PROPERTIES OF POLYIMIDAZOPYRROLONES

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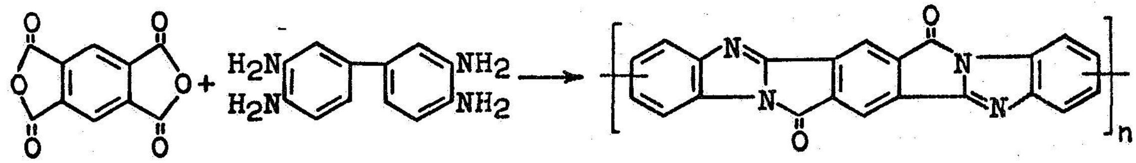
INTRODUCTION

The study of the all-aromatic polybenzimidazoles by Vogel and Marvel[1] opened the way to a number of other polymers based on aromatic-heterocyclic condensation reactions. Most of these polymers have shown remarkable levels of stability to thermal energy. The central theme which has directed research into the aromatic-heterocyclic polymers has been the confidence of polymer chemists that the "ladder" or two-strand polymer structures would show significant improvement in thermal stability. One of the most recent polymers which approaches this goal of a "ladder" structure is that class derived from the reaction of aromatic ortho-tetraacids and ortho-tetraamines. An example is afforded by the product obtained by reacting pyromellitic dianhydride (PMDA) with 3,3'-diaminobenzidine (DAB):



PMDA **DAB** **PMDA-DAB**

This class of polymers, which we have referred to as polyimidazopyrrolones (or simply Pyrrones), has been the subject of research by several groups [2,3,4,5]. This paper describes our investigation into the unusual properties of the Pyrrones for possible utilization in current and future aerospace applications.

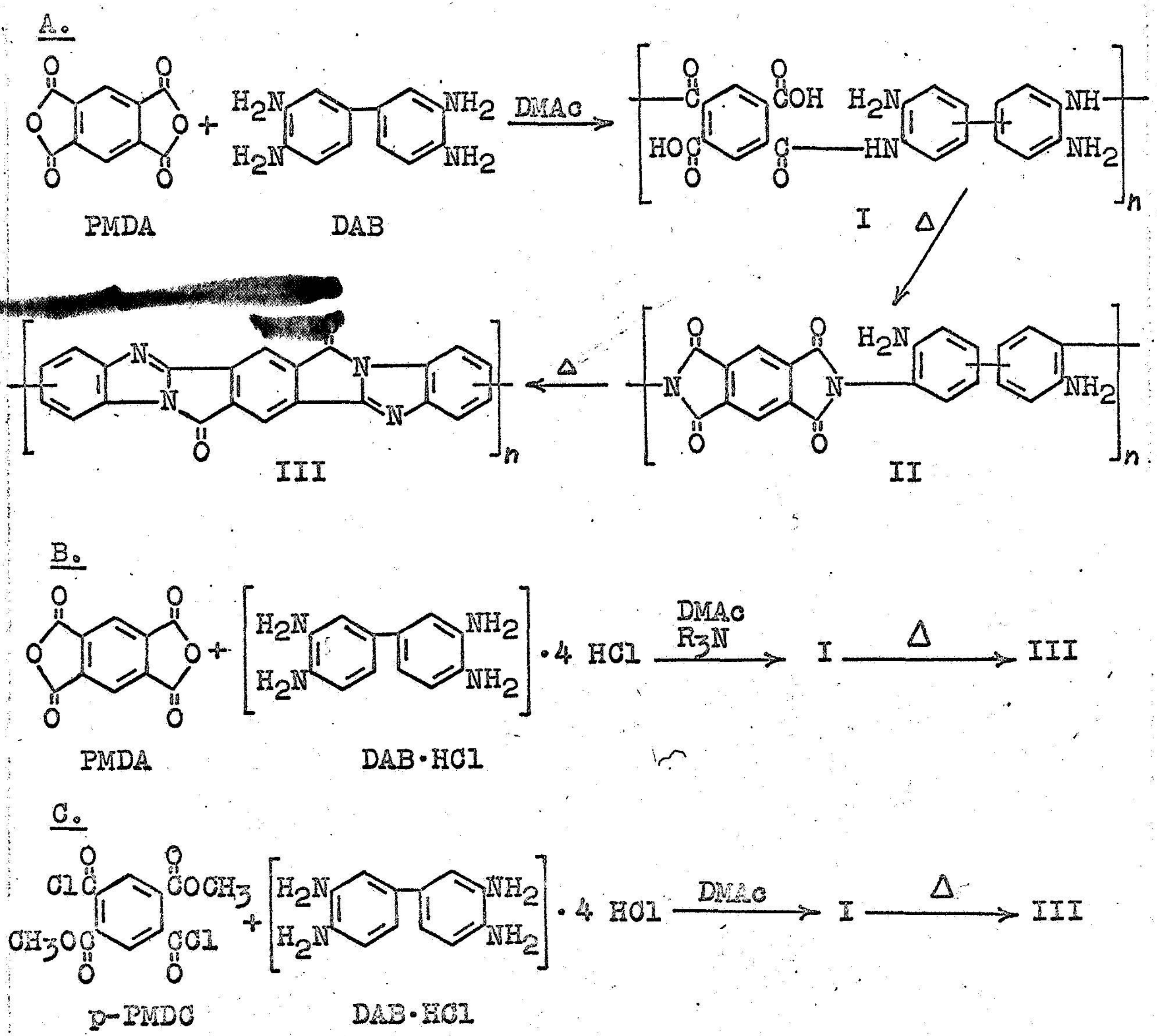
EXPERIMENTAL

The polyimidazopyrrolones described in this paper were prepared using two aromatic dianhydrides: pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA). Four tetraamines were polymerized with each of the two anhydrides: 3,3'-diaminobenzidine (DAB), 3,3',4,4'-tetraaminodiphenyl ether (TADPO), 3,3',4,4'-tetraaminodiphenyl methane (TADPM) and 3,3',4,4'-tetraaminobenzophenone (TABP). The dianhydrides and DAB were obtained commercially, while the TADPO, TADPM, and TABP were synthesized by dinitration of the corresponding 4,4'-diamines, followed by reduction of the nitro groups.

Three methods were used for preparation of the polyimidazopyrrolones. Procedure A, which involved the reaction of the dianhydride with the free tetraamine at room temperature, was the most frequently used technique. This reaction was generally carried out in a Waring Blendor by adding a solution of the dianhydride in amide-type solvents to a solution of the tetraamine with rapid stirring. Approximately 95% of the stoichiometric amount of dianhydride was added at one time, while the remainder was added carefully in a dropwise manner. If the purity of the starting materials and solvents was high, as little as one percent excess of dianhydride was required to reach the highest possible viscosity, $\eta_{int.} \cong 1.5$, before gellation occurred. This initial reaction resulted in a polyamide containing unreacted carboxyl and amino groups (I). This polyamide stage was useful for fabrication purposes since it was the only point at which the polymer was soluble. Films were obtained by solvent-casting the polymer solutions onto glass plates. The films were then dried in air ovens at 125°C for one hour, 200° for one hour and 300° for one hour. This thermal treatment converted the initial polyamide through the amino-substituted polyimide (II) and thence to the fused imidazopyrrolone structure (III).

A second method, procedure B, was a modification of procedure A which utilized the tetraamine tetrahydrochloride salt and a tertiary amine as an acid acceptor. Two advantages were realized by using the hydrochloride derivatives: first, it was a convenient way to utilize the tetraamines, some of which oxidize extremely rapidly as the free base, and secondly, the reaction of the anhydrides with the hydrochloride salts was much slower than the free amine, thus permitting better reaction control. The experimental procedure was essentially the same as procedure A, except for the addition of pyridine and the slower reaction time. Insofar as the polymers were examined, they appeared to be essentially the same as those prepared by procedure A. It is likely that the pyridine hydrochloride was sublimed away during the thermal conversion since elemental analysis of the polymers disclosed that no chloride was present.

POLYIMIDAZOPYRROLONE SYNTHESIS PROCEDURES



The third procedure (C) for preparing polyimidazopyrrolones involved the reaction of 2,5-dicarbomethoxyterephthaloyl chloride (p-PMDC) with the tetraamine tetrahydrochloride salts using dimethylacetamide as the solvent. However, the use of a tertiary amine was not essential to allow the reaction to proceed to completion. On the contrary, the diacyl chloride was so reactive that it was necessary to moderate the reaction by using the amine hydrochloride salts since the reaction with the free tetraamines was so vigorous that insoluble products were obtained. Once again, the polymers prepared in this manner were apparently identical with those prepared by procedures A and B.

PROPERTIES

A summary of the polymers which were prepared has been given in Table I. The intrinsic viscosities cited were not necessarily optimum, but should be considered as typical values since some of the polymer compositions were prepared a number of times and the viscosity levels were varied. It should be noted that polymers with intrinsic viscosities as low as 0.40 could be used for the fabrication of satisfactory films by solvent-casting techniques.

TABLE I

SOLUTION PROPERTIES OF POLYAMIDE PRECURSORS OF POLYIMIDAZOPYRROLONES

Polymer[a]	Method[b]	Solvent	Viscosity[c], Polyamide	Molecular[d] Weight $\bar{M}n$
PMDA-DAB	A	DMF	0.99	-
PMDA-DAB	B	DMAc	.47	-
PMDA-TADPO	A	DMAc	.59	8,000
PMDA-TADPM	A	DMAc	.74	-
PMDA-TABP	A	DMF	.64	14,300
BTDA-DAB	A	DMF	1.45	-
BTDA-TADPO	A	DMAc	1.11	14,700
BTDA-TADPM	A	DMAc	0.72	-
BTDA-TABP	A	DMF	.43	13,800

[a] PMDA - Pyromellitic dianhydride; BTDA - 3,3',4,4'-benzophenone tetracarboxylic dianhydride; DAB - 3,3'-diaminobenzidine; TADPO - 3,3',4,4'-tetraaminodiphenyl ether; TADPM - 3,3',4,4'-tetraaminodiphenyl methane; TABP - 3,3',4,4'-tetraaminobenzophenone.

[b] Procedure A - Dianhydride + tetraamine
Procedure B - Dianhydride + tetraaminetetrahydrochloride

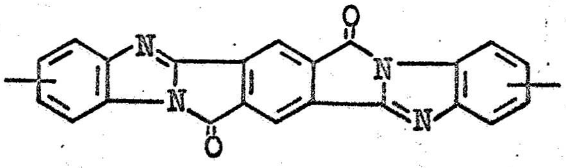
[c] Intrinsic viscosity in the specified solvent at 25°C.

[d] Via membrane osmometry in the polymerization solvent at 37°.

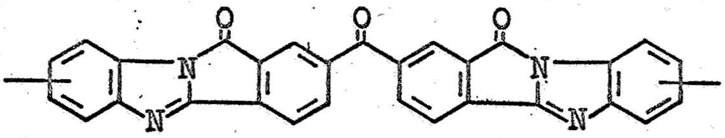
The theoretical structures of the various polyimidazopyrrolones are given in Table II.

TABLE II

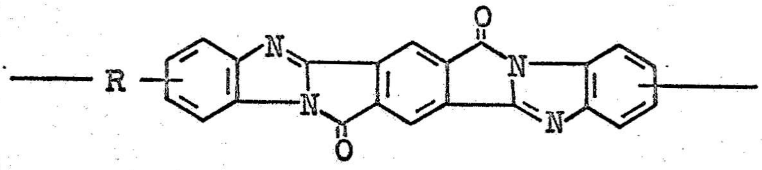
POLYIMIDAZOPYRROLONE REPEAT UNITS



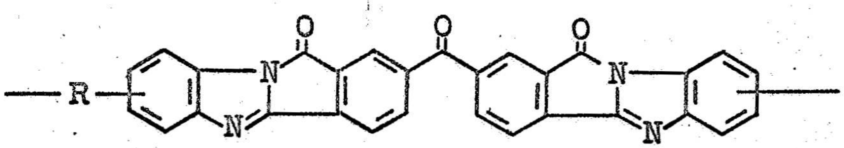
PMDA-DAB



BTDA-DAB



R= -O- : PMDA-TADPO
R= -CH_2- : PMDA-TADPM
R= -CO- : PMDA-TABP



R= -O- : BTDA-TADPO
R= -CH_2- : BTDA-TADPM
R= -CO- : BTDA-TABP

The tensile properties of a number of polyimidazopyrrolone films are given in Table III.

TABLE III

TYPICAL TENSILE PROPERTIES OF POLY(IMIDAZOPYRROLONE) FILMS[a]

Polymer[b] Composition	Tensile Strength (psi)	Elongation (Percent)	Tangent Modulus (psi)	Color
PMDA-DAB	20,400	2.8	950,000	Deep Red
PMDA-DAB[c]	13,600	2.0	810,000	Deep Red
PMDA-TADPO	21,800	4.8	812,000	Red
PMDA-TADPM	13,900	3.9	534,000	Orange
PMDA-TABP	13,300	2.6	593,000	Yellow
BTDA-DAB	20,300	4.3	601,000	Red
BTDA-TADPO	18,900	3.8	627,000	Red-orange
BTDA-TADPM	9,700	1.9	599,000	Yellow
BTDA-TABP	12,000	3.1	498,000	Yellow

[a] Films cast from amide solvents onto glass plates, dried and cured in air at 125°C/1 hr., 200°/1 hr. and 300°/1 hr. Final film thicknesses ranged from 0.7 - 1.0 mils.

[b] See Table I for explanation of abbreviations.

[c] Polymer prepared utilizing PMDA and tetrahydrochloride salt of DAB (procedure B).

The mechanical properties indicate general trends for the structural compositions. Considerable variation in film quality were observed, even from one film to another from the same polymer solution; nevertheless, the tensile strengths were usually excellent while the tangent moduli were quite high and the elongations were consistently low. As a measure of chain stiffness, the latter two values were quite in line with the expected rigid, ladder-like polymer structures although an undetermined amount of crosslinking was believed to be present in the cured, imidazopyrrolone polymers. The moduli of 950,000 psi for the PMDA-DAB composition and 498,000 psi for the BTDA-TABP films may reflect the theoretical rigidities to be expected for polymer chains containing groups of seven and four fused rings, respectively. The colors of the films also emphasized the extent of conjugation in the fused ring structures, those based on PMDA being darker than those derived from BTDA.

The film properties were found to be quite independent of the conversion (curing) atmosphere since no significant difference was observed when the films were cured in air, nitrogen or *in vacuo*. On the other hand, the ultimate curing temperature exerted a marked influence on the mechanical properties. The data in Table IV indicate a general increase in strength and modulus, together with a corresponding decrease in elongation, as the ultimate conversion temperature was increased.

TABLE IV

EFFECT OF CURING TEMPERATURE ON FILM[a] PROPERTIES

Polymer Structure	Curing Temperature	Strength, kpsi Yield	Strength, kpsi Tensile	Modulus, kpsi	Elongation (Percent)
BTDA-TADPO	150°/1 hr	11.1	16.3	509	5.4
BTDA-TADPO	225°/1 hr	13.1	17.1	545	4.1
BTDA-TADPO	300°/1 hr	14.7	18.9	627	3.8

[a] All samples from single sheet of 1-mil film.

The retention of tensile properties of films at elevated temperatures was excellent. The results given in Table V show that PMDA-DAB films (0.6 mil) retained over 65% of their room temperature tensile strength when tested at 200°C in air. The retention of elongation when the test temperature was increased from 100° to 200°C is suggestive of some measure of crosslinked structure.

TABLE V

EFFECT OF TEMPERATURE ON TENSILE PROPERTIES OF PMDA-DAB FILMS[a]

Testing Temperature	Yield Strength (psi)	Tensile Strength (psi)	Elongation (Percent)	Tangent Modulus (psi)
25°C	12,900	17,000	2.8	857,000
100°C	9,800	15,800	3.7	713,000
200°C	7,400	11,500	3.7	526,000

[a] Films were precured at 225°C for 1 hour.

Our previous work on the polyimidazopyrrolones[2] disclosed the remarkable resistance of the polymer films to degradative effects of ionizing radiation both in air and in vacuum. Additional study of this property has extended the investigation to more severe exposure levels. The data in Table VI indicate that although some degradation may have begun after 21,000 megarads of 3 MeV electrons, the tensile properties of the films after the extreme dose of 58,000 megarads were still nearly equivalent to the initial values.

TABLE VI

EFFECT OF RADIATION ON PMDA-DAB FILMS[a]

Dose, (Mr)[b]	Yield Strength (psi)	Tensile Strength (psi)	Elongation (Percent)	Tangent Modulus (psi)
0	13,300	16,700	3.2	811,100
1,100	14,200	20,900	4.5	883,000
5,500	14,400	20,900	3.9	889,000
11,000	14,600	19,100	3.1	891,000
21,000	15,600	22,200	3.3	988,000
58,300	12,500	15,300	2.7	826,000

[a] Films converted at 300°C; environment temperature during irradiation was approximately 250°C.

[b] 3 MeV electrons at a dose rate of 5,500 megarads (Mr) per hour.

The relative thermal stabilities of the eight polymer compositions (Table II) were measured by means of thermogravimetric analysis (TGA). The specimens tested were 2.0 milligram portions of 0.6-1.0 mil films which had been cured at up to 300°C for one hour. Figure 1 shows the weight loss vs. temperature relationship for the polyimidazopyrrolones when heated in air. The shaded area within the two boundary curves contain the TGA curves for all eight of the compositions studied. It was concluded that the effect of structure on thermal (oxidative) stability was moderate, with a difference of only 40-50°C separating the temperatures of maximum rates of weight loss.

Figure 2 shows the weight loss behavior of the same eight polyimidazopyrrolones when they were heated in vacuum (10^{-6} torr). Once again, the TGA curves for all eight combinations have been encompassed within the bounds of the shaded area. One unusual feature of this figure is the surprising reversal of stability which was noted for the BTDA-TABP polymer. While it displayed the greatest stability when heated in air, it was found to be the least stable when heated in a vacuum environment.

There were indications that the fully converted polyimidazopyrrolones formed a loosely hydrated structure. Figure 3 shows the weight loss as a 0.7 mil PMDA-DAB film, cured at 350°C for two hours, was cycled in air through four stages: (a) heated from 25 to 100°C, (b) maintained at 100°, (c) cooled from 100° to 25°, and (4) maintained at 25°. Each stage was 15 minutes in duration. The figure indicates a ready gain of 7 percent upon cooling in air and an equally facile loss of the same amount of water upon reheating to 100°. The theoretical percentage of water for $[\text{PMDA-DAB}]\cdot 2H_2O$ is 9 percent. The formation of a weakly complexed dihydrate was further supported by elemental analyses and vapor phase chromatography of trapped volatiles.

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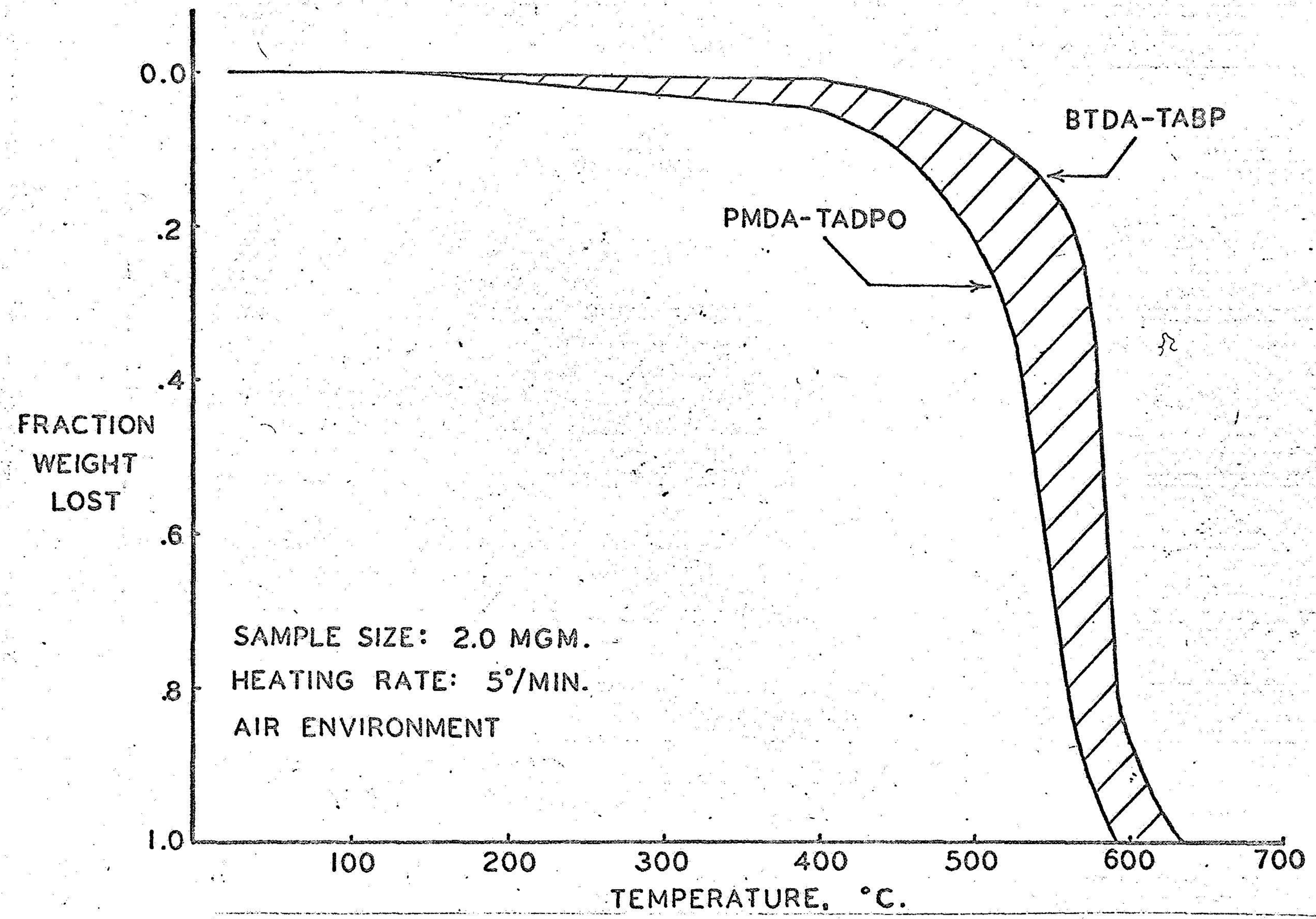

Figure 1. - Thermogravimetric analysis of polyimidazopyrrolones in air. Shaded area includes curves for all eight compositions.

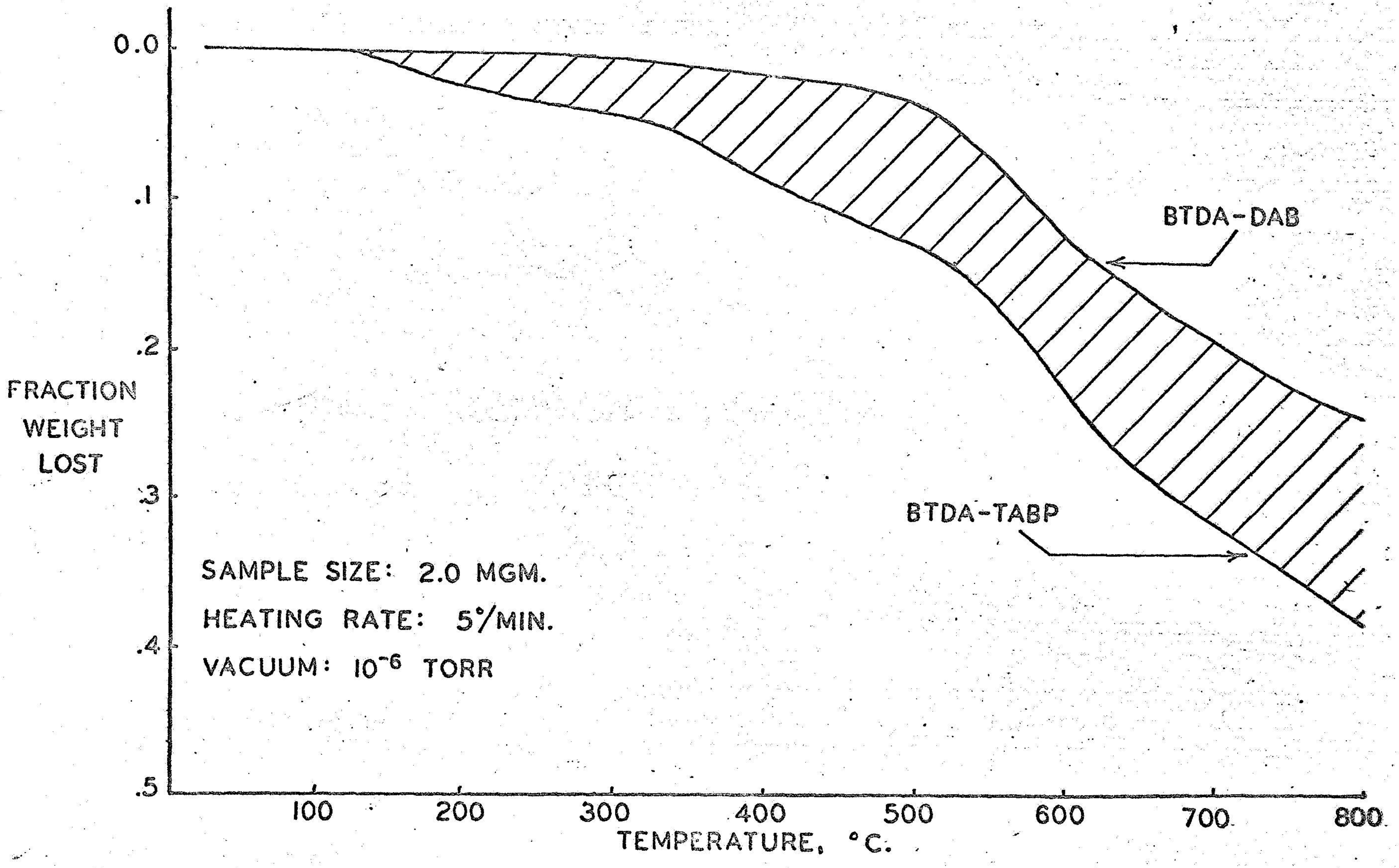

Figure 2. - Thermogravimetric analysis of polyimidazopyrrolones in vacuum. Shaded area includes curves for all eight compositions.

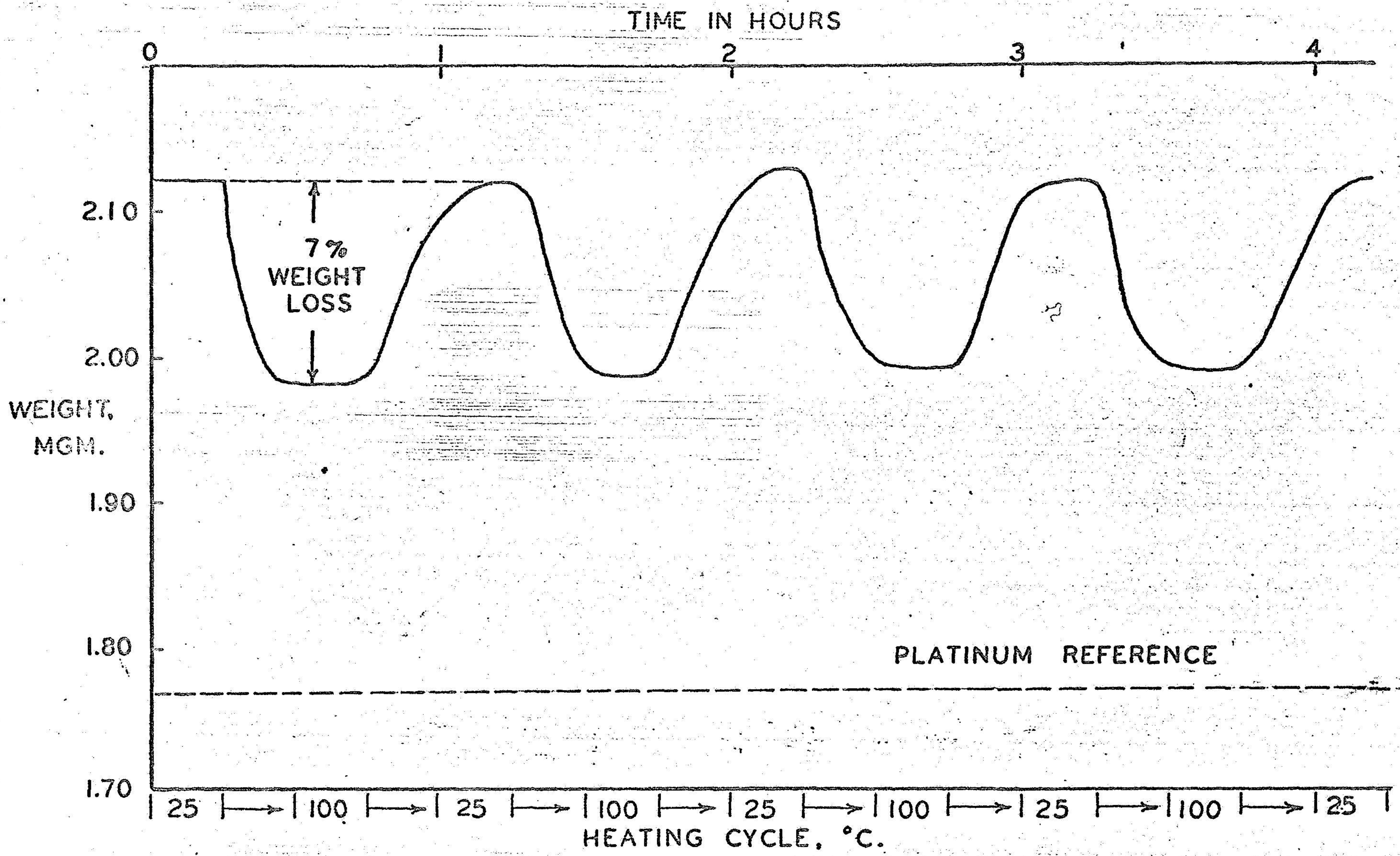

Figure 3. - Loss and regain of water from 0.7 mil PMDA-DAB film when heated and cooled in air.