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Specific Pyrolysis of Polycondensation Polymers

L.G.Gladkova, E.F.Kolpikova, Ya.S.Vygodskii, and A.S.Fialkov

The review discusses processes involving the thermochemical conversion of polymeric materials with a network structure (furfural and phenol-formaldehyde polymers) and polyimides into carbonaceous materials. The structural characteristics and properties of the carbonaceous materials based on the polymers are analysed and their applications are indicated. The bibliography includes 122 references.

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I. INTRODUCTION

The successful development of modern technology is to a large extent determined by the creation of materials capable of retaining their operating properties at a high level under extreme conditions. The aromatic polyamides, polyimides, polysulphones, and polybenzoxazoles synthesised hitherto, in which a high thermal stability and heat resistance are combined with effective strength and dielectric parameters and with radiation and chemical stability, have made it possible to solve many problems in modern technology.

However, the possibilities of thermostable polymers are limited, the temperature of their prolonged use in air does not exceed 300 to 400° in most cases, and treatment with strong chemical agents can lead to their dissolution or decomposition. A further increase in the resistance of polymeric materials to the effect of temperature in corrosive media is possible by creating on their basis secondary carbon structures. Such structures are chemically inert, are highly resistant to heating, and in many cases possess a high mechanical strength. They are obtained by the heat treatment of macromolecular compounds under non-oxidative conditions.

The main type of polymers used to prepare carbonaceous materials comprises phenolic polymers in view of their low cost, large-scale production, and the reliability of the sources of the natural raw material. However, the relatively low yield of coke, vigorous gas evolution, and pronounced shrinkage during the pyrolysis of phenolic polymers do not permit the full realisation of the potential possibilities of carbonaceous materials obtained from polymers. The inadequate assortment, the limited thickness, the appreciable brittleness, and the presence of undetectable defects in gas-impermeable articles made from carbonaceous materials based on phenolic polymers narrow their practical applications.

The above factors necessitate the search for new polymeric sources of carbonaceous materials which will make it possible to obtain articles with stable and improved characteristics. Polymers with a heterocyclic structure, among which polyimides occupy an outstanding position, can undoubtedly serve as polymers of this kind. The high coke numbers of polyimides, the small gas evolution during their pyrolysis, and the possibility of processing them in a powder form combined with the ability of certain representatives of the polymers of this type to be converted into a highly elastic and viscofluid state justify the assumption that they are promising materials for the creation of thermostable carbonaceous materials with a valuable set of properties.

The present review is devoted to the analysis of studies concerned with modern ideas about processes involving the carbonisation and graphitisation of polymeric materials.† It appeared useful to survey the results of experimental and theoretical studies on processes involving the specific pyrolysis of phenolic polymers, since these have been studied in greatest detail, and polyimides which are some of the most promising representatives of new polymers as potential sources of carbon.

This approach makes it possible to establish important characteristics of the conversion of the polymeric raw material into carbonaceous materials which influence their physicochemical properties.

II. THE FORMATION OF THE STRUCTURES OF CARBONACEOUS MATERIALS ON THE BASIS OF NETWORK POLYMERS

The preparation of carbonaceous products on the basis of polymeric materials involves several heat treatment stages during which their main properties are established.[1,2] In the general case, the stages in the manufacture of carbonaceous materials from polymers are carbonisation and graphitisation. The first stage consists in the heat treatment of the initial raw material (or articles formed from the initial raw material) up to temperatures in the range 1100 to 1300 °C (carbonisation), which makes it possible to obtain under certain conditions carbonaceous materials with a two-dimensionally ordered structure.[1,3] The second stage involves the heat treatment of these materials up to temperatures in the range 2500 – 3000 °C,[1,4] during which mainly their structural rearrangement takes place.

In many instances, additional operations are introduced—preparation of the initial raw material, the moulding of articles, hardening, etc.[1,4] The required form of the article is imparted to the initial polymer which can be cast in the form of a film or moulded in any of the usual ways—by pressing, casting under pressure, and extrusion.[1,5]

It is known[1,6] that the structure and hence also the properties of carbonaceous materials are determined by the nature of the polymer, the character of the intermediate products formed during pyrolysis,

†The review does not present information about processes leading to the formation of carbon fibres, which constitutes an independent field of study.

and the carbonisation and graphitisation conditions. Factors such as the rate of heating to the maximum temperature and maintenance at this temperature can influence significantly the specificity and extent of the thermochemical transformations of the initial raw material and the qualitative characteristics of the materials formed—the crystal and disperse structures, the carbon content, and the concentration of heteroatoms.[1,2]

1. Characteristic Features of the Carbonisation of Phenolic Polymers

The carbonisation of polymeric materials, i.e. their thermal transformation into carbon, is an important stage determining the properties of the final carbonised product. It is achieved by the slow heating of the polymers with and without catalysts in a reducing or inert atmosphere.[7-10] Inert gases (nitrogen,[3,11,12] argon,[13,14] and helium[15]), a high vacuum,[13,16] a coke charge,[17] and a powdered alumina charge[18] were used for this purpose. A reducing atmosphere (H_2, CO) is more rarely employed.[19,20]

The final temperature of the treatment of the polymer is mainly 800–1200 °C,[20,21] although it can be below (600 °C)[11] or above (1400–1600 °C)[12,22] this range. In the carbonisation stage, low-molecular-weight products of the pyrolysis of the polymers are split off, a coke residue is formed, the geometrical dimensions and density of the specimens are altered, and a porous structure and a contact surface are formed. Qualitatively new properties arise in the carbonised polymeric material as a result of these changes.

The onset of the thermochemical transformations of phenol-formaldehyde (FP) and furfural-phenol-formaldehyde (FPF) polymers is believed to be at 150 °C according to electron paramagnetic resonance data.[23-25] When FP and FPF polymers are heated above 300 °C, they begin to undergo degradative changes accompanied by weight loss.[26-29] The principal decrease in the weight of FPF polymers occurs in the temperature range 300–600 °C,[28-30] while the maximum rate of this process has been noted at 460 °C.[1,26] On heating to 1200 °C, the FP and FPF polymers vigorously evolve low-molecular-weight and volatile products[26,27] and the weight loss is then more than 50%.[1,26]

When network polymers are carbonised in the temperature range 250–450 °C, degradative processes, accompanied by the evolution of volatile pyrolysis products and the formation of condensed aromatic fragments, take place preferentially.[25,31] A sharp increase in the concentration of unpaired electrons,[24,30] reaching an extreme value at temperatures of about 600 °C,[23,24] corresponds to this period. Higher temperatures induce the recombination of the aromatic fragments and the appearance of condensed aromatic formations with higher molecular weights.[25,31] The concentration of paramagnetic centres (PMC) then falls sharply.[24]

It has been shown[31,32] that planar layers with hexagonal packing appear in carbonised FP polymers already in the temperature range 200–350 °C.[31,32] However, the hypothesis that the onset of the formation of the structure of carbonised FP and FPF polymers occurs at 500 °C appears more likely.[33] The most intense structural transformations of individual parts of the carbon skeleton of the pyrolysed FP and FPF polymers occur at 500° and 720 °C.[34]

The principal products of the gas evolution in the pyrolysis of the above types of polymers are CO, CO_2, CH_4, H_2, H_2O, and phenol[13,30,34-36] and up to 600 °C mainly carbon oxides and water are evolved, while at higher temperatures the principal products are methane and hydrogen.[36,37]

It has been established[37-39] that, when PF and FPF polymers are heated, they are dehydrated as a result of the interaction between hydroxy-groups, which can take place with cyclisation, and between hydroxy-groups and methylene bridges.

The low apparent activation energy for the dehydration of PF polymers (25–38 kJ mol^{-1}) shows that this process takes place readily.[40]

The maximum rate of evolution of carbon oxides on pyrolysis of FPF and furfural-acetone (FA) polymers is observed at 380° and 500 °C, to which correspond the maxima in the exothermic effect on the differential-thermal analysis (DTA) curves, while the maximum rates of the endothermic evolution of hydrogen and methane have been noted at 390° and 580 °C.[41]

Carbon oxides are formed in the thermal degradation of the least stable oxygen-containing groups at defective sites of the three-dimensional polymer network.[35,42] It has also been reported that CO_2 may be produced as a result of the decomposition of hydroxy- and hydroperoxy-groups formed with participation of chemisorbed atmospheric oxygen[34] and that CO may be formed on decomposition of benzene rings.[26] It has been established[29] that, even at temperatures around 1000 °C, the volatile products of the pyrolysis of PF polymers contain an appreciable amount of CO, while only traces of CO_2 have been noted above 700 °C. The explanation is that at elevated temperatures the reaction equilibrium

$$2CO + O_2 \rightleftarrows 2CO_2$$

is displaced towards the formation of carbon monoxide.

Heating of network polymers above 500 °C leads to far-reaching chemical transformations, which is indicated by the appearance of appreciable amounts of CH_4 and H_2 in the gaseous pyrolysis products.[26,35] Methane is produced as a result of the degradation of methylene bridges, which proceeds via the formation of the reactive methylene radical.[35] This process takes place most vigorously at about 600 °C, above which processes involving the evolution of CH_4 and H_2 predominate. It is emphasised[37,43] that hydrogen may be formed on pyrolysis of PF polymers and also in lower temperature ranges on decomposition of the methylene bridges. At temperatures above 500 °C, the fraction of H_2 increases in the pyrolysis products of the PF and FPF polymers as a result of the dehydrogenation of aliphatic units and the condensation of aromatic rings.[35] It is known[44] that the energy of the C–H bond in the benzene ring is lower than that of the C–C bond, so that on pyrolysis the former is dissociated first. However, Ouchi and Honda[37] have shown that dehydrogenation of aromatic units at high temperatures can be accompanied by the cleavage of the ring with formation of active thermal degradation products and condensed polyphenylene rings.

The dynamics of the specific pyrolysis of PF and FPF polymers is determined by the ratio of the rates of dissociation of the chemical bonds and of the recombination of the radicals formed.

The chemical structure of the polymers undergoes significant changes during heating: the solid coke formed after the removal of the low-molecular-weight products is gradually enriched in carbon and its content of heteroatoms diminishes.[28,32] In the initial stages of the pyrolysis, these transformations are recorded by spectroscopic analysis. Thus the intensity of the absorption bands referring to the OH, CH_2, and C–O–C groups (at 3400, 1475, and 1100 cm^{-1}) gradually decreases in the IR spectra of the heated PF and FPF

polymers.[26,38] This is accompanied by a gradual increase in the concentration of benzene rings, which can be inferred from the increase in the intensity of the 1500 cm^{-1} band.[26,38]

The FPF polymers heat-treated at temperatures up to 500 to 600 °C contain, together with carbon, still a considerable amount of hydrogen and oxygen.[1,31] The 1100 cm^{-1} absorption bands persist in the IR spectra of such materials, while the 1415 cm^{-1} absorption bands, referring to the residual CH_2 groups, completely disappear. Absorption bands charactersitic of condensed aromatic structures appear and grow at the same time.[26,38] The decrease in the concentration of PMC on heating the polymers above 600 °C also indicates vigorous formation of condensed aromatic systems.[1,35] The changes in the polymers can be inferred from their colour. Deepening of the colour to brown and black in the range 300–600 °C indicates the development of a system of aromatised rings.[5] On raising the temperature, further carbonisation of the solid residues in the polymers takes place. For example, heating of the FPF polymers above 1200 °C increases the carbon content in the coke residue from 68.3 to 97.6 wt.% with a corresponding decrease in the oxygen content from 27.1 to 0.3 wt.%.[30] The residual oxygen forms part of the composition of the hexagonal rings and aliphatic units constituting the final network structure of the carbonised material.[1] The hydrogen and nitrogen contents in the carbonised materials diminish,[30] but nitrogen persists in materials heated to 1200 °C (1.8 wt.%).[1]

The study of the processes involved in the heat treatment of resol PF polymers by EPR showed[24] that, up to 500 °C, the density of the three-dimensional polymer (resite) network does not influence significantly the carbonisation process and the structure of the carbonised residue. The greatest changes in the composition of the heat-treated products are observed[24] in the temperature range 500–700 °C, to which corresponds the maximum PMC concentration of $\sim 10^{19}$ to 10^{20} spins g^{-1}. The changes in the paramagnetic properties at temperatures above 500 °C have been attributed[24] to the fact that at this temperature the density of the three-dimensional network of the polymers begins to influence significantly their carbonisation process. The maximum PMC concentration in the region of 600 °C is determined mainly by localised unpaired electrons, which have been identified with ruptured chemical bonds—free radicals.[45–47]

At temperatures in the range 700–750 °C, parallel networks of hexagons begin to be formed in the carbonised materials.[33] It is believed[38] that isotropic regions comprising tiny "crystallites" consisting of non-ordered accumulations of graphite layers are formed at the temperatures indicated. The initial polymer structure disappears fully and the formation of a two-dimensional structure, characterised by a large amount of non-ordered substance, large dimensions of atomic networks, and their imperfect packing is completed.[30,31,33] The transformation of the aromatic molecular chains of the polymer into carbon with a two-dimensional structure takes place within a relatively narrow temperature range, which in fact explains[48] the sharp change in the properties of the materials at 700 °C.

The diamagnetic susceptibility of the carbonised PF and FPF polymers increases above 700 °C, indicating the onset of the growth of hexagonal carbon layers, which continues without interruption as the temperature is raised.[30] The growth of atomic networks, an increase in the size of the crystallites, and an improvement of order are observed in the range 1000–1300 °C.[31,32,49]

The pyrolysis of PF and FPF polymers in an inert atmosphere can be divided into three stages:[42,50,51] 300–350 °C—a slight weight loss and a slight change in volume; 350–(500–600 °C)—vigorous evolution of gaseous pyrolysis products accompanied by weight loss and a decrease in density as a result of the development of an internal porosity; (500–600)–1200 °C—an appreciable intensification of shrinkage with a comparatively small weight loss and an increase in density and thermal conductivity.

The differences between the structures of the initial polymers and in the hardening conditions are responsible for some specificity in their decomposition and influence the yield of the carbon residues.[25,52] It has been shown[53] that, depending on their chemical structure, the FA polymers afford between 53 and 60 wt.% of coke residue. The properties of the carbonised materials are also determined to a large extent by the structure of the initial polymers. Thus the study of the carbonisation of PF polymers established[42] that the density, the overall and open porosities, and the specific electrical resistance of the carbonaceous materials depend on the ratio of formaldehyde and phenol used to synthesise the initial polymers. It has been noted[42] that the PF polymers obtained using a 1.3–1.6 ratio formaldehyde and phenol and heat-treated at 1250 °C give rise to ~70 wt.% of coke residue, show the smallest shrinkage, have the smallest volume of the open porosity, and have the highest density and ultimate bending strength. The carbonisation of polymers obtained using polymer ratios below the limits indicated gives rise to 60–65 wt.% of coke residues, which has been explained[42] by a decrease in the amount of cross-links, formed via bridging methylene groups. Increased formaldehyde content tends to increase the amount of the low-molecular-weight pyrolysis products evolved as a consequence of the decomposition of the excess hydroxymethyl groups, which leads to an increase in the open porosity of the carbonised materials and an impairment of their strength properties.,

A number of workers have emphasised[50,54,55] that the carbonisation stage should be the slowest part of the overall process involving the formation of carbonaceous materials from polymers. The point is that this stage is accompanied by the vigorous evolution of volatile products, generating an internal pressure in the article, which may increase to such an extent that the article ruptures. During the aromatisation of the heat-treated polymeric structures, an impairment of their strength properties is observed with increase in their electrical conductivity.[5] In order to retain strength, it is necessary to suppress the degradation of polymer chains, which is in most cases initiated by free radicals. The procedures for the preparation of carbonised materials are therefore characterised by low rates of temperature rise (1–5 K h^{-1}).[1] The temperature conditions in the carbonisation of porous articles are characterised by higher heating rates compared with the conditions in the preparation of monolithic articles (20–2000 K h^{-1}).[12,22,56]

2. Graphitisation of Carbonised Phenolic Polymers

The graphitisation process is defined as the temperature-activated continuation of the development of the structure of the substance formed in the preceding stages of the heat treatment.[1] This process, whose name cannot be regarded as especially apt when applied to the coke residues from polymers, is accompanied by slight changes in the weight of the specimens, predominantly as a result of the removal of peripheral atoms and groups, further carbonisation, and ordering of the structure.[1–3]

The practical purpose of graphitisation is a sharp reduction of the electrical resistance, the removal of ash impurities, the reduction of reactivity, and the establishment of the required electrophysical properties of the carbonaceous materials.[57]

Polymers whose hardening takes place without the formation of a mesophase serve[2,4] as the raw material for non-graphitisable or hard types of carbon. Such polymers include, for example, the phenolic and epoxide polymers. This fact has been explained[58-61] by the decrease in the mobility of the structural elements of the substance as a result of the formation of bonds in space during the heat treatment. The non-graphitisability of the products of the carbonisation of certain polymers is also attributed to the influence of the extensive pore system, which bends the graphite layers,[48] and the presence in them of nitrogen above 1200–1500 °C, which prevents the condensation and ordering processes.[30]

The studies on the carbonisation and graphitisation processes involving polymers of the vinyl and furan series, PF and FPF polymers, and oligomeric arylenes established[62] that the graphitisability of the carbonised material can be predicted from the activation energy for the main polymer decomposition process in the range 300–500 °C. Thus the activation energies for the polymers investigated are in the range 70–470 kJ mol^{-1}, while the degrees of graphitisation of the carbonised materials vary from 0 to 90%. Processes in which exothermic polycondensation reactions predominate correspond to activation energies below 125 kJ mol^{-1} and the graphitisability of the cokes is then less than 20%. High activation energies (more than 250 kJ mol^{-1}) are characteristic of endothermic degradation reactions of the main chains of the polymer and the degree of graphitisation of such materials is more than 70%.[62]

On heat treatment of carbonised FPF polymers above 1200 °C, a rapid increase of the diamagnetic susceptibility has been noted, which continued without appreciable saturation up to 3000 °C, showing that the structural ordering processes in the test substance have not reached completion.[30]

In carbonaceous material based on PF polymers, the process leading to the perfection of the structure is inhibited, which in fact explains[47] the slow decrease in the paramagnetism of the test specimens heated to 3000 °C. The symmetrical EPR absorption line, observed up to 3000 °C, reflects the imperfection of the structures of such materials, the retention of small size of the crystallites, their enhanced defectiveness, and the absence of a distinct microtexture.[47]

The X-ray diffraction patterns of carbonised PF polymers show reflections of the (001) and (hk0) types, which are approximately at the angular positions corresponding to the graphite lines.[30,31] The high background level persisting on the diffractometer traces for the heat-treated substances is due to the incoherent X-ray scattering by the aromatically non-organised carbon and the different chemical groups consitituting the amorphous phase.[30,31] With increase in the temperature of the heat treatment of the carbonised PF and FPF polymers, their diffraction pattern changes (the reflections become narrower and more intense)—processes leading to the ordering of the material take place, which involves the orientation of the atomic networks, a decrease in the interplanar spacing, the growth of layers of condensed aromatic carbon, a decrease in the thickness of the packets of planar hexagonal layers, and a decrease in the content of the amorphous phase.[30,31] The structural parameters of the carbonised materials vary as follows: the interplanar spacing d_{002} decreases from 0.370–0.360 to 0.344–0.340 nm for the products heat-treated at 900–1200 and 3000 °C respectively. The sizes of the crystallites L_c and L_a then increase from 3–6 and 1.5–2 nm to 6–12.5 and 4.2–4.6 nm respectively.[30,31]

The character of the change in the X-ray diffraction patterns and the structural parameters as a function of the heat treatment temperature shows that the carbonised PF and FPF polymers are typical non-graphitisable materials with a turbostratic structure.[30] They are characterised by small dimensions of crystallites, are isotropic, have an extensive microporosity and transitional porosity, and their crystal structure remains of the turbostratic type up to high temperatures—as far as 2800–3000 °C.[1,2]

It has been shown[6] that, despite the appreciable changes occurring in the structure of carbonaceous materials based on phenolic polymers during heat treatment, the qualitative character of the globular-cellular structure of the initial polymer is retained up to 3000 °C. The degeneration of the globules to highly oriented regions and the subsequent formation of graphite on the latter proceed with a lag period because this structural rearrangement involves translational processes. It has also been established[6] that the process leading to the imperfection of the structure of the carbonaceous materials based on PF polymers is accompanied by a change in the shape of the globules from spherical to ellipsoidal.

The study of a series of carbonised phenolic polymers—derivatives of phenol, *m*-cresol, and 3,5-xylenol heat-treated at 3000 °C—established[63] that the graphitisability is determined by the structure of the phenolic fragment. The presence of the bulky CH_3 substituents in the phenol improves the graphitisability of the carbonised polymers. Thus non-graphitisable "hard" carbon is obtained from PF polymers, graphitisable or "soft" carbon is obtained from xylenol-formaldehyde polymers, while cresol-formaldehyde polymers give rise to a carbon of an intermediate type.[63] The three-dimensional (112) diffraction line, indicating the appearance of the graphite phase in the test substance, has been noted for carbonised xylenol-formaldehyde polymers at 1800 °C, while for the other two polymers it remained weak even at 3000 °C.[64]

It was established later[65] that mesophase mosaic formations arise in the heat-treated xylenol-formaldehyde polymers at 400–430 °C and promote the formation of large condensed aromatic structures in the test substance, which leads to effective graphitisability of carbonised polymers of this type.

It has been shown[64] that the (002) reflections for carbonaceous materials derived from PF polymers at temperatures above 2800 °C and for materials obtained from cresol-formaldehyde polymers at 2950 °C are compound, while in the case of xylenol-formaldehyde polymers single reflections are obtained. This indicates the presence in the first two specimens of regions differing greatly in the type of structural organisation.

The character of the changes in the compound (002) profile with increase in temperature made it possible to represent the graphitisation process in the following way.[63,64] The distance d_{002} in the initial crystallite of the non-graphitisable carbonaceous material gradually diminishes with increase in the heat-treatment temperature. When d_{002} and L_c reach 0.343–0.344 nm and 2–4 nm respectively, a small proportion of the heat-treated substance changes abruptly. Three components having different structural parameters then appear in the material (see Table).

A further increase in temperature leads to an increase in the amount of the graphite component where d_{002} = 0.336 nm, but even at 3000 °C all three components coexist.[64] It is noteworthy that L_c in the graphitisable carbonaceous material depends on the interplanar spacing, while in the non-graphitisable material it does not. Furthermore, the structural parameters of the graphitisable carbonaceous material vary monotonically and those of the non-graphitisable carbonaceous material vary step-wise.[64]

The study of the processes leading to the formation of the porous structure of the FPF polymers during their heat treatment up to 3000 °C has shown[56] that the pores in such materials can be represented by a honeycomb with a cell size of 10–30 nm and a wall

thickness of 5 – 15 nm. The walls of the pores have in their turn much smaller pores.[66]

As the temperature of the heat treatment is reduced, the macroporosity of the carbonaceous materials based on PF and FPF polymers greatly diminishes (from 13% at 1000 °C to 2.3% at 3000 °C).[6] The size of the intraglobular pores and the structural porosity increase under these conditions. The abrupt change in the structural parameters and the character of the distribution of the porosity during the heat treatment of carbonaceous materials suggested[6] that the decrease in porosity takes place not only as a result of the condensation and ordering of the carbonaceous material but also as a result of the generation of crystalline closer-packed graphite-like formations.

Structural parameters of the carbonaceous materials based on phenolic polymers.[64]

Initial polymer	T, °C	d_{002}, nm	L_c, nm
PF polymer	2800	0.3437	2.3
	2800	0.3427	84.0
	2800	0.3863	66.0
	3000	0.3430	3.3
	3000	0.3427	28.0
	3000	0.3370	37.0
Cresol-formaldehyde polymer	2950	0.3448	2.7
	2950	0.3430	8.0
	2950	0.3373	37.0

The graphitisability of carbonised polymers is known to depend on several factors: the rheological properties of the initial polymers, the nitrogen content in the carbonised residues, and the number and energy of the transverse spatial bonds in them[1,48,59] It has been established[67] that the graphitisability of the carbonised materials can be regulated by pressure. However, there is no information in the literature about the influence of each of the above factors on the graphitisability and structure of carbonaceous materials based on polymers.

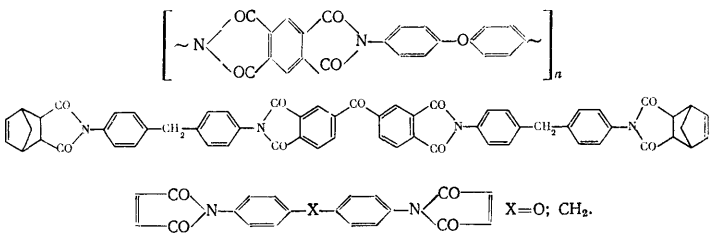
III. SPECIFIC PYROLYSIS OF POLYIMIDES

Numerous communications devoted to the thermal degradation processes involving aromatic polyimides have now been published.[68–87] Depending on their chemical structure, polyimides are distinguished by a wide variety of properties and there are numerous literature data concerning the influence of their structure on their thermal stability.[70–75] Data concerning the influence of the chemical structure of polyimides on their thermal stability in an inert atmosphere have been surveyed in a monograph.[88] It is believed[85] that the degradation of polyimides begins as a result of the decomposition of the "binding" elements—the imide ring and the bridge structures (atoms and groups of atoms).

The chemical structure of polyimides influences significantly the pathways followed in their thermal decomposition.[68,78,85] The polyimide thermal degradation processes can be determined to a large extent by the presence in them of heterounit fragments: amidoacid and isoimide structures and terminal functional groups.[88,89]

The pyrolysis of polyimides is known[85] to proceed via a series of consecutive-parallel reactions, each of which is associated with the formation of definite products. This process is accompanied by the formation of gaseous, liquid, and solid low-molecular-weight substances and of an infusible high-molecular-weight residue. The main bulk of the low-molecular-weight polyimide degradation products consist of H_2O, CO, CO_2, H_2, phenol, benzene, analine, and benzonitrile.[78,79,82,90] The solid polyimide pyrolysis products consist of aromatic carbocyclic and heterocyclic compounds with a system of conjugated double bonds. At the same time, the processes involved in the specific pyrolysis of polyimides, whose aim is to obtain carbonaceous materials, have been investigated to a much smaller extent.[90–94]

The transformations of polyimide and oligoimides having the following structure have been investigated[90] on heating to 3000 °C:



X=O; CH_2.

Carbonaceous materials have been obtained from the polymers and some of their properties have been investigated (hardness, specific surface, and tensile strength). A general scheme for the pyrolysis of polyimides has been published[69] with references to known sources (Fig.1).

In our view, the data on the temperature ranges corresponding to the formation of certain low-molecular-weight pyrolysis products obtained as a result of X-ray diffraction studies and their interpretation are controversial.

The studies on the transformations at temperatures up to 3000 °C in non-oxidising media (argon, coke charge) of polyimides obtained from pyromellitic acid and *p*-phenylenediamine (I), from pyromellitic acid and di(4-aminophenyl) ether (II), from benzophenone-3,3′,4,4′-tetracarboxylic acid and di(4-aminophenyl) ether (III), and from benzophenone-3,3′,4,4′-tetracarboxylic acid and anilinofluorene (IV) have shown[95–97] that the changes in the structure and properties of the polyimides on heating take place at temperatures in the range 300 – 500 °C in a relatively stable mass. Under these conditions, the glass points of the polyimides (III) and (IV) increase gradually and the polyimide (IV) loses it solubility, which may indicate the formation of intermediate three-dimensional structures.

Polyimides may be cross-linked as a result of the interaction of the terminal amino-groups with the imide ring,[83] the interaction of the amide and terminal amino-groups,[88] and the dehydrogenation coupling of two phenyl groups.[85]

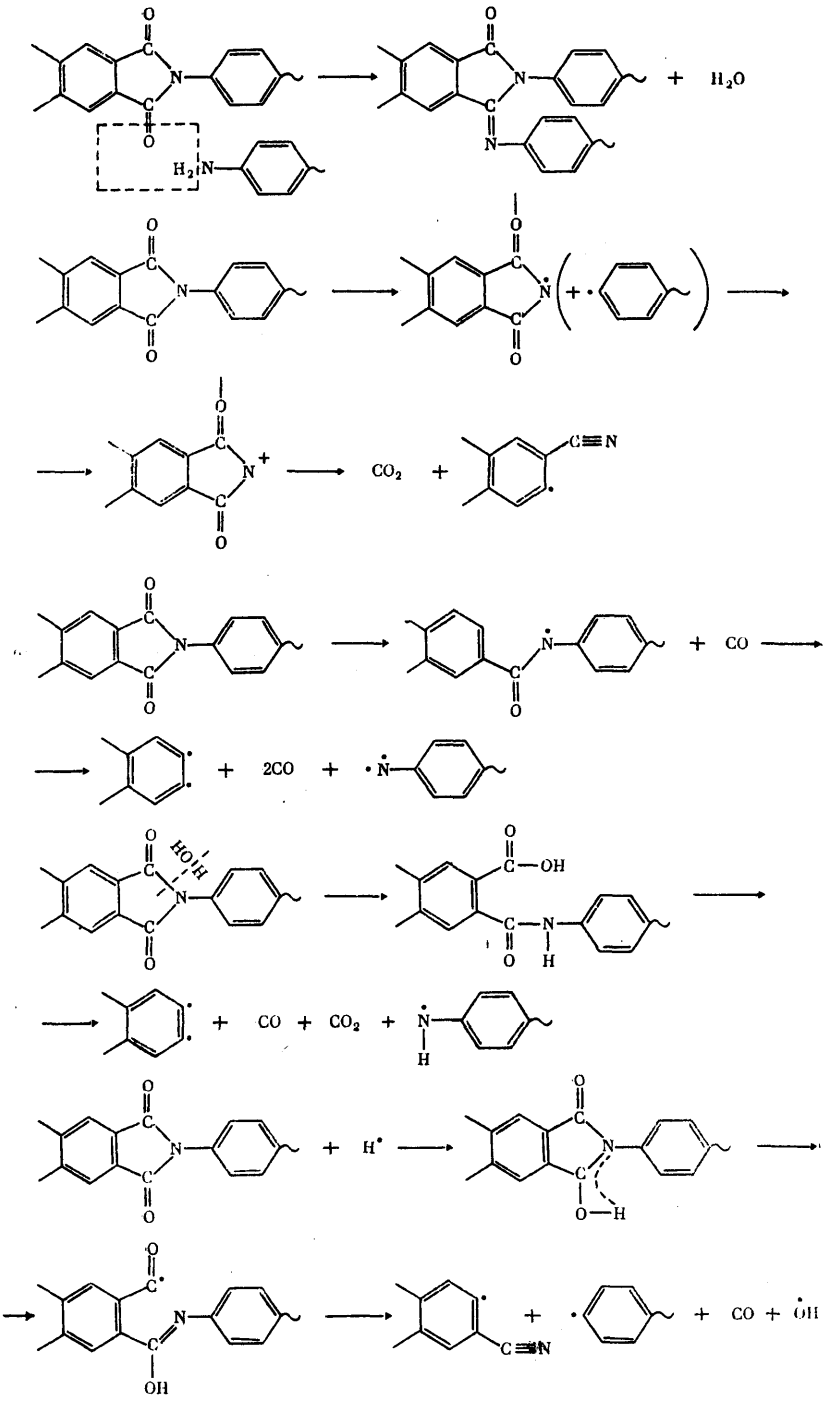
Absorption bands at 1650 cm^{-1} (amide), which can be partly attributed to the formation of a three-dimensional network in polyimides, appear in the IR spectra of heat-treated polyimides.[95,97] The fragments formed under these conditions can serve as sources of certain low-molecular-weight pyrolysis products and can influence the course of the subsequent transformations.

The heating of polyimides in argon to 520 – 540 °C and of the polyimide (I) to 580 °C reduces their weight as a result of the removal of low-molecular-weight pyrolysis products, which consist of carbon oxides and water. The formation of the above products in the initial stages of the weight loss process can occur as a result of a series of elementary reactions[98] (see below).

Under real conditions, the pattern in the thermal degradation of polyimides is much more complex even in the initial stages of the weight loss. It is known[85] that, under the conditions of dynamic heating, there is a possibility, in principle, of any bond dissociation reaction with formation of the corresponding products.

A decrease in the intensity of the 1780 (in a doublet with 1720), 1380, and 725 cm^{-1} absorption bands and an increase in the intensity of the 1650 cm^{-1} band have been observed in the IR spectra of the polyimides (II)–(IV) heat-treated at 540–550 °C.[95-97] These changes indicate the continuation of the reactions in the polyimides.

Heat treatment of the polyimides (II)–(IV) above 550 °C and of the polyimide (I) above 630 °C leads to the development of their thermal degradation processes, which are determined by competing reactions involving the rupture of the spatial cross-links and intramolecular bonds and polycondensation. Under these conditions, the rates of weight loss by the polyimides increase sharply, the



amount of low-molecular-weight pyrolysis products increases, and their composition changes (Fig.2). According to EPR data, the most intense degradative changes, accompanied by the dissociation of chemical bonds and the formation of free radicals, occur in the temperature range 550–650 °C. For the polyimide (I), these processes have been displaced by about 50 °C to the high-temperature region. Most of the weight loss by polyimides occurs in these ranges.[95-97] The degradation of polypyromellitimides, associated with large weight losses, takes place in the narrowest temperature ranges, compared with the polyimides formed from diphenyl ether derivatives and benzophenonetetracarboxylic acid.[95-97]

The rates of decrease in the weight of the polyimides (I) and (III) in the intense degradation region are higher by a factor of 3–4 than those of the polyimides (III) and (IV).

The effective activation energies for the intense polyimide degradation processes in the region of the main weight losses are E_{eff} = 170–300 kJ mol^{-1},[95] E_{eff} for polypyromellitimides being higher by a factor of ~1.5 than E_{eff} for polyimides formed from diphenyl ether derivatives and benzophenonetetracarboxylic acid.

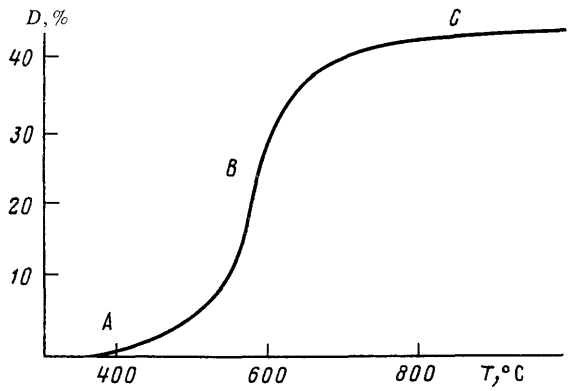
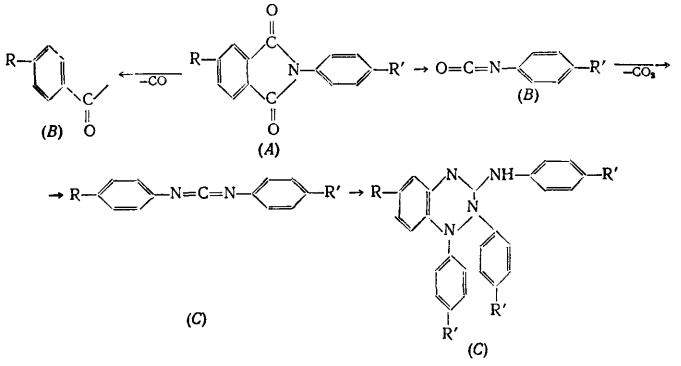


Figure 1. Schematic representation of the pyrolysis of polyimides:[90]



The letters *A*, *B*, and *C* denote regions corresponding to the existence and transformations of the corresponding structures; *D* = weight loss.

Indeed the low activation energy for thermal degradation means that, with increase in temperature, the thermal degradation of polyimides is not accelerated quite so much as that of the polymers with a high activation energy and the advantage of the former will become most apparent at high temperatures. With increase in the mobility of the polyimide macromolecules, the contribution of condensation processes in pyrolysis increases, which may be the cause of the reduced effective activation energies for the thermal degradation processes involving such polymers. Indeed, an increase in chain mobility creates favourable kinetic conditions for the recombination of the fragments produced.

The main bulk of the low-molecular-weight products, whose qualitative composition varies significantly compared with the initial pyrolysis stages, are removed from the polyimides (III) and (IV) at temperatures in the range 550–650 °C. Thus, apart from carbon oxides and water, whose formation was noted already at temperatures corresponding to insignificant weight losses and whose amount increases with increase in temperature, hydrogen, nitrogen, hydrogen cyanide, methane, benzene, phenol, benzonitrile, and diphenyl ether have been identified in the polyimide pyrolysis products (Fig.2). The formation of the above products from the polyimide (I) takes place at higher temperatures (600–700 °C).

The overall amounts of the low-molecular-weight products as well as their composition are comparable for the polymers investigated. Nevertheless, the influence of the chemical composition of the polymers on the character of their thermal degradation can be traced quite distinctly.

The main fraction of the polyimide pyrolysis side products, evolved in the region of vigorous degradation, corresponds to CO and CO_2 (Fig.2); H_2O is also formed in considerable amounts. The maxima of the peaks in the mass spectra of the above products correspond approximately to the temperatures of the highest rates of weight loss.[95-97]

It is noteworthy that the polyimides (I) and (II) evolve larger amounts of CO_2 than CO, while the polyimides (III) and (IV) exhibit the opposite behaviour. The CO_2/CO ratio for the polyimide (I) is greater than for the polyimide (II), which may be due to the high extent of the intramolecular and intermolecular interaction of the donor (diamine) and acceptor (dianhydride) sections in the polyimide macromolecules. It is known[99,100] that such interaction is accompanied by the delocalisation of electrons and the formation of intramolecular and intermolecular charge-transfer complexes. The possibility of an intramolecular rearrangement or of intramolecular oxygen transfer is facilitated in formations of this kind, which promotes the reaction involving the decomposition of the imide ring with formation of CO_2. The bridging heteroatoms or groups of atoms interrupt or greatly weaken the conjugation along the chain.[100] The electron-donating properties of the diamine residues weaken from the polyimide (I) to the polyimide (II), which can explain the changes in the ratio of the carbon monoxide and dioxide formed.

The higher CO content in the pyrolysis products of the benzophenonetetracarboxylic acid polyimides may be caused by the splitting-off of the carbonyl groups from the benzophenone structure.[101] The somewhat smaller, compared with the polyimide (III), amounts of CO formed in the pyrolysis of the polyimide (IV) are probably associated with the influence of the carbo-group.

The intensity maxima on the curves describing the formation of the low-molecular-weight liquid products of the pyrolysis of polyimides correspond to the region of high rates of weight loss (Fig.2). The greatest relative amounts of liquid compounds are formed in the thermal degradation of the polyimides (I) and (II).[95-97]

The formation of the products described indicates a far-reaching rearrangement of the chemical structures of the polyimides on heating. The evolution of such compounds by the polyimides under the

conditions of specific pyrolysis should probably be explained, by analogy with the pyrolysis of the network polymers (PF and FPF), by the removal of bulky fragments preventing the molecular condensation of the heat-treated polyimides. Such fragments may be structural elements arising in the initial stages of the pyrolysis and also sections of the macromolecules which were not altered at lower temperatures.

In the heating process, the elemental composition of the coke residues from the polyimides changes, which is particularly notable at the temperatures corresponding to the removal of liquid low-molecular-weight pyrolysis products. At 600–700 °C, the carbon content in the residues increases to 80–86 wt.%, while the fraction of hydrogen and nitrogen diminishes appreciably.[95-97]

Pyrolysis of the polyimides leads to the formation of new products—carbonised polyimides—at temperatures in the range 600 to 700 °C.

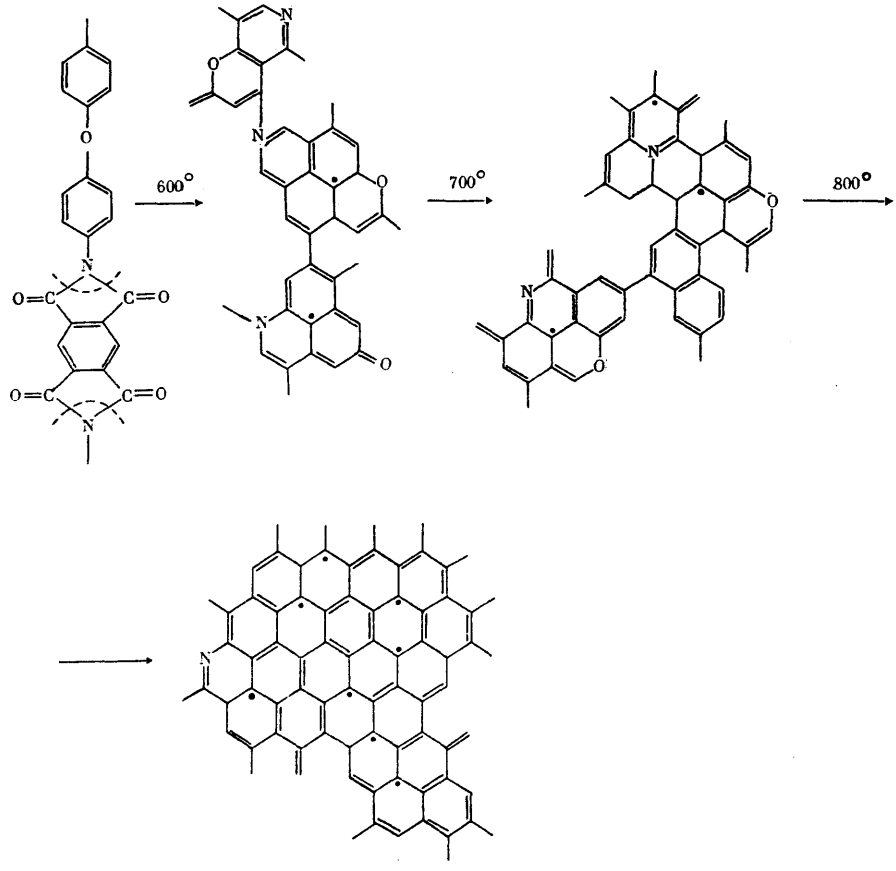
X-Ray diffraction data indicate the conversion of the chain structure of the polyimides to a polycyclic condensed structure at temperatures in the range 600–700 °C. The properties‡ of the pyrolysed materials change sharply at these temperatures—they acquire metallic lustre, their electrical resistance decreases to 180–210 Ω cm, and their thermal expansion coefficients and thermal diffusivities increase respectively from 0.2–0.3 (for the unheated polyimides) to 0.5–2.0 $W\ m^{-1}\ K^{-1}$ and from (1.1–1.3) × 10^{-7} to ~4.0 × 10^{-7} $m\ s^{-1}$.[95-97]

It has been shown[102] that the bulk-phase electrical resistance of the Kapton polyimide film decrease by 16–18 orders of magnitude after vacuum heat treatment at 600–800 °C as a result of the formation of carbon–carbon double bonds and free valences in the polymer.

The yield of coke from the polyimides (I)–(IV) at 900 °C in argon is 55–64 wt.%. The greatest amounts of residues are retained by polyimides with bridging atoms in the dianhydride residues.[95-97]

It has been shown[87] that, in polymers having a heterocyclic structure, nitrogen participates in the formation of the coke residue together with carbon. The nitrogen of the phthalimide ring, a considerable proportion of which is retained in the carbonised polyimide at 1000 °C, plays the greatest role in this process.[87]

The study of the vacuum thermal degradation of polyimides with an increased nitrogen content and based on the di- and tri-phenyl derivatives of pyridine and diamines containing pyridine, benzimidazole, and oxadiazole rings has shown[87] that the coke residues from such polymers amount to 60–65 wt.% and that their content is



‡The properties are quoted for specimens in bulk.

independent of the initial structure of the polyimides. The carbonised materials retain on average up to 50–60% of nitrogen relative to its initial amount. It has also been established[87] that, compared with the thermal degradation of polyimides containing nitrogen atoms only in the imide rings, the relative nitrogen content in the coke residue from polyimides with an enhanced [initial] nitrogen content is reduced by 10–15%. It has been suggested that the nitrogen atoms not forming part of the imide ring participate in the formation of volatile thermal degradation products, while the imide ring nitrogen is mainly concentrated in the coke residue.[87] However, the observed characteristics of the pyrolysis of polyimides having different chemical structures[95–97] [(I)–(IV)] suggest that the character of the elimination of nitrogen when they are heated is determined to a large extent by the rheological properties of the initial polymers.

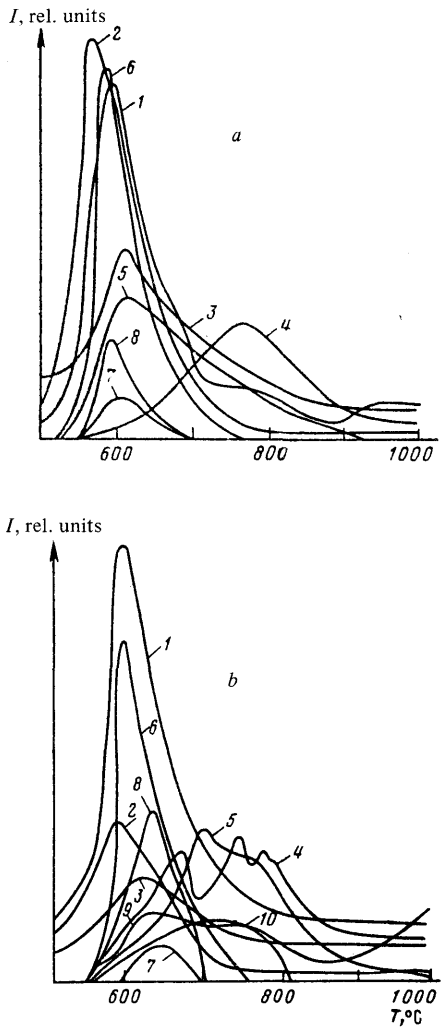


Figure 2. Differential curves for gas evolution in the pyrolysis of polyimides (II) (*a*) and (IV) and (*b*): (1) CO; (2) CO_2; (3) H_2O; (4) H_2; (5) HCN; (6) phenol; (7) benzene; (8) benzonitrile; (9) N_2; (10) CH_4.[96]

Fig.2 shows that the main fraction of the nitrogen-containing pyrolysis products in the thermal degradation of polypyromellitimides is removed before this is observed for polyimides derived from diphenyl ether and benzophenonetetracarboxylic acid.

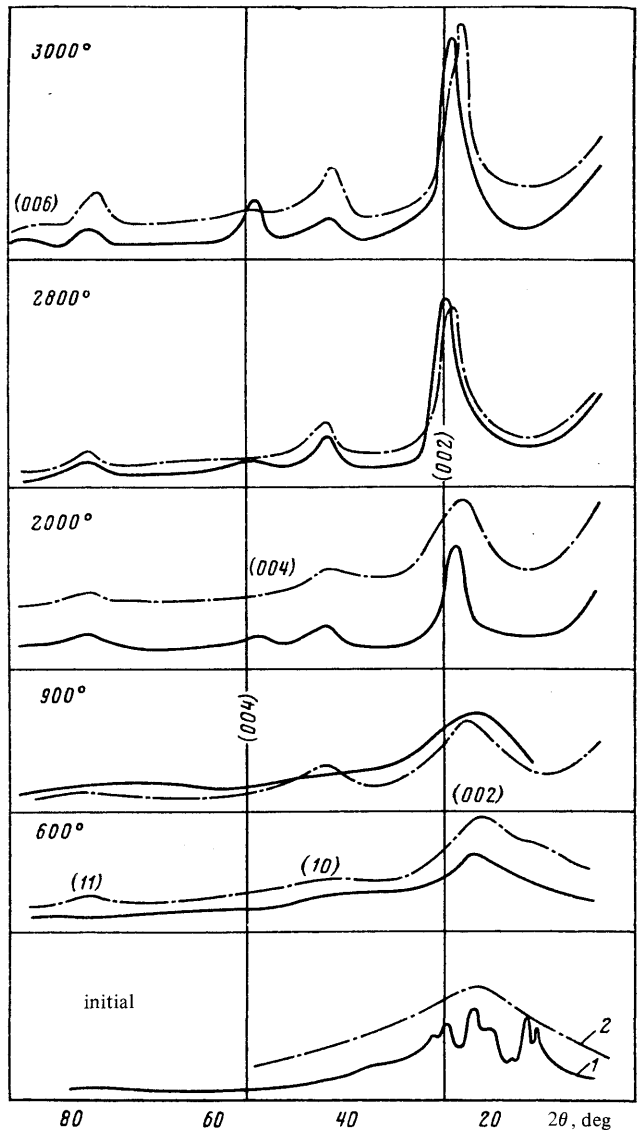


Figure 3. X-Ray diffractometer traces for the initial polyimides (II) (curves *1*) and (IV) (curves *2*) and the carbonaceous materials based on them; heating rate 5–20 K h^{-1}; the vertical lines indicate the angular positions of the principal graphite reflections.[96]

The above factors suggest that the pyrolysis of polyimides with different structures leads to the formation of carbonised materials having different structures. This is manifested particularly strongly when two groups of polymers are considered: polyimides without bridging atoms or groups of atoms in the dianhydride fragments

(polypyromellitimides) and polyimides with the benzene rings in the dianhydride and diamine components separated by such groups—polyimides derived from diphenyl ether and benzophenonetetracarboxylic acid.[95-97] Thus, when the carbonised polyimides (I) and (II) are heated, nitrogen-containing compounds are eliminated initially, which should evidently promote the condensation of these substances, and this is followed by further aromatisation accompanied by the removal of hydrogen, while in the case of the carbonised polyimides (III) and (IV) these processes take place simultaneously.

Heat treatment of the carbonised polyimides in the temperature range 900–3000 °C is accompanied by slight (from 3 to 7%) weight losses and the rates of shrinking processes diminish, approaching zero at 2000 °C. The overall shrinkage is then 16–18%.[95-97] Heat treatment of the materials above 2000 °C leads to the virtually complete elimination of hydrogen from them, the carbon content in the specimens heated to 2500–3000 °C being 99.3–99.9%. It must be emphasised that nitrogen was not detected in the carbonaceous materials based on the polyimides of the first group, obtained at temperatures in the range 1500–1800 °C, while the materials based on the polyimides of the second group retain considerable amounts of nitrogen (0.20–0.33 wt.%) after heating to 3000 °C.[95-97]

During the high-temperature treatment of the carbonised polyimides, the X-ray diffraction patterns change (Fig.3). With increase in the heat-treatment temperature, the intensities of the diffraction profiles of the polyimides increase and the (002) line shifts to the region of larger angles. The improvement of the structure of the carbonised substances is also indicated by the appearance of the (004) line on their diffractometer traces.

The narrowing of the diffraction peaks and the increase in their intensity with increase in the heat treatment temperature and the appearance of the (004) line on the X-ray diffraction patterns indicate the continuing ordering of the structures of the carbonaceous materials.

The form of the X-ray diffraction patterns and the character of the changes in the structural parameters of the carbonised polyimides demonstrate that they are typical non-graphitisable materials with a turbostratic structure.

Materials obtained from polypyromellitimides have the most perfect structure. Their X-ray diffraction patterns show the most intense reflections; after heat treatment at 2950 °C, the (006) lines appear, indicating "long-range order" in the substance (Fig.3). The interplanar spacing in the crystals of the carbonaceous materials obtained from the polyimides (I) and (II) is 0.338 nm, whereas for the remaining materials it is 0.343–0.344 nm. The fraction of the amorphous phase in materials obtained by the heat treatment of polypyromellitimides at 2800 °C is 42% compared with 48–53% for the materials based on the polyimides (III) and (IV).[95-97]

The change in the structural parameters of the crystallites of the carbonaceous materials based on polyimides (Fig.4) is associated with the changes in their chemical composition. The fastest decrease in the interplanar spacing is observed at temperatures such that the processes involving enrichment in carbon and the elimination of nitrogen proceed at high rates; this happens in the range 600 to 1200 °C for the polyimides (I) and (II) and 600–1500 °C for the polyimides (III) and (IV). Above the temperature ranges indicated, the rate of decrease in the interplanar spacing diminishes and the rate of increase in the crystallite diameter appreciably increases. For carbonised materials obtained from the polyimide (IV), this process is particularly vigorous, as a result of which their crystallites have the highest diameter among the materials investigated. Presumably this is associated with the presence in the polyimide (IV) macromolecules of fluorene groups, which, as a result of the thermal transformations in the temperature range 1200–1500 °C, acquire the ability to be located in the planes of different sections of the main chain, having the most ordered structure. The decrease in the diameter of the crystallites in materials based on the polyimide (II) (Fig.4) is due to vigorous processes involving the mutual approach of the hexagonal layers, which may induce their rupture at the most strained bonds.

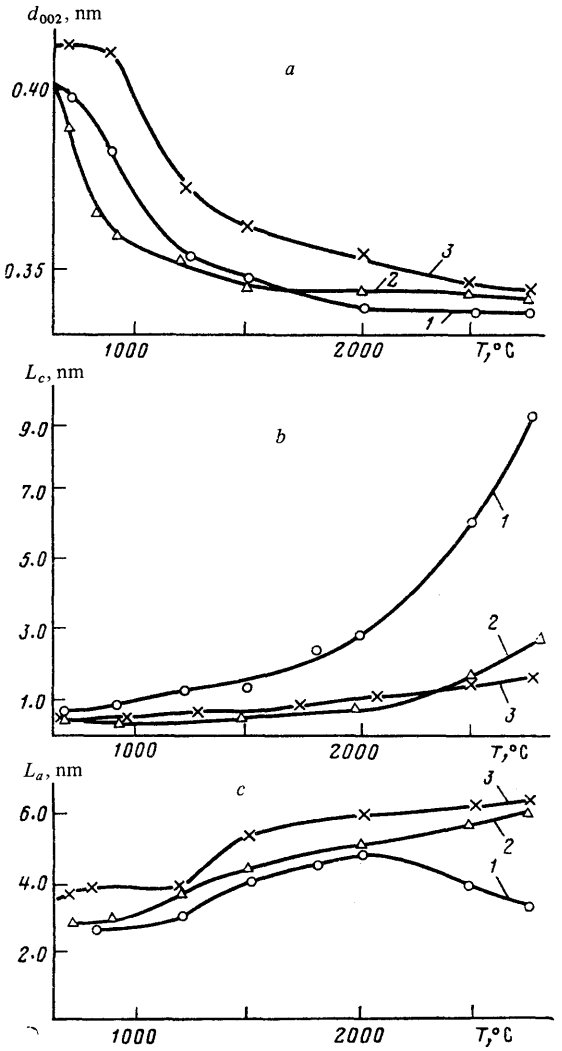


Figure 4. Variation of the interplanar spacing (d_{002}) (*a*), of the thickness of the packets (L_c) (*b*), and of the layer diameter (L_a) (*c*) in the carbonaceous materials based on the polyimides (II) (curves *1*), (III) (curves *2*), and (IV) (curves *3*) as a function of the heat treatment temperature; heating rate 5–20 K h^{-1}.

An increase in the thickness of the crystallites is observed mainly at temperatures where the materials contain the minimum amounts of nitrogen possible for them (Fig.4). Indeed, the growth in thickness of the crystallites in the specimens based on the polyimide (II) is

observed already above 600 °C. The high rates of growth of the height of their crystallites are probably associated with the absence of nitrogen from such materials, heated above 1500 °C.

The data presented show that the structural differences between the carbonaceous materials based on polyimides are mainly associated with the nature of the removal of nitrogen from them. This nitrogen, which has a relatively larger molecular volume than carbon, can prevent the ordering of the structure of the carbonaceous substances.[1,47,103]

It must be emphasised that significant differences between the characteristics of the removal of nitrogen from the polyimides investigated were noted already in the early stages of pyrolysis.

The foregoing suggests that the spatial cross-links, formed in the polyimides in the early stages of the thermal degradation, arise mainly with participation of the nitrogen of the imide ring and prevent its elimination. In carbonaceous materials with a relatively low degree of order [based on the polyimides (III) and (IV)], a considerable nitrogen content has been observed even at 3000 °C, while in the materials based on the polyimides (I) and (II) nitrogen was no longer detected above 1500 °C. One must evidently assume that the spatial cross-linking of polypyromellitimides also takes place, but in such cases it occurs at energetically unfavourable sites. Consequently spatial bonds with different thermal stabilities may arise in the heat-treated polyimides. The weakest of them are ruptured, providing the main source of nitrogen removed from the carbonised materials above 1000 °C, while the strongest are retained up to 3000 °C.

It has been shown[95-97] that the degree of ordering of the structures of the carbonised polyimides is largely determined by the stability of the intra- and inter-molecular cross-links formed in them on heating with participation of the nitrogen of the imide ring. The frequency of such cross-links is known[104] to be capable of varying significantly under the influence of mechanothermal influences, which leads to definite possibilities for regulating the structures of the carbonaceous polyimide-based materials.

The characteristics of the changes in the structural parameters of such materials are determined by the differences between not only their chemical structures but also between their supermolecular structures. Indeed, transient forms of carbon are formed as a result of the reactions in the solid phase, which leads to the possibility of the retention of the initial form of the materials.[4,105]

It has been suggested that the conformation of the skeleton of the polyimide (I) chains can be represented as a planar zig-zag,[106] while for the polyimides (III) and (IV) it can be represented by a greatly extended helix.[88] Sections with different degrees of order can exist in such structures.[107]

The size of the crystallites in the carbonised polyimides is much smaller than that of the crystallites in the carbonised PF and FPF polymers,[30,31] which leads to the expectation that the carbonised polyimides have enhanced strength properties. The wide set of interplanar spacings of the carbonaceous materials obtained from polyimides having different chemical structures provides different possibilities for regulating their physicomechanical characteristics.

The carbonaceous materials obtained from polymers consist of a broad spectrum of molecular structures and supermolecular formations: chain, layer-ribbon, globular, lamellar, diamond-like, and graphite-like formations.[108] The wide variety of structural forms of the artificial carbonaceous materials presuppose a correspondingly wide range of their possible properties.[58,108] By regulating the structure of the material by means of heat treatment or by selecting the initial raw material, it is possible to regulate its characteristics.

Thus vitreous carbon, having many specific properties which are not characteristic of the known modifications of carbon, has been obtained from many types of polymers.[109-117] These properties include an isotropic and monolithic structure, low permeability to liquids and gases, effective strength characteristics, high electrical and thermal conductivities, high thermal stability (in non-oxidising media as a function of the final synthesis temperature—1200 to 3000 °C), high resistance to thermal shock, low density, and resistance to corrosive media which is retained at elevated temperatures.[112-116] Vitreous carbon remains solid up to the sublimation temperature of carbon (3700 °C).[1]

The increase in the chemo-oxidative and thermo-oxidative stabilities and the virtually complete absence of open porosity in vitreous carbon permits its use under conditions where graphite articles break down—in corrosive media and at elevated temperatures and also at an interface between two media. Vitreous carbon articles are used as heat exchangers, components of nuclear reactors and flying vehicles, electrical conductors, electrodes and electric terminals; crucibles, bulb containers, and chemical apparatus for use in specially corrosive media, and implanted components are made from it.[111-117]

The characteristics of the structure and the properties of vitreous carbon have been investigated in detail.[118-122]

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