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THERMOANALYTICAL INVESTIGATION OF THE ROLE OF THE SOLVENTS IN THE PREPARATION OF POLYIMIDE FILMS

YU. N. SAZANOV, G. N. FEDOROVA AND L. M. SHCHERBAKOVA
Institute of Macromolecular Compounds of the Academy of Sciences of the U.S.S.R., Leningrad (U.S.S.R.)
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ABSTRACT

Polyamido acid (PAA) synthesized from pyramellitic dianhydride and diaminodiphenyl-ether has been subjected to thermal analysis by a coupled simultaneous technique (TG, DTG, DTA, TVA). It was established that amide solvents—dimethyl formamide, dimethyl acetamide and N-methyl pyrrolidone—profoundly affect the process of transformation of PAA into polyimide (PI) and thermal characteristics of the latter. It was found that the thermal stability of PI depends on conditions of the preparation of PAA films (drying time and film thickness) and on the boiling point of the solvent. The necessity for a combined approach to the evaluation of thermal stability of PI is shown.

INTRODUCTION

One of the most important problems in the synthesis of polyimides is the choice of the solvent for the preparation of the prepolymer (polyamido acid) which strongly influences the properties of polyimide materials. Analysis of the literature shows that the most widespread solvents for this purpose are solvents of the amide type and that dimethyl formamide is the most widely used solvent among them[1–5]. As has been shown previously[6–7], this solvent actively interacts with the prepolymer and profoundly affects the thermal characteristics of polyimide. In this connection, it was of interest to investigate the behavior of other amide solvents, such as dimethyl acetamide and N-methyl pyrrolidone which are also used in the synthesis of polyimides and materials based on them.

EXPERIMENTAL

The following solvents were used for the preparation of polyamidoacid (PAA) and polyimide (PI): dimethyl formamide (DMF), dimethyl acetamide (DMA) and N-methyl pyrrolidone (MP). Initial materials for the preparation of PI were pyromellitic dianhydride and diaminodiphenyl ether. The methods for the purification of the solvents and initial reagents and the preparation of PAA solutions have been described previously[6]. The transformation of the PAA solution into PAA films with their subsequent thermal degradation at high temperatures was carried out with a

MOM derivatograph (Hungary) and a DuPont-990, TG-951 thermoanalyzer. For the preparation of PI films the PAA solution was applied to flat plate holders of the balance of these thermoanalyzers. In the course of the experiment the following parameters were continuously recorded: the change in the sample weight caused by film drying at room temperature, the transformation of PAA films into PI films by thermal dehydrocyclization of PAA and thermal degradation of PI at a constant rate of the temperature rise. Simultaneously DTA was used to record thermal effects accompanying these processes. Gas evolution was investigated with a TVA apparatus by a method described previously^5. The influence of the nature of the solvent, the thickness of the PI film and conditions of its preparation on its thermal characteristics were investigated and compared. Experimental conditions and data of thermal analysis are given in Table 1.

TABLE 1

CONDITIONS OF THERMOGRAVIMETRIC ANALYSIS OF PAA AND PI AND THERMAL CHARACTERISTICS OF PAA AND PI OBTAINED FROM TG DATA

Measurements were carried out with a MOM derivatograph (Hungary), the rate of the temperature rise was 12°C min^{-1}, a standard polyplate holder was used. Q is the ratio of the PAA film weight after a period of drying at room temperature to the weight of the PAA solution used for the preparation of the PAA film. R is the ratio of the weight loss of the sample on heating from 20 to 250°C to the weight loss of the sample on heating from 250°C to complete sample volatilization. T_0 is the temperature of the start of thermal degradation of PI determined from the beginning of the deviation of the TG curve from its horizontal position in TG.

Sample No.	*No. of plates in a holder*	*Film thickness (μm)*	*Drying time at room temp. (days)*	*Solvent*	Q	T_0	P
1	1	40	1	DMA	0.33	450	2.0
2		40	3	DMA	0.21	470	1.0
3		40	1	MP	0.85	460	6.0
4		40	3	MP	0.58	440	3.2
5		40	1	DMF	0.24	480	1.3
6		40	3	DMF	0.20	490	0.85
7	5	5	1	DMA	0.17	440	0.7
8	5	5	3	DMA	0.15	440	0.65
9	5	5	1	MP	0.80	400	5.4
10	5	5	3	MP	0.49	430	3.8
11	5	5	3	DMF	0.16	500	0.65
12	5	10	1	DMA	0.55	380	1.0
13	5		3	DMA	0.32	400	0.66
14	5		1	MP	0.88	380	6.1
15	5		3	MP	0.70	380	4.75
16	5		3	DMF	0.20	410	0.59
17	5	40	1	DMA	0.87	460	5.8
18	5	40	3	DMA	0.67	480	4.7
19	5	40	1	MP	0.96	470	7.5
20	5	40	3	MP	0.94	480	4.1
21	5	40	3	DMF	0.23	420	0.83

DISCUSSION OF RESULTS

For the convenience of discussion of results the numbering of the TG, DTA, DTG and TVA curves corresponds to numbers of experiments shown in Table 1.

(I) Drying of PAA films

After the PAA solution is applied to the plate holders of the balance of the thermoanalyzer, the evaporation of the solvent from the surface begins immediately at room temperature. The evaporation rate was determined from the weight loss of the sample; it depends on many factors, the most important of them are the thickness of the layer of the PAA solution, the rate of the removal of the solvent vapors from the surface and the partial pressure of the vapors depending on the nature of the solvent. Thus, Fig. 1 shows that as the film thickness and the boiling point of the solvent increase, the relative rate of the solvent removal decreases. It is also shown that the values of Q in the initial and final stages of film drying differ greatly. Moreover, it is seen that with increasing drying time the evaporation of the solvent completely stops, particularly with DMF. However, the minimum values of Q observed in the experiments are still higher than $Q = 0.125$ characterizing complete absence of the solvent in the PAA film. Thus, PAA films dried during 3 days still contain a certain amount of the solvent which depends on its nature and the film thickness. It was impossible to remove the residual solvent by the prolongation of the drying period at room temperature; this is evidently associated with the formation of a PAA crust on the film surface and with a general increase in the solvent viscosity. Therefore, it was attempted to attain a more complete removal of the solvent by increasing the rate of the withdrawal of solvent vapors from the film surface. It was achieved by passing a stream of helium or air over the film surface at different rates and also by using open

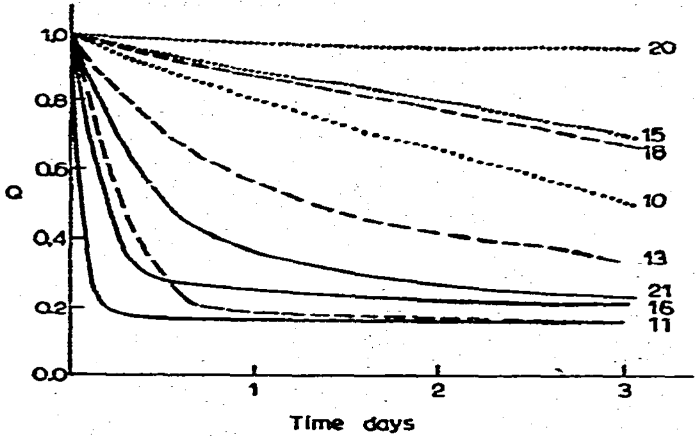


Fig. 1. Effect of drying time on the residual amount of the solvent in the PAA films. ———, DMF; — — —, DMA; ......, MP; Q, see Table 1.

plate holders in a static atmosphere (experiments 1–6). A comparison of values of Q for open and sectional plate holders shows that the evaporation from open surfaces takes place faster; nevertheless, in this case, too, the removal of the solvent stops before $Q = 0.125$ is attained. The effect of the flow-rate is shown in Table 2. As compared to film drying under static conditions the evaporation in a gas flow is more rapid but even in this case the solvent is not completely removed. The change in the gas flow-rate and the nature of the gas affect the value of Q only slightly. The evaporation of the solvent under vacuum gives good results but in this case the solvent forms bubbles during drying and this leads to film defects. Evidently, as has already been pointed out[6], it is necessary to dry PAA films under isothermal conditions at a high temperature or at a constant but rather slow rate of the temperature rise depending on the nature of the solvent and the film thickness.

TABLE 2

EFFECT OF THE RATE AND THE NATURE OF THE GAS FLOW IN TG OF PAA AND PI SAMPLES ON THEIR THERMAL CHARACTERISTICS

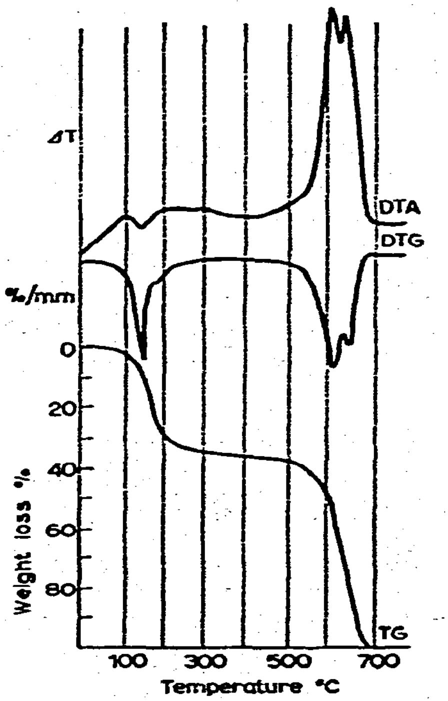
TG was carried out with a "Du Pont 990, TG-951" thermoanalyzer on a standard platinum pan at the rate of the temperature rise of 10°C min^{-1}. The thickness of the PAA film was 50 μm; drying time at room temperature was 6 h. The explanation of the symbols Q, R and T_0 is given in Table 1.

Solvent	*Gas*	*Gas flow-rate* (*cm^3 min^{-1}*)	Q	P	T_0 (°*C*)
DMF	air	150	0.22	0.51	455
DMF	helium	150	0.224	0.53	430
DMF	air	50	0.223	0.54	405
DMA	helium	50	0.284	0.76	425
Air	air	50	0.260	0.83	430
MP	air	150	0.810	5.80	440
Air	helium	150	0.840	6.00	435
Air	air	50	0.890	6.30	425

(2) *Analysis of samples at a constant rate of the temperature rise*

As mentioned above, after film drying for 1 or 3 days the film contains some residual solvent; its amount depends on the film thickness, the nature of the solvent and conditions of drying. When the dried PAA film is heated at a constant rate of the temperature rise, processes occurring in the film were recorded by a simultaneous TG–DTA method. When the temperature is raised from room temperature to 800°C, the PAA film undergoes the following typical transformations shown in Fig. 2. Immediately, after the beginning of heating, rapid weight loss of the film is observed with a maximum at 150–160°C. The weight loss is accompanied by a proportional endothermic effect. These effects reflect the process of the evaporation of the residual solvent from the film. Over the temperature range of 140–160°C endothermic transformation of PAA into PI occurs accompanied by water removal. This process is characterized by a pronounced change in the rate of the weight loss (as a rule, this change is clearly evident in the DTG curve) and by the superposition of the endothermic dehydrocyclization effect on the endothermic DTA peak of the evaporation of the solvent.

After PAA is transformed into PI, from 200°C up to the beginning of the thermal degradation of the PI film no great changes in the shape of the TG and DTA curves are observed with the exception of some special cases considered below. Thermal degradation of the PI film starts at temperatures in the range of 350–400°C and is marked in the TG curve by an accelerated weight loss until the sample is completely evaporated The degradation is accompanied by a considerable exothermic effect; as a rule there are two maxima at a temperature of about 600°C. Such is the



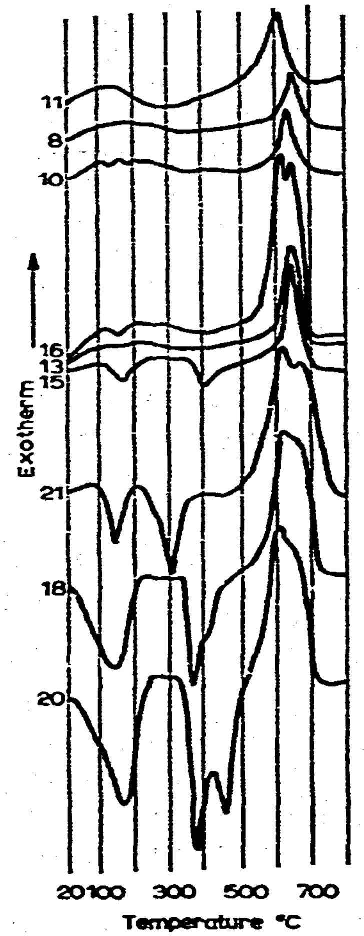


Fig. 2. TG, DTG and DTA curves for sample 16. Rate of the temperature rise, 12°C min^{-1}; feed, 50 mg; air flow-rate, 50 cm min^{-1}; sensitivity of DTA and DTG, 1/10; standard platinum polyplate holder; reference sample, aluminium oxide.

Fig. 3. Effect of thickness of the PAA film on thermal effects for PAA and PI. Conditions of DTA, see Fig. 2.

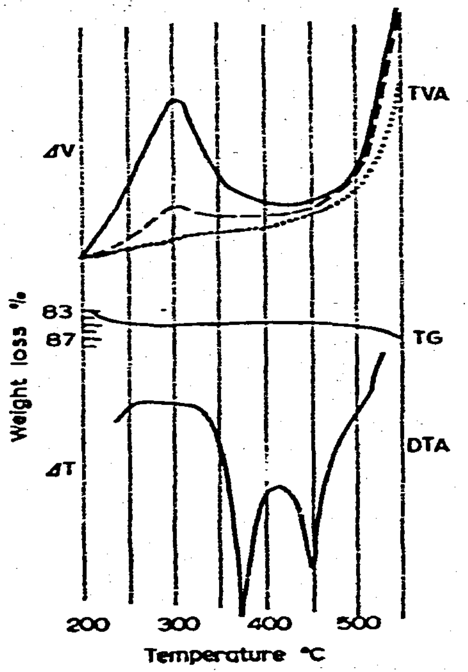
scheme of the process from 20 to 800°C characteristic of the transformation of the PAA solution in DMF. We can see the change in this scheme according to TG–DTA data when DMF is replaced by DMA or MP depending on the above parameters of the preparation of PAA films when we compare the DTA curves for samples shown in Table 1.

(*a*) *Effect of film thickness* Figure 3 shows that as the thickness of the PAA film increases, not only the quantity of heat absorbed or evolved but also the shapes of the DTA curves change with increasing temperature. Thus, for films of 40 μm thickness for all solvents not only the peak area greatly increases at 150°C as compared to thinner films but also new endothermic peaks appear at the temperature range of 350–450°C. In contrast to the first peak these thermal effects are not accompanied by a noticeable change in the sample weight (samples 18, 20, 21). It has been shown previously[5] taking as an example PAA in DMF that endothermic effects with a maximum at about 300°C (sample 21) correspond to the process of thermal degradation of residual DMF bound to the PAA structure and forming solvato-complexes. Their formation as a result of the interaction of the initial products of the PAA synthesis with amide solvents has been proved[8] and confirmed calorimetrically taking DMF as an example[7]. The use of the TVA method[9] showed that heat absorption over the temperature range of 350–450°C is accompanied by gas evolution clearly evident in the TVA curves. Figure 4 shows as an example the TG, DTA and TVA curves of sample 20 where in the TVA curve the peak at 300°C corresponding to the first endothermic effect is clearly seen. The difference in the temperature maxima of DTA and TVA peaks is caused by a difference in pressures in carrying out TG–DTA and TVA The second endothermic effect at 460°C is not accompanied by extreme gas evolution, nevertheless, the TVA curve shows that after [illegible]–70°C a new process of gas evolution begins at a considerably increased rate. In the TG curve this moment corresponds to the start of the weight loss directly after the temperature of the second DTA maximum. The character of TVA peaks indicates the presence of volatile compounds, such as products of high temperature degradation of solvents remaining in PI films.

It is noteworthy that the contents of the solvent in the sample is so low that its removal over the narrow temperature range considered does not cause any changes in the TG curve; only a combination of thermogravimetric investigations with DTA and TVA methods permitted the observation of this effect.

Thus, these data show that with increasing film thickness the effect of solvents on temperature characteristics of the film increases and favorable conditions are attained for the development of side processes at high temperature leading to degradation of PI films.

(*b*) *Effect of drying time.* Figure 1 shows that with the prolongation of film drying the content of the solvent decreases gradually approaching the limiting value *Q*. A comparison of the TG, DTA and TVA curves for samples with different drying time at room temperature shows that irrespective of the initial film thickness, the nature of the solvent or the method of drying, when the drying time increases, in the temperature range of 20–500°C, thermal effects decrease appreciably and sometimes even disappear, weight losses drop and gas evolution decreases As an illustration of the effect of drying time on the change in thermal effects we can compare the DTA curves for samples dried during 1 and 3 days: 1 and 2, 3 and 4, 5 and 6 (Fig. 5). It is clear that the increase in drying time leads to decreasing DTA peaks over the temperature range from 20 to 500°C; for MP the peak disappears at 400°C. A comparison of curves in Figs. 5 and 3 shows the combined importance of drying time and open surface of plate holder as compared to similar conditions when a closed holder is used.



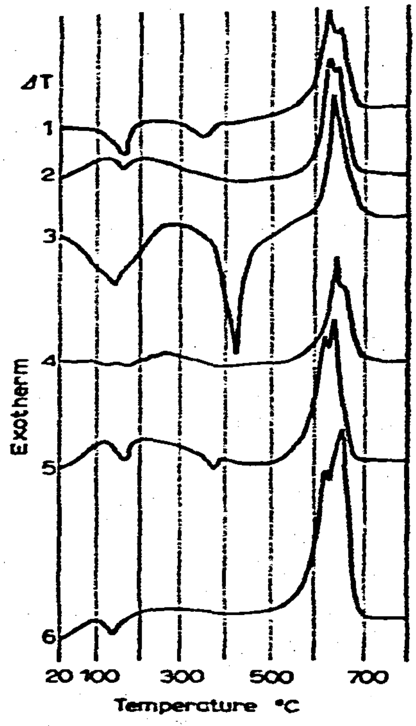
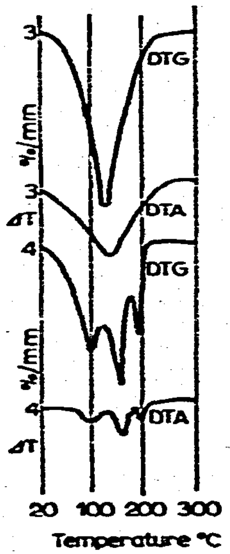


Fig. 4. TG, DTA and TVA curves for sample 20. Conditions of TG and DTA, see Fig. 2. TVA of the PAA film was carried out with sample 20 heated to 250°C according to TG conditions. ——— room temperature of the cooling trap; — — —, −75°, ..., −196°; vacuum 10^{-2} torr.

Fig. 5. Effect of heating time of the PAA films on thermal effects of PAA and PI. Conditions of DTA, see Fig. 2.

In some cases a decrease in the amount of the solvent in PAA films as a result of long drying time makes it possible to observe a distinct separation of records of processes occurring over a narrow temperature range. A comparison of the DTA and DTG curves of samples 3 and 4 (Fig. 6) is an example of this separation. Curves of sample 4 show distinct effects related to the evaporation of the solvent, dehydrocyclization and thermal degradation of the MP–PAA solvato-complex. In curves of sample 3 these effects are superimposed.

(*c*) *Effect of the nature of the solvent.* The investigation of the effect of the nature of the solvent on the process of the transformation of PAA into PI and the temperature characteristics of the latter show that DMF, DMA and MP have essentially the same effect on the properties of PAA and PI. Over the entire temperature range considered these solvents strongly influence the results of the thermal analysis of PAA and PI. After the PAA film is being heated at a regular rate, the evaporation rate of the solvent increases and its maximum approaches the boiling point of the solvent. Over the temperature range of 130–200°C dehydrocyclization of PAA and thermal degradation of the solvato-complex PAA-solvent are superimposed on the process of solvent evaporation. Depending on the amount of the solvent in the film the TG, DTG, DTA or TVA curves illustrate the overall effect with higher or lower resolution (Fig. 6). Over this temperature range the effect of the nature of the solvent becomes apparent only in different boiling points of these solvents and different temperatures of the degradation of solvato-complexes. This quantitative difference permits the separation of processes over this range according to the DTA and DTG curves (Fig. 7). Thus, the DTA curves show that as the boiling point of the solvent increases, the effects related to water removal as a result of the imidization of PAA and the effects of evaporation of the solvents and degradation of their solvato-complexes become more and more distinct in the curves.



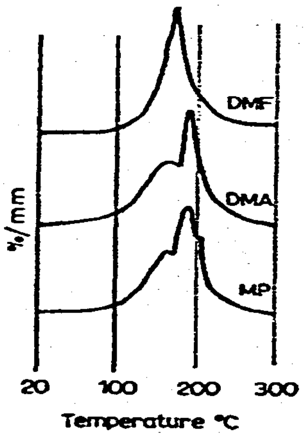


Fig. 6. DTA and DTG curves for samples 3 and 4. Conditions of DTA and TGA, see Fig. 2.

Fig. 7. DTG curves for PAA in different solvents. Curves were obtained with a DuPont thermoanalyzer at a heating rate of 10°C min^{-1}; feed, about 2 mg; sensitivity, 0.2; air flow-rate, 50 cm^3 min^{-1}.

Above 200°C the solvent influences thermal effects of PI depending on conditions of the film preparation (time of preparation, film thickness etc.). The above-mentioned gas evolution and accompanying endothermic effects over the temperature range of 320–450°C are virtually the beginning of PI degradation. This effect was observed for all solvents and the difference is only quantitative, i.e., for MP, a solvent with higher boiling point, these effects are more pronounced and are observed at higher temperatures (Fig. 2). In the stage of intense thermal degradation of PI it is difficult to estimate the effect of the nature of the solvent, since several successive degradation processes are superimposed. Nevertheless, in all DTA curves the exothermic effect accompanying thermal degradation of PI depends on the initial amount of the solvent in the PAA film.

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