

INVESTIGATIONS OF IMIDIZATION OF POLYPYROMELLITAMIDO ACIDS AND THERMAL DEGRADATION OF POLYPYROMELLITIMIDES BY MASS SPECTROMETRIC THERMAL ANALYSIS

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ABSTRACT

Processes occurring when samples of fibers of polypyromellitimido acids and polypyromellitimides based on them are heated in vacuum have been investigated by mass spectrometric thermal analysis (MTA) over a wide temperature range.

A combination of MTA methods with a comparative thermal analysis of polyimides and model compounds permits conclusions to be made concerning the main reactions responsible for the thermal stability and the start of degradation of a number of polyimide structures.

INTRODUCTION

The development of the industrial production of polymeric materials with a very high thermal stability, in particular, polymers based on polyimides, has led to detailed investigations of reactions proceeding both during the thermal treatment of these polymers in the course of their preparation and as a result of thermal effects during the exploitation of articles manufactured from them.

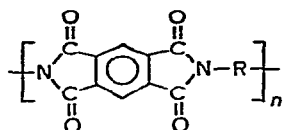
Mass spectrometric thermal analysis (MTA) is a method providing extensive information on the structure of polymers and their thermal stability¹⁻³. The distinguishing feature of the MTA method is that it permits investigations of the dynamic development of the thermal degradation of polymers.

The results of investigations carried out by this method are not only of great practical importance, but also of major theoretical significance. They make it possible to approach the solution of several fundamental problems of the thermal stability of polymers. This refers, in the first place, to the elucidation of the main factors governing the limits of the thermal stability of polymers and to the establishment of relationships between the thermal stability and chemical structure.

In this work, the method of MTA was used to investigate transformations occurring when fibres of polypyromellitimido acids (PAA) and polypyromellitimides (PI) based on them are heated in vacuum over a wide range of temperatures.

TABLE 1

CHARACTERISTICS OF INVESTIGATED PAA AND PI FIBRES* WITH THE GENERAL FORMULA



Sample no.	R	σ (kgp/mm ²)	ϵ (%)	E (kgp/mm ²)	E ₀ (kgp/mm ²)
PI-1		18 50	9 0.8	1050 8000	20,000
PI-2		20 90	8.2 0.6	1200 10,000	21,000
PI-3		22 45	7.6 0.7	1360 7000	
PI-4		16 23	16 40	450 440	1000
PI-5		14 23	18 38	340 390	900
PI-6		39 70	16 8	690 1400	2900
PI-7		M M	7.0 1.6	2100 13,000	13,000 22,000

* The upper values of the parameters correspond to PAA, the lower to PI.

EXPERIMENTAL

Materials

Structural formulae, indices of the polymers investigated and characteristics of PAA and PI fibres based on them are shown in Table 1. The selected PAA were synthesized according to the method described by Adrova et al.⁴ and the PAA fibres were spun from a dimethyl formamide (DMF) solution⁵ and vacuum dried at room temperature.

Mechanical and thermomechanical characteristics of fibres were determined with a standard tensile testing machine (span 100 mm, deformation rate 20 mm/min) and with an instrument for testing the deformational properties of fibres and films⁶. E₀ is the elastic modulus corresponding to the temperature of absolute zero obtained by extrapolating the temperature dependences of the elastic modulus to 0°K.

MTA procedure

Experiments were carried out as described in ref. 7. Fibre samples of ca. 3 mg in weight were placed in a stainless steel crucible fixed on the pipe connection of the gaseous source of ions in a MI 1305 mass spectrometer in such a way that all volatile products isolated from the sample during gas evolution passed directly into the ionization chamber. The operating vacuum in the analyzer chamber was 10^{-7} – 6×10^{-6} torr. The energy of the electrons used for ionization was 70 eV; the range of mass numbers recorded was from 1 to 200. The crucible was heated in an oven at a rate of 0.7–1.0°C/min. During heating, the mass spectra were recorded periodically with simultaneous registration of the temperature at the moment of the appearance of a peak in the mass spectrogram. Mean recording time for one spectrum was ca. 10 min.

After MTA had been carried out, dependences of heights of peaks (h) on time (t) and temperature (T) of the experiment were determined. Quantitative analysis of the volatile products formed was carried out by graphic integration of the experimental curves $h = f(t)$ and

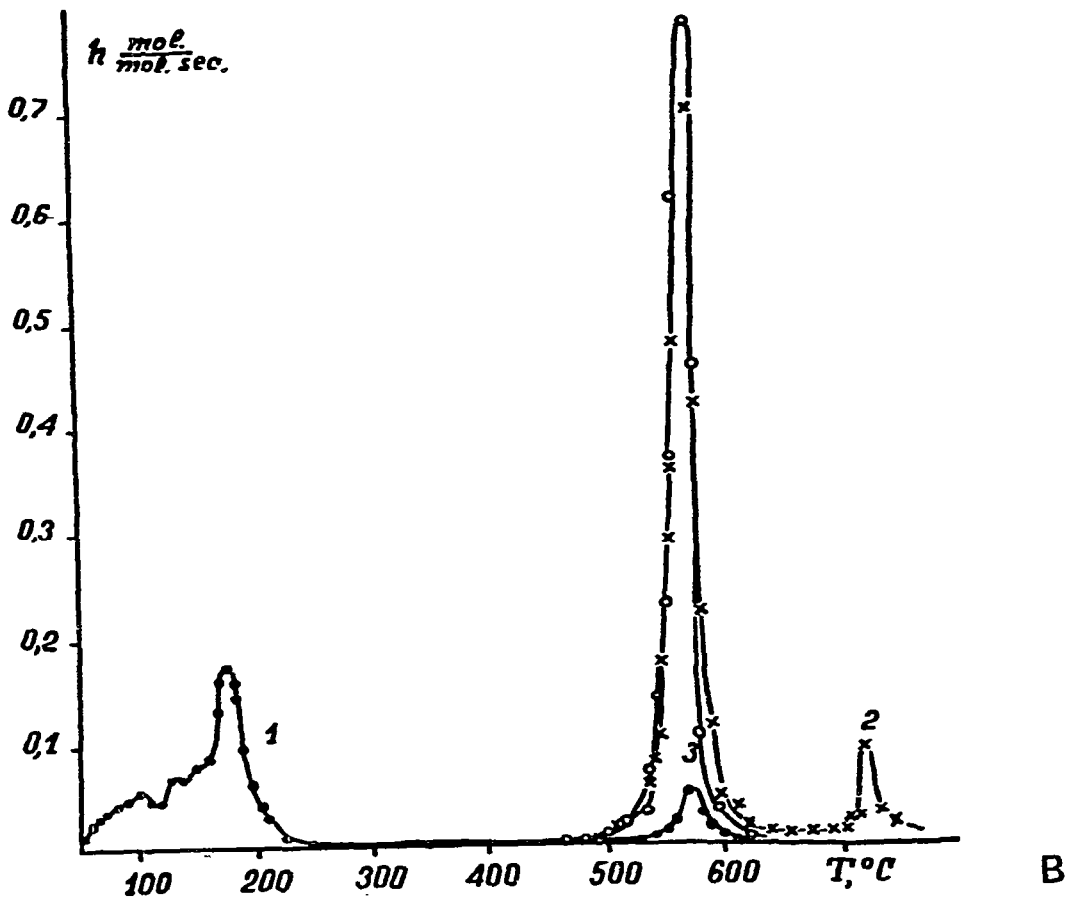
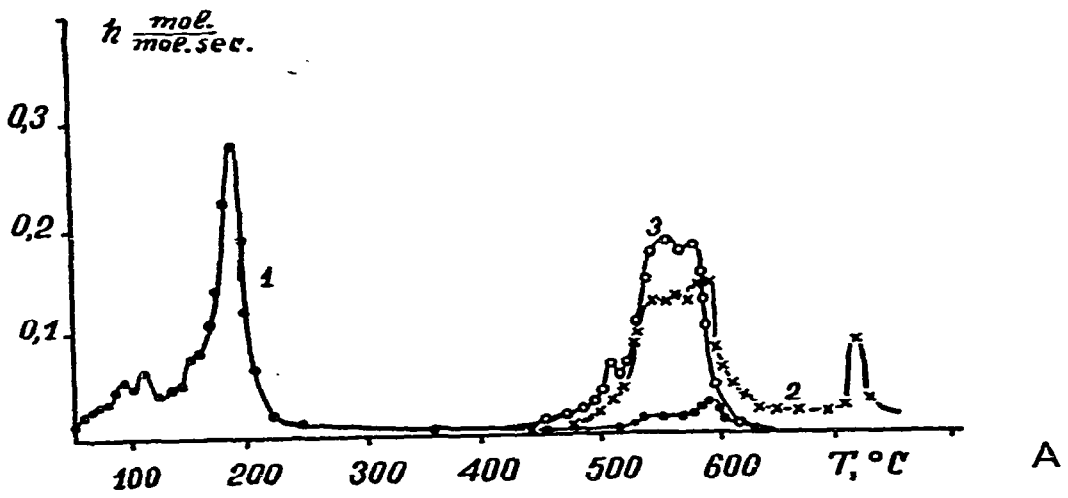
$$Q_m = \varphi \int_{t_1}^{t_2} h_m(t) dt$$

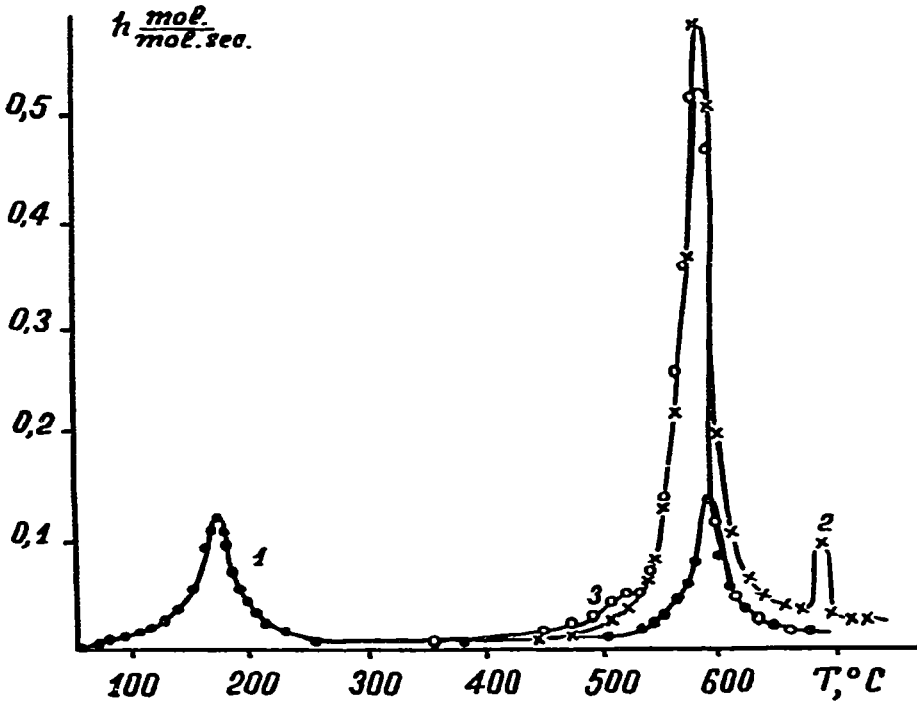
where Q_m is the content of the volatile product m over the temperature range t_2 – t_1 and φ is the sensitivity of the instrument.

RESULTS AND DISCUSSION

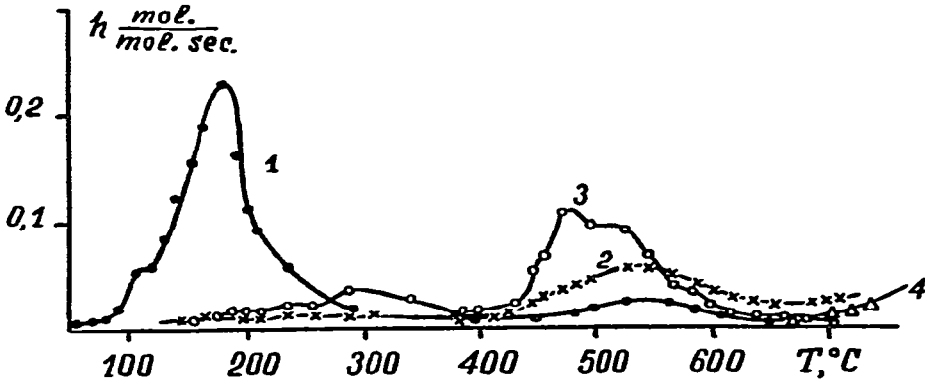
Figure 1 shows curves of the evolution of the main gaseous products H_2O , CO and CO_2 vs. temperature in the course of heating of the PAA investigated and of the PI formed after cyclization. The ordinate gives the relative rates of formation of corresponding products in moles of the substance measured per sec/mole of the initial PAA. It is clear that degradation processes are preceded by the stage of water isolation caused by the imidization of PAA. On the basis of calculations of the amount of water, the degree of imidization ($i\%$) can be determined (Table 2). In all cases, the processes of the imidization of PAA and the thermal degradation of the resultant PI are separated by a considerable time interval within which the evolution of volatile products is minimal.

In investigations of the imidization of PAA, it should be borne in mind that when the fibres are heated, the residue of DMF used as solvent in the fibre formation can be evolved. The study of the mass spectra of volatile products other than H_2O which are formed during the imidization of PAA showed the presence of small amounts of compounds, the mass spectra of which can be assigned to DMF and its decomposition products. Figure 2 shows as an example the spectra of samples of PI-4, PI-5, PI-6 and PI-7 at temperatures of maximum evolution of DMF (peak $m/e = 73$). It is shown in Fig. 2 that this maximum on the temperature scale is situated differently for different polymers. For PAA-4, -5 and -7, it ranges from 194 to 200°C

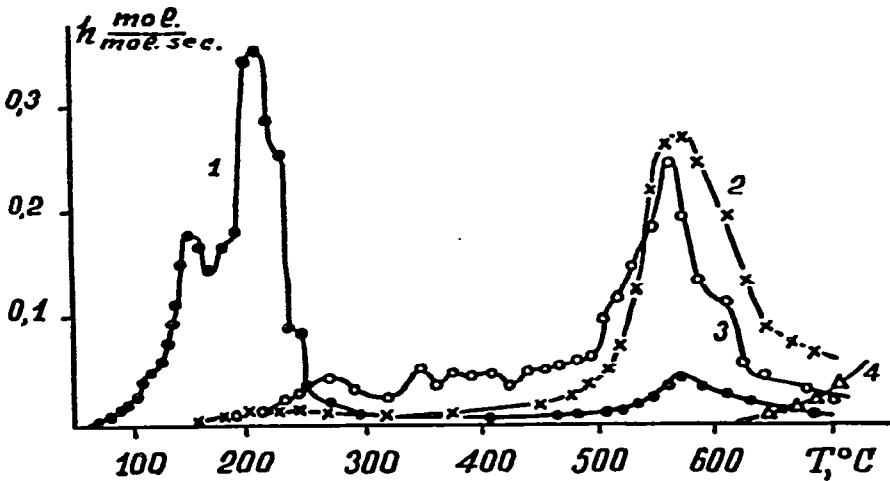




C



D



E

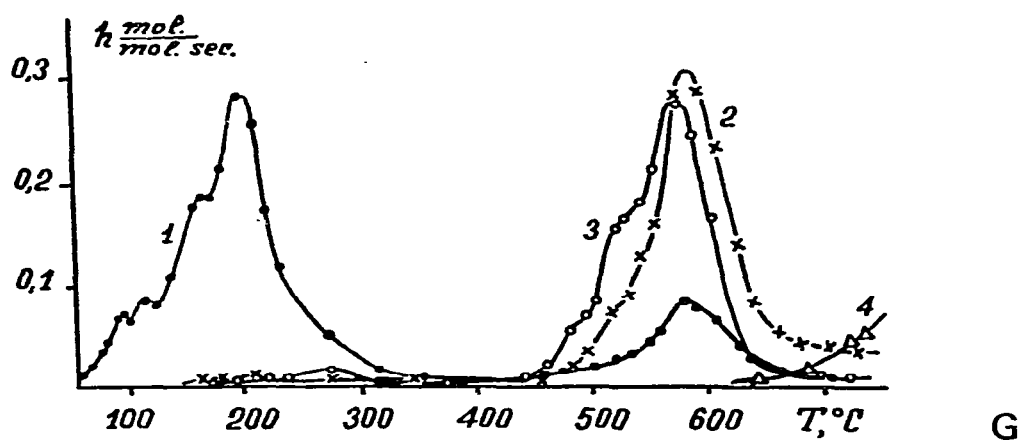
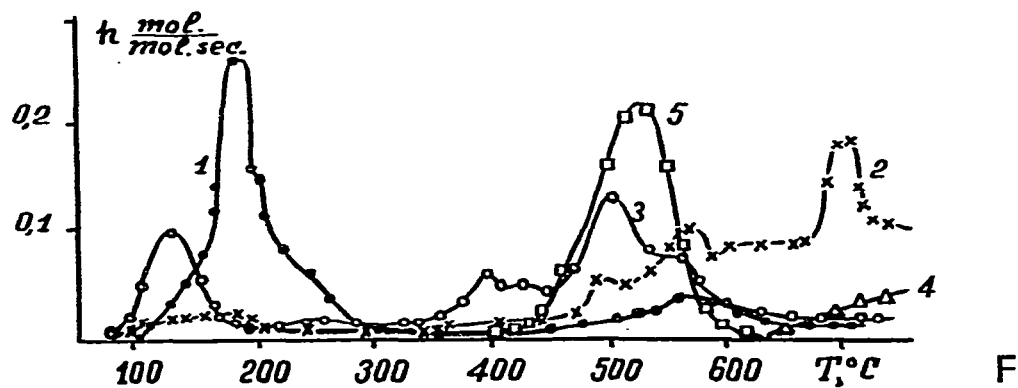


Fig. 1. Curves of the evolution of main gaseous products obtained by the MTA method. 1, H₂O; 2, CO; 3, CO₂; 4, H₂. (a) PI-1; (b) PI-2; (c) PI-3; (d) PI-4; (e) PI-5; (f) PI-6; (g) PI-7. Ordinate: $10^3 \times h$ mole (mole sec)⁻¹.

TABLE 2

DEGREE OF IMIDIZATION OF PI ATTAINED UNDER THE EXPERIMENTAL CONDITIONS DESCRIBED IN THE TEXT

Sample no.	1	2	3	4	5	6	7
<i>i</i> (%)	75	86	40	72	100	56	78

TABLE 3

RELATIVE DMF CONTENT OF PAA FIBRES

Sample no.	4	5	6	7
DMF content (wt. %)	0.08	0.12	0.33	0.16

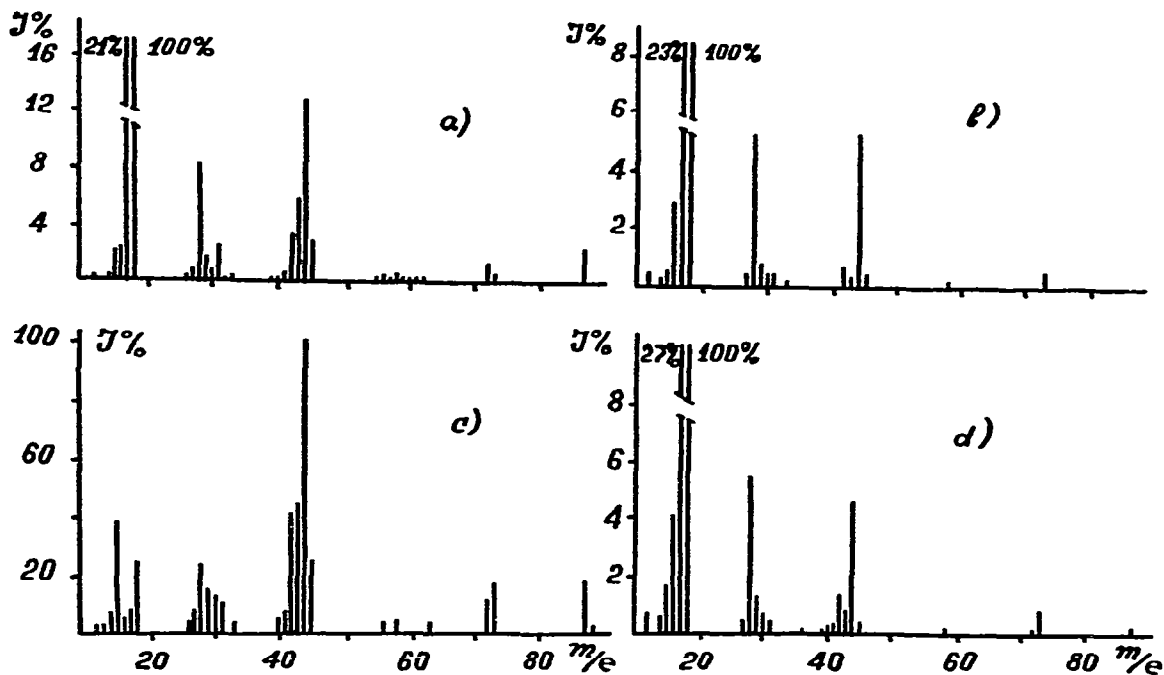


Fig. 2. Mass spectra of gaseous products obtained at the temperature maxima of DMF evolution. (a) PI-4, $T = 194^{\circ}\text{C}$; (b) PI-5, $T = 220^{\circ}\text{C}$; (c) PI-6, $T = 100^{\circ}\text{C}$; (d) PI-7, $T = 204^{\circ}\text{C}$.

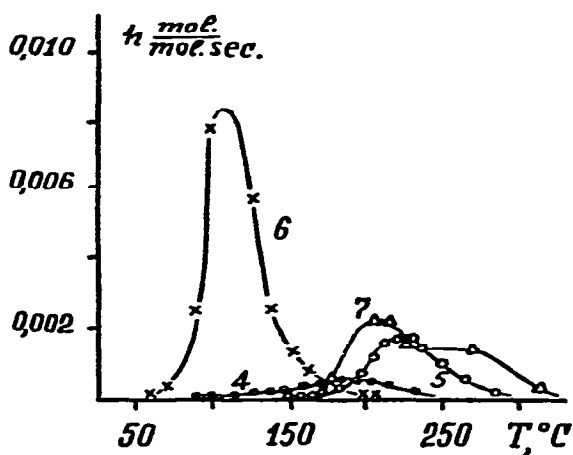


Fig. 3. Curves of DMF evolution. Curve numbers correspond to polymer indices. Ordinate: $10^3 h$ mole (mole sec) $^{-1}$.

whereas for PAA-6 it is located near 100°C ; this is confirmed by data on the dynamics of DMF evolution (Fig. 3). Apart from the difference in the amounts of recorded DMF which are calculated by using the peak with $m/e = 73$ and those shown in Table 3, a qualitative difference exists in the composition of secondary volatile products of the imidization process. PAA-4 and -6 are characterized by the presence of a strong peak corresponding to an ion with $m/e = 87$; in the case of PAA-7, this peak is small and in the mass spectrum of PAA-5 it is absent. As to the volatile

TABLE 4

THE INTENSITY OF THE MAIN PEAKS IN THE MASS SPECTRA OF THE VOLATILE PRODUCTS OF THE THERMAL DEGRADATION OF PI (%)

<i>m/e</i>	<i>Sample no.</i>						
	<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>
12	20	9	17	20	17	17	26
16	22	15	19	29	15	14	29
17	15	6	8	22	7	12	15
18	13	7	14	39	17	35	28
27				35	6	36	14
28	93	90	100	98	100	100	100
39				12		32	
44	100	100	88	100	71	72	100
50	4	2	3	15	6	14	4
65				10	3	33	
66				13	6	53	
76	3	2	2	12	4		4
78	2	1	1	18	3		1
91				27			
92				20			
93	2			37	9		
94						82	
103	5	4	3	26	5		8
106				13			
109						4	
128	2			9			1

products with $m/e = 26-32$ and $40-45$, they can be interpreted as products of DMF decomposition [CO , HCO , $\dot{\text{N}}(\text{CH}_3)_2$].

Further heating of polyimides formed from PAA leads to their thermal degradation, the character of which varies greatly depending on the chemical composition of PI (Fig. 1).

The analysis of the mass spectra (Table 4) of products of PI pyrolysis in vacuum showed that they consist mainly of CO , CO_2 , H_2O and phenol (PI-2) and, to a lesser extent, of NH_3 , HCN , benzene (all PIs except PI-6), benzonitrile, dicyanobenzene and biphenyl (PI-2).

Integrating the yield curves of the main volatile products, it is possible to estimate the relative amount (in mole %) of each component in the gaseous mixture of volatile products of the thermal degradation of PI. The results of this estimation for some PI's are shown in Table 5.

In the thermal degradation of polymers under conditions of dynamic heating up to 700° , virtually any homolytical bond breaking reaction is possible with the formation of the corresponding degradation products. The probability of breaking a certain bond at a given temperature depends on the value of the bond energy and on the chemical structure of the polymer fragment including this bond. The situation is

TABLE 5

RESULTS OF THE QUANTITATIVE ANALYSIS OF THE MAIN VOLATILE PRODUCTS FORMED AS A RESULT OF PAA IMIDIZATION AND THERMAL DEGRADATION OF THE RESULTING PI (%)

<i>m/e</i>	<i>Sample no.</i>					
	<i>1</i>	<i>2</i>	<i>3</i>	<i>5</i>	<i>6</i>	<i>7</i>
12	38	43	43	34	21	7
16	48	68	65	42	22	61
17 (imide)	30	35	19	46	22	34
17 (total)	49	60	52	60	30	66
18 (imide)	124	142	67	186	98	128
18 (total)	161	168	135	211	131	189
27				21	30	43
28	154	242	169	182	120	148
39					26	
44	165	269	188	172	136	148
50	3.2	5.8	6.9	7.7	10.8	4.5
65				3.6	33.3	
66				6.6	55.5	
76	2.6	3.4	4.3	5.9		5.1
78	1.4	3.9	5.5	5.1		1.9
93	1.8			10.4		
94					85.8	
103	5.6	9.9	7.1	5.9		11.2
109					3.7	
128	1.6		1.3			2.0

complicated by the fact that, as the temperature increases, chain processes occur in the polymer; they are related the homolytical bond breaking and lead to polymer degradation. Moreover, hydrolytic degradation of the imide structure (the possibility of which has recently been shown⁸) takes place as well as other processes of the ionic type. Hence, it becomes evident that an attempt to develop a more or less comprehensive scheme of the process of the thermal degradation of polyimides would not be justified. Consequently, in our opinion it would be reasonable to attempt to establish the elementary reactions related to the start of the thermal degradation of polyimides and responsible for the value of their thermal stability. For this purpose, we use in this work not only the results of a comparative investigation of the thermal degradation of some polyimides obtained by the MTA method, but also the results which we have obtained by a comparative thermal analysis of polymers and corresponding model compounds (CTA)⁹.

The thermal stability of polymers is known to depend on two chemical factors: (1) the structure of the elementary unit of the polymer and (2) the presence of impurities and defects in the polymer structure. When the polymer contains many defects, the latter factor is of major importance. The main defects in the polyimide chain are amido acid sequences (i.e. those polyimide units which, for some reason,

did not undergo imidization), interchain amide cross-links and terminal amine, acid and anhydride groups. The main impurity is the solvent which sometimes remains in the polymer structure at high temperatures and whose significance in the formation and degradation of polyimides has not yet been completely elucidated^{10, 11}.

In accordance with the effect of these factors, our curves of the temperature dependence of the yield of the main volatile products formed during the imidization of PAA and the thermal degradation of PI can be divided into three temperature ranges (Fig. 1).

(1) 20–300°. The main processes are the imidization accompanied by the elimination of water and the removal of solvent residues.

(2) 300–450 (500)°. The main process is the degradation of defective structures in the polymer; in some cases, the imidization process is completed and the traces of the solvent are removed.

(3) 450(500)–700°. The degradation of the main initial structure of polyimide takes place and a new structure is formed which is stable at 700° and above this temperature¹².

When the behaviour of those polymers in the first temperature range is considered, it should be noted that the degree of imidization which can be attained during heating depends on the mobility of polyimide chains. This mobility is determined by the chain structure of the elementary unit and related physical factors, the chain rigidity and the tendency of the polymer to crystallization. Consequently, the values of the degree of imidization obtained for polyimides of different structures (Table 2) cannot be interpreted uniquely proceeding from one structural formula of the elementary unit. Figure 1 shows that the ascending portions of the curves of water removal during imidization exhibit characteristic "teeth". This can be considered as a result of two processes: the process of dehydrocyclization leading to an increase in the polymer rigidity which, in its turn, causes a decrease in the cyclization rate, and the process of softening of the polymer with increasing temperature which leads to an increase in the rate of water removal and in the degree of imidization. Table 2 shows the results of determinations of i by MTA for the PAA being investigated. Of the first three samples differing in the number of phenyl rings in the diamine component, PI-3 exhibits the lowest degree of imidization. According to the data on the degree of crystallinity, PI-3 exhibits the highest crystallizability in this group of polymers. PI-6 is also characterized by a high degree of crystallinity and, hence, by a low degree of imidization. The table shows that PI-5 exhibits maximum imidization and fibres based on it have an amorphous structure.

It is possible that the process of the imidization of polyimide fibres is closely related to the removal of solvent residues from the polymer. First, it has been shown that chemical interaction is possible between polyamido acid and the solvent^{13, 14}. This should profoundly affect the extent of imidization and the amount of defects in the polymer. Secondly, the solvent affects the kinetics of the cyclization of polyimido acids with the formation of polyimides^{10, 11}.

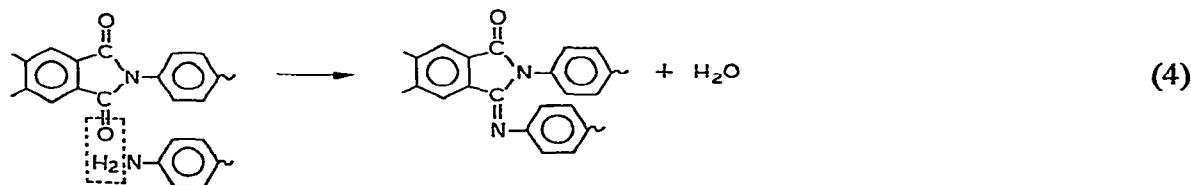
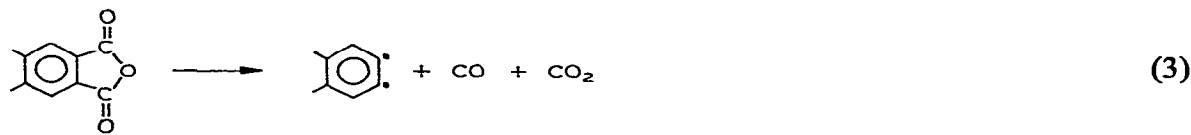
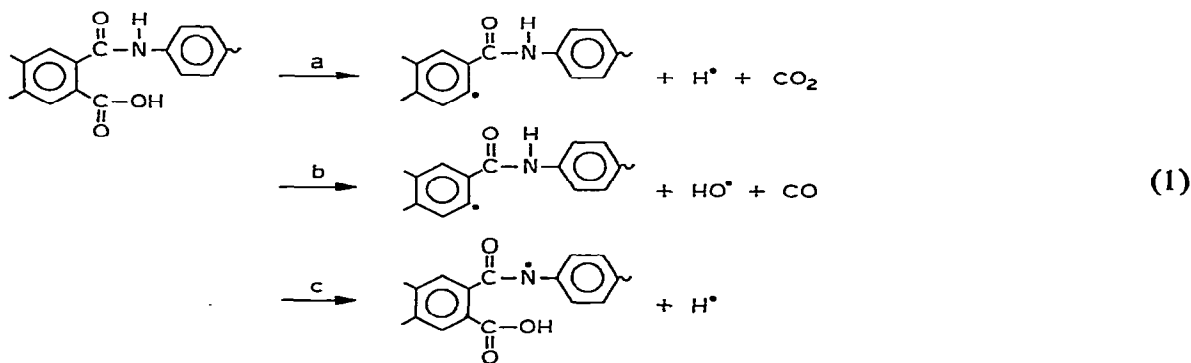
Differences in the kinetics of DMF evolution (Figs. 2 and 3) can be attributed

to different capacity of polymers to form polymer-solvent crystals with the solvent which undergo degradation at different temperatures¹⁵. In this case, it can markedly affect the course of the imidization process and its extent and, hence, the process of the thermal degradation of polyimides.

As has already been mentioned, the second temperature range is characterized by the degradation of structures exhibiting defects. It has been shown for model compounds^{16, 17} that at temperatures of ca. 400°, thermal degradation of aromatic mono- and dicarboxylic acids takes place and gaseous CO, CO₂ and H₂O are formed. At higher temperatures, the degradation of aromatic amides occurs accompanied by the formation of water which profoundly affects further stages of PI degradation. The significance of water in the degradation of the imide structure is shown taking *N*-phenylphthalimide as an example. At temperatures below 500°, the addition of water not only accelerates the degradation process but also drastically changes the composition of the pyrolysis products. Thus, at 540° the CO/CO₂ ratio varies from 50 to 0.5 and the rate of the process increases approximately 15-fold on passing from the thermal degradation in vacuum to the thermal hydrolysis of *N*-phenylphthalimide.

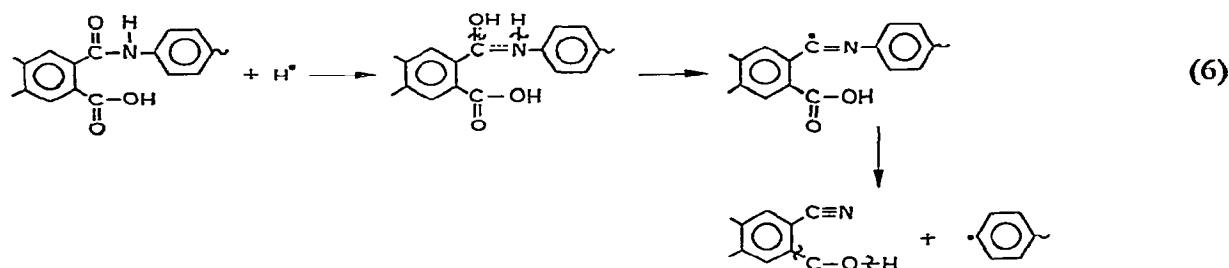
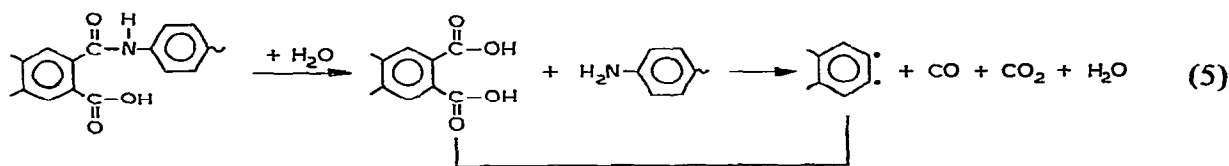
As the temperature is increased and the processes of polyimide degradation develop under vacuum, the amount of reactions leading to the formation of H₂O molecules increases. The interaction between amine end groups and carbonyl groups of imide rings is an example of these reactions¹⁸.

The results of investigations of model compounds suggest possible reactions in polyimides in this temperature range.



The structure formed according to reaction (4) is one of the sources of degradation products of the benzonitrile type.

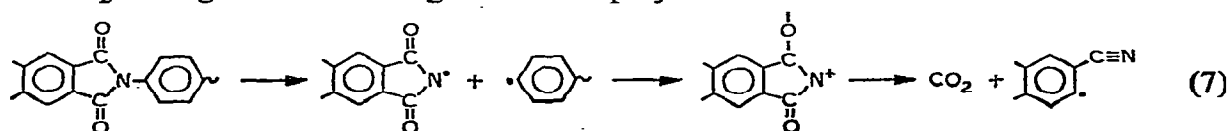
The presence of hydrogen and water leads to many transformations two of which are shown.



All these reactions can be regarded as single stages of chain processes developing in the thermal degradation of polyimides; at high temperatures, they lead to the degradation of the initial imide structure.

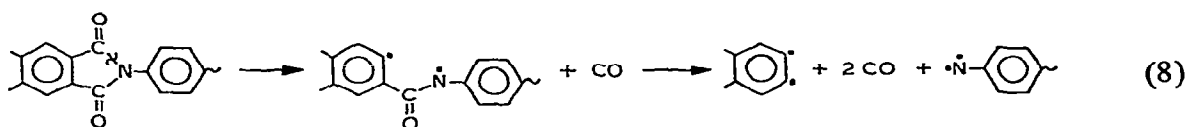
As to the thermal degradation of polyimides in the third temperature range, it should be said that according to the character of the yield curves of volatile products in Fig. 1, they can be divided into two groups. PI-1, -2 and -3 are included in the first group and PI-4, -5, -6 and -7 are in the second group. The first group is characterized by an essentially complete coincidence of peaks of CO and CO_2 with regard both to the height and to the temperature range whereas the peak maximum of H_2O shifts to higher temperatures compared with CO and CO_2 peaks. In the second group, the degradation of main structures begins earlier with the evolution of CO and CO_2 ; the temperatures of their maxima do not coincide, CO_2 being evolved earlier than CO . The maxima of CO and H_2O peaks coincide and the maximum of the H_2O peak appears earlier than in the first group (by $30-40^\circ$). These differences in the thermal degradation of these two groups of PI are caused by their different chemical structures.

If the amount of defects is not taken into account, PI-1 has the simplest chemical structure of all polyimides investigated. If it is assumed that the thermal degradation of polyimide begins from the homolytical breaking of some bond, the breaking of the $C_{arom}-N$ bond is the most probable. (The breaking of the $C_{arom}-C_{arom}$ bond is improbable, this is confirmed by the stability of the benzene structure on heating to 590°). This reaction does occur, but in the case of PI-1 its rate is probably low, as shown by the low intensities of mass peaks 78 and 76 (Table 4). Johnston and Gaulin³ consider a similar reaction to be responsible for the ionic rearrangement leading to the formation of CO_2 during the thermal degradation of polyimide.

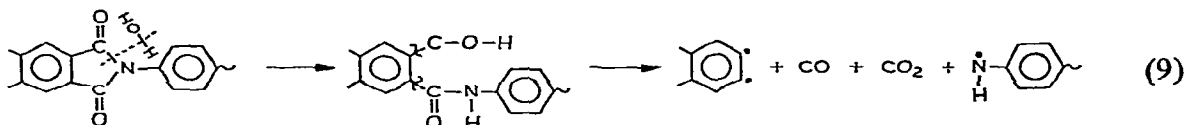


In our experiment, however, when the corresponding model compound, *N*-phenylphthalimide, decomposed and the CO/CO₂ ratio varied from 20 to 50 over the temperature range from 500 to 600° (ref. 8). At the same time, experiments with the addition of water led to a drastic change in this ratio to 0.4–0.5. Hence, it should be borne in mind that the hydrolysis of the imide bond is possible. Its role is particularly important in the initial stages of polyimide degradation (above 460°) when the C_{arom}-N bond is not yet broken.

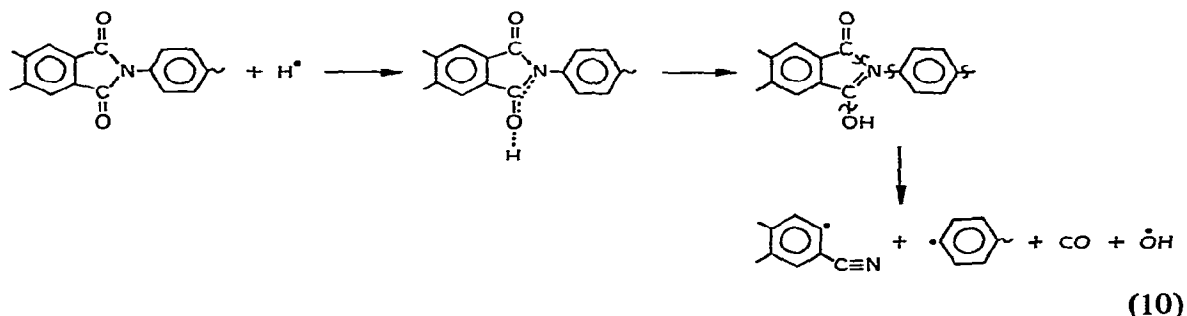
Apart from the above homolytical reactions, bond breaking in the imide ring is possible with the formation of CO molecules. However, this process does not account for approximately equal amounts of CO and CO₂ evolved over the temperature range considered.



Hence, homolytical processes alone cannot explain the quantitative and qualitative composition of products of thermal degradation. Therefore, the formation of CO and CO₂ in a 1:1 ratio can be interpreted more adequately by the reaction



Another type of reaction should also be mentioned: the reaction with the participation of atomic hydrogen formed as a result of the above reactions. Hydrogen is known to react both with aromatic structures¹⁹ and with the carbonyl groups of imide rings; thus it initiates a whole series of new degradation reactions.



The presence of many⁴ radicals and macroradicals should cause their recombination and as the temperature increases further, the structures formed undergo degradation. This is one of the sources of the formation of CO and CO₂.

An increase in the amount of phenylene rings in the diamine component of polyimides of the first group on passing from PI-1 to PI-2 and PI-3 leads to a drastic increase in the CO and CO₂ peaks in mass-spectra of corresponding polyimides. This

can be interpreted by a decrease in the stability of the diamine component in PI-2 and PI-3 as compared with PI-1. In fact, in the former polymers, a $C_{\text{arom}}-C_{\text{arom}}$ bond exists between phenylene rings and its homolytical degradation facilitates the breaking of the $C_{\text{arom}}-N$ bond as well as a further series of reactions of degradation. Indeed, the temperature of the start of degradation of model compounds, biphenyl and *p*-terphenyl, should be assumed to be 540 and 520°C, respectively²⁰. In other words, the temperature ranges of an analogous reaction in PI-2 and PI-3 and of the reaction considered above for PI-1 coincide.

Polyimides of the second group are characterized by a more complex process of thermal degradation because the diamine component in these polymers is less thermally stable than in polyimides of the first group. Hence, the start of thermal degradation is displaced towards low temperatures and the maxima of the CO and CO₂ peaks do not coincide. Thus, for PI-5, the range over which the evolution of CO is observed (450–700°) is much wider than for polymers of the first group. The amount of CO is much greater than that of CO₂; this can be attributed to a relatively easy rupture of the $C_{\text{arom}}-CO$ bond in the diamine fragment. In fact, for benzophenone, the degradation of the structure begins at 485–500° (ref. 10). Owing to this, the contribution of hydrolytic processes probably decreases compared with that of homolytic processes and the maximum of the equilibrium concentration of H₂O is displaced towards low temperatures compared with polymers of the first group.

For PI-6, the situation is more complex than for PI-5. The decisive factor is the weakness of the diamine fragment containing the polyphenylene oxide structure. Actually, as the yield curves of the main products of thermal degradation show (Fig. 1), phenol begins to evolve from ca. 430°. Presumably, the weakness of this structure is due to the presence of oxygen atoms in the *para* position in the benzene ring; this leads to a displacement of electrons in opposite directions (the saturation effect)²¹. In this case, it can be said that the thermal degradation of the ideal structure of the polymer begins with the homolytic degradation of bonds in the diamine fragment. The first peak of CO₂ with the maximum at 400° can probably be assigned to the degradation of amido acid sequences, the amount of which in this case is relatively high. The maxima of the second peak of CO₂ and of the first peak of CO are at 500°; this probably corresponds to the hydrolytic degradation of the imide structure.

A distinguishing feature of PI-7 is the presence of labile hydrogen in the fluorene structure. This should lead to an easy formation of H₂O molecules as is indicated by a marked H₂O peak in the initial stages of thermal degradation, and to the hydrolysis of the imide structure. It is clear that, beginning at 450°, CO₂ is predominantly evolved up to 530–540° when the rate of the homolytic degradation of imide bonds becomes relatively high.

Summing up the general features of the thermal degradation of polyimides, it should be said that four of the six structures considered are characterized by the formation of a new structure during this degradation; this structure remains stable up to 700° and at higher temperatures undergoes degradation with the evolution of CO and/or N₂ ($m/e = 28$). Moreover, it has been shown¹² that at 750° these polymers

lose no more than 25–30% of their weight and retain a residue stable at temperatures above 800°.

Hence, mass spectrometric thermal analysis of a number of polyimides in combination with the method of a comparative thermal analysis of polyimides and model compounds makes it possible to obtain a clear picture of processes occurring in polyimides over a wide range of temperatures and to make conclusions concerning the main reactions responsible for the thermal stability and the start of degradation of some polyimide structures.

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