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PREPARATION AND INVESTIGATIONS OF POLYIMIDES III

THERMAL INVESTIGATION OF THE IMIDIZATION OF POLYAMIDE ACID POWDERS

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Polyamide acid powders of pyromellitic dianhydride and 4,4'-diaminodiphenyl ether base were prepared in tetrahydrofuran, in the heterogeneous phase. The imidization of these powders was investigated by thermogravimetric, calorimetric and mass-spectrometric methods.

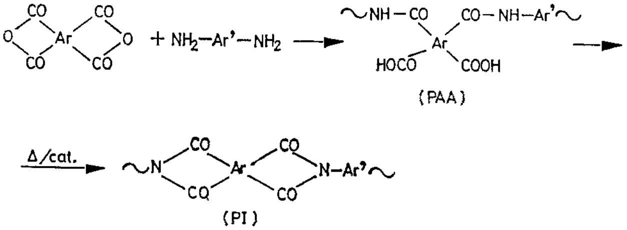
According to the TG and DSC data, the temperatures of the beginning and maximum rate of imidization increase with increasing temperature and duration of imidization.

A linear relationship has been found to exist between the weight loss and the reaction heat of the imidization process. The reaction heat corresponding to unit weight loss increases with decreasing molecular weight.

Dicarboxylic anhydrides, applied as chain-terminators, do not affect the thermal properties of polyamide acids to an appreciable extent.

Imidization has been found to be a complex process, in which decomposition of polyamide acids also takes place besides dehydrocyclization. The kinetics of imidization are satisfactorily described by a first-order dehydrocyclization and a parallel first-order decomposition. The weight loss during imidization is higher than the loss calculated on the basis of dehydrocyclization, which must be due to the release of the decomposition products of the polyamide acid, the release of solvated or complexed tetrahydrofuran, or that of possible oligomeric clusters.

The most widespread representatives of thermoresistant plastics are aromatic polyimides, prepared by the reaction of aromatic tetracarboxylic dianhydrides and aromatic diamines [1–7], according to the following reaction scheme:



The polyamide acids (*PAA*) formed in the first step of the reaction are well soluble in polar solvents. The second step is a dehydrocyclization (imidization) reaction carried out by thermal or chemical methods [4–9]. The characteristics of the imidization reaction, which basically determines the properties of the polyimides (PI), have been studied widely [9–14]. It has been found that polyamide acids are generally solvated with large amounts of solvent [10–13], and that the presence of the solvate shell interferes with the determination of the thermal properties of the dehydrocyclization process, and also affects the course of reaction [13].

In order to eliminate the interference, various authors [7, 10, 13] have applied solvate exchange with solvents of low boiling points. This method is applicable to remove strongly-bound solvents. With regard to the equilibrium nature of PAA formation, however [16, 17], extraction may change the equilibrium conditions.

With the aim of studying dehydrocyclization and eliminating the above difficulties, we have prepared polyamide acid powders in a solvent of low boiling point, tetrahydrofuran, in which the product is insoluble. The reacting monomers are dissolved in tetrahydrofuran, whereas the resulting polyamide acid precipitates in the form of a fine powder (heterogeneous reaction), and thus it can presumably be prepared in a solvent-free state. The imidization of the resulting product can be studied more easily, since now the removal of bound solvent is not superimposed on the chemical process.

We were concerned with the preparation of polyamide acids based on pyromellitic dianhydride (*PMDA*) and 4,4'-diaminodiphenyl ether (*DAE*), and with a detailed investigation of their imidizations.

However, the molecular weights of the polyamide powders prepared by the above heterogeneous reaction are relatively low (20.000 to 50.000). As a compensation, reactive end-groups were built into the polyamide acid, which, under the conditions of imidization, yield cross-linked products through a thermal transformation [18]. The reactive end-groups were formed by adding maleic anhydride (*MA*), or other dicarboxylic anhydride which yields maleic anhydride in a thermal reaction, as chain-terminator.

The investigations were generally performed by micro methods with 1–3 mg of sample, and thus the temperature and pressure gradients within the sample could be neglected in the investigation of processes involving simultaneous heat and mass transport.

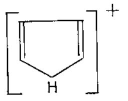
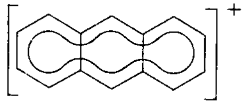
Experimental

Material and their purification

Pyromellitic dianhydride (*PMDA*, m.p. 559.8 K) and 4,4'-diaminodiphenyl ether (*DAE*, m.p.: 462.5 K) were purified as described previously [4].

Cis-3,6-endo-methylene-1,2,3,6-tetrahydrophthalic anhydride (norbornene dicarboxylic anhydride, *NDA*) was prepared in a Diels–Alder reaction from cyclopentadiene and maleic anhydride [19]. The crude product was recrystallized from benzene, and dried in vacuo (m.p. 540.3 K, decomposition at 590–600 K). The mass-spectrum of the recrystallized product can be seen in Fig. 1a.

9,10-Dihydroanthracene-9,10 endo-α,β-succinic anhydride (*ASA*) was prepared by Diels–Alder reaction from anthracene and maleic anhydride. The crude product was recrystallized from toluene, and dried in vacuo (m.p. 531.2 K). The mass-spectrum of the pure substance can be seen in Fig. 1b.

Both adducts are thermally unstable, and decompose into their constituents (*MA* and cyclopentadiene or anthracene, respectively). This process can easily be detected in the mass-spectra. The most intense fragment of NDA (Fig. 1a) is the $m/e = 66$  ion, whereas the most characteristic fragment of *ASA* (Fig. 1b) is the $m/e = 178$  ion.

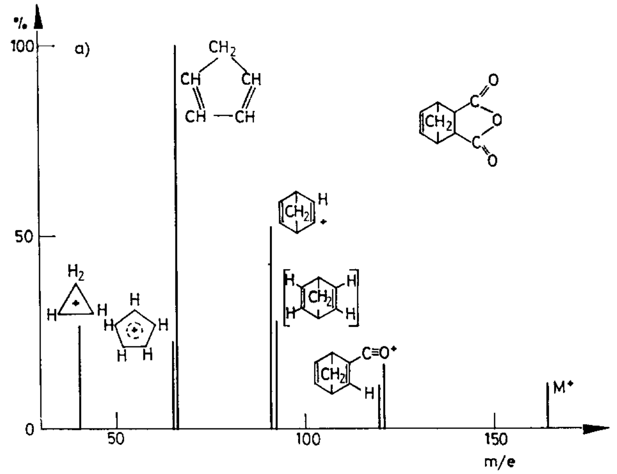


Fig. 1a. Mass spectrum of norbornene-dicarboxylic anhydride

The decomposition temperatures of both compounds are higher than the temperature of dehydrocyclization, and thus the unsaturated end-groups will be attached to completed polyimide chains.

Maleic anhydride (*MA*): The commercial substance (Reanal) was recrystallized from chloroform, and then dried in vacuo at room temperature (m.p. 323.7 K).

The reaction medium of precipitation polyaddition was anhydrous tetrahydrofuran (*THF*).

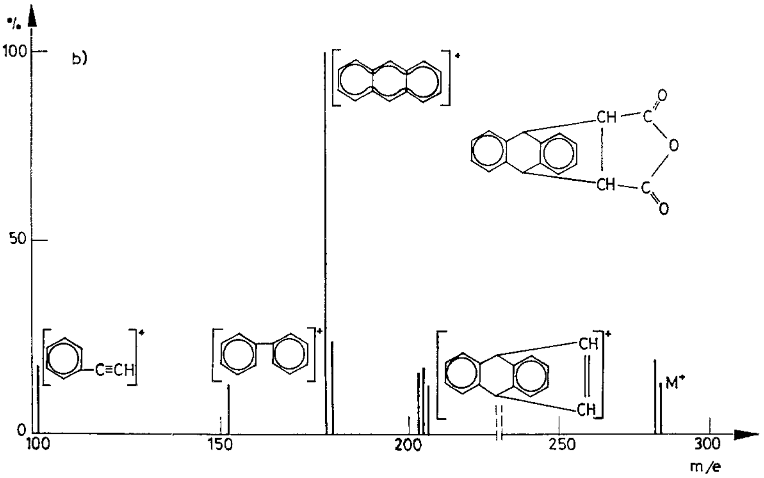


Fig. 1b. Mass spectrum of anthracene-maleic anhydride adduct

Instrumental methods

The structures of the products eliminated during imidization were determined by mass-spectrometric investigations. The mass-spectra were recorded with a Jeol JMS – 01 SG – 2 spectrometer and data processing system. The heats of imidization and the melting points of starting compounds were determined in a calorimeter (Perkin-Elmer Model DSC – 2). Thermogravimetric investigations were carried out in a Cahn-type micro thermogravimetric (TG) instrument. The molecular weights of *THF*-soluble products were determined with a Knauer-type vapour pressure osmometer (VPO), and those of *PAA* powders by viscosimetric methods [20]. EPR spectra were recorded on a Jeol JES – PE instrument.

Preparation of PAA

The heterogeneous polyaddition reaction was performed at 298 ± 0.1 K, in a three-necked flask under a stream of inert gas. Solid *PMDA* was added at a low

Table 1

Compositions and properties of polyamide acid powders

Sample	Composition, mole			Chain terminator
	DAE	*PMDA*	Chain terminator	
PAA-T	1	1	–	–
PAA-T$_1$	1	0.95	–	–
PAA-TR$_1$	1	0.95	0.1	ASA
PAA-TR$_2$	1	0.95	0.1	NDA
PAA-TR$_3$	1	0.95	0.1	MAA

rate to the stirred *THF* solution of *DAE*. Chain-terminator anhydrides were added together with *PMDA*.

After the addition of the anhydride component, the solution immediately became opaque. In order to complete the reaction, the mixture was stirred for one hour, the precipitated yellow-white *PAA* powder was filtered, washed five times with anhydrous *THF*, and then dried in vacuo at room temperature.

The compositions and properties of the *PAA* powders prepared are given in Table 1.

Results and discussion

The TG curves of *PAA* powders can be seen in Fig. 2. The characteristic temperatures, weight losses, and the heats of imidization are listed in Table 2.

Table 2

TG and *DSC* data of *PAA* powders

Sample	Δm_i, %	T_{max}, K	T_0, K	Δm_d, %	ΔH_i, J/g
PAA-T	13.9	467.0	703	3.8	143
PAA-T$_1$	13.3	461.5	663	1.4	182
PAA-TR$_1$	16.8	460.5	673	1.0	206
PAA-TR$_2$	13.8	472.0	733	0.6	159
PAA-TR$_3$	13.8	473.0	703	0.6	176

Δm_i — weight loss of imidization process
T_{max} — temperature of the maximum rate of imidization reaction
T_0 — decomposition temperature of the resulting polyimide
Δm_d — weight loss measured from start of decomposition process to 773 K
ΔH_i — reaction heat of imidization process

In order to determine the kinetics of imidization reactions, *PAA* powders were heat-treated at various temperatures for various periods. This heat-treatment was carried out in a DSC apparatus at a heating rate of 320 deg/min to predetermined temperatures, and the maintained under isothermal conditions for given periods. After heat-treatment, the samples were cooled down quickly (320 deg/min) and subjected to TG and DSC investigations.

In studies on the kinetics of isothermal imidization it must be taken into account that the reaction may progress to a certain extent during heating to the temperature of measurement (particularly at high temperatures). In order to determine the extent of transformation in the heating and cooling steps, the samples were heated at a rate of 320 deg/min, and after the desired temperature was reached, they were cooled down at the same rate. The result of this measurement was accepted as the conversion corresponding to the starting time ($t = 0$) of imidization.

As an illustration of the results obtained with thermal treatment, Fig. 3 shows the DSC curves of a *PAA—T* sample treated for 10 min at various temperatures, and Fig. 4 shows the TG curves of samples heat-treated at 448 K for various periods. The properties measured after heat-treatment are given in Table 3.

The TG curves of untreated *PAA* powders (Fig. 2) have the same run as those of *PAA* prepared in solution [13]. However, the weight losses corresponding to the imidization process are nearly 5% higher than the theoretical values (8.6%). (In the case of *PAA*—TR_1 the calculated weight loss for thermal decomposition of the end-groups is 12.4%.) The temperature pertaining to the maximum reac-

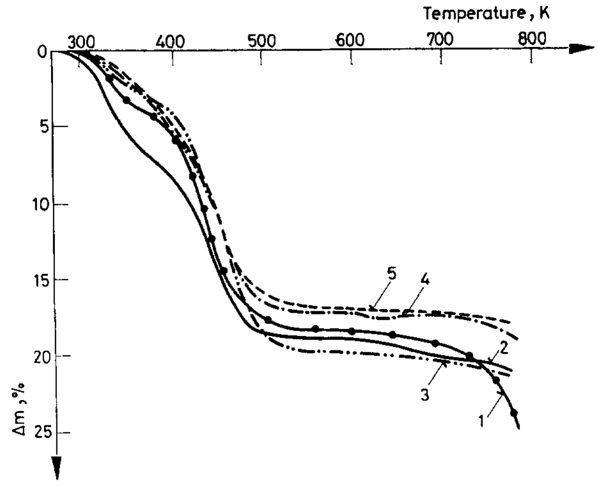


Fig. 2. TG curves of polyamide acid powders. *1* — *PAA—T*; 2— *PAA*—T_1; *3* — *PAA*—TR_1; *4* — *PAA*—TR_2; *5* — *PAA*—TR_3

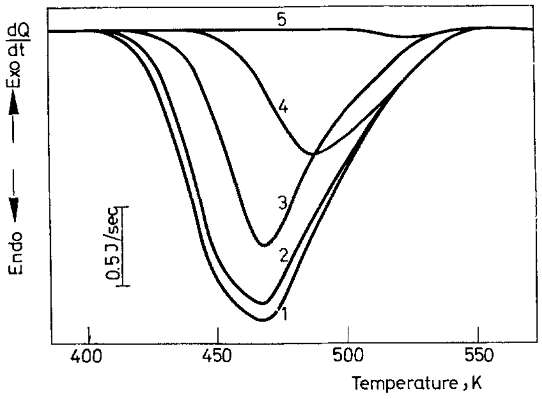


Fig. 3. DSC curves of *PAA—T* samples treated at various temperatures for 10 minutes. *1* — 398 K; *2* — 408 K; *3* — 423 K; *4* — 448 K; *5* — 498 K

Table 3

TG and *DSC* data of heat treated *PAA* powders

Sample	Heat treatment		Δm_t %	T_E K	T_{max} K	T_0 K	ΔH_i J/g
	Temperature, K	Duration, min					
PAA-T	423	0	13.0	406	466	728	135
		10	9.4	416	470	718	100
		28	7.0	421	480	693	94
		45	6.3	435	476	713	94
		120	5	426	484	728	49
	448	0	13.0	403	467	723	135
		5	6.6	424	482	710	82
		10	6.7	430	486	718	77
		28	3.4	438	497	710	47
		120	1.8	459	507	718	8
PAA-T_i	448	0	12.1	399	463	673	180
		5	6.0	410	480	718	98
		10	4.8	421	485	713	94
		15	3.7	441	490	713	47
		45	2.0	448	495	720	52
		127	0.8	435	500	670	22
	473	0	9.5	398	467	713	123
		5	2.0	408	477	716	—
		10	0.8	453	513	716	—

T_i — starting temperature of imidization reaction

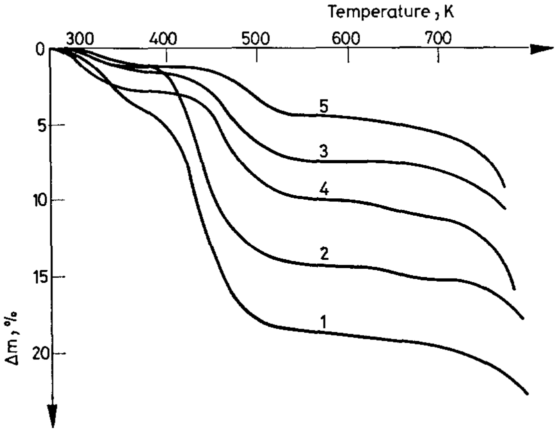


Fig. 4. TG curves of *PAA—T* samples treated at 448 K for various periods. *1* — untreated; *2* — 0 min; *3* — 5 min; *4* — 10 min; *5* — 28 min

tion rate is higher than that of *PAA* prepared in the homogeneous phase [13]. In the course of heat-treatments of samples, the initial temperature of imidization increases, and the weight loss and reaction heat corresponding to imidization decrease when the temperature or the duration of heat treatment increase (Table 3). A linear relationship was found between the weight loss and the reaction temperature (Fig. 5).

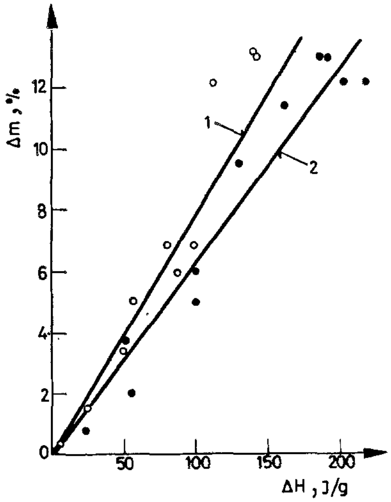


Fig. 5. Relationship between imidization weight loss and reaction heat with *PAA—T* (*1*) and *PAA—*T_1 (*2*) samples

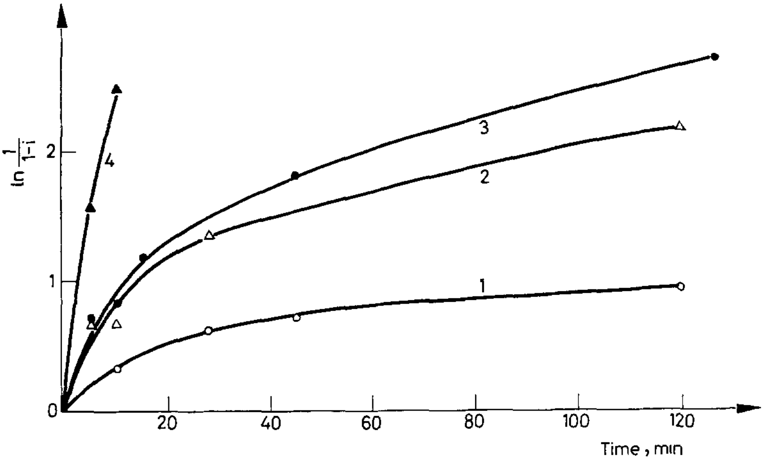


Fig. 6. Evaluation of the TG curves of samples heat treated under isothermic conditions on the basis of first order reaction ($i = 1 - \Delta m_t/\Delta m_0$) *1 — PAA—T* at 423 K; *2 — PAA—T* at 448 K; *3 — PAA—*T_1 at 473 K

The Figure 5 clearly shows that with increasing temperature or duration of heat-treatment (low weight losses or reaction heats), the deviation of the experimental results decreases. This is due to the fact that the evaluation of DSC curves taken on samples with high conversions becomes more accurate because of the smaller changes in specific heat [13]. For the two products with different molecular weights, the weight losses related to unit reaction heat are close to one another. In the case of *PAA–T* (M_w ≈50.000) this is 0.7 g/mJ, and for *PAA–*T_1 (M_w 8.000 to 10.000) 0.9 g/mJ. Consequently, the reaction heat corresponding to unit weight loss increases with decreasing average molecular weight.

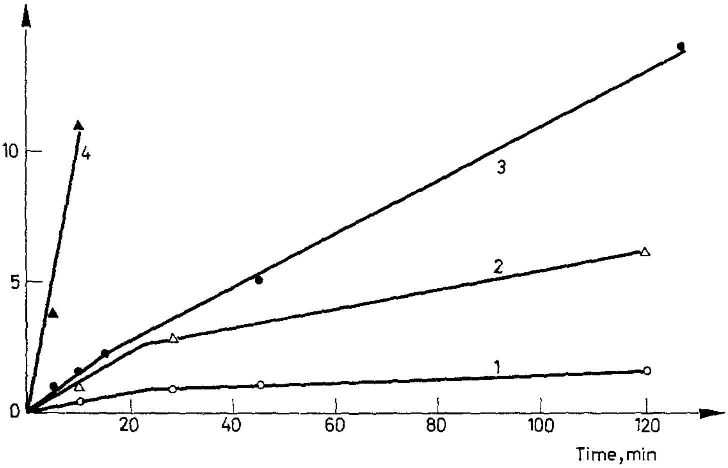


Fig. 7. Evaluation of TG data according to [17]. *1 –PAA–T* at 423 K; 2. – *PAA–T* at 448 K; *3 – PAA–*T_1 at 448 K; *4 – PAA–*T_1 at 473 K

From the thermogravimetric data of isothermal heat-treatments, kinetic calculations [17] were performed under the assumption of a first-order reaction. Figures 6 and 7 show the kinetic curves obtained. (DSC data, owing to their high deviations, cannot be used for kinetic calculations.)

It is clear from the Figures that imidization cannot be described by the equation of first-order reactions. Moreover, the data cannot be linearized on the basis of second-order reactions, either. Since the imidization process cannot be described by a single equation, the kinetic data were analyzed in terms of the reaction scheme suggested by Kamzolkina et al. [17], which also takes into account the degradation of *PAA* (process with rate constant k_2):

$$\mathrm{PMDA} + \mathrm{DAE} \underset{k_2}{\overset{k_3}{\rightleftharpoons}} \mathrm{PAA} \xrightarrow{k_1} \mathrm{PI}$$

According to this model, the maximum rate of the decomposition of *PAA* is located at 448 K, and $t = 15-20$ min. After this point the dehydrocyclization reaction, in which *PI* is formed, becomes increasingly dominant. The rate constants calculated for *PAA–T* at 448 K are $k_1 = 0.04$ min^{-1} and $k_2 = 0.02$ min^{-1} and those for *PAA–T*$_1$ are $k_1 = 0.07$ min^{-1} and $k_2 = 0.03$ min^{-1}. The value of k_3 could not be determined from the measured data.

The reaction scheme which takes into account the decomposition of *PAA* is in accord with the observation that the imidization weight loss of untreated samples is higher than the loss calculated from the dehydrocyclization reaction.

With the aim of the direct detection of the products formed in the decomposition of *PAA*, mass-spectrometric investigations were carried out. The mass-spectra measured after the thermal treatment of *PAA* powders are shown in Fig. 8.

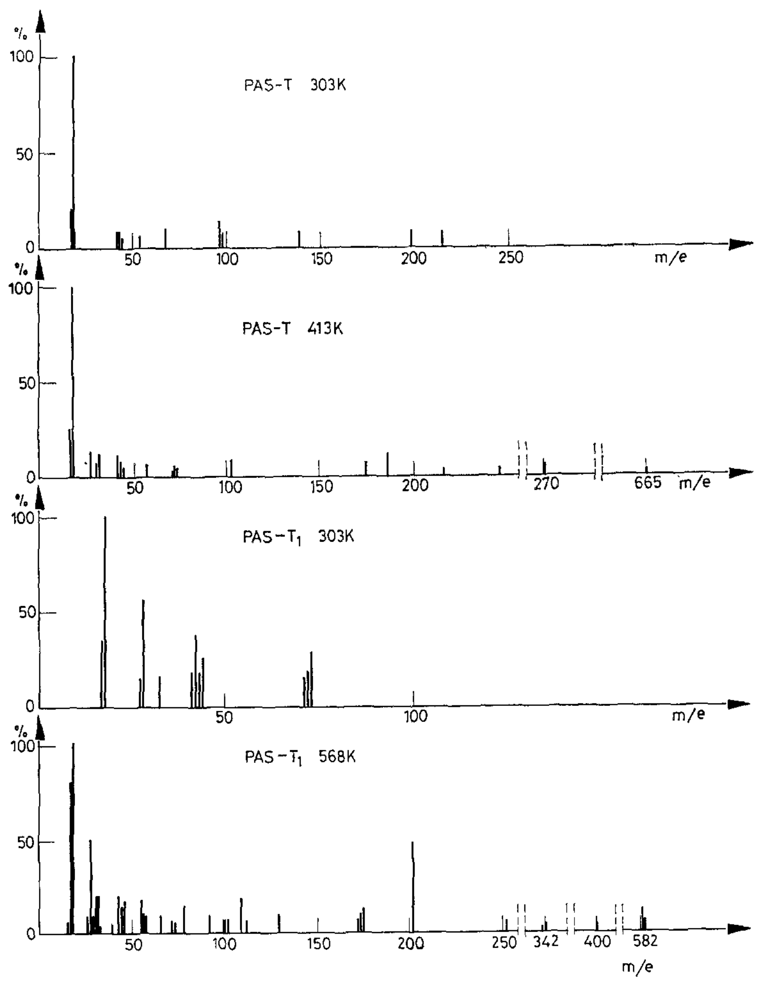


Fig. 8. Mass spectra of various polyamide acid powders

It can be seen that in addition to the characteristic fragments of the monomers [4], fragments with high mass number ($m/e > 218$) also appear in the spectrum. They are most probably doubly-charged fragments of oligomers. Surprisingly, *THF* ($m/e = 72$) can also be detected in the spectrum; this is released from the sample only after heat-treatment, at high temperatures (373–383 K).

The presence of *THF* can be attributed, in our opinion, to two factors:

(a) *THF* has a certain solvation effect on *PAA* powders too, and

(b) it may form a charge-transfer complex with *PMDA* or with the terminal anhydride groups [22], which decomposes at higher temperature with the release of *THF*. The presence of such a complex is confirmed by the observation that *PAA* powders give an EPR signal (Fig. 9) which can be assigned to the radical ion form of the charge-transfer complex.

Fig. 9. EPR spectrum of untreated *PAA–T*

In addition to the degradation process, the traces of monomers and oligomers in the mass-spectrum may also be due to the fact that they are present as clusters in the *PAA* powders.

In order to prove this assumption, we analyzed the small amount of material which remained in *THF* solution. A portion of the filtered mother liquor was evaporated at room temperature, in vacuo, and the solid residue was pulverized and dried again. The greyish product was investigated by TG, DSC and MS methods.

The TG curve shows four overlapping weight loss processes. Up to 373 K moisture is released ($\Delta m \sim 5\%$). This is followed by the imidization process ($\Delta m \sim 9.5\%$), which has a maximum rate at 420 K. The weight loss step corresponding to the imidization process partly overlaps with a process causing a weight loss of ca. 20% up to 673 K (decomposition temperature). DSC measurements have shown that this latter can be divided into two steps. The maximum rate of the first process is at 500 K ($\Delta m \sim 11\%$), and that of the second at 568 K ($\Delta m \sim 9\%$). These two processes correspond to the release of oligomers. According to the MS, too, the solid residue contains large quantities of dimers and trimers (fragments at $m/e = 200$ to 300). The same fact is indicated by the average molecular weight $\bar{M}_n = 700 \pm 15$ determined from the mother liquor. This molecular weight arises from the large amounts of dimers ($M = 636$ and $M = 618$) and trimers ($M = 836$).

In the TG curves of untreated samples a 1–2% weight loss step, starting at 553–563 K and terminating at decomposition, could be observed. This corresponds to the second step of the release of oligomers. The first decomposition step overlaps with the weight loss step of imidization. However, taking into account the data obtained from the investigation of the distillation residue, this value does not exceed 3%. The remaining weight loss excess of ca. 2% is due to the release of oligomers and monomers obtained from the decomposition of *PAA*.

The results indicate that, even when the thermal investigation of *PAA* powders is thoroughly planned, several complications may arise; one must reckon with possible complex formation, the weak solvation effect of the solvent, and the release of clustered monomers and oligomers, which may all affect both the calorimetric and the thermogravimetric results.

It is noted finally that when the data of dynamic TG measurements were evaluated by means of the Horowitz–Metzger formal kinetic equation, a second-order reaction was obtained (with an apparent activation energy of (90 ± 21 kcal/mole). In the light of the above results, it can be stated that in the application of such types of equation one must proceed very carefully, and the conclusions drawn should also be checked by other methods.

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Résumé — Les polyamides en poudre résultant du dianhydride pyromellitique et de l'éther 4,4'-diaminodiphénylique ont été préparés en phase hétérogène dans le tétrahydrofuranne. La formation d'imides à partir de ces poudres a été étudiée par thermogravimétrie, calorimétrie et spectrométrie de masse.

D'après les résultats obtenus par TG et DSC, les températures du début de la formation d'imide et la vitesse maximale de la réaction augmentent avec l'accroissement de la température et de la durée de la réaction.

On a trouvé une corrélation linéaire entre la perte de poids et la chaleur de formation de l'imide. La chaleur de réaction correspondant à l'unité de perte de poids augmente quand le poids moléculaire diminue.

Les anhydrides dicarboxyliques utilisés en bouts de chaines n'ont pas d'effet appréciable sur les propriétés thermiques des polyamides.

On a établi que la formation d'imide est un processus complexe, au cours duquel, outre la déshydrocyclomérisation, une décomposition des polyamides a également lieu. La cinétique de la réaction peut être décrite de façon satisfaisante par une déshydrocyclomérisation du premier ordre et une réaction de décomposition parallèle également du premier ordre. Lors de la formation d'imide la perte de poids est plus élevée que celle calculée à partir de la déshydrocyclomérisation, ce qui provient sans doute du dégagement des produits de décomposition du polyamide, du dégagement du tétrahydrofuranne solvaté ou complexé ou bien de celui des inclusions oligomères éventuelles.

Zusammenfassung — Polyamidsäurepulver von Pyromellitdianhydrid und 4,4'-Diaminodiphenyläther wurden in Tetrahydrofuran in heterogener Phase hergestellt. Die Imidisierung dieser Pulver wurde durch thermogravimetrische, kalorimetrische und Massenspektrometrische Methoden verfolgt.

Nach TG- und DSC-Angaben steigt die Temperatur des Beginns und der Maximalgeschwindigkeit der Imidisierung mit steigender Temperatur und Imidisierungsdauer an.

Ein linearer Zusammenhang wurde zwischen Gewichtsverlust und Reaktionswärme des Imidisierungsvorgangs gefunden. Die der Einheit des Gewichtsverlustes entsprechende Reaktionswärme nimmt mit abnehmendem Molekulargewicht zu.

Als Kettenende angewandte Dicarboxylanhydride beeinflussen die thermischen Eigenschaften der Polyamidsäuren nicht in merklichem Maße.

Es wurde festgestellt, daß die Imidisierung ein komplexer Vorgang ist, in dem außer der Dehydrocyclisierung auch eine Zersetzung der Polyamidsäuren stattfindet. Die Kinetik der Imidisierung kann durch eine Dehydrocyclisierung erster Ordnung und eine parallele Zersetzungsreaktion erster Ordnung befriedigend beschrieben werden. Der Gewichtsverlust während der Imidisierung ist höher als der aufgrund der Dehydrocyclisierung berechnete Verlust, was der Abspaltung von Zersetzungsprodukten der Polyamidsäure, der Freisetzung von solvatiertem oder komplexgebundenem Tetrahydrofuran oder eventueller oligomerer Einschlüsse zuzuschreiben ist.

Резюме — Были получены порошки полиамидной кислоты в гетерогенной фазе и в растворе тетрагидрофурана из диангидрида пиромеллитовой кислоты и 4,4-диаминдифенилового эфира. Имидизация этих порошков была исследована термогравиметрическим, калориметрическим и масс-спектрометрическим методами. Согласно данным ТГ и дифференциальной сканирующей калориметрии, температура начальной и максимальной скорости имидизации увеличивается с увеличением температуры и продолжительности имидизации. Найдена линейная зависимость между потерей веса и теплотой реакции имидизации. Теплота реакции, соответствующая единице потери веса, увеличивается с уменьшением молекулярного веса. Ангидриды дикарбоновых кислот, используемые в качестве обрывателей цепи, не оказывают заметного влияния на термические свойства полиамидных кислот. Найдено, что имидизация является сложным процессом, в котором кроме дегидроциклизации, также имеет место разложение полиамидных кислот. Кинетика имидизации удовлетворительно описывается реакцией дегидроциклизации первого порядка и параллельно протекающей реакцией разложения тоже первого порядка. Потеря веса при имидизации выше, чем потеря веса, вычисленного на основе реакции дегидроциклизации. Это должно быть обусловлено выделением продуктов разложения полиамидной кислоты, выделением сольватированного или закомплексированного тетрагидрофурана или выделением возможных олигомерных включений.