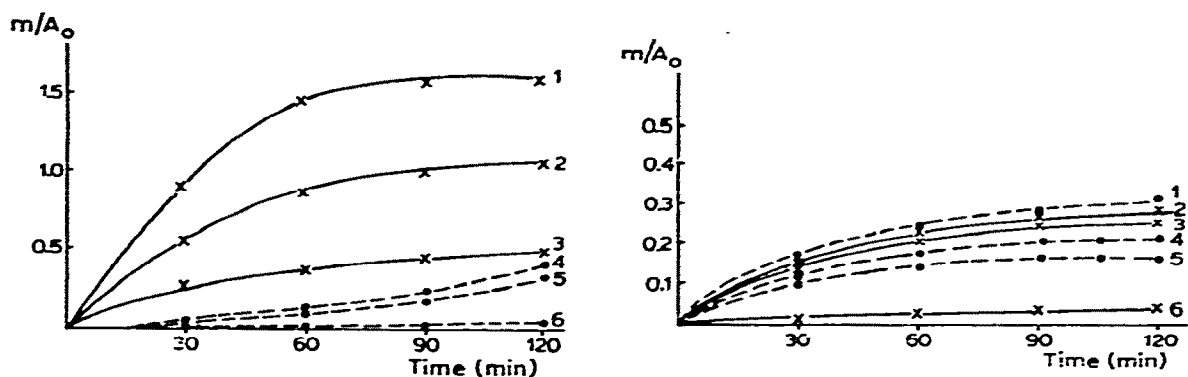


Fig. 4. Comparison of processes of gas evolution in thermal (dotted line) and thermohydrolytic (full line) degradation of PhI. Curves: 1,4 = CO + CO₂; 2,6 = CO₂; 3,5 = CO.

Fig. 5. Comparison of processes of gas evolution in thermal (full line) and thermohydrolytic (dotted line) degradation of PhBA. Curves 1,3 = CO₂; 2,4 = CO; 5,6 = H₂.

at 580°C. This indicates that hydrolytic processes develop with increasing temperature. The appearance of solid degradation products in thermal and hydrolytic degradation of PhI is markedly different. In the first case the product is a dark brown film reminding of polyimides in color, and in the second case the products are colorless. The importance of hydrolytic reactions becomes particularly evident when kinetics of thermal and hydrolytic degradation of PhBA are compared. Figure 5 shows curves of formation of gaseous products in thermal (curves 6, 2, 3) and hydrolytic (curves 4, 5, 1) degradation of PhBA at 510°C. In contrast to PhI (Fig. 4), in the case of PhBA there is no pronounced difference between the curves of thermal and hydrolytic degradation. Actually, in these cases the values of the overall degradation rate and the CO/CO₂ ratio are similar. Their principal difference is that in thermal degradation reaction products contain much smaller amounts of hydrogen. This hydrogen deficiency in the case of thermal degradation may be attributed to the participation of hydrogen in H₂O formation. As a result the initial thermal process virtually becomes a hydrolytic process. Figure 6 shows the curve of PhI degradation in the presence of water. The temperature range of the degradation of PhI, BA and PA and the order of magnitude of degradation constants almost coincide. This suggests that PhI hydrolysis is caused by an equilibrium shift towards the formation of acid because its thermal degradation rate is higher than that of PhI.

It is interesting to note that when the pyrolysis of a compound modelling another main fragment of the polyimide chain—DE—proceeds in vacuum in the presence of water, its high temperature hydrolysis does not occur under those conditions when thermohydrolytic degradation of PhI occurs (Fig. 7).

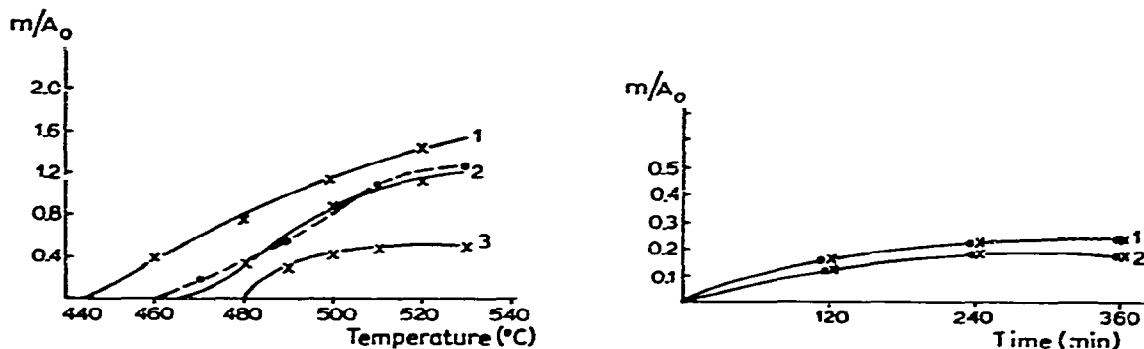


Fig. 6. Temperature dependence of the rate of thermal degradation of PA (curve 1), BA (curve 2) and PhBA (curve 3) and thermohydrolytic degradation of PhI (dotted line).

Fig. 7. Curves of thermo- (—○—) and thermohydrolytic (—×—) degradation of DE; curve 1 = H_2 , curve 2 = CO .

Thus, a possibility of hydrolysis of imide rings at high temperature leading to CO_2 formation was established on the basis of the analysis of degradation of model compounds.

Thermooxidative degradation of model compounds

Degradation of PhI, DE PhBA, PD and DADE in an atmosphere of oxygen was carried out over a wide temperature range in order to evaluate relative stability to thermal oxidation of main fragments of the polyimide chain, amido acid fragments and end groups (Fig. 8). Figure 8 shows that DADE reacting with oxygen at $170^\circ C$ exhibits the lowest thermooxidative stability. This is confirmed by kinetics of oxygen absorption (Fig. 9). In this process water formation is evident, and starting from $210^\circ C$ other gaseous degradation products appear: CO and CO_2 . The anhydride ends of the polyimide molecule are more stable to thermooxidation (PD degradation starts at $310^\circ C$). PhBA modelling amide chain fragments starts to decompose at $330^\circ C$. PhI and DE exhibit the highest stability to oxidation, just as in vacuum.

Under actual conditions of thermooxidative degradation of polyimides macromolecules undergo a combined action of oxygen and water. Since even for compounds modelling "weak" fragments of the polymer chain thermal oxidation is accompanied by the action of water isolated from these compounds, we checked the effect of water on thermooxidative degradation of PhI and DE. Figure 10 shows a pronounced decrease in the temperature of the beginning of thermooxidative degradation of PhI and DE in the presence of water whereas hydrolysis in the absence of oxygen begins for PhI at a temperature $70\text{--}80^\circ C$ higher and DE does not undergo any

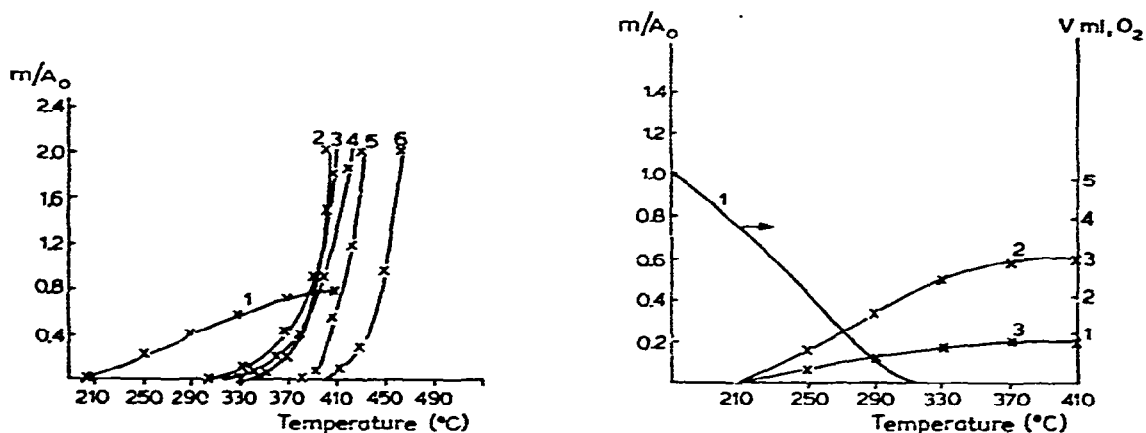


Fig. 8. Temperature dependence of thermooxidative degradation of DADE (curve 1), PD (curve 2), PhBA (curve 3), BA (curve 4), PhI (curve 5), DE (curve 6).

Fig. 9. Curves of gas evolution in thermooxidative degradation of DADE; curve 1 = O_2 absorption, curve 2 = CO_2 evolution, curve 3 = CO evolution.

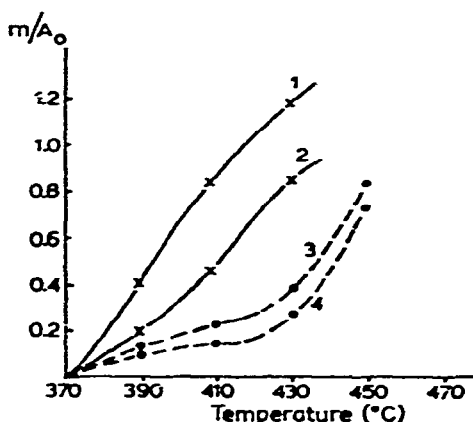


Fig. 10. Gas evolution curves in thermooxidative degradation of PhI (full line) and DE (dotted line) in the presence of H_2O ; curve 1, 4 (CO_2), curve 2, 3 (CO).

hydrolysis in the absence of oxygen. Evidently, hydrolysis of PhI is possible both in vacuum and in oxygen, but in oxygen it proceeds faster owing to the shift in the equilibrium: hydrolysis–dehydrocyclization because the degradation rate of products of PhI degradation is higher than that of PhI itself.

Acceleration of DE oxidation in the presence of water probably occurs as a result of hydrolysis of products of DE oxidation.

CONCLUSIONS

The investigation of compounds modelling single fragments of polypyromellitediphenyloxideimide (PPI) showed that thermal stability of these compounds

depends on the composition of the surrounding atmosphere and on the presence of reactive groups in their structure. Thermal stability of PPI depends on that of compounds modelling "weak" fragments of PPI, in particular, compounds containing free amine and carboxyl groups. Thermal stability of PhI and DE modelling the main PPI structure is much higher than that of the common polymer.

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