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KINETICS OF THE THERMAL DEGRADATION OF POLYIMIDES

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A number of temperature and kinetic parameters of thermal degradation of polyimides over the temperature range from 20 to 1000° have been determined on the basis of thermogravimetric investigations of a polyimide sample obtained from pyromellitic dianhydride and diaminodiphenyl ether. It was shown that such kinetic parameters as the reaction order and the activation energy of thermal degradation are directly dependent on the conditions under which the thermal analysis is carried out. It was found that when the static and dynamic conditions of the environment of a polymer sample are varied, the thermochemical processes occurring in a polyimide over the temperature range investigated are drastically changed.

A critical analysis of the possibility of comparing the kinetic data on thermal degradation with the criteria generally used for the evaluation of the thermal stability of polyimides was carried out. The dynamic kinetic characteristics of the degradation of polyimide were correlated to prolonged thermal stability.

At present the intensive development of various methods of thermal analysis has resulted in the wide use of these procedures for the investigation of numerous chemical and physical processes. The adoption of these methods in polymer physics and chemistry allowed the solution of various problems; in particular, it allowed a closer approach to the determination of some thermochemical and thermophysical characteristics [1–6]. It should be noted that although there is no doubt that thermal analysis is very useful in the study of the structure and properties of polymers, the possibilities of using it are sometimes overestimated. This is particularly noticeable in the study of the kinetics of thermal degradation of polymers. Some workers have attempted to describe the mechanism of thermal degradation of polymers by using classical parameters, such as the energy of activation, the reaction order and the pre-exponential factor calculated from the TG and DTA results. These attempts are justified for the simplest cases of the effect of high temperatures on polymers, and therefore their results have a certain physical sense for such polymers as polymethyl methacrylate and some polystyrene samples the thermal degradation of which proceeds in a single stage and follows the depolymerization mechanism. For other polymers, in particular polycondensation polymers, the mechanism of thermal degradation is so complex and depends on so many factors that kinetic calculations have no physical sense.

Numerous workers, including the present author [7–10], have shown that the experimental conditions under which thermal analysis is carried out actually determine the type of thermal degradation of polymers. In this connection it should be noted that the conditions of thermal investigations profoundly affect the kinetic parameters of the degradation of such simple inorganic compounds as calcium carbonate, ferric hydroxide, etc. These observations and conclusions have been clearly stated in a very interesting paper by Hungarian scientists [11]. Hence, the problem of the advantages of the calculation of kinetic parameters and their use for the chemical or physical characterization of thermal degradation and, particularly, the thermal stability of such complex compounds as polymers, seems to be meaningless at this stage of development of thermal analysis. Naturally, it is possible to use the values of activation energy or reaction order for the comparison of the processes of thermal degradation occurring under identical and precisely reproducible conditions. However, these values are only formal criteria and their calculation leads to additional difficulties in the mathematical treatment of the curves of thermal analysis. From the standpoint of evaluation of the comparative stabilities of polymers it is more advantageous to carry out a mathematical treatment of the curves that would yield the values characterizing definite points relating to the time and temperature of thermal degradation. These points, obtained during the primary treatment of curves of thermal analysis, are widely used by many workers.

In particular, for TG the following points are used: the temperatures of 0, 5, 10, 50 and 100% weight loss, the weight losses are determined over a particular temperature range at a constant heating rate or for a particular time interval at a constant temperature, etc. Most of these parameters have a real physical sense and are of practical value for the estimation of operating characteristics of polymers. Doubtless, the values characterizing these points depend on the conditions of thermal analysis, but since these conditions can be approximately compared to the actual operating conditions for polymers, it is possible to establish valuable characteristics of the thermal stability of polymers by varying the conditions of analysis.

Since the behaviour of polyimides with high thermal stability is of great interest; a series of experiments was carried out to determine the thermal stability of a commercial polyimide film of the PM type 40μm thick. This film (in portions of 50 and 100 mg) was subjected to thermal and thermo-oxidative degradation on a MOM derivatograph.

The following sample holders were used: plate holders consisting of six (10) and one (9) plate, platinum crucibles 9 mm in diam. and 12 mm in depth without a lid (1), with a lid (4) and with a lid and a layer of Al_2O_3 (7), crucibles 9 mm in diam. and 5 mm in depth without a lid (3) and with a lid (6), and ceramic crucibles 12 mm in diam. and 18 mm in depth without a lid (2) and with a lid (5). The numbers in parentheses are the symbols denoting the holders. When closed crucibles were used, samples were heated without an air flow and for open crucibles the air flow rate was 50 cm^3/min. Experiments with plate holders were carried out both in an air flow and without it. The heating rates were 2.5, 5, 10 and 20°/min.

The following temperature parameters of polyimide degradation were determined. The values of T_0, T_5, T_{10}, T_{50} and T_{100} were estimated from the TG curves. These data were used to calculate T_{av1} and T_{av2}, equal to the arithmetical average of the values of $T_5 + T_{10} + T_{50}$ and $T_5 + T_{10} + T_{50} + T_{100}$, respectively.

In addition, the dependence of the criterion for the thermal stability of polymers according to Doyle [12] on the above experimental conditions was investigated.

Discussion of results

The comparison of the TG curves obtained in all these experiments shows a distinct dependence of the temperature parameters on the composition of the atmosphere surrounding the sample during degradation. This dependence is related to oxidative processes accelerating polymer degradation, and to the rate of the removal of gaseous products of thermal degradation. Figure 1a shows a family of curves each of which represents the dependence of the corresponding temperature characteristics on the shape of the sample holders and hence on the composition of the surrounding atmosphere.

The symbols of the holders are arranged in the order corresponding to the increase in the T_0 value of the sample; this order actually reflects the interdependence of the oxidation and hydrolysis of the polyimide in the early stages of thermal and thermo-oxidative degradation. In these stages the weight loss of the polyimide is the resultant of several competing reactions. The main ones are the evolution of

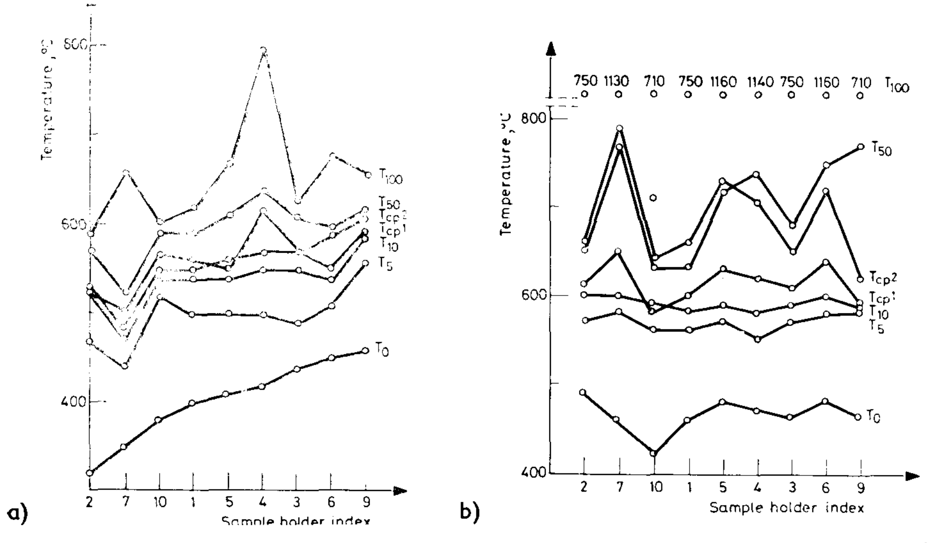

Fig. 1. Temperature characteristics of thermal degradation of PM polyimide *vs.* shape of sample holder: see text for the designation of numbers on the abscissa; sample 50 mg; heating rate a) 2.5°/min and b) 10°/min

water and CO_2 as a result of the degradation of single bonds, complete cyclization and structurization. The effect of oxygen in these reactions is also determined by the ratio of kinetic and diffusion processes, and hence the shift of the equilibrium degradation $\rightleftarrows$ structurization occurs fairly easily under the conditions of the unsteady state near the temperature T_0.

Thus, according to the data of curve T_0 in Fig. 1a, the lowest values of T_0 were observed on heating in a deep open ceramic crucible and in a crucible in which the sample was closed with an aluminium oxide layer and a lid. Under these conditions the most probable result is the evolution of CO_2 due to hydrolytic reactions favoured by low heating rate and a limited rate of water diffusion from the sample. It is noteworthy that not only the adsorbed water, but also the water evolved as a result of complete imidization (most complete at a low heating rate) participates in the reaction.

The further increase in T_0 on passing to holders of a different shape can be interpreted by the superposition of the processes of degradation and structurization. Thus, for samples placed on plate holders the part played by hydrolysis is insignificant, but the overall effect is attained when the reactions of oxidation and structurization occur simultaneously.

It is well known that the value of T_0 is very sensitive to changes in many methodological factors and it is not surprising, therefore, that there is no direct proportionality between it and the values of T_5 and T_{10}, that for polyimides reflect the early stages of degradation of the main polymer chain. It can be seen from Fig. 1a that the curves representing the dependence of the changes in the temperatures of 5 and 10% weight loss on the shape of the holders show a considerable dependence only for very open and very closed holders. The curves expressing the changes in the values of T_{100} and T_{av}, also show the specific feature of the degradation of polyimides: the carbonization process is most pronounced in a closed volume and at high polymer conversion [12].

This feature is still more pronounced if the heating rate is increased: this leads to a sharp shift to the right in the thermochemical degradation $\rightleftarrows$ structurization equilibrium in particular, in closed holders. Figure 1b shows the dependences similar to those in Fig. 1a at a heating rate of 10°/min. It can be seen that the maximum values of T_{100} exceed 1100° only in closed holders. However, the increase in the heating rate seems to be smoothed down by the differences in the temperature characteristies in the early stages of polyimide degradation. The regular increase in the absolute values of T_0, T_5 and T_{10} on the one hand and the smoothing down of these values on the other hand also indicate that the mechanism of thermal degradation undergoes a change towards structurization under the influence of methodological factors.

When all temperature characteristics obtained on heating polyimides in different holders of the derivatograph at four different rates are analyzed, it is possible to plot a temperature vs. time diagram within which the values obtained are located. This diagram (Figs 2a and b) reflects an interesting peculiarity of the dependence of the temperature characteristics on the heating rate. At low heating rates

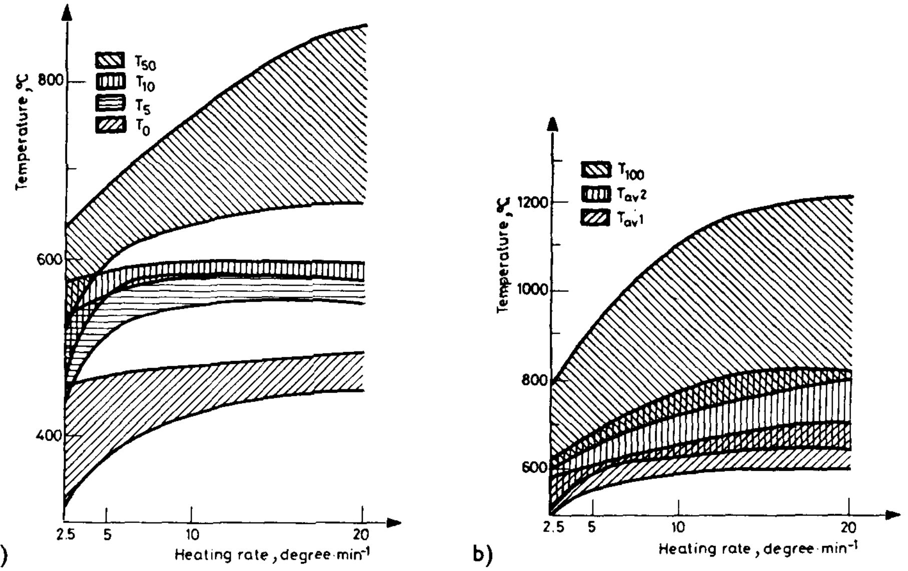

Fig. 2. Diagram of temperature characteristics of the thermal degradation of PM polyimide *vs.* heating rate; sample 50 mg. a) values of T_0, T_5, T_{10} and T_{50}; b) values of T_{av1}, T_{av2} and T_{100}

a wide spread in temperatures is observed; it reflects the predominant influence of the crucible shape on the initial stage of polymer degradation. This spread increases with increasing temperature in the later stages of degradation. Moreover, as can be seen in Fig. 2, the temperatures of polyimide weight loss after the half-life depend to almost the same extent on the heating rate and the holder shape and cover a wide range from 600 to 1200°. The diagram shown in Fig. 2 can serve to some extent as a comparative criterion for the thermal stabilities of polymers operating under conditions comparable to those of thermal analysis.

In connection with the criterion for comparative thermal stability, it was of interest to analyze the thermal stability according to Doyle [12].

With this end in view, the observed integral degradation temperature T^*_A and the thermostability index A^*K^* were calculated.

Table 1 gives the values of T^*_A, A^*K^* and T^*_A, taking into account the correction for some thermoanalytical experiments, and Fig. 3 shows the corresponding dependences.

These data provide further evidence in favour of the decisive effect of methodological factors on the formal criteria for the thermal stability of polymers. The absence of a correlation between the heating rate and the T_{values} for the same polymer also indicates that if the conditions of analysis change, the mechanism of thermal degradation of polyimides and in general that of other complex polymers undergoes great changes. This fundamental difference between the thermochemistry of polymers and the corresponding processes for inorganic substances

Table 1

Values of comparative thermal stability of polyimides at different heating rates in holders 4, 5 and 10

Holder number	Heating rate, °/min	T^*_A °C	A^*K^*	T, °C
4	2.5	719	0.6888	628
4	5	695	0.6823	622
4	10	685	0.67122	648
4	20	634	0.6631	605
5	2.5	796	—	—
5	5	724	0.7175	653
5	10	670	0.7258	660
5	20	647	0.6713	612
10	2.5	846	—	—
10	5	829	—	—
10	10	788	—	—
10	20	720	0.7003	638

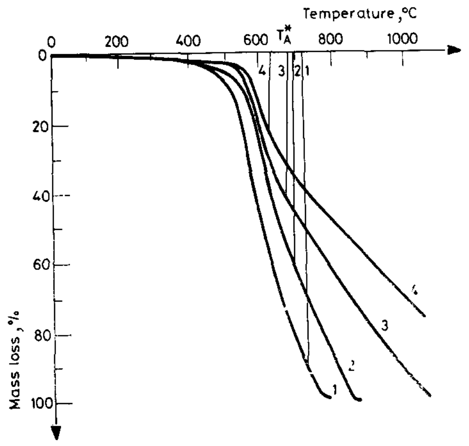

Fig. 3. TG curves for polyimide, holder 4; sample 50 mg; heating rates 1) 2.5, 2) 5, 3) 10 and 4) 20°/min

shows that much greater caution should be exercised in the use of some kinetic and formal criteria for the evaluation of the thermal stability of polymers and the processes of their degradation in general than for the characterization of thermal degradation of inorganic substances. One of the indispensable conditions for comparison of the behaviour of polymers upon heating is the absolute identity of all the conditions of thermal analysis. Another condition for deriving practical advantages from the data of the thermal analysis of polymers is the possibility of comparing the conditions of this analysis with the thermal service conditions for these polymers.

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Zusammenfassung — Eine Anzahl von Temperatur- und kinetischen Parametern des thermischen Abbaus von Polyimiden wurde im Temperaturbereich von 20 bis 1000° aufgrund von an aus Pyromellitdianhydrid und Diaminodiphenyläther erhaltenen Polyimidproben durchgeführten Untersuchungen bestimmt. Es wurde gezeigt, daß kinetische Parameter wie die Reaktionsordnung und die Aktivierungsenergie der thermischen Zersetzung unmittelbar von den Bedingungen abhängig sind, unter welchen die Thermoanalyse durchgeführt wurde. Es wurde gefunden, daß im Falle der Änderung der statischen und dynamischen Bedingungen der Umgebung einer Polymerprobe, die in einem Polyimid in dem untersuchten Temperaturbereich stattfindenden thermochemischen Vorgänge drastisch geändert werden.

Eine kritische Analyse der Möglichkeit des Vergleichs kinetischer Angaben bezüglich des thermischen Abbaus mit den zur Bewertung der Thermostabilität von Polyimiden allgemein gebräuchlichen Kriterien wurde durchgeführt. Die dynamischen kinetischen Charakteristika des Abbaus von Polyimiden wurden mit der verlängerten Thermostabilität korreliert.

Резюме — На основании термогравиметрических исследований образцов полиимида, полученного на основе пиромеллитового диангидрида и диаминодифенилового эфира, определены ряд температурных и кинетических параметров термодеструкции в интервале температур 20—1000°. Показано, что такие кинетические параметры, как порядок реакции и энергия активации процесса термодеструкции находятся в прямой зависимости от методических условий проведения термического анализа. Установлено, что при изменении статических и динамических условий окружающей полимера среды существено изменяются термохимические процессы, протекающие в полиимиде в исследованном интервале температур.

Проведен критический анализ сопоставимости кинетических данных по термодеструкции с критериями термостабильности, используемыми для оценки термостабильности полиимидов. Проведена корреляция между динамическими кинетическими характеристиками деструкции полиимида и длительной термостабильностью этого полимера.