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COMPARATIVE THERMAL ANALYSIS (CTA) OF THERMALLY-STABLE POLYMERS AND MODEL COMPOUNDS. POLYIMIDES AND MODEL COMPOUNDS

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The method of comparative thermal analysis has been used to determine the thermal stability of polyimides and their model compounds. The extent of defects in the investigated polyimides was determined by gas chromatography. The dependence of the extent of the defects on the chemical structure of the initial components and the supermolecular structure of the polyimides was established.

It has previously been shown (taking as examples polyphenylenes and polyketophenylene oxides, as well as corresponding model compounds [1–3]) that CTA can be used to evaluate both the thermal stability of the main structure of these polymers and the extent of distortions of the structure. This method is still more important for the investigation of the most widely-used and promising, thermally-stable polymers: polyimides. There is no other class of thermally-stable polymers in which such a number of compounds differing in the structure of the elementary unit have been synthesized. The main difficulty in establishing a relationship between their structure and properties is that polyimides differ not only in the chemical structure of the main unit, but also in the number of defects along the chain. This sometimes leads to similar properties of polyimides with different chemical structures. Hence, to solve the principal problem, that of the establishment of the relationship between the structure and the properties, it is necessary to develop a method for the synthesis of "non-defective" polyimides or, at least, to establish the extent of the distortions in the structure with comparatively high precision.

The results of most existing methods for the determination of the extent of these distortions, and in particular the extent of incompleteness of imidization in polyimides, are unreliable, and the unreliability of their results increases at high degrees of imidization. Thus, the determination of the extent of incompleteness of imidization by quantitative analysis of the IR-spectra of polyimides [4] is complicated by band superposition and by the difficulty of interpreting the spectra at degrees of imidization of 80% and higher, although the preparation of polyimides with a degree of imidization close to 100% is of particular interest for the attainment of optimum physico-mechanical properties. Moreover, this method is useful for the determination of the extent of structural distortions for polyimides in solutions, in films and, to a lesser extent, in powders, but it does not give good results for fibres.

During thermal treatment the defective structures are usually degraded earlier than the main polyimide structure. Hence, it is quite reasonable to attempt to determine the degree of imidization by mass-spectrometric investigation of the products of thermal degradation of polyimides [5]. This method consists in the measurements of the amount of carbon dioxide in the products of thermal degradation at 420–470°. It is based on the concept that during heating the unimidized amido acid units of polyimide undergo hydrolysis, with subsequent decomposition of carboxylic groups and the formation of carbon dioxide molecules. However, it is uncertain whether the hydrolysis proceeds to the end and whether other degrading processes in amido acid sequences, leading to the formation of gaseous products, are possible.

In this work, data on the thermooxidation of polymers and model compounds obtained during isothermal heating in a closed volume are used to determine the structural distortion in polyimide materials: powders, films and fibres (mostly the latter).

Experimental

Thermal oxidation of samples of the polymer and model compounds in the amounts of 0.0200 g was carried out in sealed double chamber pyrex ampoules with a breakable partition [1, 6]. The initial pressure of O_2 in the ampoule was 0.25 atm at 20°.

The ampoules were placed in a furnace in which the temperature was maintained to within ±0.5%. Thermal oxidation was carried at a certain temperature in the range from 200° to 450°.

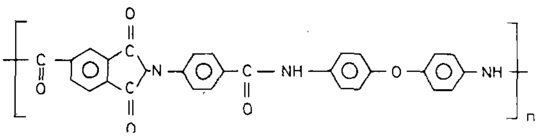
The volume of gaseous pyrolysis products was determined as follows. In order to avoid the penetration of air into the ampoule the partition was broken under a layer of a saturated NaCl solution. Gaseous products were introduced into measuring burette with a syringe. The amount of gaseous products ($CO + CO_2$) evolved in the course of thermal oxidation was measured with a Tsvet-4 gas chromatograph [7].

The method for the preparation of model compounds has been described in ref. [8]. Polyimide fibres were obtained according to the data in ref. [9].

Discussion of results

Figure 1 shows the rates of formation of gaseous products ($CO + CO_2$) *vs.* temperature when the thermooxidation in a closed volume is carried out for polyimide fibres with the following structures:

B-1



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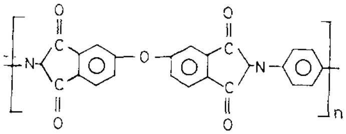

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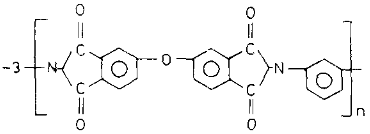

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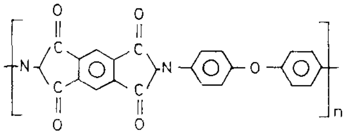
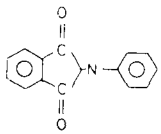


As a rule, these curves exhibit three parts: the initial portion up to 330°, the shoulder region from 330° to 390° (400)° and the final sharp rise above 390°. This character of the curves may be explained (by analogy with refs. [1, 2]) by study of the thermal oxidation of model compounds. For thus purpose the following model imides were synthesized:

1



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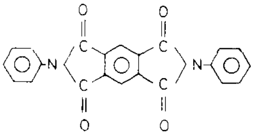

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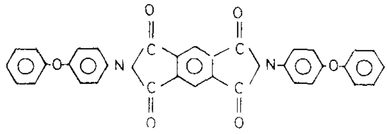

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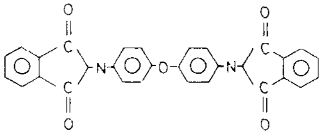

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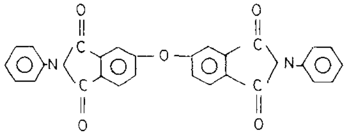


Figure 2 shows the curves of thermooxidation of these models in a closed volume in an oxygen atmosphere during isothermal heating for 1 hr. Each point on the curve corresponds to the rate of thermooxidation in g.mole of the gas evolved per g.mole of the sample per hr at the same temperature. All the curves have one common feature: thermooxidation starts above 390°, i.e. all these models remain

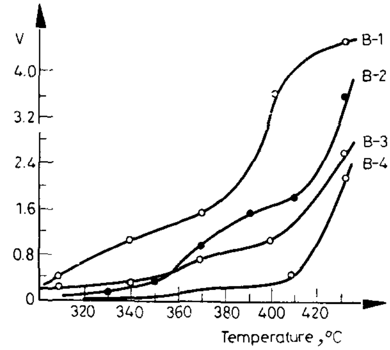


Fig. 1. Rates of formation of gaseous products (CO + CO_2) *vs.* temperature in the thermo-oxidation of polyimide fibres in a closed volume. Ordinate: g.mole of gas/g.mole of sample per hr

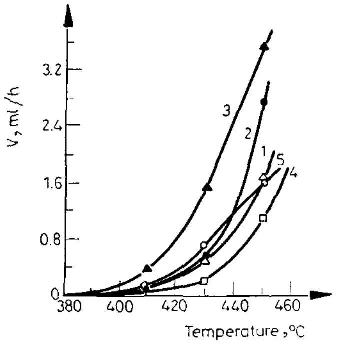


Fig. 2. Rates of formation of gaseous products (CO + CO_2) *vs.* temperature in the thermo-oxidation of model imides in a closed volume

stable during heating in an oxygen atmosphere for 1 hr (oxygen pressure in the ampoule at room temperature is 0.25 atm). Figure 3 shows the thermooxidation curve of diphenyl ether (DE). It is clear that this compound, which serves as model for fragments often present in polyimides, is also stable up to approximately the same temperatures. Evidently these data suggest that phthalimide, pyromellitimide and diphenyl oxide structures are very stable. It should be noted that the third portion of the thermooxidation curves of fibres, relating to a sharp increase in the evolution of gaseous oxidation products, also lies above 390°. If it is assumed that above this temperature thermooxidation of the main imide structures occurs, the gas evolution in the temperature range from 330 to 390° should be explained by the thermooxidation of less thermally-stable, defective structures. Benzoic acid (BA), N-phenylbenzamide (PhBA), pyromellitic dianhydride (DP) and diaminodiphelyl ether (DDE) were used as models for these structures in polyimides. Figure 3 shows the thermooxidation curves of these compounds. It is clear that the curves of the first three of these lie in the temperature range denoted by us as the second portion in the thermooxidation curve for fibres. Hence, these compounds, differing greatly in their thermal stability from imides and diphenyl ether, are probably actually models for similar defective structures in polyimides, and the characteristic shoulder in the curves of the thermooxidation of fibres in the temperature range from 330 to 390° (Fig. 1) appears because, under these conditions, the process of thermooxidation is of the successive character, i.e., the defective fragments are "burned out" before the main structures are oxidized. The formation of gaseous products at temperatures below 330° may be due to two factors. First, as Fig. 3 shows, diaminodiphenyl ether starts to decompose at temperatures below 200° and, consequently, it might be expected that amine end-groups in polyimides will also oxidize at very low temperatures. Secondly, some amounts of residual solvents, such as dimethylformamide (DMF), N-methylpyrrolidone, etc., are present in polyimides. Figure 4 shows the thermooxidation curve of DMF,

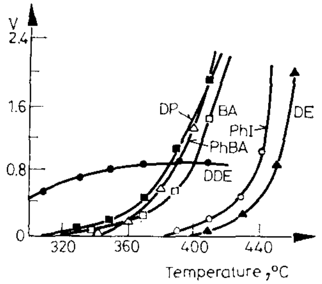


Fig. 3. Rates of formation of gaseous products (CO + CO_2) in the thermooxidation of mode compounds. Ordinate: g.mole of gas/g.mole of sample per hr

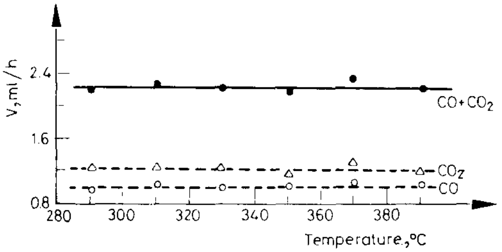


Fig. 4. Rate of the formation of CO and CO_2 in the thermooxidation of dimethylformamide

indicating that DMF is completely oxidized at a much lower temperature than 330°.

The fact that each curve obtained in the thermooxidation of polyimide fibres differing in their chemical structure and physical characteristics (such as glass transition temperature) exhibits three portions, each of which lies in a certain temperature range, shows that the processes of phase transition of the polymer do not affect the rate and order of the thermooxidation of solvent residues in the fibre and defective and main polyimide structures. The probable explanation is that, under these conditions, at high temperatures the rate of oxygen diffusion into the fibres is not the limiting stage of the entire thermooxidation process.

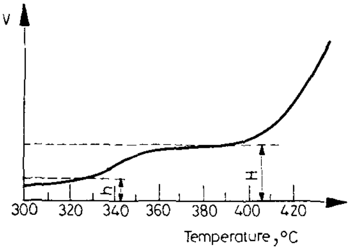


Fig. 5. Schematic plot of thermooxidation rate of polyimides *vs.* temperature

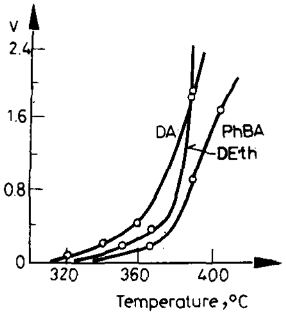
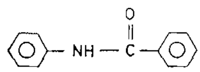


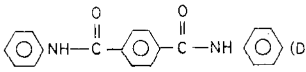
Fig. 6. Rates of formation of gaseous products ($CO + CO_2$) in the thermooxidation of model compounds. Ordinate: g.mole of gas/g.mole of sample per hr

It thus follows that the portion in the thermooxidation curve for fibres from 330 to 390 (400)° and, more precisely, the height of the shoulder, characterizes the extent of distortions in the polyimide structure. Gas evolution in the first portion of the curve may sometimes be neglected, but when it is high, the height of the shoulder should be "corrected" for it, i.e. decreased by it. The schematic curve of the thermooxidation of polyimide fibres, films and powders is shown in Fig. 5. The value of (H-h) characterizes the extent of structural distortions in the polyimide, or, more precisely, the gas evolution occurring as a result of the thermooxidation of amide and amido acid sequences, as well as anhydride and acid end-groups. It can be shown that for polyimide fibres and films, the molecular mass of which usually exceeds 20,000–30,000, the amount of gaseous products formed after the thermooxidation of anhydride and acid end-groups does not exceed 1–2% of the total amount of gaseous products.

As no independent method of determining the degree of imidization was available for the establishment of its relationship to the value of (*H-h*), another approach to the calculation of the degree of incompleteness of imidization was used to increase the reliability of the proposed method [10]. This approach was based on the observation of the oxidation rate (in g.moles of gases per g.mole of the sample per hr) of model compounds containing an amide bond. Figure 6 shows thermooxidation curves for model amides:

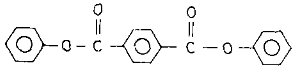


(Ph BA) and

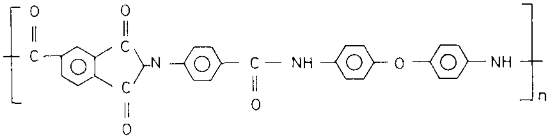


(DA)

The thermooxidation rate of PhBA and DA at 390° was 1 and 2 g. mole of gas/g.mole of sample per hr, respectively. It should be noted that for a model ester



(DEth) the oxidation rate was also 2. In other words, in the thermooxidation of these models at 390° for 1 hr, one mole of gas was evolved per each amide or ester bond. These bonds can be regarded as a preliminary structure for CO and CO_2 formed during thermooxidation. The reaction conditions (the amounts of sample and oxygen, and the temperature and duration of thermal oxidation) were chosen in such a manner that oxygen was consumed first for the thermooxidative breaking of these bonds, whereas aromatic structures were degraded later. It was of interest to elucidate whether this regularity is maintained on passing to polymer samples. The thermooxidation rate was determined for fibres of polyamidoimide, the elementary unit of which has the following structure:



i.e., it contains two amide bonds per elementary unit. The value of (*H-h*) for this polymer was 2 g.mole of gas per g.mole/hr. Hence, it seems possible to use these data to calculate the degree of incompleteness of imidization in polyimide. When incomplete imidization is related to interchain crosslinking, occurring as a result of the formation of an amide bond between two polyimide molecules, one elementary unit in which imidization has not proceeded contains four amide groups. In this case thermooxidation at 390° for 1 hr should lead to the formation of 4 moles of gas per unit. When incomplete imidization is due to the presence of a free acid group, the unit that did not undergo unimidization contains two amide and two acid groups. For the thermooxidation of benzoic acid at 390°, the values of the thermooxidation rate were close to unity. Assuming that, just as for amides, the thermooxidation rate of fragments containing an acid group is approximately the same as that of the model acid, we suppose that in this case too the thermooxidation of one unimidized unit at 390° yields four molecules of gas per hour.

Hence, the degree of incompleteness of imidization, D, can be calculated from the following equation:

$$D = \frac{(H-h)}{V} \cdot 100\%$$

where $(H\text{-}h)$ is the measured thermooxidation rate at 390° for polyimide units that are not imidized, and V is 4 g. mole of gas/g.mole per hr, i.e. it is the hypothetical thermooxidation rate of the polymer if it is assumed that imidization has not occurred at all.

This relationship was checked in the determination of the degree of incompleteness of imidization for model imides. Actually, it is not always possible to complete cyclization even in the synthesis of model imides. Thus, in the synthesis of N-phenylphthalimide various authors have obtained samples differing in the melting temperature by 7–8° [11, 12]. In contrast to polyimides, for model compounds the number of amido acid units that have not undergone cyclization can be determined spectroscopically with high precision [13]. The percentage of amido acid in three samples of N-phenylphthalimide, determined spectroscopically and from the results of thermooxidation, is given below.

		Amido acid content	
Sample No.	Melting temperature	Spectroscopic method	From the results of thermooxidation
II	206–207°	1%	2%
IV	201–204°	9%	13%
V	204°	9%	13%

In other words, the "degree of imidization" of N-phenylphthalimide determined spectroscopically was 99, 91 and 91%, and according to the results of the thermooxidation method it was 98, 87 and 87%, respectively. These data may be considered to be in good agreement.

The good agreement of these results with the values obtained in the study of the mechanical properties of the fibres proves indirectly that it is possible to determine the degree of incompleteness of imidization from CTA data.

It is known [14] that the Young modulus of crystalline oriented polymers depends on the elastic moduli of crystallites E_{cr} and amorphous parts E_{am} and on the degree of crystallinity κ:

$$E = \frac{E_{cr} \cdot E_{am}}{E_{cr}(1 - \kappa) + E_{am} \cdot \kappa}$$

If we consider polyimides as random copolymers of the corresponding imides and amido acids, and use the models of alternating introduction of rigid (E_{cr}) and flexible (E_{PAA}) elements, it is possible to calculate formally the degree of imidization:

$$i = \frac{E_{cr}(E_{fib} - E_{PAA})}{E_{fib}(E_{cr} - E_{PAA})} \cdot 100\%$$

where E_{cr}, E_{fib} and E_{PAA} are the elastic moduli of the crystallite, the investigated fibre and the polyamic acid fibre, respectively, and i is the degree of imidization [15].

Date in Table 1 show that the values of the degree of incompleteness of imidization, D, and those of $(100 - i)$ for a number of fibres determined by the two above methods (calculation and the CTA method) are in good agreement.

Table 1

Degree of incompleteness of imidization of polyimide fibres according to the data of thermal degradation and mechanical tests

No.	Initial reagents		Degree of incompleteness of imidization	
	Dianhydride	Diamine	Thermal degradation D, %	Calculation from model (100%)
1	Pyromellitic acid	Bis-(4-aminophenyl ether) of hydroquinone	19	20
2	Pyromellitic acid	Bis-(4-aminophenyl ether) of resorcine	10	9
3	Pyromellitic acid	Phenylene-diamine	10	10
4	Pyromellitic acid	Phenylene-diamine	8	—
5	3,3',4,4'-Tetracarboxy-diphenyl oxide	Phenylene-diamine	19	17
6	3,3',4,4'-Tetracarboxy-diphenyl oxide	Phenylene-diamine	10	—
7	3,3',4,4'-Benzophenone tetracarboxylic acid	Phenylene-diamine	7	—
8	Pyromellitic acid	4,4'-Diaminodiphenyl sulphide	4	—
9	Pyromellitic acid	2,7-Diaminofluorene	8	8
10	Pyromellitic acid	4,4'-Diaminobenzophenone	4	—
11	Pyromellitic acid	Benzidine	11	9
12	3,3',4,4'-Diphenyl tetracarboxylic acid	Benzidine	4	6
13	Bis-(3,4-dicarboxyphenylic ether)-hydroquinone	Phenylene-diamine	15	—

Assuming that these values of D actually characterize the degree of incompleteness of imidization, it may be concluded that the limiting degree of this process is related to the chemical structure of the polyimide unit (under the condition that the same method of fibre preparation is used). A comparison of the values of D for fibres 1 and 2, 3 and 4, and 5 and 6, shows that a change in the position of the phenylene rings in the diamine component from the para- to the meta-position leads to a considerable increase in the homogeneity of the fibre structure. This can be due to the fact that this change in structure leads to the formation of less rigid polyimide chains, because in the meta-configuration of the benzene ring the chain segments rotate more freely [16]. In fact, fibres with amorphous structure (Nos. 8 and 10) exhibit the lowest degree of incompleteness of imidization. Hence, the distortion in the chemical structure and the thermal stability of polyimides are related to the molecular mobility of the polyimide chains. The latter can be determined by crystallization processes occurring during the imidization of fibres, by hindrances to the rotation of single fibres and interchain cross-linking.

These data show that the CTA method can be used to evaluate the thermo-oxidative stability of single fragments in the polyimide unit and the extent of structural distortions in the polymers, to carry out changes in the method of preparation of polymers so as to decrease these defects, and also, in some cases, to establish the relationship between them and the supermolecular structure of the polymer.

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Résumé — La méthode d'analyse thermique comparée (CTA) a été utilisée pour étudier la stabilité thermique des polyimides et de leurs composés modèles. On a déterminé par chromatographie en phase gazeuse l'étendue des défauts dans les polyimides étudiés. On a établie de même les rapports qui existent entre l'étendue des défauts dans la structure chimique des composants initiaux et la structure supermoléculaire des polyimides.

Zusammenfassung — Die Methode der vergleichenden Thermoanalyse wurde zur Bestimmung der Hitzestabilität von Polyimiden und ihren Modellverbindungen eingesetzt. Das Ausmass der Defekte in den untersuchten Polyimiden wurde gaschromatographisch bestimmt. Die Abhängigkeit des Umfangs der Defekte von der chemischen Struktur der Ausgangskomponenten und der supermolekularen Struktur der Polyimide wurde festgestellt.

Резюме — Методом сравнительного термического анализа проведено исследование термоокислительной стабильностн ряда полиимидов, синтезированных на основе ароматических диаминов и диангидридов с различным количеством и расположением оксифениленовых звеньев. Показана зависимость термостабильностн полиамидов от степени их дефектности и строения элементарного звена полимера. Получена хорошая корреляция метода термическим и спектральным способом определения степени имидизации полимерных образцов.