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THERMOCHEMISTRY OF POLYMERS

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ABSTRACT

Some examples of problems solved by derivatography in polymer chemistry are reviewed, such as the effects of the sample holder, thermal characteristics of degradation and evaporation.

INTRODUCTION

In the last two decades, the derivatograph, a Hungarian thermoanalytical instrument, has been widely used in the U.S.S.R. and enjoys great popularity in the study of the thermophysical and thermochemical processes that occur in various substances. Investigations of polymers have acquired a particularly wide scope, and the following three factors favoured this development: first, a considerable increase in the range and amount of polymer materials manufactured industrially and developed in various research institutes and laboratories; second, a rapid development and improvement of methods of thermal analysis, which has virtually become a large independent branch of analytical chemistry; and third, a continuous improvement of the derivatograph on the basis of the latest technical achievements, permitting the application of this instrument to the solution of many various problems in the chemistry and physics of polymers.

It is impossible to cover in a single paper all the problems in polymer chemistry that have been investigated by thermal analysis with the aid of a derivatograph. Hence, it seemed reasonable to direct attention to the solution of some interesting and important problems in the field of thermochemistry of polymers of very high thermal stability. We shall take as an example polyimides, which are at present the most thermally stable industrially manufactured high-molecular-weight compounds used in many fields of science and technology under very high temperature conditions.

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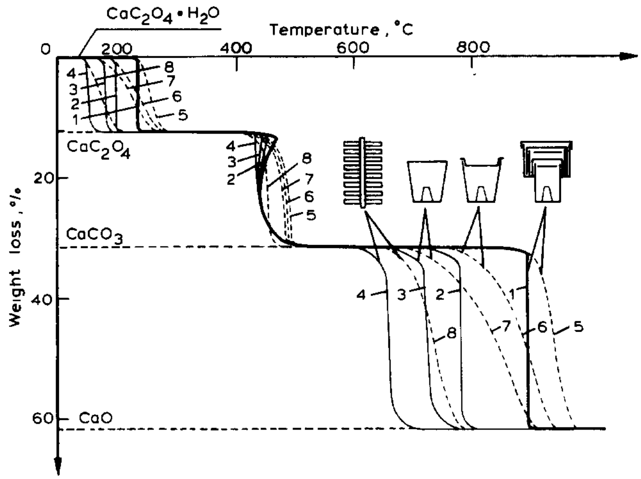


Fig. 1. Dependence of TG curves of calcium oxalate on the shape of derivatograph holders (I).

Before reviewing various problems of the thermochemistry of polyimides solved recently with the aid of the derivatograph, it is necessary to consider briefly the main features of the thermal analysis of high- and low-molecular-weight organic compounds. Our experience with these substances over many years shows that in many instances, in contrast to inorganic compounds, when organic substances and particularly polymers are heated, their physical and chemical characteristics depend on several factors, which may tentatively be divided into three groups: (1) the design of thermoanalytical instruments, particularly sample holders; (2) the composition and state of the gaseous atmosphere surrounding the sample during analysis; and (3) kinetic and diffusion factors determining the direction of thermochemical reactions of polymers.

In order to illustrate the major importance of these factors, some examples will be cited. Paulik and Paulik have convincingly shown the effect of the shape of sample holders using calcium oxalate (Fig. 1). It is clear that the temperatures characterizing dehydration, decarbonylation and decarboxylation reactions are profoundly affected by the shape of sample holders.

The first group of factors also includes some methodological features. For example, the heating rate of an organic polymer sample affects the temperature of thermal degradation, mainly as a result of changes in the nature of thermochemical reactions. Figure 2 shows the temperature characteristics (temperatures of the start and 5, 10, 50 and 100% mass loss) of the thermo-oxidative degradation of PM polyimide. The wide temperature ranges shown clearly characterize the strong dependence of the temperature on the heating rate and the conditions of high-temperature treatment. This example is also an illustration of the second group of factors, because the upper limit

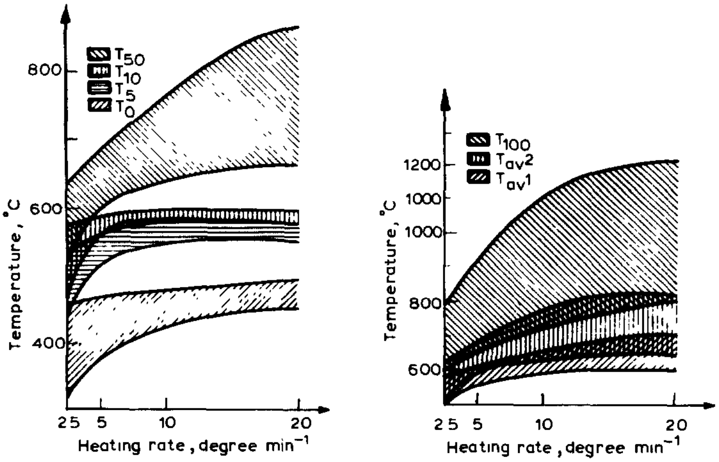


Fig. 2. Ranges of temperature characteristics (T_0, T_5, T_{10}, T_{50}, T_{100}, T_{av^1} and T_{av^2}) obtained with a derivatograph from the TG curves of thermo-oxidative degradation of PM polyimide at various heating rates in open and closed crucibles.

of each temperature range refers to experiments in which maximum isolation of the sample from the surrounding atmosphere of air was ensured, whereas the lower limit refers to the temperature characteristics obtained under

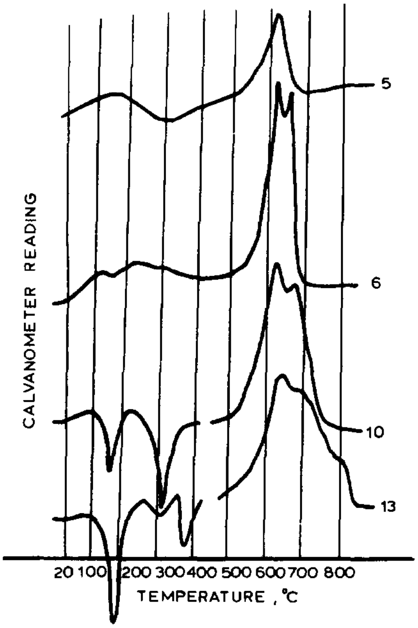


Fig. 3. DTA curves of samples of polyamic acids obtained under conditions indicated in the text.

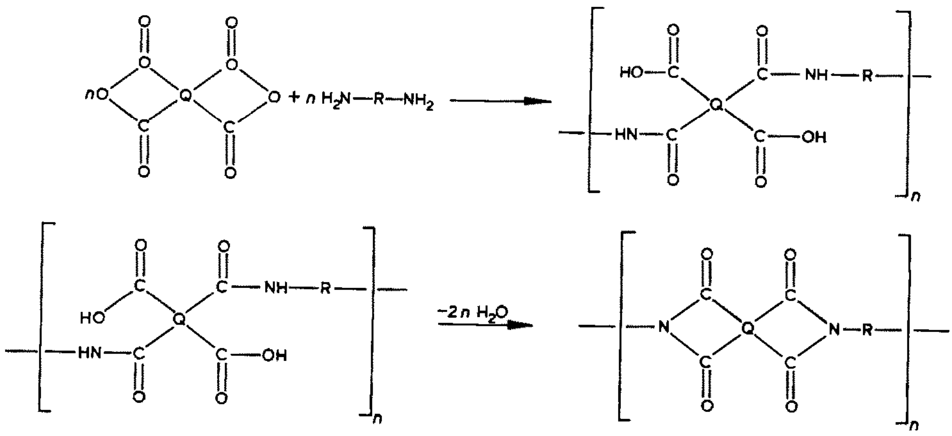


Fig. 4. Scheme of polyimide synthesis in which Q and R are any (mainly aromatic) radicals.

oxidizing conditions. Considering the third group, the DTA curves for a number of polyimide films of various thickness (Fig. 3) show that diffusion factors determine the rate of thermochemical reactions in the polymer bulk and lead to the formation of new structures, the existence of which is determined from these curves and from the physico-chemical characteristics of samples undergoing thermal treatment.

The above considerations are a necessary digression from the main subject of the paper, in which the versatility of the derivatograph in the study of various aspects of polyimide thermochemistry is demonstrated. This digression is a reminder that some caution is necessary in the interpretation of thermoanalytical data and that all the above factors should be taken into account in the characterization of the processes occurring in polymers on heating. Hence, passing to the description of the possibilities provided by the derivatograph in the study of polyimides, we should recall that polyimides belong to polymers with the highest thermal stability and articles manufactured from them are widely used in many branches of industry. Also, polyimides are synthesized from tetracarboxylic dianhydrides and diamines (Fig. 4). In the first stage, a solution of polyamic acid is obtained from which an article (film, fibre, coating, etc.) is to be prepared and subsequently converted into polyimide by thermal cyclodehydration. This is the classical route still carried out in industry. Nevertheless, new variants of synthesis and technology are being developed.

Our experience has shown that with the aid of methods of thermal analysis it is possible to observe and evaluate all the stages of the synthesis of polyimides, the technology of the preparation of articles based on them and the changes that occur in these materials over a wide temperature range. Some of these investigations do not concern directly the operation of the derivatograph and hence will be mentioned only briefly. Thus, the relation-

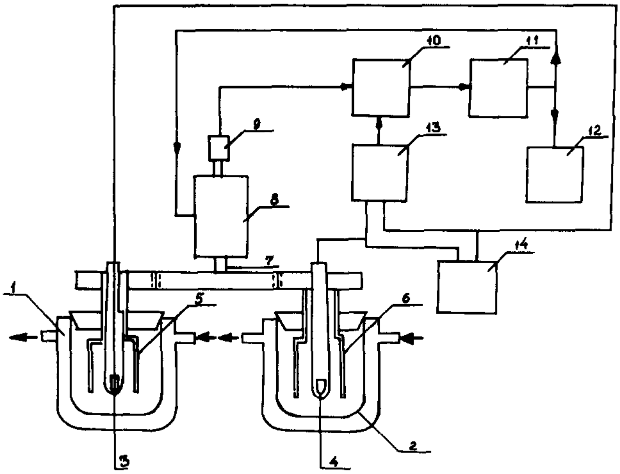


Fig. 5. Schematic diagram of a BTA-01 ballistic thermoanalyser. (1) Operating reactor, (2) reference reactor, (3,4) thermosensors, (7) axis and (8) motor of electric engine, (9) sensor of tachogenerator, (10) comparator unit, (11) regulating unit, (12) viscosity recording unit, (13,14) units of differential scheme of thermosensors.

ships of dissolution and interaction between the initial substances in the synthesis of polyamic acids were studied with a ballistic thermoanalyser designed on the basis of the DTA method in solution (Fig. 5).

With regard to the study of various reactions of polyimides involving transformations into a solid, the derivatograph has rendered invaluable service.

Kinetic curves of solvent evaporation and of the formation of a polyamic acid film at room temperature were obtained (Fig. 6) using plate holders to which a solution of polyamic acid was applied. These results indicate that

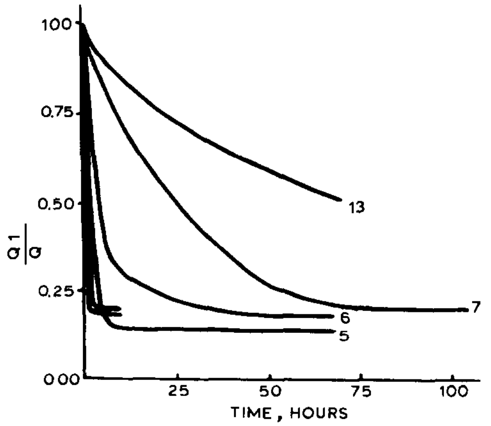


Fig. 6. Kinetic curves of evaporation of dimethylformamide in the preparation of polyamic acid films.

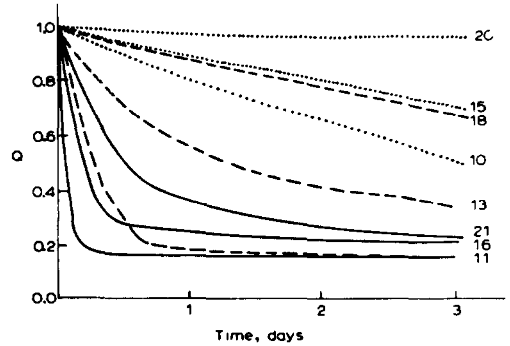


Fig. 7. Kinetic curves of evaporation of amide solvents in the preparation of polyamic acid films.

the amount of dimethylformamide (DMF) remaining in the film is profoundly affected by the film thickness and the drying temperature and time. Even under the most favourable conditions of DMF evaporation this amount remains equal to 7–8% (w/w) of the polyamic acid. A similar picture is observed when other amide solvents are used, such as dimethylacetamide, *N*-methylpyrrolidone and dimethylsulphoxide (Fig. 7). Moreover, in this instance the dependence of the amount of residual solvent in the film on its properties and, in particular, on the boiling temperature can be clearly seen. These data are closely related to the thermal characteristics of polyimides prepared from these films, which is confirmed by the TG curves of thermo-oxidative degradation. The differences in the conditions of drying of polyamic acid films lead to considerable variations in mass loss and to the displacement of the temperature characteristics of the thermal stability of polyimide films (Fig. 8).

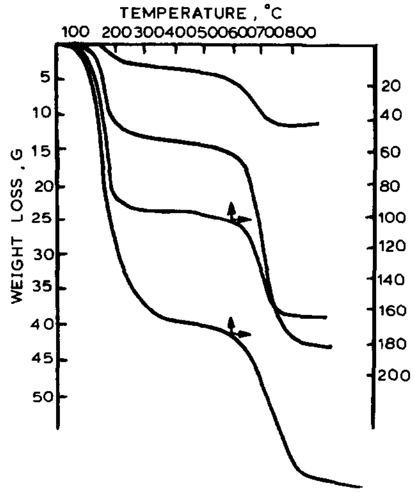


Fig. 8. Ta curves of thermo-oxidative degradation of PM polyimide films of various thickness. Feed, 50 mg; heating rate, 4.5 °C min^{-1}.

Figure 8 is an excellent illustration of the possibilities of application of the derivatograph. With its aid, using both TG and DTA data and comparing them, it is possible to observe and record all changes occurring in a polyimide beginning from its formation from polyamic acid and including its complete degradation and the evaporation of volatile products of thermo-oxidative degradation or the formation of coke residues in an inert atmosphere. In this connection a series of investigations were carried out for the elucidation of the effect of various factors on the formation, degradation and structuring of polyimides in film and fibre samples.

The main feature of and difficulty with polyimide synthesis for the preparation of articles of high thermal stability is the formation of a perfect structure, i.e., of a macromolecule that does not contain reactive groups. The presence of these groups drastically decreases the thermal stability of polyimide articles and leads to their degradation at temperatures much lower than the theoretical temperature. Hence, attempts have been made to develop methods for the preparation of polyimides with 100% imidization. For this purpose various conditions of thermal treatment of polyamic acids have been used in which the temperature and time of thermal treatment were varied. In these investigations the derivatograph has been widely used as a high-speed control instrument, making it possible to determine the optimum conditions of thermal treatment according to the temperature and mass characteristics. Thus, the data in Table 1 show the dependence of the temperature characteristics of powder, film and fibre of PM polyimide undergoing thermal treatment in an air flow at 400°C on the time of treatment. Apart from purely thermal cyclodehydration, various dehydrating

TABLE 1
Temperature characteristics of polyimide materials thermally treated in an air flow at 400°C

Sample	Treatment temperature (°C)	Time (min)	Weight loss (%)	T_0	T_5	T_{10}	T_{50}	T_{100}
Powder	400	5	1.5	440	540	555	585	630
		15	2.3	450	535	550	585	635
		30	3.0	460	540	555	580	630
		60	4.0	465	535	550	585	625
Film	400	5	1.8	420	520	550	585	630
		15	2.7	430	525	550	585	630
		30	3.2	445	525	550	585	630
		60	4.8	455	525	550	585	630
Fibre	400	5	2.0	420	490	520	560	600
		15	3.6	430	510	535	560	600
		30	5.2	440	510	535	560	600
		60	7.0	450	515	535	560	600

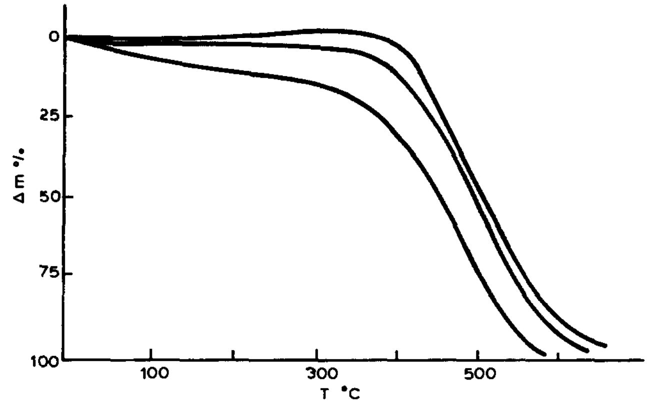


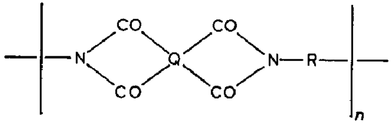
Fig. 9. TG curves of thermo-oxidative degradation of DFO fibre. 1, Thermal imidization; 2, chemical thermal imidization; 3, chemical imidization.

agents were used for the preparation of polyimides. According to the TGA data, the difference in the behaviour of polyimides obtained in different ways can also be clearly seen (Fig. 9). Hence, any changes in the preparation of polyimide products can easily be recorded with a derivatograph from the changes in temperature and mass characteristics.

As the requirements for thermal stability of polyimides and of the necessity to combine thermal stability with other valuable properties became more stringent, attention was drawn to a search for new structures, Q and R. Particular attention was devoted to the use of various aromatic and heterocyclic diamines and tetracarboxylic dianhydrides.

As a result of the wide range of synthetic experiments carried out in our Institute, it became possible to test a large number of polyimides synthesized from over 30 aromatic and heterocyclic tetracarboxylic dianhydrides and 70 diamines. This thermoanalytical study, carried out with a derivatograph under identical conditions, made it possible to determine a number of relationships between the chemical structure of the elementary unit of a polyimide and its thermal stability and other characteristics. As the details of the polyimides investigated would occupy several pages, the discussion is restricted to the main conclusions of the measurements. For polyimides containing oxyphenylene groups differing in isomeric composition and the number of oxyphenylene units, it was shown that the most thermally stable polyimides are formed from para isomers. An increase in the number of oxyphenylene groups leads to a gradual decrease in the thermal stability of the polymer. The thermal stability of polyimides based on diphenylmethane derivatives depends on the chemical nature of substituents at the quaternary carbon atom. The temperature characteristics of polyimides of this group can be arranged in ascending order from hydrogen to alkyl and further to aryl substituents. A large group consists of polyimides containing different

TABLE 2
Thermal characteristics of rigid-chain polyimides



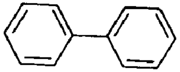
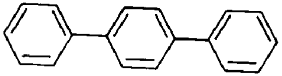
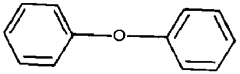
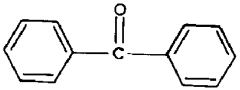
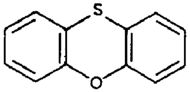
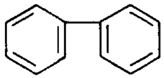
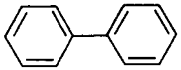
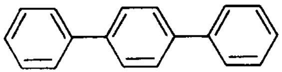
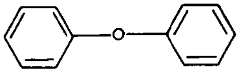
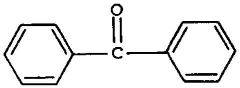
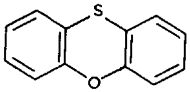
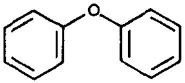
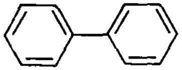
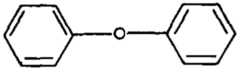
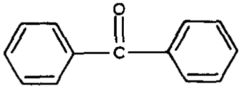
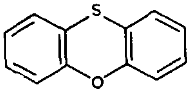
Q	R	T_0 (°C)	T_{10} (°C)	T_{50} (°C)	T_{100} (°C)	K_a (kcal mol^{-1})
		400	530	590	650	42±2
		370	540	620	670	48±2
		370	520	580	640	43±4
		330	500	600	640	39±4
		420	560	610	670	56±2

TABLE 2 (continued)

Q	R	T_0 (°C)	T_{10} (°C)	T_{50} (°C)	T_{100} (°C)	K_a (kcal mol^{-1})
		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	51 ± 2
		350	490	540	610	40 ± 4
		380	480	560	630	36 ± 4
		400	520	560	630	50 ± 2

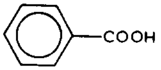
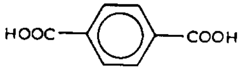
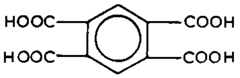
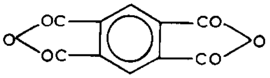
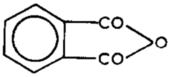
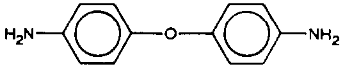
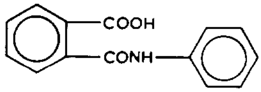
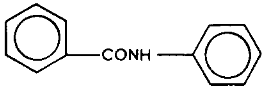
numbers of nitrogen atoms in the main chain. The thermal stability of these compounds is characterized by three main features. When nitrogen atoms are introduced into the diamine or the dianhydride component, the thermal stability of the resulting polyimides changes markedly. It depends on the chemical structure of the heterocycle containing nitrogen, the highest thermal stability being observed with polyimides based on pyrimidine and oxodiazole derivatives. Nitrogen atoms introduced into the polyimide molecule are of major significance in the formation of carbonized structures in high yields in the high-temperature pyrolysis of polyimides. Sulphur-containing polyimides have an interesting feature. Bivalent sulphur plays a positive role, its introduction into the main polyimide chain leading to a large increase in the thermal stability of polyimides under the conditions of thermo-oxidation and thermo-hydrolysis. The sulphoxide group does not exhibit this effect, and in many instances the thermal stability of polyimides containing this group is lower than that of their oxygen-containing analogues.

The so-called rigid-chain polyimides display the highest thermal stability. The molecule is saturated with aromatic and heterocyclic units of the type diphenyl, terphenyl, naphthalene, anthracene, fluorene, phenoxathyn, etc. Examples of polyimides of this class and their temperature characteristics are given in Table 2.

These examples of the application of the derivatograph to comparative measurements of the temperature characteristics of thermal and thermo-oxidative degradation show the possibility of readily conducting investigations of the chemical structure-property type, with the aim of finding reagents that ensure the preparation of compounds with the highest thermal stability. In this connection the derivatograph in combination with other methods and instruments of thermal analysis has been used successfully for solving the problem of modelling some thermochemical reactions of low-molecular-weight compounds imitating individual fragments of polyimide molecules. This investigation was necessary because of the difficulty of interpreting certain results of the thermal analysis of polyimides in correlation with the chemical structure of the reacting compounds such as monomers, solvents and catalysts. For this purpose numerous low-molecular-weight compounds were synthesized, representing the following elements of the polymer system: (1) fragments of polyamic acids; (2) solvato complexes of fragments of polyamic acids; (3) fragments of defective parts of the polyimide molecule; and (4) fragments of a "perfect" structure of polyimide. The formulae of some model compounds are shown in Table 3 and Fig. 10.

As all these low-molecular-weight compounds sublimate relatively easily on heating, special closed crucibles of the derivatograph were used for the study of more extensive transformations at high temperatures. This device made it possible to obtain interesting data which, in combination with the results of other thermoanalytical methods, led to the determination of some

TABLE 3
Model compounds and "imperfect" polyimide units

No.	Formula	Compound	Symbol
1		benzoic acid	BA
2		terephthalic acid	TA
3		pyromellitic acid	PA
4		pyromellitic dianhydride	PDA
5		phthalic anhydride	PhA
6		diaminodiphenyl ether	DADE
7		*o*-carboxyphenylbenzamide	CPhBA
8		*N*-phenylbenzamide	PhBA

relationships of thermochemical reactions of the formation and degradation of polyimides. Figure 11 shows as an example TG curves characterizing the thermal degradation of solvato complexes of pyromellitedianilic acid with one and two molecules of DMF and free from solvent. These data, compared with the results of mass spectrometric thermal analysis, permitted the establishment of the mechanism of interaction between polyamic acids and solvents and the significance of the latter in the formation of polyimides.

Let us consider two other examples showing the possibility of detecting various stages of the thermal degradation of model compounds by using various methods of operation with a derivatograph. Figure 12 shows the DTA curves for the heating of diphenylpyromellitimide in an open and a

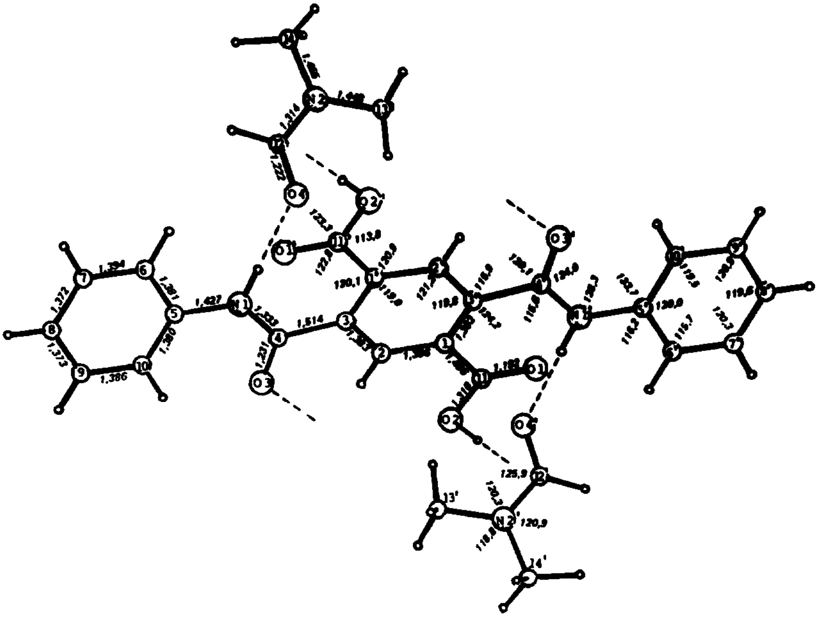


Fig. 10. Solvato complex of pyromellitedianilic acid with dimethylformamide.

closed crucible. It can be clearly seen that in the former instance only the endothermic effect of sublimation was observed, whereas in the latter the melting effect and three exothermic effects accompanying various stages of thermal degradation of the sample were recorded. Figure 13 shows the possibilities of studying the thermal degradation of 4,4′-diphthalimide diaminodiphenyloxide in holders of different constructions and in different

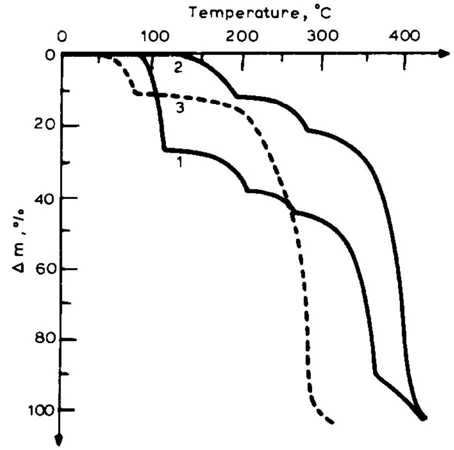


Fig. 11. TG curves of degradation of pyromellitedianilic acid in a complex with (1) two and (2) one solvent molecule and (3) without solvent.

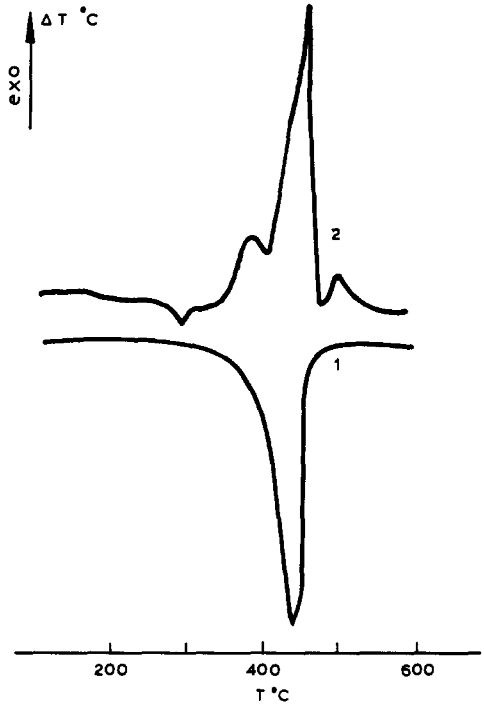


Fig. 12. DTA curves of diphenylpyromellitimide on heating in (1) open and (2) closed crucibles.

gaseous atmospheres. These results permitted the determination of the effect of the structure of the diamine fragment on the thermal stability of the polyimide and also the establishment of the mechanism for thermo-oxidative processes occurring in the perfect structure of the polymer. From the methodological standpoint these results proved that the derivatograph may be used for carrying out various investigations of low-molecular-weight organic substances the analysis of which has previously been limited to measurements only of some physical parameters such as the temperatures of melting, sublimation and boiling.

Apart from these conclusions, the investigation of low-molecular-weight compounds with a derivatograph for the study of various factors affecting the thermal stability of polyimides made it possible to solve the problem of the identification of the thermo-stabilizing effect of some organic compounds. Two characteristic examples will be considered. It was established by many independent chemical and physical experiments that some aromatic dicarboxylic anhydrides increase the thermal stability of polymers of the hetero-chain series (polyethers, polyamides, polyurea, etc.). A series of experiments with PM polyimide showed that these anhydrides, particularly those with halogen-containing substituents, also stabilize this class of thermally stable polymers. Thermogravimetric analysis carried out under dy-

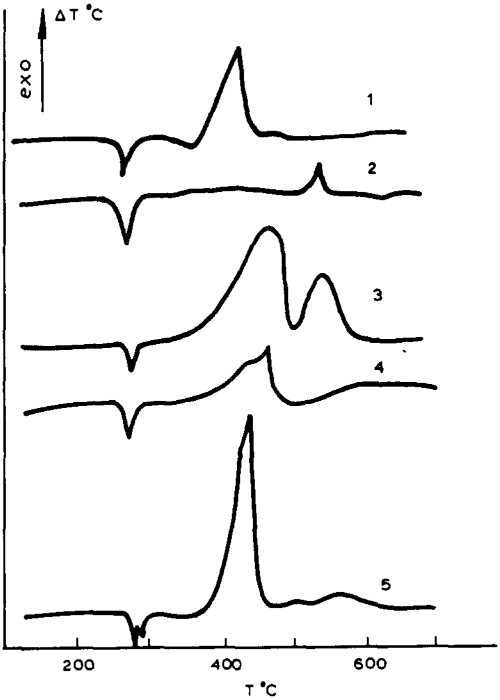


Fig. 13. DTA curves of 4,4′ = diphthalimide diaminodiphenyloxide on heating (1) on a plate holder, (2) in a quartz ampoule, (3) in a closed crucible, (4) in an open crucible in a helium flow and (5) in an air flow.

namic and isothermal conditions for a number of polyimides containing a 2% addition of anhydrides listed in Table 4 showed that the temperature characteristics of many stabilized samples exceed by 30–60°C those of the

TABLE 4

Results of dynamic and isothermal TGA of samples of PM polyimide with a 2% addition of mono- and dianhydrides

Anhydride	T_0 (°C)	T_5 (°C)	T_{10} (°C)	T_{100} (°C)	Weight loss (%) at 350°C, 250 h
No addition	350	470	530	640	55
Phthalic	320	490	520	640	40
Tetrahydrophthalic	340	495	520	640	38
Maleic	390	540	560	650	37
Dichloromaleic	320	500	540	650	45
Dibromomaleic	360	500	550	660	31
Dibromphthalic	410	530	550	680	29
Tetrabromphthalic	360	500	520	700	26
Dibromopyromellitic	320	450	510	670	35
Dichloropyromellitic	300	480	530	730	49

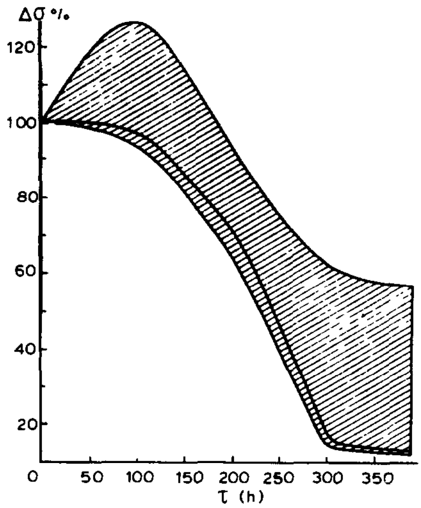


Fig. 14. Dependence of changes in stability (as a percentage of the initial samples) for a PM polyimide film containing additions of di- and tetra-bromphthalic anhydride at 330° C.

unstabilized samples. This difference is particularly pronounced after long thermal treatment in which the mass loss for 250 h at 350°C for samples treated with di- and tetrabromphthalic anhydride is half that for the unstabilized polyimide. The effect of thermal stabilization achieved by these compounds is very marked in the results of mechanical tests (Fig. 14). These results show that the tensile strength of a film containing di- or tetra-bromophthalic anhydride increases by 30–40% after 3 days of thermal treatment at 330°C and remains at the level of 65% after 10 days of thermal treatment. The broken curve shows the behaviour of the unstabilized film.

Triphenylphosphate (TPP) is another effective thermostabilizer of polyimides. Its action is also clearly shown by TGA data obtained with a derivatograph under dynamic and isothermal conditions. Figure 15 shows that on thermo-oxidative treatment at 430°C the unstabilized PM polyimide is completely degraded in less than 24 h, whereas the mass loss of a sample stabilized by triphenylphosphate is only 5% in the same period and its complete evaporation takes 4 days. These data, in combination with the results of other methods of investigation, made it possible to suggest a mechanism for the thermo-stabilizing effect of triphenylphosphate. This mechanism consists of four stages in which triphenylphosphate acts as a plasticizing agent, a promoter of the cyclodehydration of polyamic acids, an inhibitor of high temperature hydrolysis of polyimides and a stabilizer of thermo-oxidation.

In conclusion, it should be said that work in this area will continue because new directions in the thermochemistry of polyimides and other thermally stable polymers are appearing. Our experience of the thermal

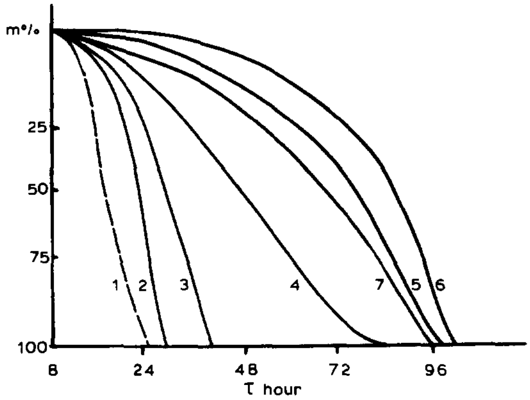


Fig. 15. TG curves (air, 430 °C) of polyimide films stabilized with triphenylphosphate. (1) Unstabilized PM; (2) PM–PF; (3) PM–MF; (4) stabilized PM with 2% of TPP; (5) with 5% of TPP; (6) with 10% of TPP; (7) with 20% of TPP.

analysis of this class of polymers conducted in close collaboration with chemists and the constructors of the instrument, permitted the transformation of thermal analysis from a passive method of recording physico-chemical changes occurring in polymers on heating into a method exerting an active influence on polymers. This is the principle of a directed thermochemical synthesis of new high-molecular-weight compounds by effecting a controlled change in the structure of initial polymers by using calculated schedules of thermal treatment under various conditions. This trend is technically and methodologically based on constant developments of the design of thermoanalytical instruments generally and the derivatograph in particular. This trend makes it possible to hope that progress in this field will lead not only to the development of more up-to-date thermo-analytical instruments but also to the appearance of thermo-synthetic instruments.

REFERENCE

1 F. Pavlik and J. Pavlik, Thermochim Acta, 4 (1972) 189.