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Special Review

THERMOANALYTICAL INVESTIGATION OF HIGH-TEMPERATURE TRANSFORMATIONS OF POLYIMIDES

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The results of thermoanalytical investigations of polyimides are considered. It is shown that combined application of methods of thermal analysis makes it possible not only to determine the thermal and structural characteristics of polyimide articles but also to observe the formation of polyimides, their thermal degradation and transformation into new structures under the influence of high temperatures.

It is well known that polyimides are unique thermally stable polymers exhibiting important properties that permit their use for the manufacture of items operating under very severe conditions (high, or extremely low temperatures, high radiation levels, aggressive media, etc.).

The properties of these polymers and materials made of them, have been described in a number of monographs and review papers. Thermal analysis which provides the possibility of investigating this class of high molecular weight compounds over a wide temperature range, has been widely used. Over a thousand publications have appeared in which the application of thermal methods to the investigation of polyimides in the temperature range from -190 to $+1500°$ has been described. However, most papers deal with the temperature range from room temperature to 900–1000°. This range may be tentatively divided into three parts: 1) from room temperature to 300°, 2) from 300 to 500° and 3) from 500 to 1000°. What are the characteristic features determining the thermal behaviour of polyimides at these temperature ranges? Up to 300°, polyimides does not undergo any changes in its chemical structure and physicochemical properties for a long time, for many samples even for several years. From 300° to 500°, the polyimides

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retain their properties for only limited periods of time that in many cases decrease exponentially with temperature. At about 450–500°, the chemical structure of the polymer is transformed fairly rapidly. The temperature range above 500° is characterized by violent reactions. Depending on conditions, polyimides undergo oxidative and hydrolytic degradation reactions, reactions of thermal cracking, restructuring, carbonization and graphitization. All these processes together determine the overall kinetics of chemical reactions and the properties of the products formed in this temperature range. The high thermal stability of polyimides in the first temperature range, limits the possibility of obtaining useful information with the aid of thermal analysis. Only some methods, such as TG, mass spectrometric thermal analysis (MTA), or DSC, can be used for determination of defects of polyimide materials due to poor processing from prepolymers. In this temperature range the thermochemical transformations of prepolymers into polyimides is of interest and thermal analysis methods have been consideraly used for the solution of some practical and theoretical problems in this field [1–9]. For instance, with prepolymer of the best known polyimide PM, based on pyromellitic dianhydride and diaminodiphenyl ether in a dimethylformamide solution, the methods of thermal analysis were used to study in detail the process of its thermal transformation into polyimide both under iso- and non-isothermal conditions at 100–300° [10–12]. The combination of these methods with mass-spectrometric thermal analysis (MTA) has permitted the determination of the mechanism of this reaction, the structure of the solvates and their role in the thermochemical transformation of the prepolymer into polyimide [13–24]. At this range the MTA method has made it possible to determine the chemical structure of the reagents [25–28] and of the technological conditions of the processing of items [29, 30] on the mechanism of formation of polyimides of different chemical structures. The thermomechanical analysis of prepolymers has made it possible to follow up the formation of a polyimide with the optimum combination of mechanical properties [31–37]. To summarize, the formation mechanism of polyimides has been investigated in detail by methods of thermal analysis in combination with spectral and other physical methods.

The temperature range 300–500° is the range of the widest application of polyimide materials and products and hence many thermoanalytical investigations of polyimides relate to this range. These investigations may be divided into two categories. One of them includes results of routine analyses which appear in almost all papers on polyimides; the other consists of sophisticated studies which lead to definite conclusions on the mechanism of thermochemical transfomations, the effect of chemical and physical characteristics on the course of reactions and the properties of products and enable us to predict possible changes which may occur during the thermal treatment of polyimides.

Reaction in the temperature range 500–1000° can be divided into those occurring below 800° and those which occur above this temperature, but the attention of most investigators was directed to the initial stage of the high-temperature degradation. Depending on the method of analysis, different parameters were employed. These parameters characterize one or several quantitative changes as functions of temperature or of time at isothermal conditions. These quantities include mass loss, gas evolution, heat absorption or evolution, changes in mechanical properties at the beginning of the reaction, at extreme points and at arbitrarily chosen temperatures, etc. On the basis of this information combined with other physical characteristics obtained by independent methods of analysis under similar conditions, the authors reveal the relationships between structure and properties.

The main problem in the thermoanalytical investigation of polyimides is the determination of the dependency of thermal stability on a number of conditions. The solution to this problem depends on the practical purposes of the investigations, consequently, the therm "thermal stability" is often defined differently by different authors. It can be seen from the literature that the thermal stability of polyimides is determined by thermal analysis and is related to the chemical structure of the reagents [38–58], the method of synthesis of polyimides and manufacturing technology of the products made from the polyimides [59–74] the macromolecular structure [75–85], conditions of use [86–90], and conditions thermal analysis [91–94], etc.

Apart from the determination of thermal stability by the methods of thermal analysis, either per se, or towards specific goal, problems related to the degradation mechanism, the interaction with other substances, the environmental effect of the degradation products and other problems related to the overall problem of reactivity of organic polymers have also been studied. The results of these investigations are in part reported in the above mentioned publications. They are not discussed in the present Review Article.

The temperature range above 500° has been studied recently. Although, as mentioned above, many experiments on thermal stability of polyimides have been carried out up to 1000°, most authors reported only the parameters determining the temperature of complete degradation of polyimides, or the percentage of the carbonized residue. However, detailed studies of polyimide coke-like products, and of the formation mechanisms at temperatures above 500° became recently of considerable interest. It is well known that in this temperature range (± 30–50°), the chemical structure of polyimides undergoes the most profound changes accompanied by the evolution of considerable amounts of gaseous products relatively simple in composition. The quantity of gaseous products is profoundly affected by the same factors as thermal stability of the polyimide. In addition, the surrounding gaseous medium is of particular importance. Thus, under the conditions of thermal oxidation, the polyimide is entirely transformed into volatile products at 650 ± 20°. In an inert atmosphere or under vacuum a carbonized residue is formed at 900–1000° in the amount of 40–80% of the initial weight of the sample. The amount and the chemical composition of this residue depend on whether it was formed under vacuum or in the presence of an inert gas.

One of the earliest descriptions of the formation of the carbonized residue upon thermal degradation of polyimide PM is due to Bruck [95, 96]. By isothermal TG, he found that when polyimide PM was heated in vacuum at 585–632° for two hours, a carbonized residue was formed in the amount of 60% of the weight of the initial sample. The gas products consisted mainly of CO_2, CO and H_2O. The quantity of CO_2 depended on the degree of cyclization of the polyimide prepolymer. The quantity of evolved CO_2 is the greatest difference between the thermal degradation of commercial H-films and of films that have been carefully freed of impurities (H-film, Kapton and polyimide PM are different names of the same polyimide). When the temperature was increased from 620 to 850°, the isothermal treatment showed that the restructuring of polyimide (H-film) profoundly affected its properties (Fig. 1) [96]. As a result of this restructuring, a polymer compound was formed exhibiting semiconductor properties. In the same paper a scheme is given for speculated structures which are formed at various stages of the thermoanalysis of the H-film (Fig. 2). However, this scheme has not been confirmed by adequate experiments. No data is given on material balance of gaseous and solid products of the thermal degradation. The reported results of elemental analysis indicate that the change in composition for C, H, O and N in this temperature range is small and these results

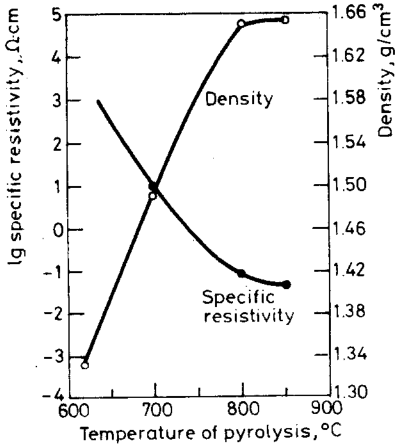


Fig. 1 Specific resistivity and density of H-film as a function of temperature of pyrolysis

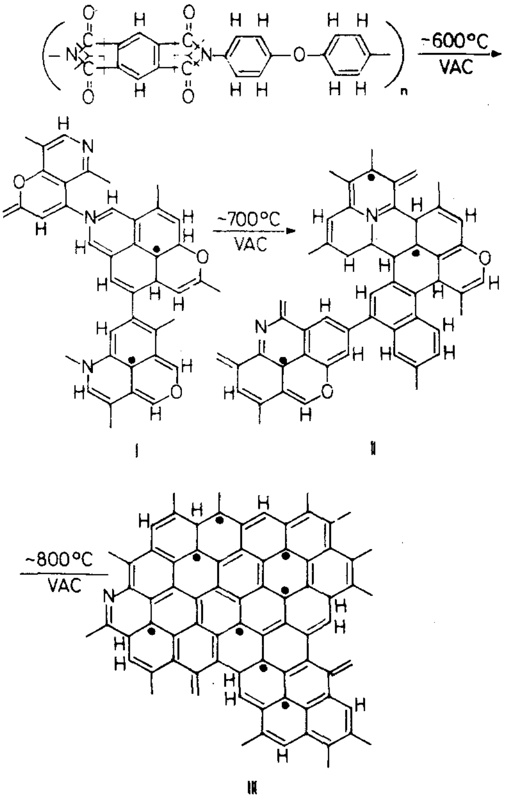


Fig. 2 Scheme for the formation of products of thermolysis of the H-film

do not correspond to the approximate composition of these elements in accordance with the proposed scheme.

Further investigations of high-temperature degradation of polyimides have shown that mass spectrometric thermal analysis (MTA) is one of the most informative methods. This method makes it possible to follow the kinetics of gas evolution in the thermal degradation of polymers, just as the thermovolumetric method [97, 98] but differs from the latter in the possibility of carrying out simultaneously qualitative analysis of gaseous products. Thus, a combined TG–MTA method (Fig. 3) showed that at 700° and at highest temperatures the main gaseous products of the vacuum thermoanalysis of polyimide fibers with various chemical structures are H_2 and CO (Fig. 3) [99]. In this case the polyimide fibers undergoing pyrolysis retain their shape. At 750° their weight decreased by not more than 25–30%, and did not change even at higher temperatures. The main gaseous products in the thermolysis of polyimide fibers [100] based on pyromellitic

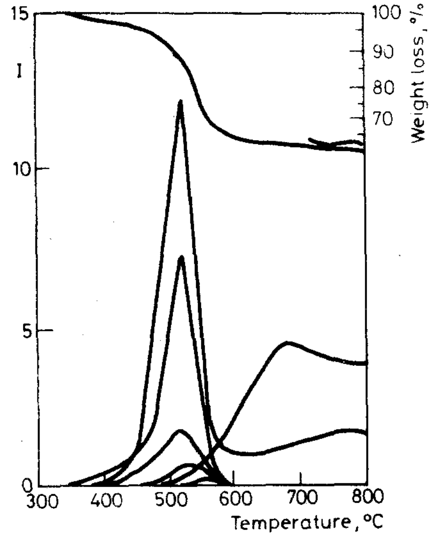
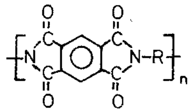
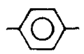
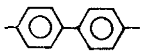
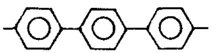
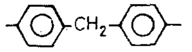
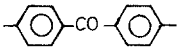
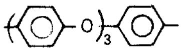
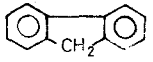


Fig. 3 Curves of simultaneous TG–MS of the polypyromellitinimide benzidine

Table 1 Characteristics of PAA and PI fibers with the general formula



Sample number	R	σ, kgp/mm^2	ε, %	E, kgp/mm^2	E_0, kgp/mm^2
PI-1		18 50	9.0 0.8	1050 8000	20000
PI-2		20 90	8.2 0.6	1200 10000	21000
PI-3		22 45	7.6 0.7	1360 7000	
PI-4		16 23	16.0 40.0	450 440	1000
PI-5		14 23	18.0 38.0	340 390	900
PI-6		39 70	16.0 8.0	690 1400	2900
PI-7	 M M	60 165	7.0 1.6	2100 13000	13000 22000

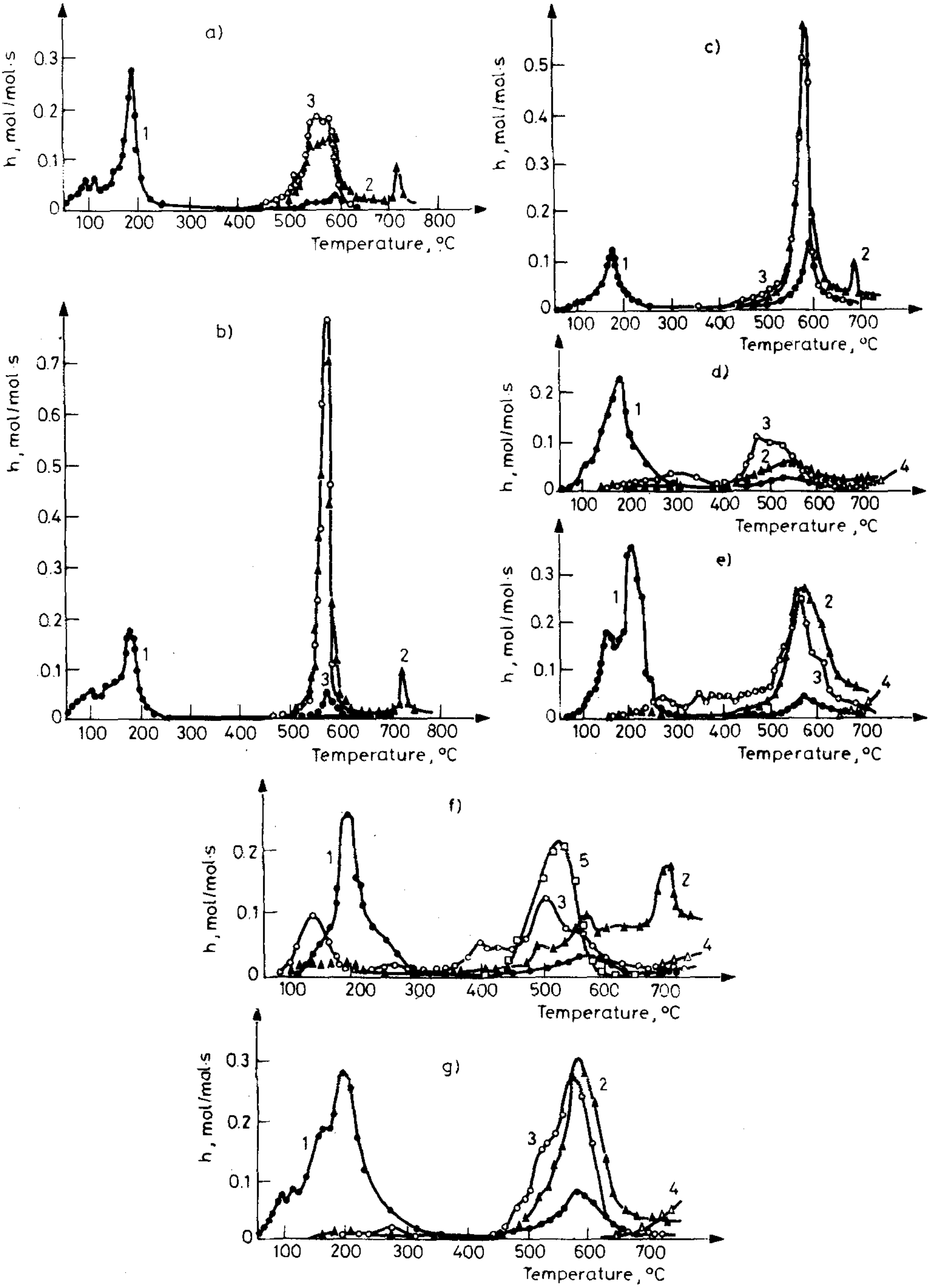


Fig. 4 MTA curves of main gaseous products of thermal degradation of polyimide fibers listed in Table 1: 1) H_2O, 2) CO, 3) CO_2, 4) H_2, a) PI–1, b) PI–2, c) PI–3, d) PI–4, e) PI–5 , f) PI–6, g) PI–7

dianhydride and some aromatic diamines (Table 1), are CO, CO_2, H_2O and H_2 (Fig. 4). Their ratio varies markedly with the chemical structure of the aromatic diamine. A relatively small amount of gaseous nitrogen compounds is obtained, although two nitrogen atoms are present in each polyimide unit. This peculiarity

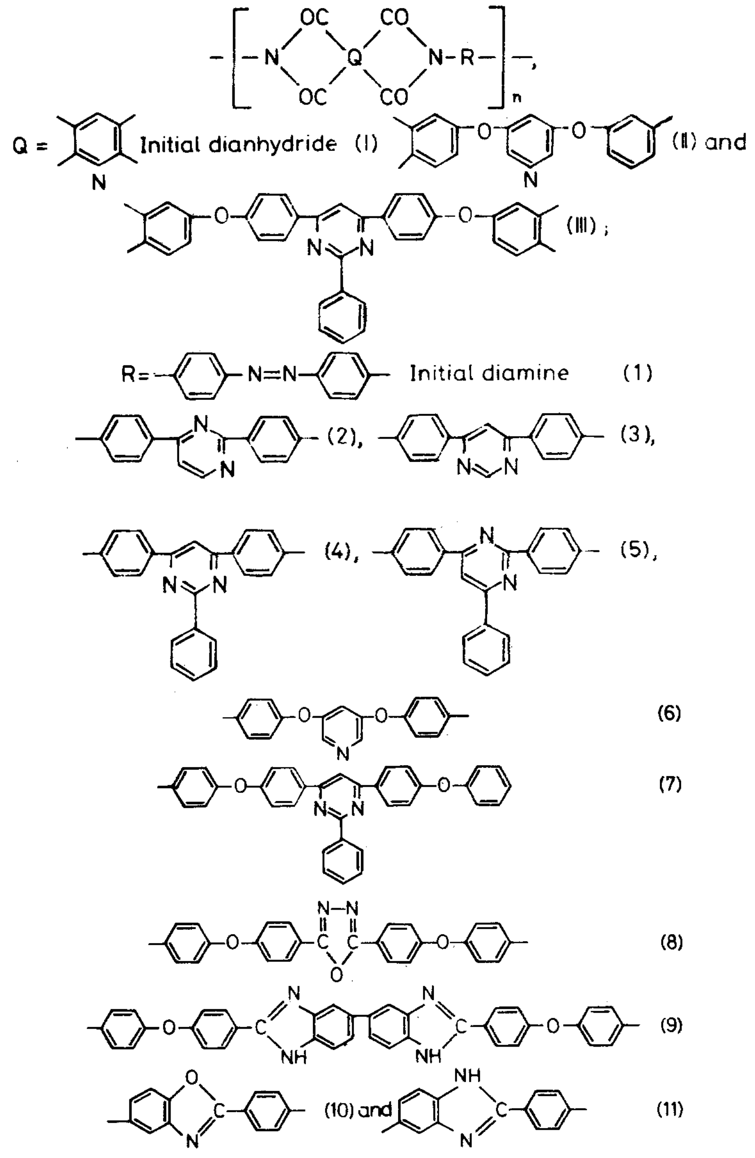


Fig. 5 Formulae of diamines used in the synthesis of nitrogen-containing polyimides

has been neglected by most authors, but it has been realized [101–103] that the nitrogen of the imide ring remains in the pyrolized products. More detailed investigations of the role of nitrogen in thermal and thermooxidative degradation of polyimides have shown that nitrogen increases the thermal stability of polyimides in which its content is higher than in the conventional polyimide PM (Fig. 5). Nitrogen atoms also play a certain role in the formation of a coke residue, amounting up to 75–80 weight % of the initial sample.This value depends on the position of the nitrogen atom in the polyimide structure. Elemental analysis has shown that nitrogen content decreases on the average to 55–60% with respect to the initial amount for polyimides containing "additional" nitrogens which are not a part of the imide ring. Ring nitrogen on the other hand, remains almost completely in the coke residue. In order to confirm this fact, the thermal analyses of acrylonitrile, polyphenylene oxadiazol, nylon-6,6-phenylone and polypyromellitimides based on diaminodiphenyl ether and *p*-phenylene diamine were carried out under similar conditions. The nitrogen content of these polymers is 26.2, 19.3, 12.3, 11.0, 7.3 and 9.6%, respectively. After thermolysis up to 900°, the residues of these polymers contained 1.5, 32.3, 0, 48.2, 70.7 and 84% nitrogen, i.e. the nitrogen of the imide ring takes hardly any part in the gaseous products of the thermolysis.

As a result of the wide use of polymeric polyimide materials under extreme thermal conditions, some papers on the study of carbonization of polyimides and the properties of the resulting products formed during carbonization have appeared recently [104, 105]. These papers deal with isothermal treatments of the reactants at high temperatures. The analysis of the products is made mainly by spectroscopic methods and not by conventional thermal analysis.

Thermal analysis of polypyromellitimides (PPI) combined with spectroscopic measurements (NMR and IR) and electric conductivity have made it possible to determine some features of carbonization of aromatic PPI [106]. When PPI is heated in vacuum, carbonized products are formed and the coke residue is equal to 60–75%, depending on the initial chemical structure (Fig. 6). These values suggest that during the thermal degradation PPI undergoes restructuring into compounds similar to glassy carbon. High yields of the carbonized residues in the pyrolysis of PPI have suggested that these samples are similar to various carbon-graphite materials.

Figure 7 shows the TG curves for the thermooxidative degradation of graphite, soot, charcoal and PPI–PM pyrolyzed at 550°. If the rates of weightloss (2.5%/min) are compared with heating rates (5 deg/min) it can be seen that the degradation process of pyrolyzed polyimide approaches that of soot and graphite. In the temperature scale the thermal stability of PPI occupies an intermediate position among the carbon-like samples investigated. The absence of data on the thermal hydrolysis of PI above 900° prevents the possibility of drawing unequivocal

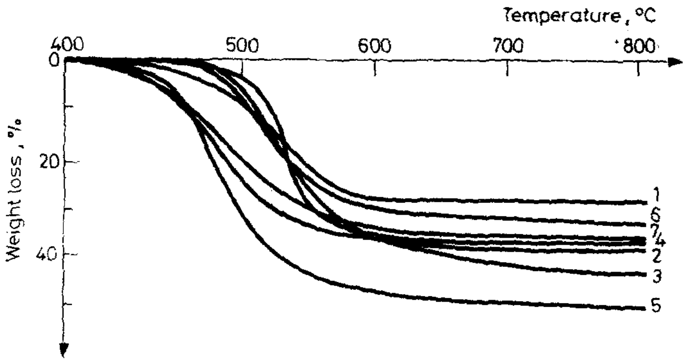


Fig. 6 TG curves of PPI based on diamines: 1) p-phenylene diamine, 2) benzidine, 3) 4,4′-bis (p-aminophenyl) diphenyl, 4) 3,3′-diaminobenzophenone, 5) 4,4′-diaminodiphenyloxide, 6) 4,4′-diaminodiphenylmethane and 7) diaminofluorene

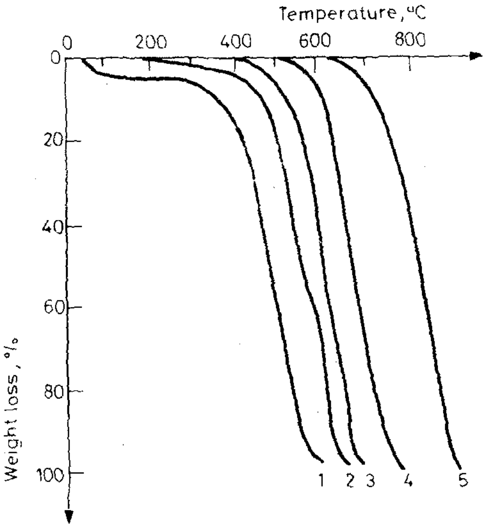


Fig. 7 TG curves of thermooxidative degradation of 1) charcoal, 2) a pitch-graphite mixture, 3) PPI–PM, 4) soot and 5) graphite

conclusions. The above difference is evidently due to the insufficient information on the high temperature treatment of PPI when the carbonization of the polymer structure starts.

In order to establish the changes occurring in PPI with increasing temperature of pyrolysis, PPI samples were prepared in different temperatures between 500 and 900° under conditions analogous to those performed during the thermovolumetric study of polyimide PM [107]. In their appearance the PPI films differ from the usual

PI–PM films only in the intensity of colour: with increasing pyrolysis temperature, the film colour turns from yellow to black passing all the shades of orange-brown. Above 700°, a metallic glitter appears and becomes more pronounced at higher temperatures. Elemental analysis reveals a considerable decrease in the content of oxygen and hydrogen in PPI in the temperature range 500–900° (Fig. 8). This effect is particularly marked in the 550–680° range, as confirmed by the chromatographic and mass-spectrometric data (a drastic increase in the amounts of the evolved CO, H_2 and water is observed). The content of elements in the PPI pyrolyzed up to 500–900° is 80–85% C, 4–5% N and 1–1.5% H. Subsequent heating of PI above the temperature of carbonization shows that traces of nitrogen remain in PPI up to 1500°.

The NMR ^{13}C spectra of representative PPI samples are illustrated in Fig. 9 showing that the heating of PM up to 600° profoundly affects its structure, that is the spectral line at 165.0 ppm due to the carbonyl group in the inside ring completely disappears, the intensity of the signal at 155–151 ppm of the carbon atom of ether bond in the diamine component drastically decreases, the signal at 136.7 ppm of the benzene ring conjugated with the imide ring is transformed and a general broadening of the bands at 127–124.3 ppm is observed, which indicates that

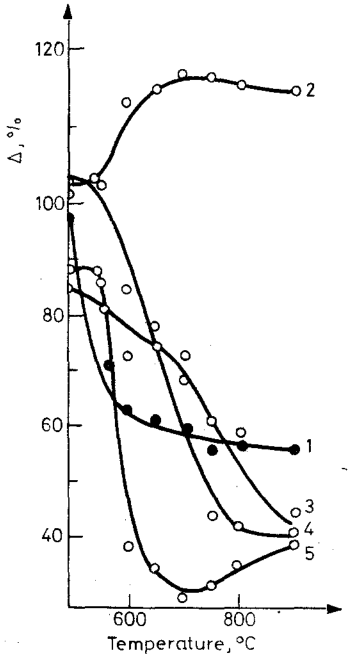


Fig. 8 Relative dependence of 1) the mass of PPI and its elemental composition, 2) C, 3) O, 4) H, 5) N on the thermolysis temperature

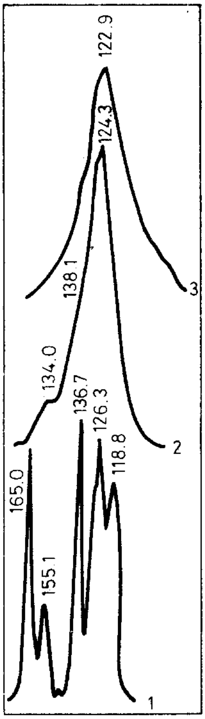


Fig. 9 NMR spectra ^{13}C of 1) initial PPI, 2) samples pyrolyzed at 600° and 3) samples pyrolyzed at 900°

the degree of aromatization of the entire polymer increases. The PPI spectrum at 900° essentially corresponds to that of carbon-graphite materials. The IR spectra of the PPI samples also unequivocally show that the most important changes in the PPI structure occur in the temperature range 500–600°. The appearance of the 985 cm^{-1} band in the IR spectrum suggests the formation of interchain crosslinks. Broadening of the 820–880 and of the 1600 cm^{-1} bands confirms the aromatization of the polyimide structures as the pyrolysis temperature increases with the simultaneous formation of the $C=N$ bond. At the same time the 1020 cm^{-1} band diappears indicating that the bonds in the diamine component are broken. When the samples are heated to 700° or higher temperatures, the IR spectra exhibit the presence of the 1680 cm^{-1} band indicating the presence of the $C=O$ groups in the extended chain.

An interesting feature of these PPI samples which shows their similarity to carbon-graphite materials is the marked decrease in the ϱ value with increasing pyrolysis temperature (Fig. 10). With regards to their stability to thermal oxidation, according to the TG data, the stability of PPI samples in the temperature range investigated, remains on the same level as for PM (Fig. 11). Moreover, PPI pyrolysed at 750–900° contains a portion subjected to low temperature oxidation with a weight loss from 5 to 12%. This phenomenon is evidently caused by the

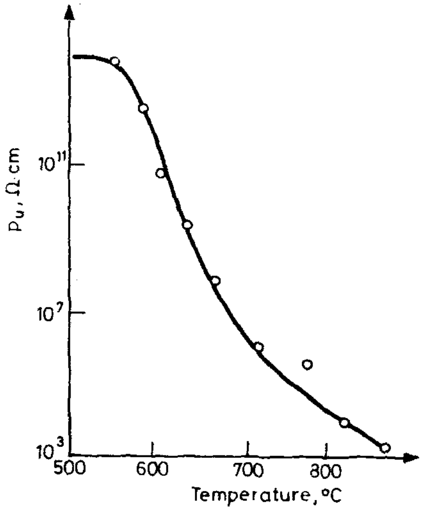


Fig. 10 Specific resistivity *vs.* temperature of PPI thermolysis

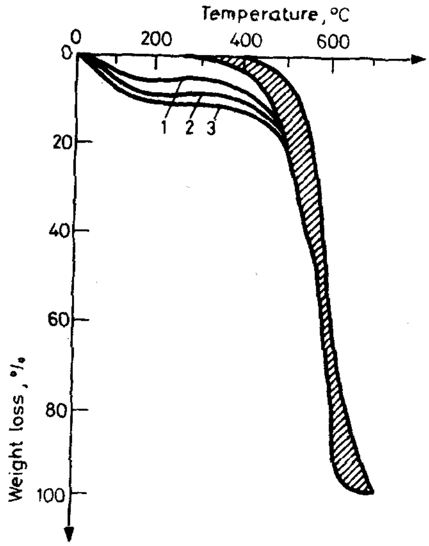


Fig. 11 TG curves of PPI samples subjected to thermolysis at 1) 750°, 2) 800° and 3) 900°; shaded area: 500–700°

Table 2 Elemental composition of cord polyimide heated to 3000 °C

T, °C	Found, %		
	C	H	N
Untreated sample	79.08	3.56	4.50
500	80.08	3.40	3.82
550	86.79	1.30	3.53
600	86.52	1.44	3:29
650	87.52	1.36	2.86
700	92.50	1.30	2.50
900	93.52	0.88	2.20
1200	96.57	—	1.30
1500	98.05	0.44	1.26
2000	98.86	0.19	0.89
2500	99.09	Het	0.58
3000	99.60	Het	0.33

formation of a porous surface of samples at temperatures above 750°. Due to its porosity, this surface is highly exposed to air oxygen.

The study of the carbonization and graphitization of cord polyimide based on 3, 3^1, 4, 4^1-benzophenontetracarboxylic acid and aniline fluorene in an inert atmosphere in the temperature range 500–3000° [108] showed that the elemental composition of the samples subjected to thermolysis suffered drastic changes and that traces of nitrogen were detected even at very-high temperatures (Table 2). The gases evolved in vacuum thermolysis support the suggested mechanism of the thermal degradation of the polyimide with the given structure (Fig. 12). Hence, at

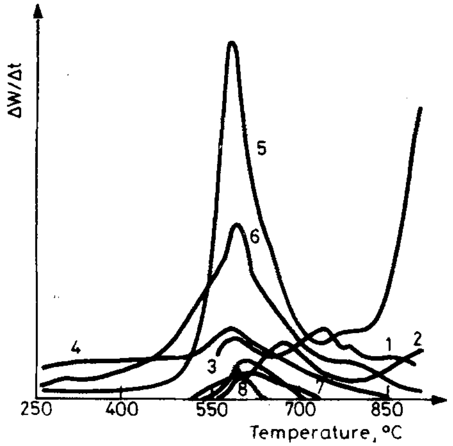


Fig. 12 MTA curves for the thermolysis of cord polyimide 1) H_2, 2) N_2, 3) HCN, 4) H_2O, 5) CO+N_2, 6) CO_2, 7) benzene and 8) phenol

700–750°, the formation of the coke residue consisting of 92.5% carbon is essentially completed (Table 2). At these temperatures, the properties of polyimide change markedly: electric resistance becomes 180–210 Ohm m^{-1} and the coefficients of thermal conductivity and diffusivity decrease from 0.230 (for the unheated sample) to 0.700 wt/m deg and from 1.10 to (3.5–4) 10^{-7} wt/m deg, respectively.

Investigation of solid pyrolysis products heated above 700° has been mainly carried out by X-ray analysis and EPR. These studies show that above 700° fragments of polyimide molecules are recombined into larger condensed aromatic species.

Higher temperatures lead to a gradual carbonization of the material and to the perfecting of the structure of the carbonized products. The diffractograms and the characteristic X-ray parameters which depend on the heating temperature, show that these thermal products are typical nongraphitized materials with the turbostratic structure. The absence of graphitization in these thermal products may be due to the structural features of the preheated material: considerable macroporosity and the occurrence of crosslinks between the carbon chain polymers which are thermally transformed into a crosslinked carbonized product.

When these products are heated in the temperature range 1300–1600°, a second maximum of the EPR absorption appears. The excessive paramagnetism of nitrogen-containing polymers is induced by nitrogen atoms. Above 1700°, the nitrogen content in the carbonized products decreases and the concentration of PMC decreases.

When the carbonized products are heated to 2900°, their X-ray diffractograms exhibit the composite line (002) indicating the presence of two crystalline phases with interplanar distances $d = 0.344$ and 0.336 nm. The latter value is characterized by much larger crystallite dimensions.

The photographs of materials undergoing thermal treatment up to 1200 and 2800° show that they contain virtually no pores.

Figure 13 shows the TG curves of the initial carbonized products and of those obtained after various stages of thermal treatment. The figure shows that the thermal oxidative stability of carbonized materials is much higher than that of the initial polymer. This stability increases with the treatment temperature.

These data suggest that it is advisable to use carbonized products for the preparation of carbonized materials, in particular glassy carbon. The above considerations show that the classical methods of thermal analysis are quite satisfactory for the investigation of high-temperature transformations of polyimides if used in combination with spectroscopic methods, in particular, with those applicable for the determination of the chemical changes occuring on the surface and in bulk of the solid products. In this field the method of photoelectronic X-ray spectroscopy (XPS) is very promising. For instance the surface analysis of

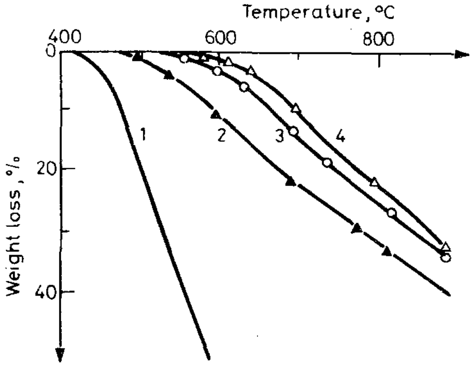


Fig. 13 TG curves of cord polyimide: 1) initial sample and samples heated to 2) 900°, 3) 1200° and 4) 2000°

aromatic polyimides based on diaminodiphenyl ether and dianhydrides of pyromellitic and benzophenontetracarboxylic acid in an example for the combination of methods. In this study the analysis of carbon, oxygen and nitrogen was used to show their chemical interdependence for the samples of the polyimide prepolymer as well as for the polyimide itself, to determine the cyclization mechanism of the prepolymer and to determine the relationship between the chemical bonds on the surface of the polyimide and the technology of its preparation. The XPS method in combination with TG was used for the study of thermolysis of the Capton film in argon at 600 and 900° [110]. As in other papers, it has been shown that above 600° the weight loss of the sample is small and the changes in the chemical structure as a result of breaking of the C—N and C—O bonds lead to the formation of a new condensed structure. The electric conductivity of the new phase is higher by a factor of 10^{20} as compared to the initial Capton film. The authors explain this effect by the possibility of the existence of the tunnel effect of conductivity. A carbonized film obtained by heating the Capton film between two quartz plates exhibits high thermal stability in air, very good adhesion to glass, ceramics and metal and satisfactory mechanical properties. The study of the thermal degradation of polyimide PM by the XPS method has been described in greater detail in [111]. In this study a series of samples heated under vacuum at temperatures 650, 820, 890, 1000 and 1200 K has been investigated. The XPS method permitted the detection of changes in the chemical structure of surface layers of the polyimide film subjected to thermolysis in the temperature range of the most intensive processes of thermal restructuring of polyimides. It was found that the structure of the surface layers of polyimide cyclized at 650 K slightly differs from the stoichiometric structure. Analysis of oxygen, nitrogen and carbon bonds shows that upon heating the film in vacuum, the bonds undergo great changes.

When the absolute quantity of oxygen in the film decreases with increasing temperature, it is distinctly observed that the carbonyl bonds disappear first. Ether bonds in the diamine fragment are thermally more stable. The restructuring of nitrogen-containing fragments was characterized by the formation of the four possible structures of imine-, nitrile-, amide- and nitrogen-containing heterocycles, in particular at temperatures above 800 K. The structure of carbon bonds varied as nitrogen, oxygen and hydrogen were burned out, and at high temperatures polynuclear structures were formed but up to 1200 K graphitization was not observed. The methods of PGC and XRS were used for the study of thermochemical transformations occurring on the surface of the polyimide PM film subjected to the temperatures of about 900° [113]. From the yield of the gaseous products by pyrolysis gas chromatography (PGC) and the investigation of solid pyrolyzed residues (XPS) it was concluded that the main degradation processes occur in the temperature range 500–650°. In this range, considerable evolution of carbon oxides due to the opening of the imide ring and a change in XPS are observed. The peaks of carbon and oxygen of the carbonyl group upon heating up to 600° decrease in intensity. The XPS spectra of nitrogen exhibit a change in the bond energy from 400.4 to 400.1 eV. The decrease in the bond energy indicates that the electron density on the nitrogen atoms increases and qualitatively confirms the decrease in the concentration of carbonyl groups. The diphenyloxide fragment is more stable to the temperature effect, and the intensity of lines of carbon and oxygen of this group is virtually invariable up to 650°. These results are in good agreement with the data of MTA and high resolution NMR in a solid body. At temperatures of 650° and higher, the degradation processes become more pronounced. Phenol, benzene, benzonitrile and hydrocarbons by PGC and MTA are detected among the volatile products. In other words, thermal degradation affects all the elements of the polyimide structure. These thermal transformations are reflected in the XPS spectra, and at a given temperature, the intensities of the photoelectron lines CIs and OIs of the carbonyl and diphenyloxide groups decrease. The broadening and splitting of nitrogen lines show that chemically non-equivalent nitrogen atoms appear in polyimide. Upon further increase in temperature (700–850, 900°), the polyimide structure is aromatized but the presence of nitrogen and oxygen in the structure of the pyrolyzed residues suggests that some heterocyclic structures which were formed during heating, are retained. Hence, as a result of the temperature effect, the polyimide undergoes restructuring and the structure of polymeric carbon is obtained. The dynamics of this restructuring may be represented by a scheme which is given in Fig. 14 [113, 114]. At three temperatures, 525, 575 and 625°, averaged over the investigated range, a group consisting of three units of polyimide PM is considered. These units are separated by the authentic intermolecular distances at which a condensation between the individual groups of atoms occurs

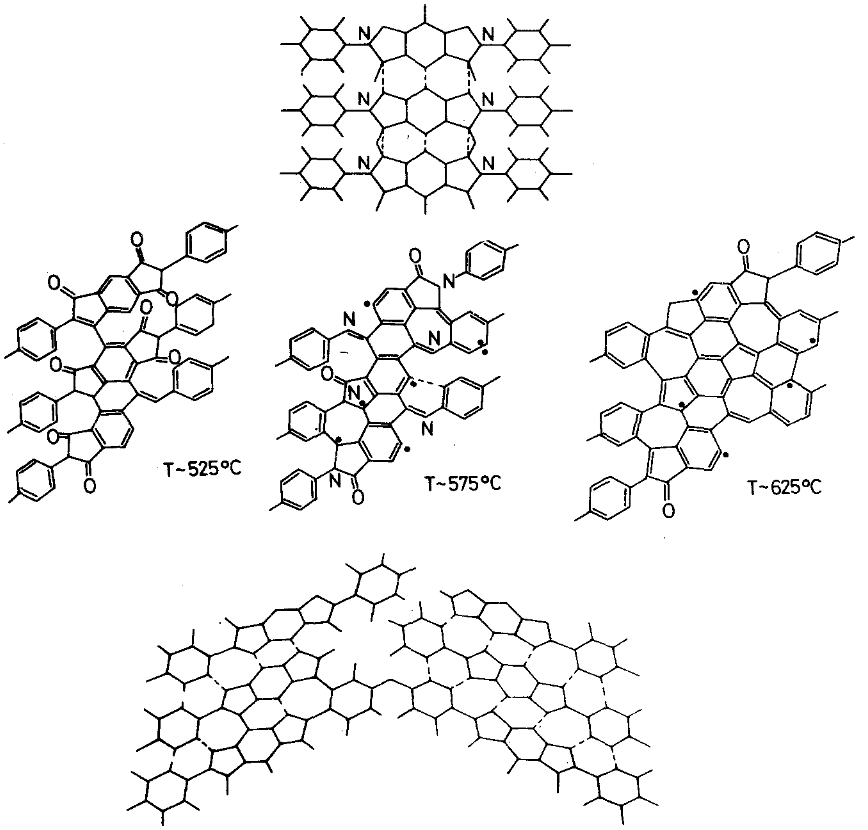


Fig. 14 Scheme for the formation of carbonized products of PPI at temperatures 1) 525, 2) 575, 3) 625° and 4) higher

with the formation of crosslinked structures. This condensation is accompained by the evolution of a number of gaseous products. There is a correlation between the amount and composition of volatiles which may be determined by MTA, TVA and TG, and the amounts and composition of the solid residue which are determined by XPS, NMR, IR spectra and elemental analysis. Weight loss which is determined by TG, is attributed to the evolution of gases during the condensation of individual groups coincide in the range of 10°. At 525°, the "memory" of the polyimide structure is still distinctly detected, although gas evolution is considerable. Subsequently radicals are generated as a result of hydrogen removal. Their recombination is confirmed by MTA and EPR. At 650°, the temperature of the most intensive degradation, a condensed aromatic skeleton is obtained with hydrogen heteroatoms in the structure and with oxygen atoms on the periphery of the condensed structure.

Further increase in thermolysis temperature leads to an increase in the density of the entire carbonized structure and to condensation which result in the removal of oxygen of the diamine fragment in the form of phenol (Fig. 14, scheme 4). In conclusion, it should be noted that the investigations in the range of high-temperature transformations of polyimides deal in a more detailed study with the properties of carbonized polyimide materials [115, 116]. The main emphasis of these papers is on the electrical properties of these materials: the generation of the conductivity and semiconductivity effect. The results indicate that the properties of the pyrolyzed material can be described by the formation of carbonized islands in the matrix of the insulator and that the current is carried by charge hopping or tunneling between carbonized islands. The far IR spectroscopy, the transmittance and reflectance and the resistivity as a function of temperature, all suggest that the pyrolyzed H-films are composed of two-phase, one phase being essentially pure carbon, the other an organic "glue". The evidence for this is very persuasive if not decisive. The strongest evidence is the far IR spectroscopy and its resemblance to that for carbon black including the wavelength dependence of transmittance which is characteristic of Rayleigh scattering. The temperature dependence of resistivity and charge limited tunneling model are remarkably well. In this modell tiny carbon grains are isolated from one another by an insulating matrix and electronic conduction takes place by tunneling. On the other hand, this temperature dependence is identical with that of two dimensional, variable range hopping in a single-phase, conducting polymer. Parenthetically we note that we fitted the resistivity data to the fluctuation-induced tunneling model Pingsheng used to describe the electrical properties of carbon black in a polymer matrix. Statistically significant departures from this model were observed at the highest and lowest temperatures.

Hence, at present the thermal analysis studies of the mechanism of thermolysis of polyimides and the properties of the resulting carbonized products have passed into the new phase of fundamental investigations of entirely new polymer structures.

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Zusammenfassung — Die Ergebnisse thermoanalytischer Untersuchungen von Polyimiden wurden ausgewertet. Es wird gezeigt, dass eine kombinierte Anwendung thermischer Analysenmethoden nicht nur die Bestimmung der thermischen und Strukturmerkmale von Polyimidprodukten ermöglicht, sondern auch die Beobachtung der Bildung von Polyimiden, sowie deren thermischer Zersetzungs- und Umformungsprozesse zu anderen Strukturen unter dem Einfluss höherer Temperaturen.

Резюме — Обзор посвящен проблеме использования термоаналитических методов для исследования термохимических превращений полиимидов, их форполимеров и модельных соединений в широком температурном диапазоне. Кроме классических методов термического анализа, рассмотрены результаты спектральных и других аналитических методик в подтверждение данных термического анализа. Библиогьафия 116 наименований.