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THERMOCHEMISTRY OF CARBONIZATION OF POLYPYROMELLITIMIDE

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The mechanisms of thermal degradation processes in polypromellitimide films were investigated by mass-spectrometric thermal analysis and high-resolution NMR spectroscopy in the solid state. Both the structures of the solid residues of pyrolysis products of the PM polyimide and the process of carbonization proper up to 1200° were studied. It was established that the breaking of the C_{ar}—O—C_{ar} bond in the diamine moiety is not the primary act of degradation of the molecular structure of the polymer, as might be expected on the basis of the value of the bond energy. The process of intermolecular crosslinking following polymer degradation under high-temperature conditions is completed by the formation of a complex nitrogen-containing heterocyclic structure.

The search for promising methods of increasing the thermal stability of polyimides is related to the investigation of thermochemical processes occurring when polymers are heated at temperatures higher than that of the beginning of degradation [1]. The directed process of the carbonization and graphitization of polyimides to prepare artificial carbon from them [2] is also impossible without investigation of the main relationships of the high-temperature transformations of the polymers.

A number of papers have been published on the processes of thermal degradation of polyimides under vacuum and in an inert medium [3–7]. The problem of a detailed mechanism for the degradation of polyheteroarylenes, and polyimides in particular, remains unsolved, although many hypotheses and mechanisms have been suggested to explain the qualitative and quantitative compositions of the thermal degradation products [4, 5, 8, 9]. In most papers, the mechanism of

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thermal degradation has usually been derived to account for the gaseous products evolved from the polymer. Information about the structures of the solid products of polyimide pyrolysis is much more scarce, although these products can provide important information about the relationships of the transition of polyimide into artificial carbon upon high-temperature heating [2, 10, 11].

The present paper considers some concepts of the mechanism of degradation processes in polyimides by making use of the data both from the well-known method of mass-spectrometric thermal analysis (MTA) and from the relatively new method of high-resolution NMR spectroscopy in a solid body (NMR HR SB). This method, just as the usual method of high-resolution NMR, provides useful information on the structures of macromolecules, and in particular polyimides. Moreover, in this case the insolubility of the samples does not preclude the investigation of their structures [12].

Experimental

The samples under investigation were polyamic acid films based on diaminodiphenyl ester and pyromellitic dianhydride (PAA PM) and Arimide PM, an industrial polyimide film. PAA PM films 20–30 μm thick were prepared by casting PAA solutions in DMF on a glass support, with subsequent drying at 40°.

Gaseous products evolved during the heating of the polymers were analysed by means of MTA using a commercial MKh–1320 mass-spectrometer (USSR). A polymer sample (1 mg) was placed in a quartz ampoule fixed to a valve unit for direct input into the ion source of the mass-spectrometer. The ampoules containing the samples were heated in the oven of a MOM derivatograph (Hungary) at a rate of 3.5 deg/min. In order to avoid the plugging of the ionic-optical system of the mass-spectrometer with resinous products of PM degradation, a refrigerator cooled with running water was placed between the valve unit and the ampoule. The quartz ampoule was connected to the refrigerator through a special connector also cooled with water.

The ^{13}C NMR spectra were obtained with a CXP–200 Bruker spectrometer (BRD). The thermal treatment of the film samples was carried out under vacuum at a rate of 5 deg/min up to 900°.

Discussion

In the description of the processes of thermal degradation of polyimides, the problem of the formation of such products as H_2O and CO_2, for which no "blanks" exist in the elementary unit of this polymer, is still unsolved. Traditionally, it is considered that polyimide contains a sufficient number of amic acid groups and end-groups to ensure the introduction into the reaction zone of a sufficient amount of water molecules and hydrogen, leading to the hydrolytic and free-radical reactions. These reactions occur at low activation energy values, thereby resulting in the accelerated degradation of the main polyimide structure. The compositions of the products of polyimide thermal degradation, and also the types of the reactions leading to the formation of these products, are profoundly affected by the medium in which the process takes place (vacuum or an inert gas) and by the conditions of thermal treatment (dynamic, isothermal or stepwise heating). The higher the rate of dynamic heating, the more rapidly the temperatures at which the homolytic processes of the degradation of the macromolecules occur can be attained. In this case the significance of defective amic acid units, end-groups and the corresponding reactions is at a minimum. At a low heating rate, with the transition to isothermal conditions, after a certain period of time the situation can become just the opposite.

In this investigation the degree of imidization of the PM film was 94–96%, the molecular weight was several ten thousand, and thermal degradation was carried out under relatively high vacuum at a high heating rate (3–5 deg/min). Therefore, it may be assumed hat the water formed as a result of the degradation of a small number of defective end-units in the early stages of heating will have little effect on the type of degradation of the main polyimide structure; hence, it will not be taken into account in the subsequent discussion.

Another main product of the thermal degradation of the polyimide, CO_2, has been a subject of discussion since the first publication on this subject. The absence of a "blank" for this molecule in the elementary unit of polyimide has led to the development of a number of hypothetical mechanisms for the formation of this compound [8]. The most important of them include:

1) the degradation of "defective" units in anhydride and carboxy groups,

2) the tautomeric transformation of the imide into the isoimide ring,

3) the condensation of isocyanate groups formed in the free-radical opening of the imide ring,

4) the hydrolysis of the imide ring.

From our standpoint, these reactions of formation of CO_2, including reaction 4), cannot explain its amount and the character of its evolution, if for no other reason that that there is no explanation of the formation of H_2O in sufficient amounts during thermal degradation. Another mechanism for the formation of CO_2 should also be mentioned: this is oxygen transfer, proposed by Johnston and Gaulin [4]; there is also a similar, but less likely mechanism of interaction between the carbonyl groups, with the formation of a crosslinked structure [5].

As regards the formation of CO, most authors are of the opinion that this product is a result of homolytic opening of the imide ring. However, this mechanism is realistic at temperatures much higher than 500°, since the imide ring loses its relatively high stability. It is usually assumed that the degradation of polyimides starts as a result of the degradation of the "joining" of "linking elements" in the structure of polyheteroarylenes, namely heterocycles and "pin-joint" atoms and groups [8]. However, at least in the case of the PM polyimide, this does not seem evident to us. Let us consider the MTA data on PAA PM film in the temperature range 20–1200° at a heating rate of 3 deg/min under vacuum (Fig. 1). The choice of the PAA PM film as a sample rather than that of the polyimide iself is due to the fact that the water evolved during cyclodehydration, in an amount of 2 moles per elementary unit of the polymer, makes it possible to carry out the normalization of the spectra with respect to H_2O for the main products of thermal degradation (CO, CO_2, H_2O, benzene, benzonitrile and phenol). Figure 2 shows the picture of thermal degradation in the range of the start of degradation of the main polyimide structure (560°). The ordinate gives the rate of evolution of the product in moles per unit time. It is clear that CO and CO_2 are evolved simultaneously and at approximately the same rate. H_2O and phenol (in a much smaller amount) are evolved in the same range. The numbers of CO, CO_2 and H_2O molecules evolved per phenol molecule are 15, 10 and 4, respectively. Alternatively, it might be assumed that the breaking of the C_{ar}—O—C_{ar} bond in the diamine component is not the primary act of structure degradation, although from an energetic aspect these bonds are not stronger than those of the five-membered imide ring. This suggestion is confirmed by the results obtained with the aid of high-resolution

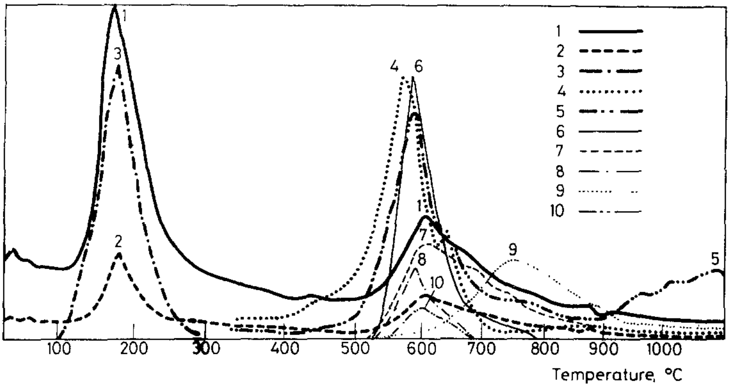
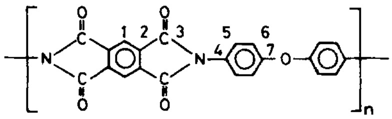
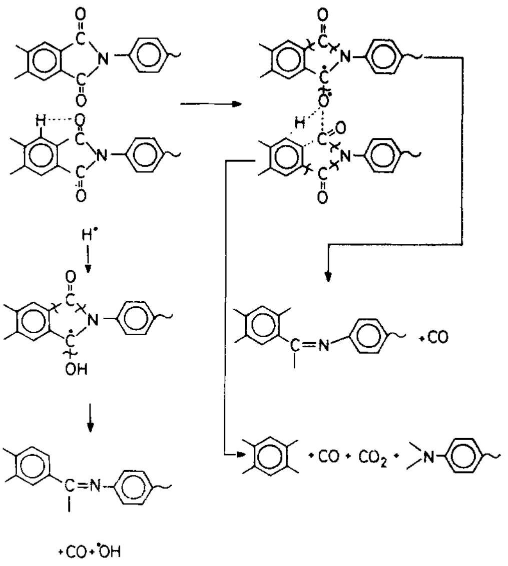


Fig. 1 Output curves: 1) m/e 18 (H_2O), 2) m/e 17 (OH, NH_3), 3) m/e 73 (DMF); 4) m/e 44 (CO_2), 5) m/e 28 (N_2, CO, C_2H_2), 6) m/e 94 (phenol), 7) m/e 27 (HCN), 8) m/e 103 (benzonitrile), 9) m/e 2 (H_2), 10) m/e 78 (benzene)

NMR in the solid state. Figure 3 shows the high-resolution ^{13}C NMR spectrum of a commercial PAA PM film taken after dynamic heating of the film under vacuum at a rate of 5 deg/min. It can be seen that an appreciable broadening of the absorption bands occurs in the same temperature range as that in which the main gaseous degradation products begin to be evolved in the MTA. The changes in intensity of the 165 and 136 ppm lines of the spectrum relate to the same temperature range. According to Ref. [12], this fact corresponds to a decrease in the contents of C_3 and C_2 atoms in the polyimide:





The intensities of the signals of the C_2 and C_3 nuclei are approximately equal and decrease regularly with increasing temperature (Fig. 4). However, the signal with centre at 156 ppm in the spectrum, and corresponding to carbon 7, decreases relatively slowly and does not disappear completely until the main signal is markedly broadened. In this case the residue of the 156 ppm signal is absorbed by the left wing of the main signal. Hence, the formation of water molecules is possible mainly as a result of the participation of hydrogen atoms in the reaction of oxygen contained in the dianhydride component because, as has just been shown, this oxygen remains for a long time in the solid residue.

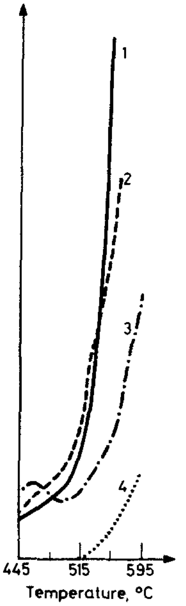


Fig. 2 Output curves: 1) m/e 28 (CO), 2) m/e 44 (CO_2), 3) m/e 18 (H_2O), 4) m/e 94 (phenol)

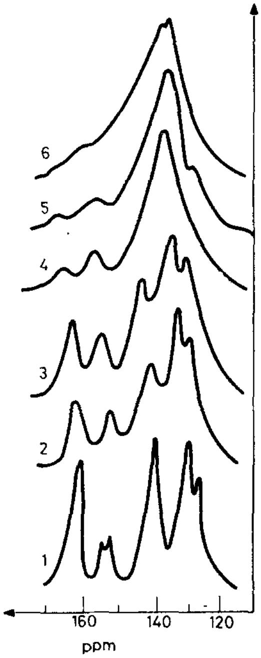


Fig. 3 HR NMR spectra in SS in heated PM films at the following temperatures in °C: 1) 30, 2) 500, 3) 540, 4) 560, 5) 580, 6) 600

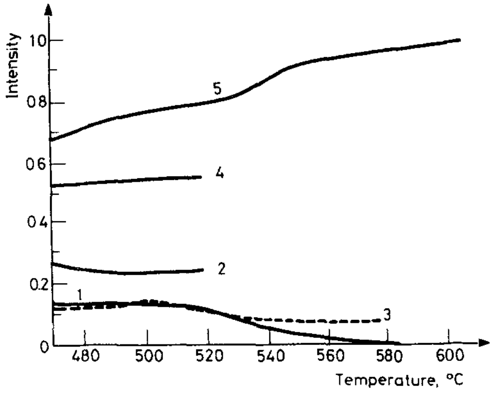


Fig. 4 Change in the intensity of PM lines in the NMR ^{13}C spectra: 1) C_3, 2) C_2, 3) C_7, 4) $C_1+C_4+C_5+C_6$, 5) C_{arom}

It is clear from Fig. 1 that the formation of large amounts of CO, CO_2 and H_2O is not accompanied by the appearance of free hydrogen. It might be suggested that at first the reaction between the carbonyl group and hydrogen takes place until the C—H bonds are completely broken as a result of thermal motion. To put it another way, it is the bimolecular reaction that occurs, rather than the monomolecular degradation of the aromatic structure with subsequent reaction of hydrogen with the carbonyl group.

When the temperature is increased to 500°, atomic hydrogen appears in the MTA curves (Fig. 1); hence, above this temperature, chain processes with the participation of atomic hydrogen become possible.

As a result of the interaction between the hydrogen contained in the aromatic fragments and the carbonyl group of the imide ring, hydroxyl radicals and, subsequently, water molecules are formed. Their formation, in turn, leads to the hydrolysis of imide rings and the formation of carbon dioxide.

Another result of this interaction may be the intermolecular transfer of oxygen, again with the formation of CO_2 molecules (see reaction scheme).

Coming back to the problem of the relative stability of the diamine and the dianhydride moieties of the elementary unit of PM polyimide, it should be pointed out that nitrogen-containing degradation products are formed at higher temperatures than the main degradation products: CO, CO_2, H_2O and phenol. Thus, the maximum of benzonitrile evolution is at 615°, while that of hydrogen cyanide evolution is 635°; the evolution of the latter continues up to 900°. The first intensity maximum of an ion with mass 14 is in the range of evolution of the main degradation products, whereas the second maximum is observed at 1100°. Similar effects have previously been reported for polyimide fibres [13]. Hence, these data show that the diamine moieties are more stable and that nitrogen plays a specific role in the stabilization of a number of intermediate structures in the carbonization of the polyimide structure. In the temperature range 520–650°, this effect is probably due to the formation of nitrile groups instead of the imide rings undergoing degradation, and to the process of cyclization and formation of heterocyclic nitrogen-containing condensed systems, the final rearrangement of the structure of which occurs with nitrogen evolution at 1000–1200°. This suggestion is confirmed by the appearance of a slight shoulder in the range of 110 ppm on the envelope of the broad NMR signal at temperatures above 580° (Fig. 3). This shoulder may be assigned to heteroaromatic rings, because polycyclic aromatic compounds containing no heteroatoms do not exhibit absorption signals in this range.

All the processes of degradation of the primary and intermediate structures occur on the background of the crosslinking and condensation of aromatic structures accompanied by hydrogen evolution. The maximum of this evolution is at 745°

(Fig. 1), after its start at 560°, and evolution in appreciable amounts continues up to 1200°. A considerable broadening of the adsorption lines in the NMR spectra with increasing temperature of heating of the film (Fig. 3) indicates the occurrence of intense intermolecular crosslinking in the temperature range 520–600°. This change in the signals has usually been interpreted in terms of an overall decrease in the molecular mobility of the polymer under investigation. With increasing temperature, the spectrum undergoes further changes. Above 600°, it loses its discrete character and becomes relatively broad, with a centre in the range of absorption of aromatic and polyaromatic compounds.

Analysis of the data of the methods used in this work (MTA and high-resolution NMR in the solid state) definitely suggests that upon the high-temperature heating of polypyromellitimide the imide ring is the weakest link, rather than the diamine moiety. The subsequent process of intermolecular crosslinking is completed by the formation of a complex nitrogen-containing heterocyclic structure, as has already been suggested [9].

However, additional methods should be employed in order to obtain a complete picture of the thermochemical process of polyimide carbonization.

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Zusammenfassung — Der Mechanismus der in Polypyromellitfilmen ablaufenden thermischen Zersetzungsprozesse wurde durch massenspektrometrische thermische Analyse und hochauflösende Festkörper-NMR-Spektroskopie untersucht. Sowohl die Struktur des festen Rückstandes des Pyrolyseproduktes des PM-polyamids als auch der Prozeß der Verkokung bis 1200 °C wurden Untersucht. Es wurde festgestellt, daß das Aufbrechen der Bindung C_{ar}—O—C_{ar} im Diaminteil nicht der primäre Schritt der Zersetzung der molekularen Struktur des Polymers ist, wie nach dem Wert der Bindungsenergie zu erwarten wäre. Der auf die Hochtemperatur-Polymerzersetzung folgende Prozeß der intermolekularen Vernetzung endet mit der Bildung einer komplexen stickstoffhaltigen heterozyklischen Struktur.

Резюме — В статье проводится анализ данных методов масс-спектрометрического термического анализа (МТА) и спектроскопии ядерного магнитного резонанса высокого разрешения в твердом теле (ЯМР ВРТТ) так о структуре твердых остатков продуктов пиролиза полиимида ПМ, так и самом процессе карбонизации вплоть до температуры 1200 °C. В работе рассматриваются некоторые представления о механизме деструктивных процессов в полиимиде. Показано, что разрыв связи $C_{\text{ар}}$—$C_{\text{ар}}$ в диаминной компоненте не является первичным актом разрушения структуры хотя энергетически эта связь не прочнее, чем связи имидного цикла, а в целом при глубоком прогреве полипиромеллитимида последующий за деструкцией полимера процесс межмолекулярных сшивок завершается образованием сложной азотосодержащей гетероциклической структуры.