Journal of Thermal Analysis, Vol. 7 (1975) 165–171

THERMOGRAVIMETRIC STUDY OF THE EFFECT OF THE CHEMICAL STRUCTURE OF POLYIMIDES ON THEIR THERMAL STABILITY

M. M. Koton and Yu. N. Sazanov

Institute of Macromolecular Compounds at the Academy of Sciences of the USSR, Leningrad, USSR

(Received May 4, 1973)

Thermogravimetry of polyimides based on dianhydrides of pyromellitic, diphenyl- and diphenyloxidetetracarboxylic acids and a series of diamines has been used to determine their temperature characteristics and calculate their activation energies. The dependence of the thermal stability of the polyimides on the structure of their diamine component was established. It was shown that the effect of the thermal stability of the polyimides progressively weakens with the increase in the rigidity of their chemical structure.

Investigations of the thermal stability of polymers by thermogravimetric analysis are very widely used for rapid determination of their relative chemical resistance to high temperature. A method for establishing weight losses with progressively and linearly increasing temperature used in TG permits a relatively rapid determination of the effect of the chemical structure on thermal stability for polymers of the same class synthesized under similar conditions. In this respect a widely-used method of isothermal analysis yielding more information on the polymer behaviour in the course of prolonged heating at a fixed temperature has an important disadvantage: when a polymer sample is maintained for a long time at a high temperature, cross-linking occurs. Thermogravimetry enables us to avoid this disadvantage to a considerable extent and to determine the contributions of different chemical structures to the thermal stability of the polymer on the basis of several comparative criteria obtained under identical conditions of analysis. One of these criteria used in recent literature [1] is the temperature characterizing a definite point on the TG curve, such as the temperature of the onset of weight loss (T_0), determined in most cases as the point in which the TG curve deviates from the initial horizontal portion. These criteria also include temperatures of 5, 10, 50 and 100% weight loss, and the values of the weight loss at fixed temperatures (200, 300, 400°, etc.).

Much work is in progress on the synthesis and investigation of high-temperature-resistant polymers of the polyimide class, which, owing to their thermal stability and many valuable physico-mechanical properties, occupy a very important place in the manufacture of polymer materials. A comparison of the thermal stabilities of different aromatic polyimides and establishment of their temperature characteristics make it possible to determine the effect of the chemical structure of the polyimides on their properties and to improve the methods for their synthesis. In recent years many polyimides have been synthesized with different aromatic groups and heteroatoms in the diamine and dianhydride components [1–3]. Polyimides based on pyromellitic acid are very widely used. Polyimides based on other aromatic tetracarboxylic acids have also been prepared [3–8]. Nevertheless, investigation of the thermal characteristics of these polyimides and determination of the optimum conditions of their thermal treatment and behaviour at elevated temperatures are not progressing as rapidly as the work on synthesis.

Using in this work some of the above criteria for evaluating thermal stability from TG data, and in particular using the value of T_0, we have made an attempt to characterize the thermal stabilities of a series of polyimides synthesized in our laboratory in accordance with the chemical structures of the diamine and dianhydride components, and to follow the effects of different substituents on the thermal stability of the polymers.

Experimental

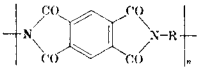
The synthesis and preparation of the polymer films cast from polyimides analyzed in this work have been carried out by the usual procedure – a two-stage process described previously [9–13]. Thermogravimetric analysis has been carried out with a "MOM" Derivatograph (Hungary) in an air flow (200 ml/hr) at a heating rate of 4.5°C/min over the temperature range from 20 to 900°.

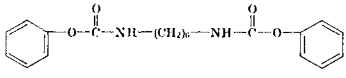
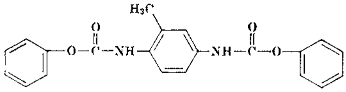
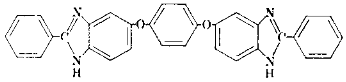
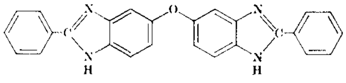
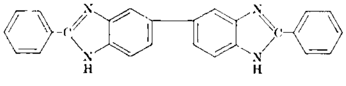
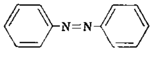
Results and discussion

Temperature characteristics of the thermal degradation of a series of polypyromellitimides with different structures of the diamine component are shown in Table 1. A comparison of the T_0 values of the polyimides investigated shows that the polymers with aliphatic units in the diamine component exhibit the lowest thermal stability. The replacement of a hexamethylene chain by a tolyl group increases the thermal stability of the polymer slightly, but the presence of two labile NH–COO-groups in the diamine structure prevents the increase of T_0 by more than 15–20° as compared to sample 1. On passing from a flexible nitrogen-containing urea group to a more rigid benzimidazole bond (samples III–V), the rigidity of the whole polymer molecule increases and, correspondingly, the thermal stability of the polyimides increases to 310°. It is interesting to note that samples III–V serve as examples showing the relationship between the increase in the thermal stability of the polymers and the distance between two benzimidazole rings. This factor, defined in the literature as the degree of ring fusion [6], is evidently essential for characterizing the thermal stability from the standpoint of chemical structure. As the structure of the polyimides is saturated with aromatic and heterocyclic units, the thermal stability progressively increases. However,

Table 1

Temperature characteristics of polypyromellitimides with the general formula



	–R–	T_0	T_{10}	T_{max}	T_{100}	E_a, $\frac{kcal}{mole}$
		°C				
I		205	270	540	610	25 ± 7
II		220	260	540	600	25 ± 7
III		250	400	570	660	31 ± 5
IV		280	415	590	640	35 ± 5
V		310	420	570	640	33 ± 3
VI		340	480	580	690	40 ± 2

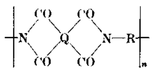
after passing the thermal stability limit determined by the T_0 value of 350°, the change in the chemical structure of the polyimides affects their thermal stability less and less. Thus, the results given in Table 2 for polypyromellitimides containing diphenyl, terphenyl, diphenyloxide, benziphenone and phenoxthine groups in the diamine component show that they exhibit a high thermal stability in the range from 370 to 420°. Polyimides based on the same diamines and anhydrides of diphenyl- or diphenyloxidetetracarboxylic acids differ as little in their thermal stability as do polymers of pyromellitic acid. In the polyimide series investigated the polyimides with a phenoxthine group in the diamine component exhibit the highest thermal stability. This effect is quite natural since in this case the phenyl rings are attached by two bonds ensuring the high thermal stability of the diamine component. The above-mentioned decreasing effect of the chemical structure on the thermal stability of the polyimides is presumably due to a considerable increase in the ridigity of the macromolecule. This increase leads to a marked decrease in the mobility of the macromolecules, to the formation of infusible products and to considerable difficulties in the final stage of imidization.

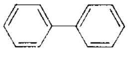
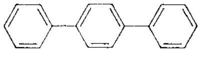
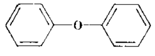
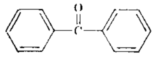
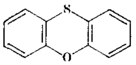
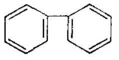
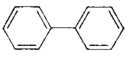
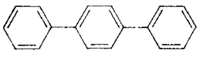
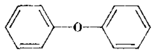
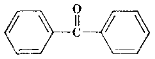
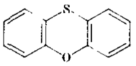
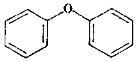
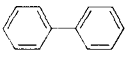
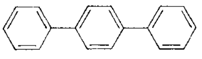
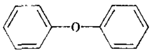
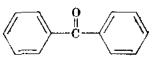
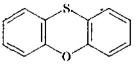
Thus, for rigid-chain polyimides stable up to 350° thermal degradation starts at those weak points or bonds which are essentially independent of the chemical structure of the diamine or dianhydride components of the polyimide.

Another parameter characterizing the thermal degradation of the polymers is the temperature of a 10% weight loss according to TG data. As a rule, this value refers to that stage of pyrolysis in which the initiation of thermal degradation has

Table 2

Temperature characteristics of polyimides with the general formula

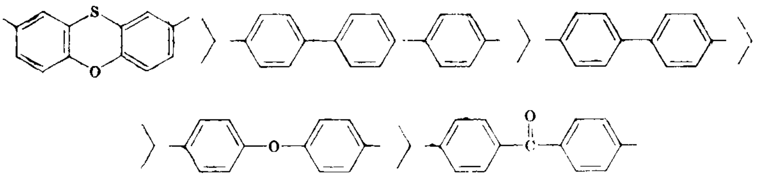


	R	T_0	T_{10}	T_{max}	T_{100}	E_a, $\frac{kcal}{mole}$
		°C				
		400	530	590	650	42 ± 2
		370	540	620	670	48 ± 2
		370	520	580	640	43 ± 4
		330	500	600	640	39 ± 4
		420	560	610	670	56 ± 2
		360	510	570	660	41 ± 2
		400	600	640	800	45 ± 2
		390	520	600	700	40 ± 4
		360	490	570	660	35 ± 4
		400	540	600	710	51 ± 2
		400	560	610	720	44 ± 2
		360	590	670	780	50 ± 2
		350	490	540	610	40 ± 4
		380	480	560	630	36 ± 4
		400	520	560	630	50 ± 2

already been completed but the process has not yet attained the maximum rate. Nevertheless, this value permits certain qualitative comparisons to be made when the mechanism of thermal degradation does not change with time. Thus, an analysis of the T_{10} values shows a correlation between the chemical structure of the diamine component and the thermal stability determined from the values of T_0 for samples I – VI (Table 1). In many cases the values of T_{10} for rigid-chain polyimides (Table 2) are close to each other. However, a regular increase in the T_{10} value is observed in passing from heterocyclic to carboxylic units with the exception of the polyimides with phenoxthine groups.

The absence of heteroatoms from the diamine and dianhydride components evidently accelerates the carbonization of the polyimides in the course of their thermal degradation. The carbonized residues of polyimides based on diphenyl and terphenyldiamines are characterized by a high value of T_{max}, and particularly of T_{100} (the temperature of complete weight loss). Thus, the value of T_{100} for terphenyl-containing polyimides exceeds by 100 – 150° the corresponding values for other polyimides.

Considering the values of the activation energy (E_a) of thermal degradation of polyimides calculated for the entire range of weight loss from the TG curves [14], it should be noted that these data are averaged values reflecting the overall effect of thermal degradation. Consequently, it is natural that in the cases in which thermal degradation is a complex process with thermal effects overlapping each other (samples I – III to a greater extent, samples IV – VI to a lesser extent), the scattering of the calculated values of E_a is high. When thermal degradation proceeds at a high rate up to 85 – 90% (which is evidenced by close values of T_{max} for rigid-chain polyimide – Table 2) and is essentially characterized by one high exothermic effect according to the DTA data, the values of E_a are determined with a much greater precision. When the E_a values for the different polyimides investigated, as well as their temperature characteristics, are compared, a regular increase in the values of E_a with thermal stability is observed for samples I – VI (Table 1). As for the rigid-chain polyimides in Table 2, the activation energy in the thermal degradation of these polymers is much higher than for samples I – VI. When the structure of the diamine component is changed, the identical change in the E_a values is observed for each of the three dianhydrides in the following order:



When the structure of the dianhydride component in the polyimide is changed, but the diamine remains the same, the values of the activation energy for the polyimides based on diphenyl and diphenyloxide dianhydrides are equal; they are slightly higher for polypyromellitimides.

Thus, the observed temperature characteristics and the values of the activation energy of the polyimides investigated yielded important initial information concerning the effect of chemical structure on the thermal stability of polyimides and permitted determination of the temperature ranges of their thermal degradation.

Conclusions

1. Temperature characteristics and values of the activation energy in thermal degradation have been determined for polyimides based on dianhydrides of pyromellitic, diphenyl- and diphenyloxidetetracarboxylic acids and a series of aromatic diamines.
2. The dependence of the thermal stability of the polyimides investigated on the chemical structure of the diamine component has been shown.
3. It has been established that an increase in the degree of ring fusion in the polyimides leads to a progressive weakening of the effect of chemical structure on the thermal stability of the polyimides.

References

1. V. V. KORSHAK, "Khimicheskoe stroenie i temperaturnye kharakteristiki polimerov", Moscow, "Nauka", 1970.
2. V. V. KORSHAK, "Termostoikie polimery", Moscow, "Nauka", 1969.
3. N. A. ADROVA, M. I. BESSONOV, L. A. LAIUS and A. P. RUDAKOV, "Poliimidy — novyi klass termostoikikh polimerov", Leningrad, "Nauka", 1968.
4. G. I. KUDRIAVTSEV, L. F. BAKALEISHCHIKOVA, A. M. SCHNETININ and L. V. CHIKURIN, Vysokomolekul. Soedin., A12 (1970) 2205.
5. E. P. KRASNOV, V. P. AKSENOVA, S. N. KHARKOV and S. N. BARANOVA, Vysokomolekul. Soedin., A12 (1970) 873.
6. P. N. GRIBKOVA, V. V. RODE, YA. S. VYGODSKII, S. V. VINOGRADOVA and V. V. KORSHAK, Vysokomolekul. Soedin., A12 (1970) 220.
7. A. N. PRAVEDNIKOV, I. E. KARDASH, E. N. TELESHOV and B. V. KOTOV, Vysokomolekul. Soedin., A13 (425) (1971).
8. D. P. BISHOP and A. D. SMITH, J. Appl. Polymer. Sci., 14 (1970) 345.
9. A. P. RUDAKOV, N. A. ADROVA, M. I. BESSONOV and M. M. KOTON, Dokl. Akad. Nauk SSSR, 172 (1961) 89.
10. USSR, 192 400, Bull. Izobr. 5 (1967).
11. N. A. ADROVA, M. M. KOTON and A. M. DUBNOVA, Vysokomolekul Soedin., 10 B (1968) 354.
12. A. P. RUDAKOV, F. S. FLORINSKY, M. I. BESSONOV, K. N. VLASOVA, M. M. KOTON and P. M. TAKUNINA, Plastmassy 9 (1967) 26.
13. N. P. KUZNETSOV, M. I. BESSENOV, T. M. KISELEVA and M. M. KOTON, Vysokomolekul. Soedin, 14A (1972) 2034.
14. H. H. HOROWITZ and G. METZGER, Anal. Chem., 35 (1963) 1464.

RÉSUMÉ — On utilise les données TG des polyimides à base des dianhydrides des acides pyroméllitique, diphényl et diphényloxydetétracarboxylique ainsi que d'une série de diamines pour établir leurs caractéristiques thermiques et leurs énergies d'activation. On établit la corrélation entre la stabilité thermique des polyimides et la structure de leur composant diamine. On montre que la stabilité thermique des polyimides diminue progressivement avec l'augmentation de la rigidité de leur structure chimique.

ZUSAMMENFASSUNG — Die dynamische TG von Polyimiden wurde an Dianhydrides von Pyromellit-, Diphenyl- und Diphenyloxydtetracarbonsäure, sowie einer Reihe von Diaminen zur Bestimmung ihrer Temperaturcharakteristika und zur Berechnung ihrer Aktivierungsenergien herangezogen. Die Abhängigkeit der Thermcstabilität der Polyimide von der Struktur ihrer Diaminkomponenten wurde bestimmt. Es wurde gezeigt, daß der Thermostabilitätseffekt der Polyimide mit zunehmender Rigidität der chemischen Struktur progressiv geschwächt wird.

Резюме — Методом динамического ТГ определены температурные характеристики и расчитаны энергии активации процесса термодеструкции полимидов, синтезированных на основе диангидров пиромеллитовой, дифенил- и дифенилоксидтетракарбоновой кислот и ряда диаминив. Установлена зависимость между химическим строением диаминной компоненты и термостабильностью полимида. Показано, что по мере увеличения степени конденсированности циклических звеньев в макромоекуле происходит постепенное ослабление влияния химического строения полиамида на его термостабильность.