

Thermoanalytical Investigation of Transformation of Polyamido Acid into Polyimide

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Synopsis

The effect of solvent and schedules of treatment of solutions of polyamido acid synthesized from diaminodiphenylic ether and pyromellitic dianhydride on its transformation into polyimide, and the effect on thermal characteristics of the latter, has been investigated by simultaneous thermogravimetric and differential thermal analysis. It was shown that dimethylformamide strongly affects the formation and properties of polyimide film. Optimum conditions of preparation of polyimide films were determined with the authors' taking into account the high reactivity of dimethylformamide. A possibility of using a water-acetone mixture as a medium for the preparation of polyimide films was shown.

INTRODUCTION

At present considerable attention is being directed to new methods for increasing the thermal stability of industrially manufactured polyimides.¹⁻⁵ A number of papers deal with various factors affecting their thermostability.⁶⁻⁹ Nevertheless, the role of the solvent, in particular of dimethylformamide (DMF), has not been elucidated in detail although DMF is nearly always used as a medium in the processes of polyimide formation starting from the interaction of diamine with tetracarboxylic dianhydride. Some aspects of the effect of DMF upon the kinetics of the formation of polyamido acid (PAA) have been shown earlier.^{10,11} But the part played by DMF in the process of the transformation of PAA into polyimide and its effect on the thermal stability of the latter have not yet been investigated, with one exception.¹²

The purpose of the present work was to study by simultaneous thermogravimetric analysis and differential thermal analysis (TGA-DTA) method the processes that occur in the PAA solutions depending upon the duration, temperature, and other technological parameters of their treatment.

EXPERIMENTAL

Preparation of PAA Solutions

Pyromellitic dianhydride and diaminodiphenylic ether carefully purified by sublimation under vacuum were used as initial reagents in equimolar ratios. DMF dried over 5A zeolite and distilled on a rectification column was used as the solvent; the fraction with bp of 58.0/20 was used. PAA was prepared by the method described by Adrowa and co-workers.¹ In order to investigate the

TABLE I
Conditions of Experiments and Data of Analysis According to TGA Curves

Exp. no.	Number of plates in the sample holder	Film thickness on 1 plate, μ	Drying time of PAA		Rate of temperature rise in dynamic TGA, $^{\circ}\text{C}/\text{min}$	Remarks ^a	T_0 , $^{\circ}\text{C}$	R_1 ^b	R_2 ^c
			solution, isothermal schedule, hr	in dynamic TGA, $^{\circ}\text{C}/\text{min}$					
1	1	40	120	12	12		500	0.50	0.25
2	1	40	72	12	12		490	0.50	0.27
3	1	40	24	12	12		480	0.65	0.30
4	1	40	0	1	1		440	8.00	0.088
5	5	5	72	12	12		380	0.37	0.25
6	5	10	72	12	12		410	0.54	0.33
7	5	40	120	12	12		440	0.64	0.21
8	5	40	5	5	5	drying at 80 $^{\circ}\text{C}$	440	0.09	0.091
9	5	40	72	1	1		460	0.83	0.15
10	5	40	72	12	12		420	1.20	0.71
11	5	40	72	12	12	the air flow in TGA, 100 ml/min	390	0.48	0.32
12	5	40	48	12	12		430	2.00	0.69
13	5	100	72	12	12		340	1.19	0.80
14	5	40	5	12	12	drying under vacuum (10 ⁻² mm Hg)	400	0.63	0.26
15	5	—	—	12	12	20 mg of powdered PAA	460	0.29	0.21
16	5	20	72 + 5 vacuum	12	12	film prepared on glass	400	0.33	0.28

^a For all experiments with the exception of No. 11, drying and heating were carried out without air flow.

^b $R_1 = (P_1/P_2)$ where P_1 is the weight loss up to T_0 , P_2 is the weight loss after T_0 .

^c $R_2 = (P_1 - P_0)/P_2$ where P_0 is the weight loss up to 152 $^{\circ}\text{C}$, T_0 is the temperature of the beginning of weight loss in thermal degradation of polyimide formed upon heating of the PAA film.

effect of the nature of the solvent on the transformation of PAA into polyimide, a water-acetone mixture was used instead of DMF. In this case, diamine solution in a water-acetone mixture (4% water by weight) was added dropwise to an acetone solution of dianhydride under stirring for 40 min. The reaction temperature was 13–15°; the concentration of the initial reagents was about 7.5%.

Preparation of PAA Film

The solution of PAA in DMF of about 0.4 was poured on a glass plate and dried in a thermostat at room temperature for 72 hr and then under vacuum (10^{-2} – 10^{-3} mm Hg) for 4 hr. The films were about 20 μ thick. When the water-acetone mixture was used as solvent, the film on the glass plate was dried at room temperature for 30 min. For determination of the kinetics of the removal of the solvent (DMF) from the film, the PAA solution was poured on the plates of a polyplate holder of a MOM Derivatograph (manufactured in Hungary). The thickness of the PAA films was varied from 5 to 100 μ .

Preparation of Powdered PAA

A dilute PAA solution in DMF (2% concentration) with addition of tetrahydrofuran was added dropwise to toluene under stirring. The precipitated PAA was filtered off, repeatedly washed with dry ether, and dried under vacuum at room temperature for 2 days.

Thermal Analysis

The process of transformation of PAA into polyimide and its subsequent thermal degradation was followed by using the results of simultaneous TGA and DTA carried out with a Derivatograph. The following parameters were determined in the experiments:

1. The run of the TGA curve in the course of DMF evaporation at constant temperature as a function of the time of exposure and the thickness of the PAA films;
2. The run of the TGA and DTA curves when the temperature was linearly increased at a rate of 1° and 12°C/min up to 900°C both for the PAA solution and for the PAA film of different thicknesses (5, 10, 40, and 100 μ) obtained at different drying times (from 24 to 120 hr). In the course of dynamic TGA and DTA, the effect of other factors on the run of the curves was determined (see "Remarks," in Table I).

RESULTS AND DISCUSSION

For convenience in discussing the results, the data of experiments and the main parameters determined and calculated from the TGA curves are summarized in Table I. The numbers of the TGA and DTA curves in the figures correspond to the experiment numbers as given in Table I.

Removal of DMF by Using Isothermal Schedule of Drying of PAA Films

Figure 1 shows the examples of the TGA curves characterizing the kinetics of DMF removal from the PAA solution as a function of the thickness of the layer and of the conditions of solvent evaporation.

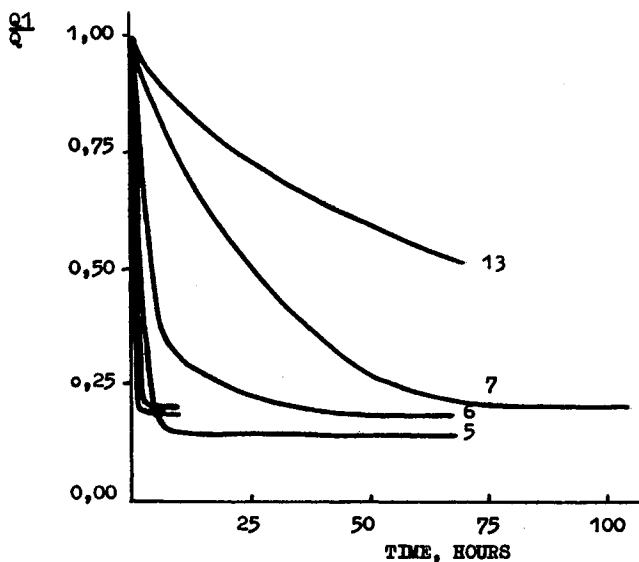


Fig. 1. TGA curves for isothermal drying of samples 5-8, 13, and 14. Q = Weight of the sample. Q_1 = Weight of evaporated DMF.

Thus, the comparison of curves 5, 6, 7, and 13 shows that as the thickness of the initial layer of the PAA solution increases, the time required for the removal of equal specific amounts of DMF increases. Moreover, the amount of the solution retained by the PAA film increases too, although the drying period is longer.

The change in the schedule of DMF removal in films drying at high temperature (curve 8) or under vacuum (curve 14) leads to a marked increase in the rate of DMF evaporation from the film. However, it should be noted that even the most favorable conditions promoting maximum DMF evaporation do not result in complete removal of the solvent and that its residual amount is not lower than 5 to 8% of the weight of PAA. These data show that DMF interacts with PAA and that evidently, as a result, a part of the solvent molecules remains chemically or physically bonded with the PAA macromolecules. The existence of such bonds in the stage of formation of PAA in DMF solutions has already been reported.¹⁰ Probably, these bonds are relatively strong and the usual methods for the removal of the solvent from the polymer film are not sufficient in the case of DMF. The residual DMF markedly affects the process of transformation of PAA into polyimide and the thermal characteristics of the polyimide film as shown by the results of dynamic thermal analysis.

Effect of Drying Time on PAA Films

Figures 2 and 3 show TGA and DTA curves for samples 1-4. These films were prepared on one open plate of a polyplate holder of a Derivatograph and dried during different periods of time.

The TGA curves, which are also typical of other PAA samples shown in Table I, exhibit a two-stage process of weight loss of the sample. The first stage, in the temperature range from 20° to 200°C, corresponds to weight losses related to the removal of the residual solvent and to the removal of the water formed as a result of

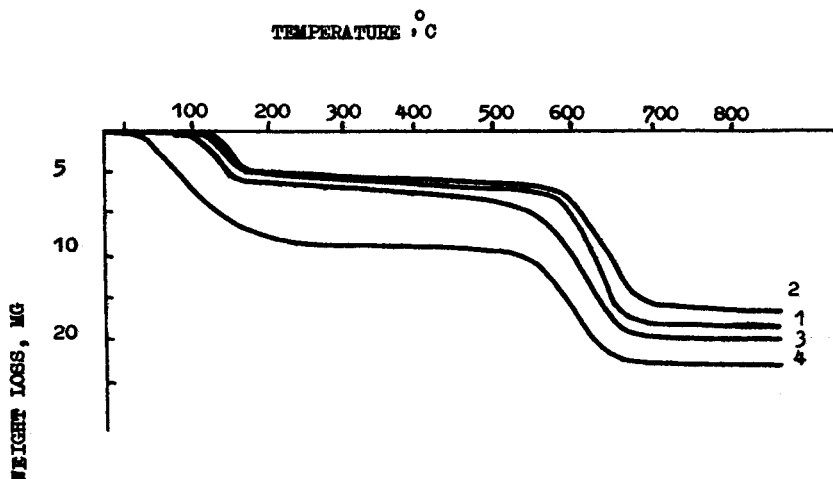


Fig. 2. TGA curves for samples 1-4.

the transformation of PAA into polyimide. The second stage, in the temperature range from 350° to 700°C, shows the weight loss of the polymer as a result of its thermal degradation, which mostly consists of two or more successive, superimposed reactions. The ratio of the weight losses in these two stages (R_1 and R_2) may serve as a criterion of the effect of DMF and methods of its removal on the properties of polyimide film and the picture of its thermal degradation.

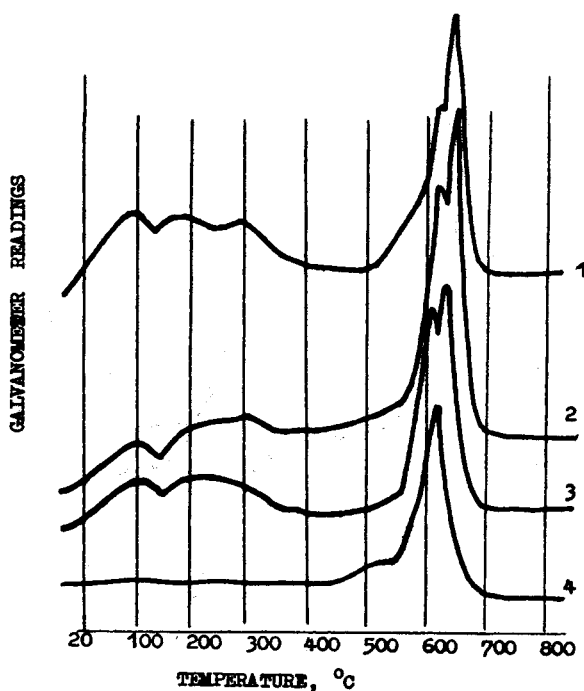


Fig. 3. DTA curves for samples 1-4.

Consideration of the first stage of weight loss in samples 1-4 shows that the increase in drying time of the PAA film at room temperature contributes to further removal of DMF. Nevertheless, after 72 hr the R_1 value remains virtually unchanged. Under these conditions the change in this value is very pronounced during the first 8 to 10 hr of drying. High effect is attained when the temperature of exposure of the PAA film is slowly raised. This is illustrated by sample 4, for which the R_2 value of 0.088 corresponds to the amount of water isolated in the course of transformation of PAA into polyimide. (Weight loss of the PAA sample resulting from the water isolated during dehydrocyclization of PAA may vary from 4.5 to 9.4% when the degree of polycondensation is changed from 1 to 10 $^\circ$.) Moreover, this effect is achieved without preliminary film drying at room temperature. The change in the drying schedule is also noticeable in the DTA curve for sample 4 (see Fig. 3) which does not exhibit the endothermic peak with a maximum at 155-160 $^\circ$ C, showing the overall effect of isolation of DMF and water. The exothermic peak of polyimide degradation exhibits only one maximum at 630 $^\circ$ C, unlike the exo-effect of most other PAA samples which show two or more maxima. DTA curves of samples 1 and 2 show small exothermic effect with maxima near 300 $^\circ$ C, their nature is discussed below. The thermal stability of polyimides formed under these conditions and determined by T_0 is high and changes in the same direction as the drying time of PAA films.

Effect of Thickness of PAA Films

Data in Table I and Figures 4 and 5 show that under the same conditions of thermal treatment of the film the R_1 and R_2 values noticeably increase with the

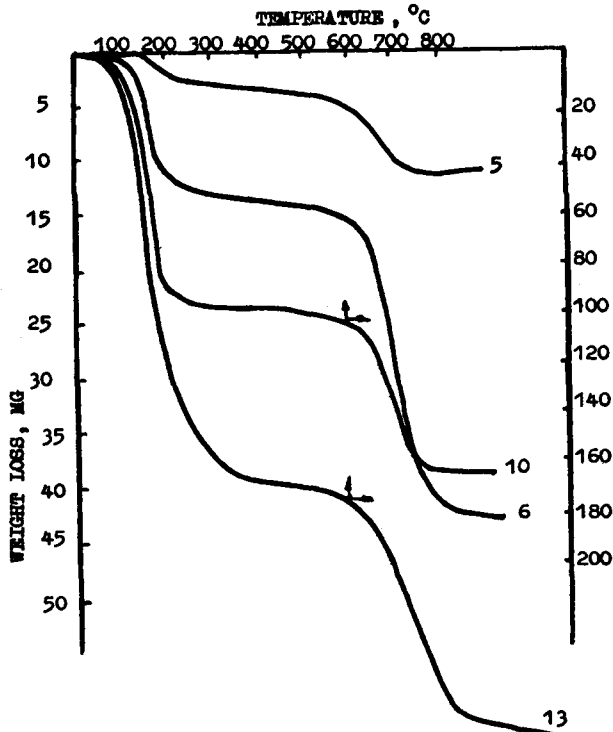


Fig. 4. TGA curves for samples 5, 6, 10, and 13.

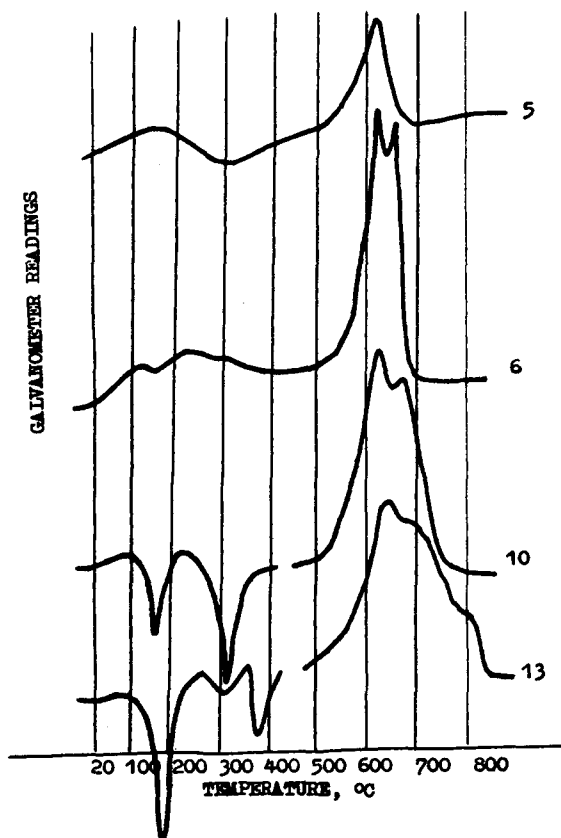


Fig. 5. DTA curves for samples 5, 6, 10, and 13.

film thickness, whereas the increase in drying time at room temperature (with the exception of sample 13) does not lead to further removal of DMF. The DTA curve of sample 5 shows clearly that in a thin PAA film the removal of residual DMF proceeds without any pronounced thermal effects before the start of thermal degradation of the polyimide formed. Exothermic effect of the thermal degradation of polyimide with one maximum similar to degradation of sample 4 confirms the absence of the effect of DMF upon this process.

The increase in the film thickness and the corresponding increase in its DMF content lead to proportional increase in the area of the first peak and the appearance of the second maximum at 670°C in the peak of thermal degradation of polyimide (sample 6) with subsequent complication of this process in the final stages of pyrolysis (sample 13). Special attention should be drawn to the very pronounced peaks in films 40 and 100 μ thick with a maximum at 300°C characteristic of sample 10 and particularly of sample 13. When the latter was heated, distinct endo- and exo-effects appeared at 300°, 350°, and 400°C. A faint effect at 300°C is also observed in the DTA curve of sample 6 and, as mentioned above, for samples 1 and 2. The peculiarity of these thermal effects is that they are not accompanied by any pronounced weight changes of the sample at these temperatures. As has been shown previously by the TVA method¹² and confirmed by chromatograms at a temperature of about 300°C,

considerable evolution of gaseous products of the thermal degradation of DMF is observed. Since this may be the result of decomposition of small weight amounts of DMF remaining in the PAA or polyimide film, no appreciable weight change of the sample is observed. Nevertheless, thermal effects confirm the occurrence of this phenomenon. Thus, the bonds between DMF molecules and PAA are of different nature and different strength. As a consequence of this, the apparently simple process of DMF removal from the PAA film is in fact a complex multistep process governing to a large extent the properties of polyimide articles.

Effect of Special Conditions of Treatment of PAA Film

In order to establish conditions ensuring maximum removal of DMF from PAA some changes in the standard conditions of the preparation and thermal treatment of PAA films were made. Figures 6 and 7 show TGA and DTA curves for some samples for which the preparation schedules are presented in Table I. A comparison of the R_1 and R_2 values shows that the most pronounced effect of DMF removal was observed when the PAA film was previously heated at temperatures up to 100°C (samples 8 and 9). Preliminary DMF removal under vacuum gives great time economy (sample 14); the use of vacuum at the

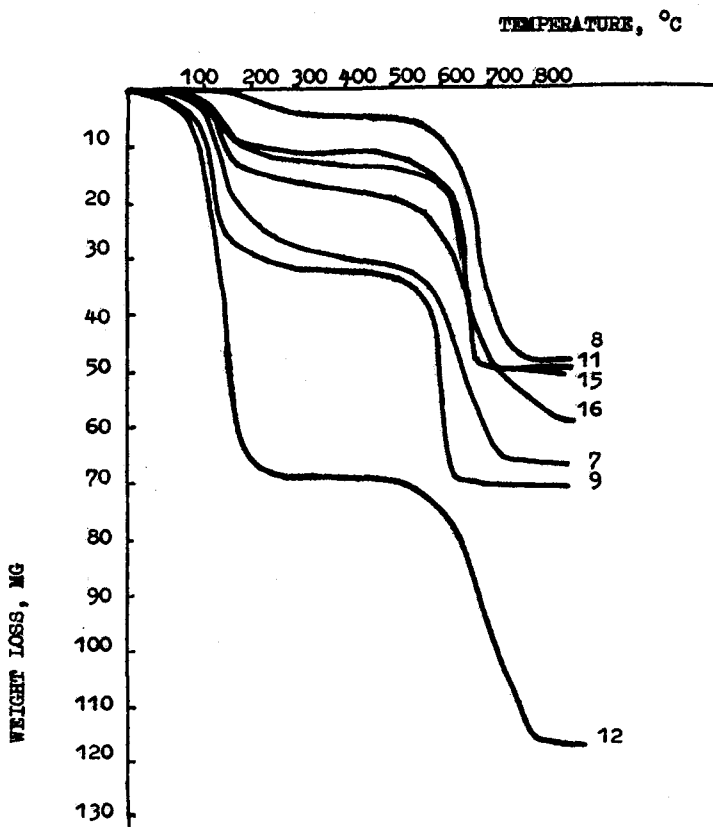


Fig. 6. TGA curves for samples 7-9, 11, 12, 15, and 16.

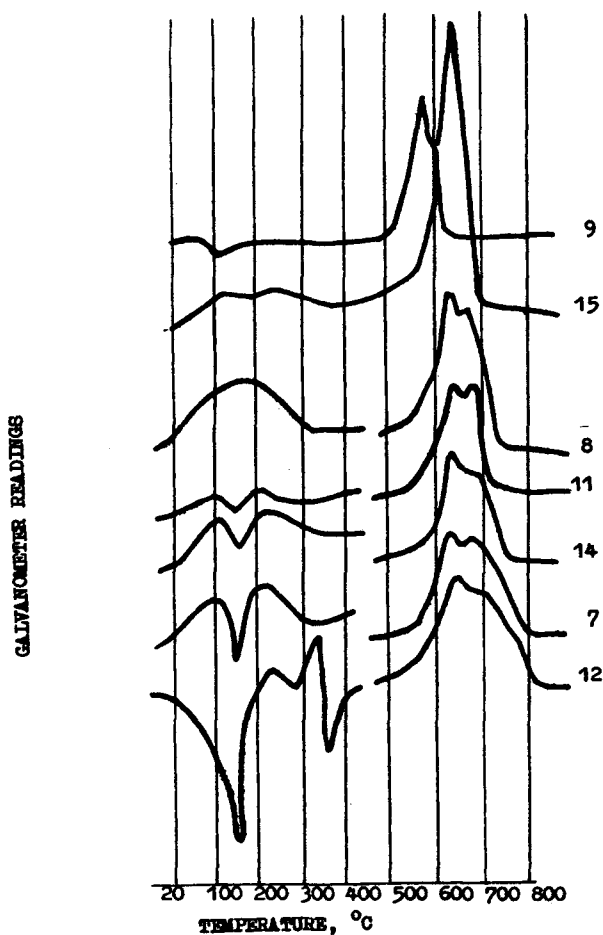


Fig. 7. DTA curves for samples 7-9, 11, 12, 15, and 16.

end of drying also decreases the R_1 and R_2 values (sample 16). The DTA curves of these samples do not show any thermal effects associated with thermal degradation of residual DMF at 300°C. Sample 12, which is comparable to sample 10 but was not so well dried, is an exception. However, the presence of a double peak of thermal degradation of polyimide with the exception of powdered PAA (sample 15) proves that even under these conditions DMF influences the formation of polyimide. Evidently, this influence is felt even in the early stages of PAA transformation into polyimide, particularly when DMF residues are removed at high temperatures (sample 8).

PAA Film Prepared from the Water-Acetone Mixture

Figure 8 shows the TGA and DTA curves for the PAA film prepared from the water-acetone mixture. The TGA curve shows that up to 145°C there is a linear weight loss of about 5%, evidently caused by the removal of the residual solvent. Then PAA is transformed into polyimide; this process is accompanied by the increase in the rate of weight loss and the appearance of endothermic effect with a maximum at about 200°C. Thermal degradation of the polyimide

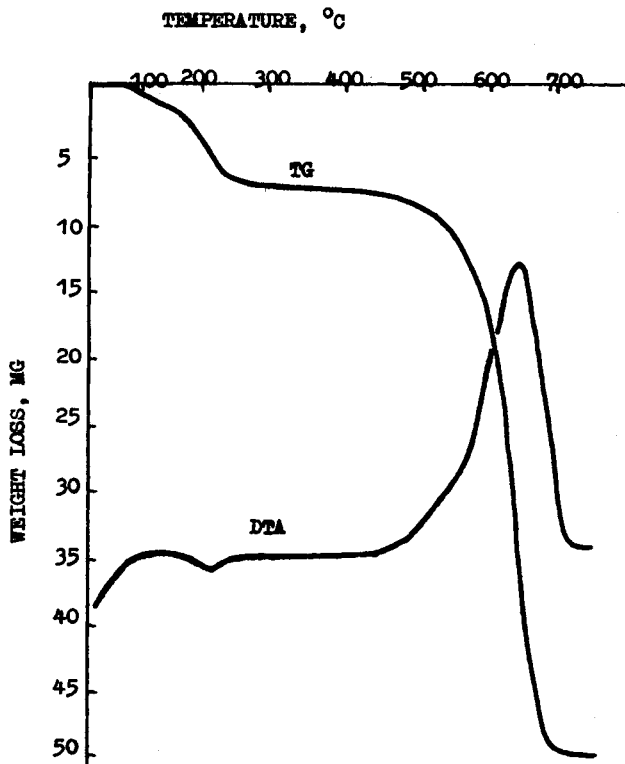


Fig. 8. DTA-TGA curves for PAA samples obtained in a water-acetone mixture.

formed starts at about 420°C, and the exothermic effect exhibits one maximum at a temperature of 620°C.

CONCLUSIONS

These experiments show that the process of PAA transformation into polyimide, and the thermal characteristics of polyimide synthesized from pyromellitic dianhydride and diaminophenylic ether largely determining the properties of films and coatings made from this polymer, depend on the nature of the solvent. At present DMF is widely used for synthesis of PAA and its transformation into polyimide, but its use requires a well-developed technological schedule for ensuring maximum removal of DMF from the PAA films and taking into account the peculiarities of the interaction of DMF with the PAA macromolecules. Chemical interaction of DMF with reactive PAA groups cannot be ruled out, and the nature of this phenomenon will be considered in subsequent papers.

In our opinion, one optimum method for obtaining polyimide films of high quality from PAA solution in DMF is the preparation of films not more than 5 to 7 μ thick, with preliminary drying at 40–60°C and dehydrocyclization by raising the temperature slowly to 180–200°C.

From the industrial standpoint, the replacement of DMF by a less reactive medium for the preparation of polyimide films is more promising.

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Received June 26, 1974

Revised November 15, 1974