

PRODUCTION AND INVESTIGATION OF POLYIMIDES II

INVESTIGATION OF THE THERMAL IMIDIZATION OF POLYAMIDE ACIDS

By

K. BELINA, K. POLGÁR, O. BIRÓ and J. VARGA

Department of Plastics and Rubber, Technical University, Budapest

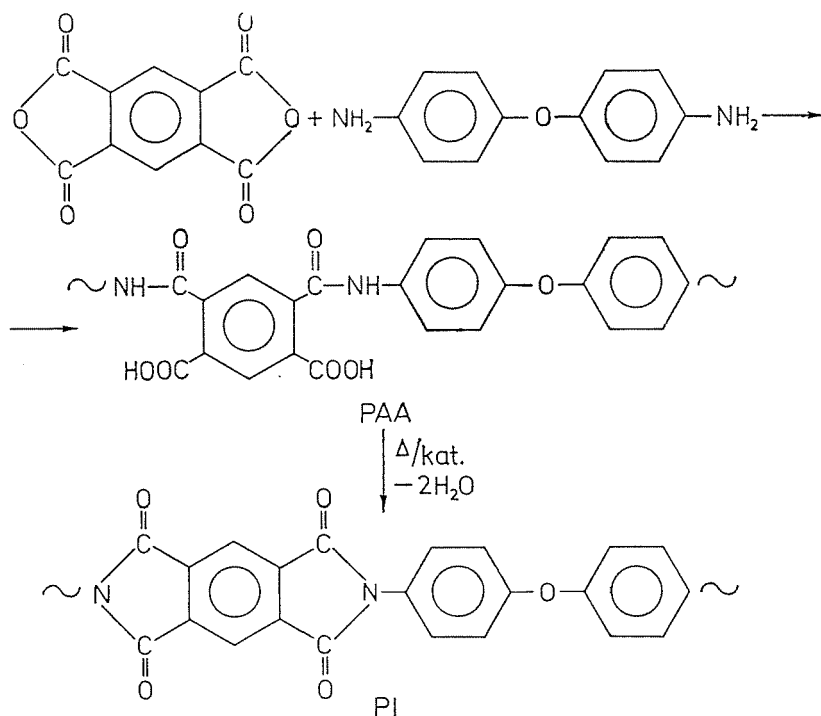
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Introduction

Among the thermo-stable polymers an outstanding place is taken by the aromatic polyimides which are produced by a two-step synthesis [1-5]. In the first step polyamide acids (PAA) are produced by the polyaddition reaction of diamines and dianhydrides in strongly polar solvents, then these polyamide acids transform into polyimides (PI) while water is leaving.

The imidization is carried out either by thermal or by catalytic method [1-9].



This paper intends to report on the simultaneous thermoanalytical and calorimetric (DSC) investigations of the thermal characteristics of PI-s derived from PAA-s of the thermal imidization of PAA-s produced in N-methyl-2-pyrrolidone (NMP) solution based on pyromellitic acid dianhydride (PMDA) and 4,4'-diaminodiphenylether (DAE). The effect of the solvent content of films as well as that of the terminal groups of PAA-s on the thermal characteristics (weight change due to the imidization, decomposition temperature of polyimides produced and that of the highest rate of ring closure reaction) has been studied. The optimal conditions for imidization reaction have been determined.

Experimental

The purification of PMDA and NMP, similarly to the production of resin solution, is dealt with in our previous paper [10]. The DAE was crystallized thrice from isopropyl alcohol. The characteristics of PAA-s used in our imidization examinations are summarized in Table 1.

Table 1
Characteristics of polyamide acid resin solutions examined

Sign of resin solution No.	Molar ratio PMDA/DAE	Viscosity, Ns/m ²
1	1.000	201.67
2	1.002	262.85
3	1.005	167.10
4	1.008	48.25
5	1.015	32.65
6	1.030	10.50
7	1.045	8.79
8	0.995	1266.00
9	0.985	128.50
10	0.980	25.55
11	0.971	12.04

To the experiments films made of PAA-s dissolved in NMP cast on a glass plate were applied which then were dried in horizontal position at room temperature.

The simultaneous thermal analysis was performed with derivatograph (MOM). The amount of material examined was about 120 mg. The experiments were carried out in streaming air atmosphere, the heating rate was 2.5°/min

in the temperature range 300 to 773 K. The enthalpy change owing to the imidization of PAA films was recorded by a differential scanning calorimeter produced by Perkin-Elmer, Model DSC-2 in streaming nitrogen atmosphere. Some 5 mg of the sample were taken and a heating rate of 10°/min was applied.

The tensile strength and modulus value were determined by a fibre tensile testing machine Chevenard MI-45. The test specimen was 15 mm in length and 3 mm in breadth.

Results and evaluation

The imidization conditions of PAA resin solutions have significant influence on the thermal, physicommechanical and other characteristics of the polyimides formed from them. Therefore, great attention should be directed to the parameters affecting the imidization reaction and to the determination of the optimal imidization conditions, as well. One important factor influencing the imidization process is the residual solvent content of the PAA films. The effect exerted upon the ring closure reaction of the solvent was investigated in PAA films dried at room temperature for different time periods. The duration of drying and the experimental results are given in Table 2.

Table 2

The effect of drying time on the thermal characteristics of PAA-s

Symbol of the PAA films	Duration of drying at room temp. (hour)	Δm %	T_{\max} K	T_0 K	T_{10} K	Note
1A	24	51	413	706	778	Second peak at 438 K
1B	72	37	413	676	743	Second peak at 435 K
1C	720	34	413	675	753	Breaking point at 431 K
1D	1440	31	418	674	748	—
1E	—	9.3	438	628	698	Extracted by acetone

Δm — weight loss measured during imidization process

T_0 — initial decomposition temperature of PI produced, determined from the TG curve

T_{10} — temperature of the 10% decomposition of PI

T_{\max} — temperature of the highest rate of imidization process

In Figs 1 and 2 the TG and DTA curves of PAA films containing different quantities of the solvent due to drying for different time periods are demonstrated. For comparison the data of a PAA film (1E) extracted by acetone are also given. (The denotation of the curves is similar to that in Table 2.)

Based on the thermoanalytical data (TG and DTA curves) of PAA films three phases can be observed in dependence of temperature. The DTA peak

and TG step observed at low temperature (between 313 and 383 K) are connected to the leave of humidity adsorbed by PAA and the polar solvent. The second phase taking place between 383 K and 503–553 K can be attributed to the imidization process. During the third phase (above 673 K) the intense thermal decomposition of polyimides produced in the course of imidization has

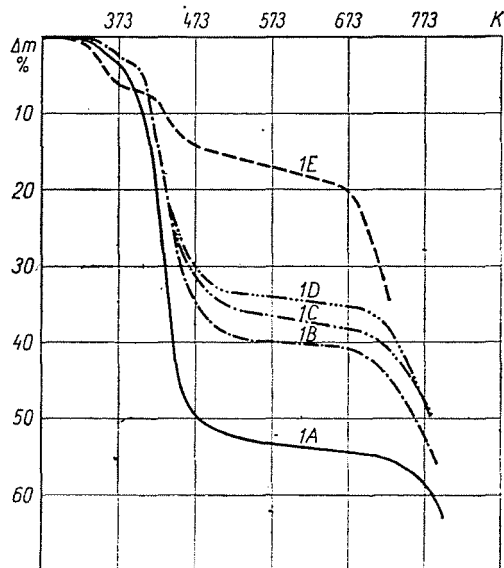


Fig. 1. TG curves of polyamide acid films extracted by acetone and dried for different times, resp.

taken place. The three phases are clearly visible on the sample denoted by 1E, while on samples 1A–1D the transition between the first and second phases is partially indistinct.

The thermogravimetric data provided by films (1A–1D) dried for different times show that in the second phase the weight loss significantly exceeds the 8.6% dehydration weight loss theoretically accompanying the transformation of PAA into polyimide. This proves the fact that the polyamide acid adsorbs a quite great quantity of solvent which cannot be removed totally by drying (“adsorbed solvent”). The 30 to 50% weight loss observed in the second phase is due to the fact that the adsorbed solvent is leaving simultaneously with the progress of the imidization process. Although by increasing the drying time, the weight loss decreases in the imidization step, however, following a 1440 hours drying its value remains still 31%. Considering the imidization weight loss, this corresponds to 22–23% adsorbed solvent content. Supposing that the *o*-carboxylic acid amide bonds are responsible for adsorbing the solvent

and one NMP molecule is connected to each monomer unit, the imidization degree calculated from the total weight loss is found to be 82%. This is in good agreement with the 80% value obtained by IR spectroscopy [7].

The 9.3% imidization weight loss of the practically solvent-free sample (1E) extracted by acetone stands close to the theoretical value.

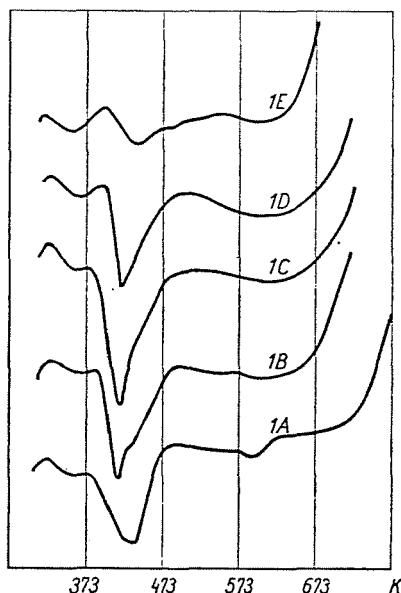


Fig. 2. DTA curves of polyamide acid films extracted by acetone and dried for different times

When the DTA curves are examined as a function of drying time, it can be stated unambiguously that the endothermal signal belonging to the second phase observed in the temperature range 383 to 503 K is varying. In the case of sample 1A the above signal has two maxima (413 and 438 K). By increasing the drying time, the second maximum is decreasing and the DTA curve of the sample 1C shows only a break at 431 K. The conclusion can be drawn that the first peak is due to the imidization and the second one to the leave of the azeotropic mixture of NMP and water (438 K) formed during imidization. When the drying time is long, the imidization peak appears at higher temperatures. In the case of the solvent-free 1E sample the DTA maximum is found at 438 K. As a consequence of the above data it can be noted that the imidization takes place more favourably in the presence of a solvent.

The drying time influences also the thermal stability of the polyimide produced what was characterized by the initial decomposition temperature (T_0) and by the temperature belonging to the 10% decomposition (T_{10}). Here,

the longer the drying time, the lower the thermal stability — contrary to the results obtained for dimethylformamide [8].

After drying the polyimides for 72 hours, their thermal stability practically does not change. The stability of polyimides formed from a film extracted by acetone is unexpectedly low.

A good comparison of the thermal stability of samples is provided by the value of T_{10} [9]. This temperature means a degree of degradation where the initial phase of decomposition has already finished, but the process is not yet at its highest rate. The sequence obtained by this evaluation corresponds to that got on the basis of T_0 .

In the temperature range between the second and third step of weight loss, the TG curves show a monotonous weight loss which increases to a small degree with the prolongation of the drying time. In the case of the 1E sample his weight loss was found to be extremely great (4%). In this temperature range a wide endothermal signal is observed on the DTA curves. The probable explanation of the process will be exposed later on.

The effect of the molecular weight and of the terminal groups upon the thermal characteristics of PAA films

In polyaddition and polycondensation reactions the mol weight of polymers can be regulated by the mol ratio of monomers. The component being in excess has namely a chain closing effect [10]. By changing the ratio of monomers PAA-s having anhydride or amine terminal groups of different mol weights can be produced. In Table 3 the results got by thermal examinations of PAA-s of different mol weights are summarized.

The TG and DTA curves of samples having anhydride terminal group (samples 2—7) are presented in Figs 3 and 4, while those of samples having amine terminal group (samples 8 to 11) in Figs 5 and 6.

The great weight loss occurring during imidization (22—23%) refers to a high quantity of adsorbed solvent contained in the dried films. The terminal groups have little effect upon the thermal stability (T_0 , T_{10}) of samples. The sequences prepared on the basis of both T_0 and T_{10} are in good agreement with each other. From the data it is clear that the thermal stability of resins having anhydride terminal group is higher compared to those having amine terminal group prepared under similar conditions. The thermal stability decreases in the sequence of the increasing monomer excess (decreasing mol weight). Considering this fact it can be concluded that the terminal groups have significant role in the decomposition processes. On the basis of the TG and DTA curves it is seen that imidization is followed by an endothermic process which is accompanied by monotonous weight loss. In our opinion, this phenomenon is due to two processes, on the one hand to further imidization, on the other hand to

Table 3

The effect of mol · weight and terminal groups on the imidization process

Symbol of PAA film	Δm %	T_{\max} K	T_0 K	T_{10} K	ΔH mJ/mg
1A	51	413	706	778	350
2	31	418	673	765	209
3	26	428	673	758	209
4	31	420	658	753	264
5	31	415	655	761	193
6	30	424	643	748	218
7	30	427	643	743	209
8	28	438	653	748	214
9	28	420	648	733	205
10	23	440	633	728	209
11	29	423	641	729	264

- Δm — weight loss measured during imidization process
 T_{\max} — temperature of the highest rate of imidization
 T_0 — initial decomposition temperature of PI
 T_{10} — temperature of the 10% decomposition of PI
 ΔH — enthalpy change of imidization process

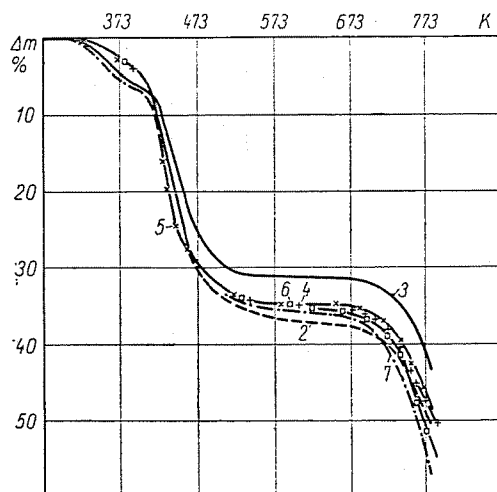


Fig. 3. TG curves of polyamide acid films having anhydride terminal groups

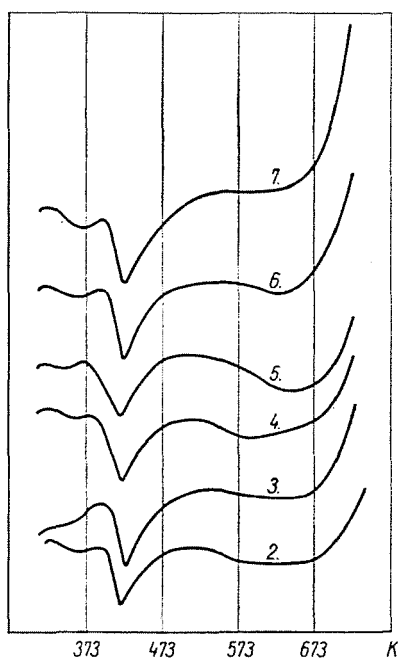


Fig. 4. DTA curves of polyamide acid films having anhydride terminal groups

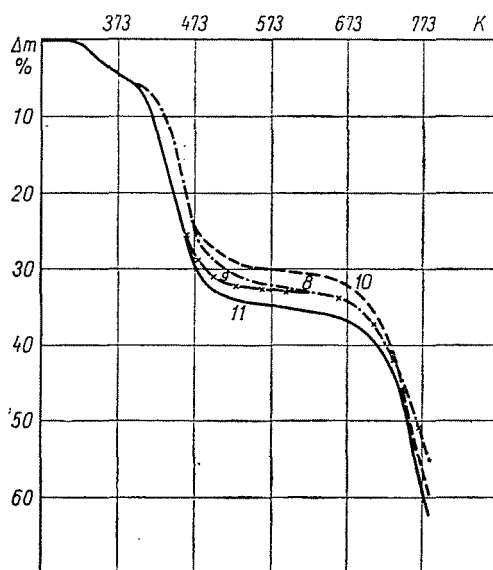


Fig. 5. TG curves of polyamide acid films having amine terminal groups

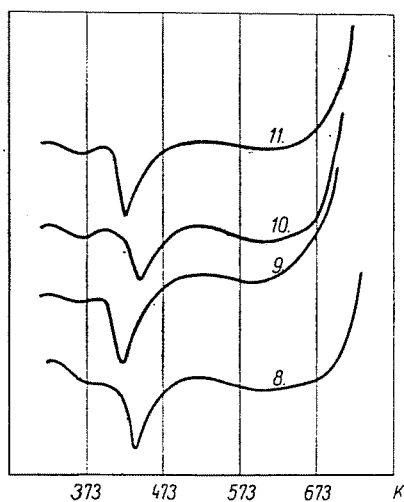


Fig. 6. DTA curves of polyamide acid films having amine terminal groups

the leave of products of low molecular weight present in PAA films (monomers, dimers, trimers). The latter hypothesis is supported by the fact that increasing the drying time the weight loss grows in this phase from 0.8% to 1.1%. It is well known [3] that the solutions of PAA are unstable, in the course of storage their viscosity lessens, caused by the hydrolysis of acid amide bonds (on the effect of the humidity of the surroundings or of the water formed during imidization). It can be concluded from the thermoanalytical investigations that the PAA films are essentially concentrated solutions, and can be regarded as plasticized systems containing about 20% solvent, thus in these films hydrolysis is also taking place. This decomposition process (decrease of the molecular weight) provides an explanation for the decrease of thermal stability for a longer drying time.

Determination of the optimal temperature of imidization reaction

The thermal, mechanical and other features of the forming polyimide are strongly influenced by the conditions of thermal imidization — the temperature and duration of thermal treatment. To determine the optimum conditions for imidization the PAA films have been thermally treated for different time intervals at temperatures 413 K, 493 K and 513 K, then based on the thermal analysis (TG and DTA curves) of the thermally treated samples the stage of imidization has been determined. The mechanical characteristics of the thermally treated films have been determined, too. As it is seen in Figs 7 and 8, and in Table 4, the imidization was not complete under the thermal conditions

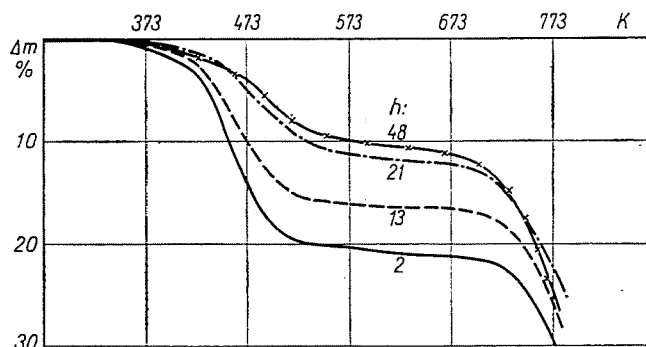


Fig. 7. TG curves of polyamide acid films treated thermally at 413 K

used; a certain degree of delayed imidization could be observed on the samples. With increasing temperature and duration of thermal treatment the weight loss corresponding to the delayed imidization is found to be less, and both the initial imidization temperature and that of the highest rate increases.

It is noteworthy that at a temperature of 413 K with a longer period of thermal treatment the thermal stability of the forming polyimide decreases, although its tensile strength increases.

Table 4

The effect of the temperature and duration of thermal treatment on the thermal and mechanical characteristics

Thermal treatment		Δm %	T_i K	T_{max} K	T_0 K	T_{10} K	σ N/mm ²	E N/mm ²
K	hour							
413	19	19	409	443	683	775	130	1810
	13	14	413	468	685	773	123	1741
	21	11	433	483	688	772	125	2129
	48	7	443	483	645	755	132	2178
493	0.17	18	373	443	678	783	103	1339
	0.5	3.7	448	505	683	765	124	1624
	2	3.0	498	—	678	766	—	—
513	10	1.7	535	—	678	762	132	2158
	0.25	5.5	453	510	693	788	137	1540
	0.5	1.8	573	—	693	783	160	2345

- Δm — weight loss between temperatures T_0 and T_i
 T_i — initial temperature of imidization process
 T_{max} — temperature of highest rate of imidization
 T_0 — initial decomposition temperature of PI
 T_{10} — temperature of the 10% decomposition of PI
 σ — tensile strength of the sample
 E — modulus of elasticity of the sample

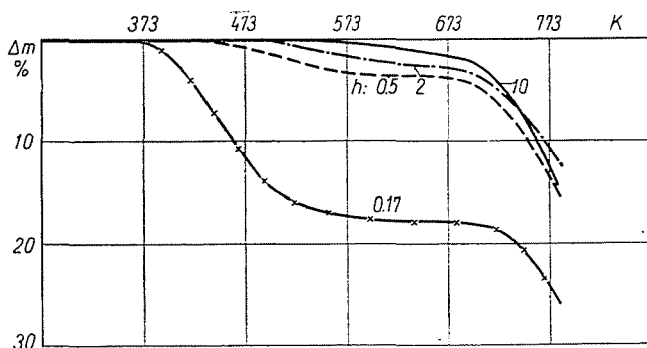


Fig. 8. TG curves of polyamide acid films treated thermally at 493 K

In the case of samples treated thermally at 493 and 513 K the beginning of decomposition of the forming polyimide is practically independent of the duration of the thermal treatment, while raising the temperature of the thermal treatment the beginning of decomposition is delayed.

The mechanical characteristics (tensile strength, modulus of elasticity) show unambiguous increase with the progress of imidization process. On the basis of the above statement the imidization is expedient to be carried out at high temperature.

Calorimetric measuring of imidization process

The enthalpy change determined calorimetrically (DSC) occurring in the course of imidization is given in Table 3. A characteristic DSC record is demonstrated in Fig. 9.

This record is very similar in character to the DTA curve obtained by simultaneous thermal analysis. Due to the more favourable resolution power of this method even in the case of extremely long time of drying, it can be shown that the imidization of films made of PAA resins is a complex process. After

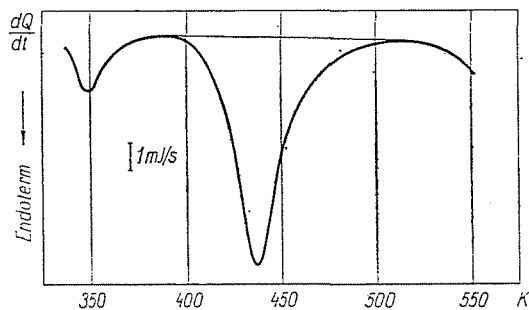


Fig. 9. DSC record of polyamide acid film

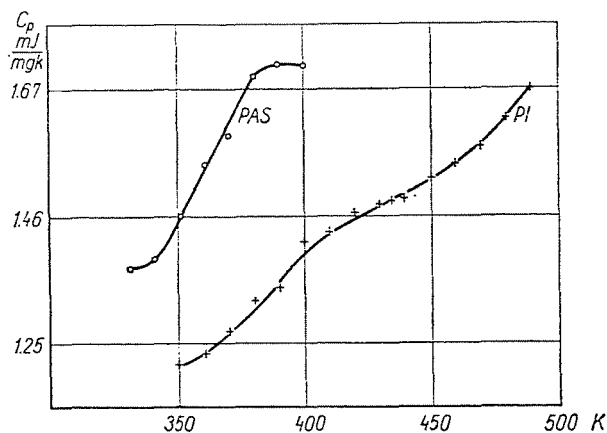


Fig. 10. The change of the specific heat of polyamide acid and polyimide as a function of temperature

several months of drying, a breaking point between 443 K—453 K can be observed on the DSC curves. Because of the complex character of the reaction the determined enthalpy changes include the heat of the dehydrocyclization reaction, as well as the enthalpy change deriving from the departure of the imidization water and the adsorbed solvent.

In addition, in DSC examinations a further problem is caused by the change of the specific heat appearing in the course of the reaction (Fig. 10), shifting the base-line of the DSC curve. The values of enthalpy changes given in Table 3 have been determined by means of the base-lines of Fig. 9.

Summary

The thermal imidization of polyamide acids produced from pyromellitic acid dianhydride and 4,4'-diaminodiphenyl ether in *N*-methyl-2-pyrrolidone is a composed process. The films prepared from resin solutions contain adsorbed solvent agent in great quantity, that leaves the system only during the imidization process. The solvent favourably influences the dehydrocyclization reaction and its removal impedes the imidization. The thermal stability of the forming polyimide is significantly influenced by the drying conditions of films. Increasing the drying time decreases the stability.

The thermal stability and decomposition of polyimides were found to be strongly dependent of the terminal groups. The thermal stability of polyimides having anhydride terminal group is better than of those having amine terminal group.

The value of enthalpy change occurring in the course of polyamide acid — polyimide reaction was determined by calorimetric (DSC) method. This enthalpy change includes the heat of the dehydrocyclization reaction and the enthalpy change deriving from the departure of the imidization water and the adsorbed solvent.

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Károly BELINA
Katalin POLGÁR
Dr. Odette BIRÓ
Dr. József VARCA

} H-1521 Budapest