The Effluent Analysis of Several Pyrrone and Polyimide Precursors During Cyclization

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Synopsis

A study was conducted to determine the degree of cyclization occurring in a series of four pyrrone and two polyimide prepolymers. These materials were heated from 25° to 400°C at 2°C/min in a helium atmosphere, and the effluent was sampled at regular intervals by a gas chromatograph/mass spectrometer technique. Quantitative analysis of this effluent indicated that the pyrrone polymers were less than 80% converted under these conditions while the polyimides were essentially fully converted. Significant amounts of carbon dioxide were found to be eliminated as the pyrrone polymers cured. This evolution was attributed to the loss of carbon dioxide from intermediate stages during cure and, in some cases, to the decarboxylation of unreacted groups. Support data obtained on model compounds are also presented.

INTRODUCTION

Stepladder and ladder polymers based on the polymerization of aromatic five-membered ring dianhydrides with bis(o-diamines) have been reported.[1–6] These polymers are commonly referred to as pyrrones. They are usually prepared in solution at room temperature, either precipitated or cast as films, and then given thermal treatment to effect cyclization. Water is eliminated during this cyclization:

dianhydride   bis(o-diamine)   amide-acid-amine   precursor
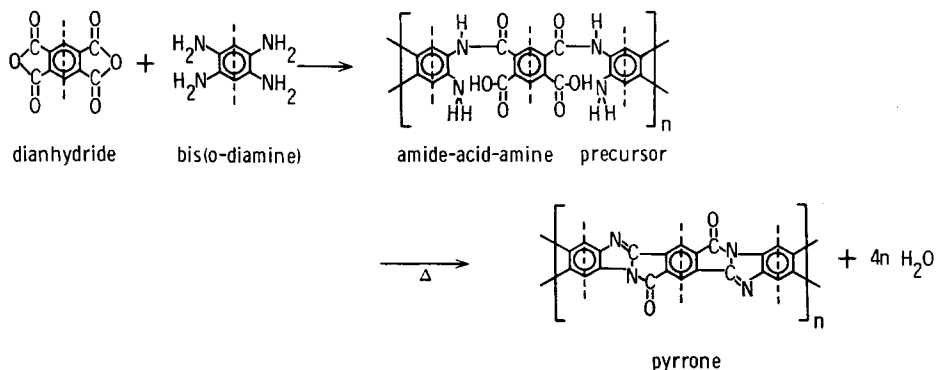
pyrrone

Initially, pyrrones were expected to possess unusual thermal properties since two bonds in the same ring had to be broken for loss of polymer integrity compared to only one bond for most other polymer systems. Despite these expec-

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tations, pyrrones did not always live up to their anticipated thermo-oxidaive stability. A possible explanation to be considered was the likelihood that the amide-acid-amine was not completely cyclodehydrated to the theoretical pyrrone structure. With few exceptions,[7,8] little quantitative information was available on this cyclodehydration of the precursor through various intermediate stages en route to pyrrone. The present investigation was made to provide an insight into these cyclization reactions.

The degree of ring closure should be readily determined by measuring the amount of water eliminated as the polymer is cured. An earlier model compound study involving stepwise thermal treatment and gas-chromatographic analysis for water verified that this approach could provide meaningful information.[9] However, this earlier study also indicated that reactions other than simple cyclodehydration were occurring and that a more complete analysis of the effluents was needed. Therefore, the present study employed an improved gas-chromatographic/mass-spectrometric technique and provided a quantitative identification of all major effluents as a function of cure temperature for a series of pyrrone precursors. Two polyimide precursors were included for comparison. Model compounds were also run under identical conditions for correlation with polymer results.

EXPERIMENTAL

Model Compounds

The synthesis and characterization of model compounds used in this study have been reported elsewhere.[10,11] They were prepared by reacting phthalic anhydride (PA) or pyromellitic dianhydride (PMDA) with o-phenylenediamine (OPD) in aprotic solvents. Each was synthesized to represent a portion of the polymer repeat unit at various stages of cyclization. The structures of these compounds are given below:
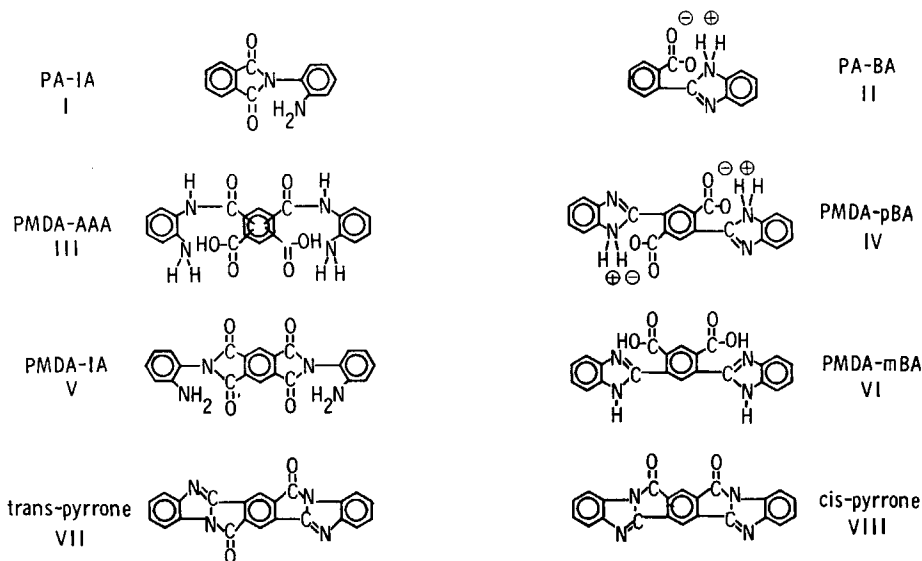
All compounds were isomerically pure, except the PMDA-OPD amide-acid-amine III which was a mixture of meta and para isomers.

Polymers

The four pyrrone precursors were prepared by the polymerization of two dianhydrides, pyromellitic dianhydride (PMDA) and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), with each of two tetraamines, 3,3′-diaminobenzidine (DAB) and 3,3′,4,4′-tetraaminobenzophenone (TABP). For comparison, two polyimide precursors were also prepared using PMDA and BTDA with 4,4′-diaminodiphenyl ether (DADPO). The polymerizations were conducted at room temperature in N,N-dimethylacetamide (DMAc) using procedures reported elsewhere.[12,13] Table I gives the inherent viscosity of each polymer solution. The products were precipitated into methanol and the resultant powders were vacuum dried for 18 hr at room temperature and stored in a desiccator until used. Theoretical repeat units of the six polymers are given below; each is presumed to be a mixture of isomers:
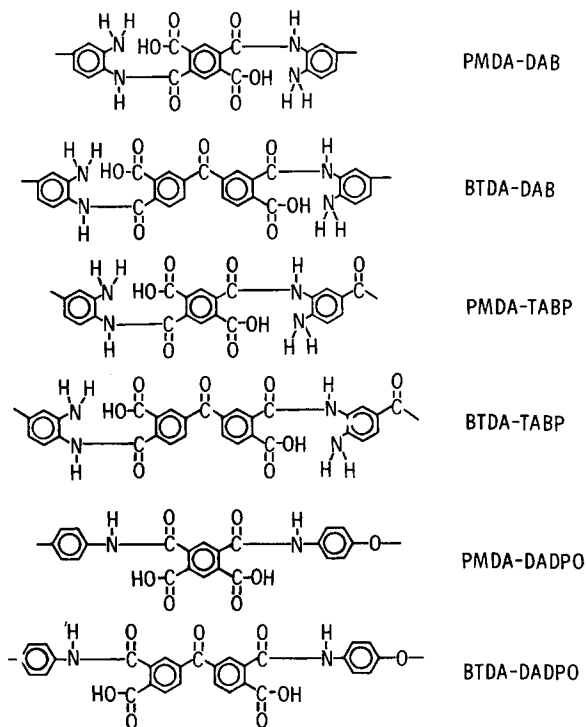

PMDA-DAB

BTDA-DAB

PMDA-TABP

BTDA-TABP

PMDA-DADPO

BTDA-DADPO

TABLE I
Solution Viscosity of Test Materials

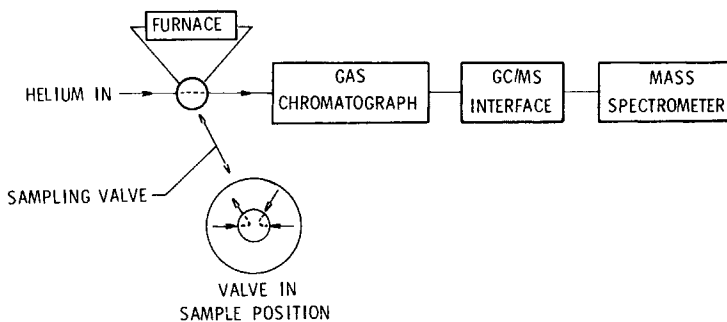| Precursor polymer	Inherent viscosity 0.5% DMAc, 35°C[a]
PMDA-TABP	0.57
PMDA-DAB	0.81
BTDA-TABP	0.36
BTDA-DAB	0.56
PMDA-DADPO	1.55
BTDA-DADPO	0.95

[a] DMAc = N,N-Dimethylacetamide.

Fig. 1. Schematic of gas analysis system.

Test Procedure

A schematic of the experimental equipment used for analysis of the gaseous effluents is shown in Figure 1. The equipment was composed of a furnace assembly for heating the sample materials, an automatic sampling valve for periodic sampling of the furnace atmosphere, and a tandem gas chromatograph/mass spectrometer with interface for removal of helium carrier gas. The individual sample materials were retained between porous plugs of quartz fibers in 0.457-cm-I.D., 15.2-cm-long stainless steel furnace tubes. Each furnace tube was cleaned prior to use by heating under vacuum to 800°C and stored in a desiccator at ambient temperature. The quartz fibers were cleaned in a vacuum furnace and also stored in a desiccator until used. Tests with the system using blank sample tubes (no sample) indicated no significant background changes between ambient and 400°C when the sample tubes were cleaned in this manner.

The sample mass was determined to the nearest 0.1 mg in the furnace tube, and the tube was placed in the furnace with a helium carrier purge for a minimum of 1 hr before the test was started. The sample mass for each test was about 5 mg.

In operation, the sample furnace was programmed from ambient to 400°C at a rate of 2°C/min. The automatic sampling valve (schematic, Fig. 1), normally kept in the bypass position, was switched to the sample position for 15 sec every 8 min (valve sample position shown in inset of Fig. 1). This sample time allowed for a complete purge of all tubing between the furnace and sampling valve. In order to prevent condensation, all tubing and connections between the valve, furnace, and chromatograph were wrapped with heating tape and insulation to maintain these parts at 175°C.

A Varian Model 1800 gas chromatograph containing a thermal conductivity detector was employed for effluent detection. For all tests, the detector current was 200 mA and the helium carrier flow rate was 18 cc/min. A Waters Associates Porapak Q column, 0.238 cm I.D. by 90 cm and maintained at 80°C, was used for product separation. The column and chromatograph were calibrated for quantitative analysis of the gaseous products of interest by injecting known quantities of each identified product into the instrument and noting the detector response. Each peak observed on the chromatogram was identified from mass spectra obtained on an EAI Quad 250 B mass spectrometer connected through an interface to the gas chromatograph. The mass spectrometer had a range of 1 to 500 amu and was always operated at 10^{-6} torr.

RESULTS AND DISCUSSION

Preliminary experiments showed that water and carbon dioxide were the two major effluents given off during the curing process of both the models and polymers. The chromatographic conditions which yielded quantitative data on these were then determined and optimized.

The total amounts of water and carbon dioxide yielded by each model compound and polymer are given in Tables II and III, respectively. The results are normalized to a 10-mg test specimen. The next-to-last column in the tables, the percent conversion, is the ratio of observed water to the theoretical amount of water which should be eliminated after complete cyclization. The progress of the cyclization reactions was followed by plotting observed water versus temperature. These data are given for the model compounds in Figures 2 and 4, the four pyrrone precursors in Figure 6, and the polyimide precursors in Figure 8. Similar data for the elimination of carbon dioxide from the model compounds are given in Figures 3 and 5. Data for the elimination of carbon dioxide from the pyrrone and polyimide precursors are given in Figures 7 and 9, respectively.

Model Compounds

Except for the PMDA-mBA (VI) model, Table II shows that none of the PMDA or PA model compounds achieved essentially complete cyclodehydration

TABLE II
Results of Effluent Analysis on Model Compounds

Model compound	MW	Calculated[a] H_2O, mg	Observed H_2O, mg	Conver- sion,[b] %	Observed CO_2, mg
PA-IA (I)	238.25	0.76	0.67	89	0.03
PA-BA (II)	238.25	0.76	0.67	89	0.04
PMDA-AAA (III)	434.41	1.66	1.29	78	0.11
PMDA-pBA (IV)	398.38	0.90	0.68	75	0.35
PMDA-IA (V)	398.38	0.90	0.77	85	0.19
PMDA-mBA (VI)	398.38	0.90	0.87	96	0.06
trans-Pyrrone (VII)	362.30	0	0	—	0.03
cis-Pyrrone (VIII)	362.30	0	0	—	0.02

[a] Normalized to a 10-mg sample size.
[b] Based on the ratio of observed to calculated water.

TABLE III
Results of Effluent Analysis on Polymers Heated to 400°C

Precursor polymer	MW[a]	Calculated[b] H_2O, mg	Observed[b] H_2O, mg	Conver- sion,[c] %	Observed[b] CO_2, mg
PMDA-TABP	460.41	1.56	1.02	65	0.35
PMDA-DAB	432.40	1.66	1.13	68	0.38
BTDA-TABP	564.62	1.27	0.97	76	0.18
BTDA-DAB	536.51	1.34	1.06	79	0.22
PMDA-DADPO	418.37	0.86	0.81	94	0.07
BTDA-DADPO	522.48	0.69	0.64	92	0.05

[a] Molecular weight of the idealized repeat unit.
[b] Normalized to a 10-mg sample size.
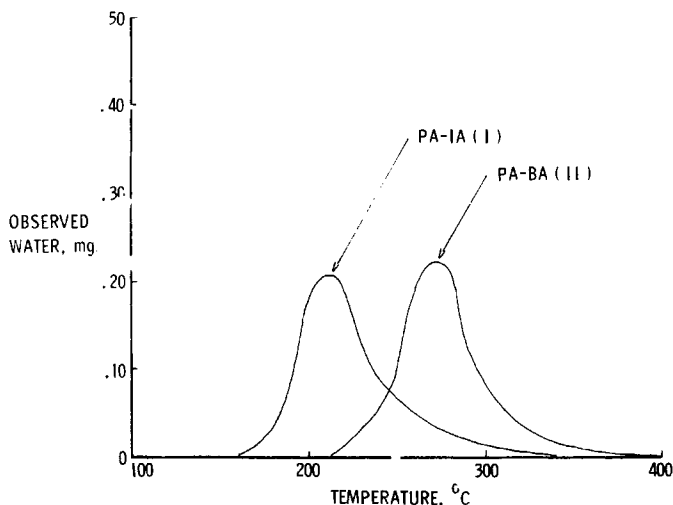[c] Based on the ratio of observed to calculated water.

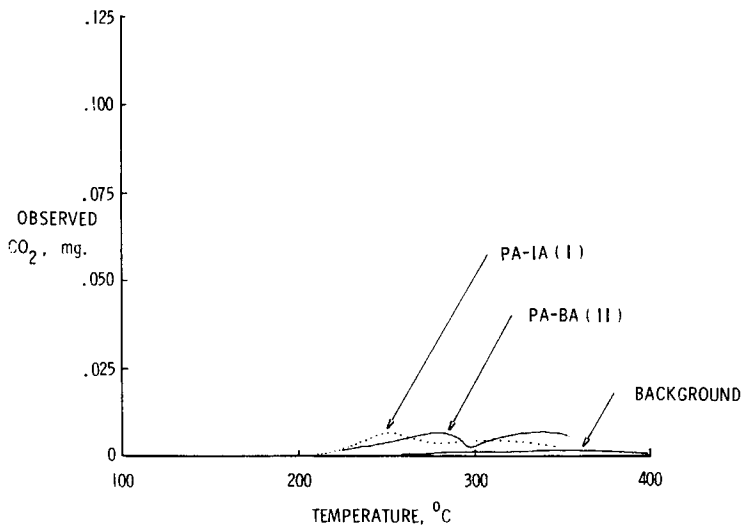Fig. 2. Evolution of water during cure of PA model compounds.

Fig. 3. Evolution of carbon dioxide during cure of PA model compounds.

under the conditions of this experiment. Substantial amounts of carbon dioxide were observed for those models which did not convert efficiently. This carbon dioxide was eliminated in two general regions, where maximum water loss occurred and at elevated temperatures. The early evolution of carbon dioxide from the amide-acid-amine model (III) as it loses water might be attributed to decarboxylation and hydrolytic cleavage of amide bonds as proposed by Bruck,[14] while the early evolution of carbon dioxide from the imide-amine models (I and V) may result from rearrangement and subsequent isoimide degradation.[15] The benzimidazole-acid models (II, IV, and VI) apparently partially decarboxylate during cyclodehydration as proposed in earlier polymer studies.[2,8,16] This is particularly evident for the PMDA model (IV). The thermal decarboxylation
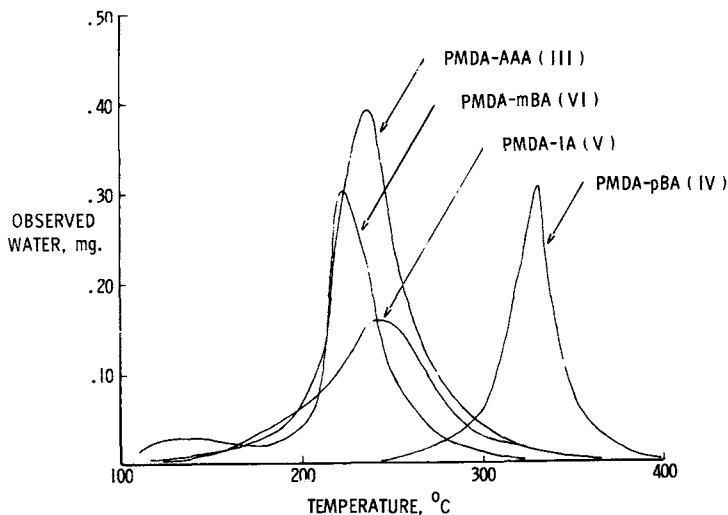
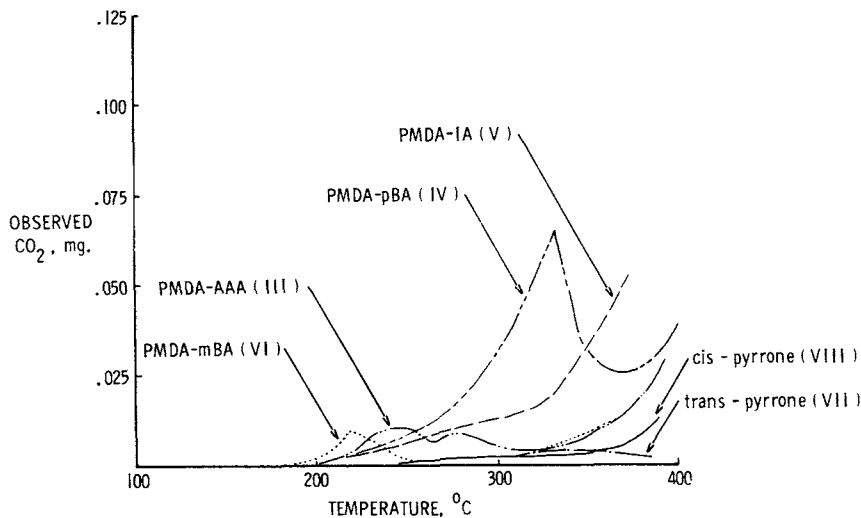Fig. 4. Evolution of water during cure of PMDA model ompounds.

Fig. 5. Evolution of carbon dioxide during cure of PMDA model compounds.

of aromatic acids is a fairly common phenomenon and is promoted by the close proximity of electron-withdrawing groups.

Since the benzimidazole-acid model (IV) eliminated more carbon dioxide than any other model, an independent experiment was conducted to confirm that it did indeed partially decarboxylate during the thermal cyclization process. Approximately 100 mg of this compound was heated to 200° at 5°C/min in a helium atmosphere and then programmed to 350° at 3°C/min. Upon cooling, the residue was extracted with chloroform and a sample of insoluble portion was introduced directly into the ionization chamber of a mass spectrometer by a solid inlet probe. The probe was then heated to vaporize the sample. Figure 10 gives the resulting mass spectrum. In this spectrum, background has been subtracted
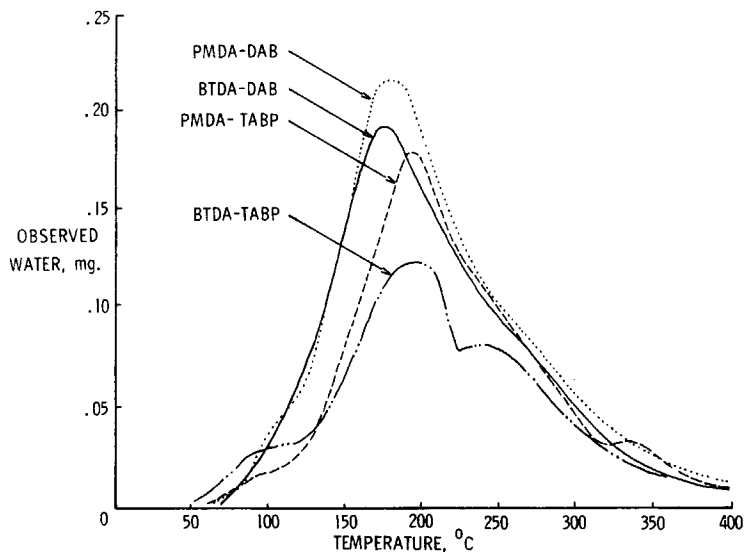
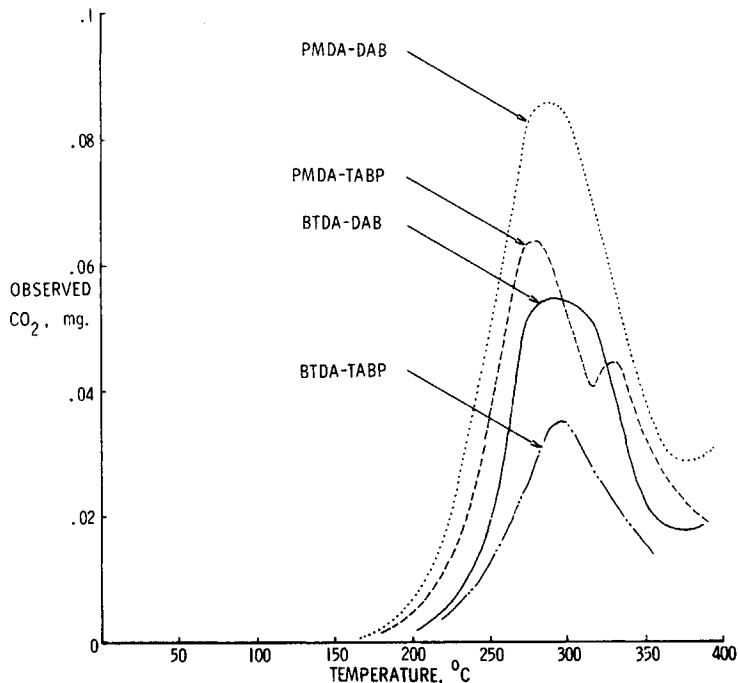Fig. 6. Evolution of water during cure of four pyrrone precursor polymers.

Fig. 7. Evolution of carbon dioxide during cure of four pyrrone precursor polymers.

and the data normalized to the highest peak, m/e 362. The parent ion peak at m/e 362 is assigned to *trans*-pyrrone (VII). However, the peak at m/e 336 can only occur if one side of the PMDA-pBA model (IV) decarboxylated while the other side converted to pyrrone such that a benzimidazole-pyrrone structure resulted. This helps explain the source of carbon dioxide during maximum water evolution from this model and probably confirms Thiele's earlier observations on the PA-BA model (II) as well.[17]
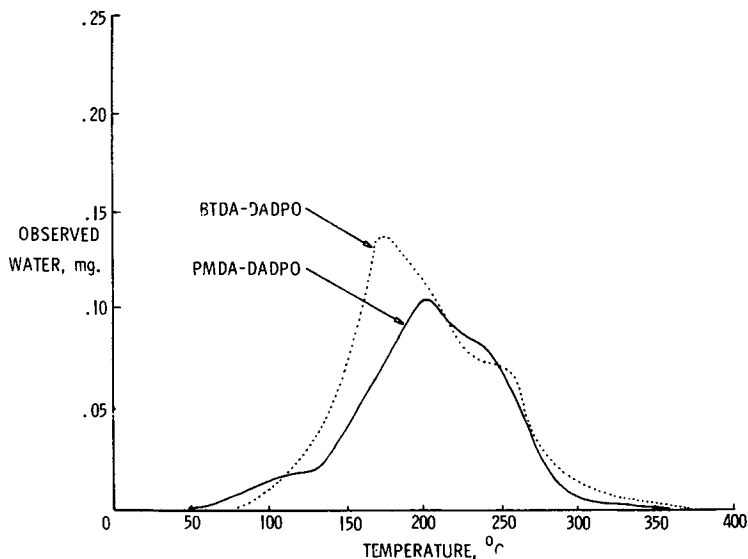
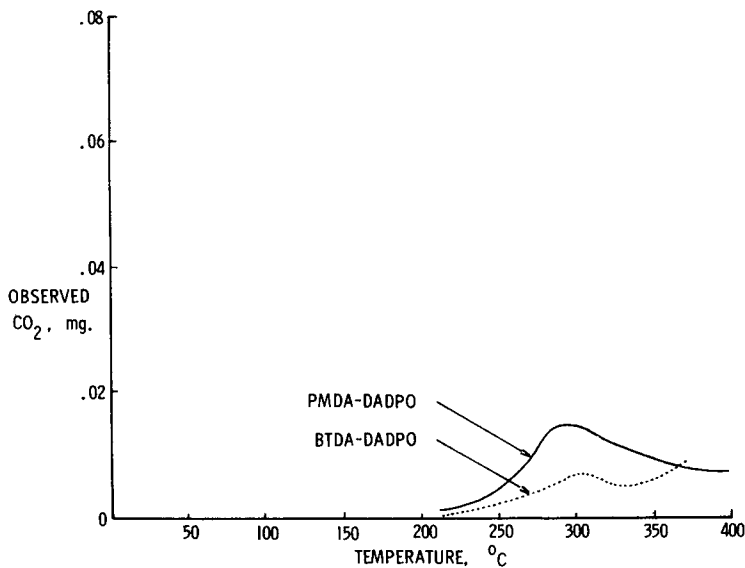Fig. 8. Evolution of water during cure of two polyimide precursor polymers.

Fig. 9. Evolution of carbon dioxide during cure of two polyimide precursor polymers.

Figures 3 and 5 show that very little carbon dioxide is lost from the fully cyclized *trans-* or *cis-*pyrrone models (VII and VIII) over that coming from background. However, all of the other models exhibited carbon dioxide loss at temperatures above where cyclodehydration occurred. Since this could not have come from any pyrrone present, the initial cyclization reactions must also yield products which degrade at elevated temperatures to produce the observed carbon dioxide. These unidentified model products may be of the type which would
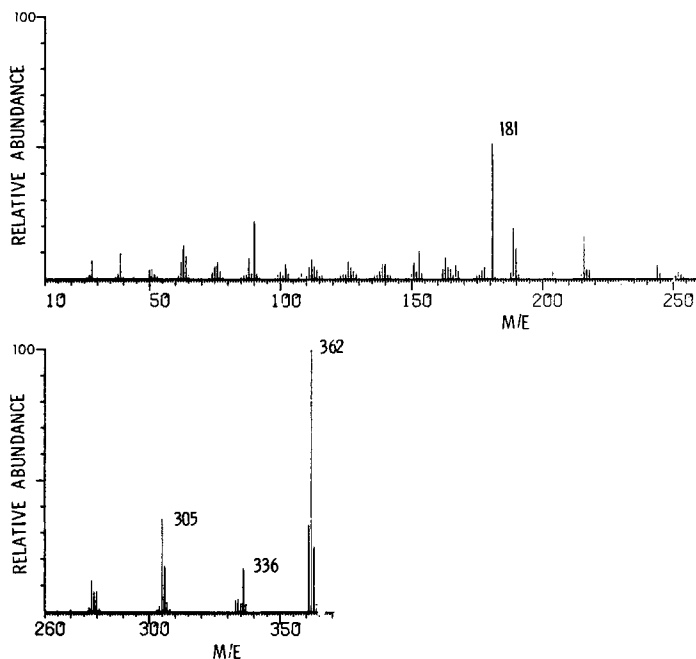
Fig. 10. Mass spectrum of PMDA-pBA (IV) model.

produce crosslinks if similar reactions occurred during the cure of pyrrone polymers.

Polymers

BTDA polymers gave better conversion to the pyrrone structure than did PMDA polymers. However, the results in Table III show that all four of the pyrrone precursors exhibited less than an 80% conversion under the conditions of this study. Inspection of Figures 6 and 7 reveals that during the cure process, significant amounts of carbon dioxide were also eliminated. A comparison of Figures 4 and 6 and Figures 5 and 7 suggests a similarity between the curing reactions occurring in the models and polymers. Thus, the incomplete conversion (Table III) can be partly explained by assuming that the carbon dioxide resulted from the same sources previously suggested for the model compounds. Whenever carbon dioxide is lost, complete cyclodehydration to the pyrrone structure cannot occur and the conversion must be less than 100%.

Incomplete conversion may also be a result of the increase in chain rigidity which is inherent in the pyrrone ladder structure.[18] As the polymer chains become more rigid, unreacted groups may find it difficult to attain the proper orientation in order to participate in cyclodehydration. Some decarboxylation of these unreacted groups also seems likely to occur under these conditions. There are several other possible reasons why complete cyclization was not observed. First, infrared spectra of the precursor polymers indicated that some cyclization during workup of the amide-acid-amine may have occurred prior to GC/MS analysis. Second, the assumption that the precursor polymer is linear may not be valid; some branching may have occurred during polymerization.[12,19]

Finally, the precursor polymers could contain an overly large number of end-groups, although the viscosity data given in Table I and solution property determinations reported earlier on PMDA-DAB polyamide-acid-amine precursors[20] tend to discount this. While these explanations might account for low yields of pyrrone, they cannot be applied to the model compounds which also exhibited low yields, although not quite as low as for the polymer. The reactions occurring in the polymers and models are probably the same, except that the polymers begin reacting at a slightly lower temperature.

The two polyimides were found to cyclize with little difficulty and, as shown in Figures 8 and 9, both were essentially converted at 350°C. Only a minor amount of CO_2 was observed up to this temperature. These results are consistent with the published results of Teleshova et al.[8] for PMDA-DADPO, and the agreement further verifies the viability of the GC/MS technique. Comparing the curves for the evolution of water and CO_2 in the imide precursors with that observed for the pyrrone precursors (Figs. 6 and 7) suggests that cyclodehydration occurs in a similar fashion for both polymer systems.

The double-stranded stepladder pyrrone structure should inherently be more thermally stable than the polyimide structure. However, in reality, no improvement in thermo-oxidative stability is afforded by pyrrones over polyimides. This is probably because polyimides largely attain their theoretical structure while pyrrones do not. This work shows that PMDA-mBA (VI) was the only model compound which achieved essentially complete cyclization. If a synthesis could be conducted which went exclusively by this route, the resulting cis polymer should have very nearly the theoretical pyrrone repeat unit. The true contribution of the complete pyrrone structural unit to the thermal stability of the polymer could then be evaluated with certainty.

CONCLUSIONS

The conclusions drawn from the study of the effluents produced during the thermal cyclization of these materials are:

1.   The GC/MS technique as described herein was used effectively to characterize the cyclization of pyrrone and polyimide precursors.

2.   The four pyrrone precursors studied did not achieve complete cyclization under the conditions of this experiment, while the polyimide precursors were almost completely converted.

3.   The low conversion to pyrrone was due in part to the loss of carbon dioxide during thermal cyclization.

4.   Based on model compound studies, a high conversion of the precursor to the pyrrone structure probably would be obtained if the precursor could be made to cyclize exclusively through the *meta*-benzimidazole-acid intermediate.

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