

## Preparation and Properties of Imide-Pyrrone Copolymers

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### Synopsis

Two series of copolymers containing imidazopyrrolone (pyrrone) and imide groups were prepared by solution polymerization. Thin films of the copolymers showed a general increase in the tangent modulus and a decrease in elongation with increasing pyrrone content. The copolymers were more resistant to degradation by strong acids and bases than the corresponding polyimides. The thermal stabilities of the copolymers in air improved with increasing imide content, while the thermal stabilities in a vacuum improved with increasing pyrrone content. These copolymers represent a way to combine the desirable properties of both classes of homopolymers.

### INTRODUCTION

It has become apparent during the past decade that the conventional plastics developed during the first half of the 20th century have been unable to meet the more demanding needs of aerospace research and technology. However, two new classes of polymers, the polyimides<sup>1,2</sup> and the polyimidazopyrrolones (pyrrones)<sup>3-7</sup> show promise of meeting some of these critical materials needs. These new polymers derive their unique properties from the fact that the main chain is comprised of a combination of aromatic and heterocyclic structures with their high orders of chemical, thermal, and radiation stability. The commercially available polyimides are currently being evaluated and even utilized in numerous aeronautical applications. The pyrrones, a class of heteroaromatic polymers developed at the Langley Research Center, represent an extension of the scheme of fusing aromatic and heterocyclic units into polymers of the ladder, or two-strand, variety that begin to approach the general structure of graphitic materials.

Though close similarities in the properties of the two polymer classes exist, there are features unique to each class. The polyimides are considered to be essentially linear because of their solubilities in fuming nitric acid.<sup>2</sup> However, the pyrrones, which are prepared by nearly the same solution polymerization technique as the polyimides, are virtually insoluble in strong acidic solvents<sup>7</sup>; this insolubility suggests a certain element of non-linearity by reason of cross-linked sites. The Pyrrone films exhibit higher tangent moduli and lower elongations than the polyimides, which is indicative of greater chain rigidity. Thermogravimetric behavior of the two classes under vacuum is also different. The Pyrrones have lower weight losses in the extreme temperature range of 600° to 900°C.

Either or both of these two polymer classes could be used in specific aerospace applications. However, it was thought that by combining the two polymer structures by copolymerization, a series of copolymers could be obtained with a range of properties. The resulting versatility can be imagined; for example, consider the properties that a polymer film must have in order to perform as a cell separator in an alkaline battery. For this end use, a Pyrrole film would probably resist the chemical action of the caustic electrolyte yet would likely be too brittle to serve as an unsupported membrane. Even though the polyimides are quite flexible as films, they are dissolved by caustics. One approach could be to use a Pyrrole-polyimide copolymer if their respective desirable properties, alkali resistance and film flexibility, could be merged into the copolymer.

The preparation of imidazopyrrolone-imide copolymers from aromatic dianhydrides and aromatic triamines have been reported.<sup>8,9</sup> However, these have the limitation of affording copolymers with only a 50:50 imidazopyrrolone:imide composition. To establish the scope of the properties of the copolymers, two chemically differing series of copolymers were prepared, eqs. (3) and (4). The compositions ranged from a pure Pyrrole to a pure polyimide with intermediate copolymer compositions. The copolymers were characterized by solution properties of the intermediate pre-

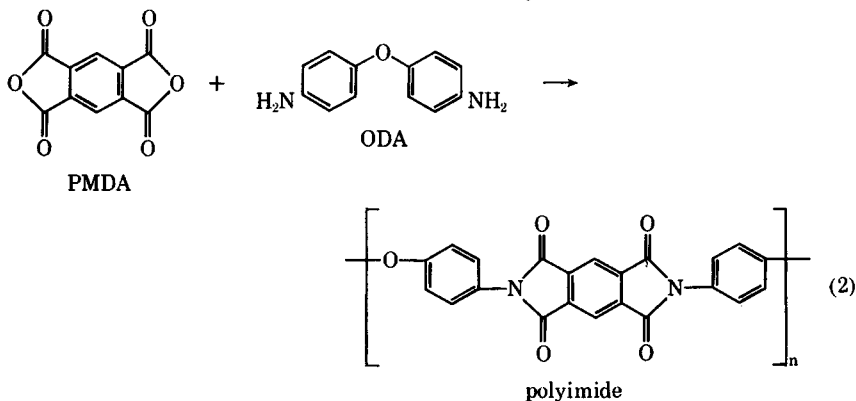
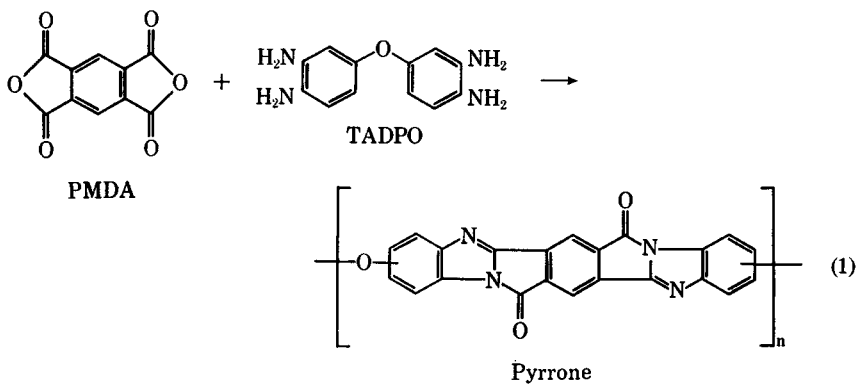


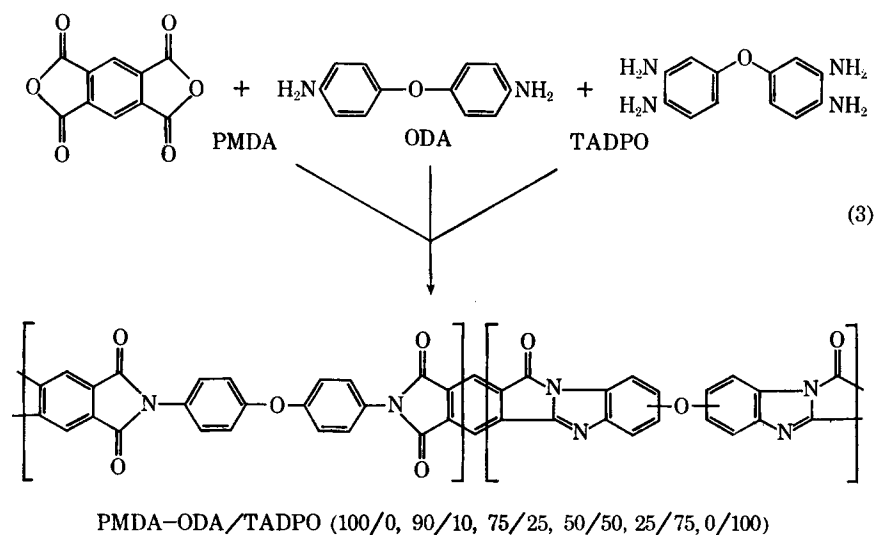
TABLE I  
Summary of Polymerizations for PDMA-ODA/TADPO Copolymers

ODA/- TADPO ratio	Reactants			Solvent (DMAc), ml	Intrinsic viscosity, dl/g
	ODA, mmoles	TADPO, mmoles	PMDA, mmoles		
100/0	20.0	—	20.8	74	1.47
90/10	18.0	2.0	20.8	75	1.65
75/25	15.0	5.0	20.8	75	2.55
50/50	10.0	10.0	20.6	75	2.78
25/75	5.0	15.0	21.1	75	1.08
0/100	—	20.0	21.0	75	0.99

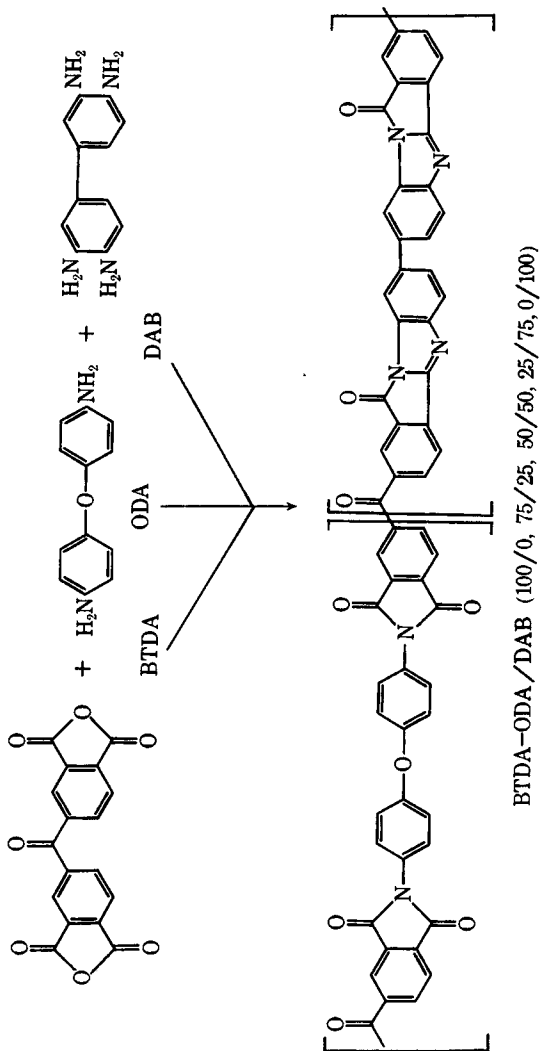
cursor polymers, the chemical resistance of the cured films, and the mechanical properties of the films.

The schematic representations for the reactions leading to both Pyrrone polymers and polyimides are given in eqs. (1) and (2), respectively, using pyromellitic dianhydride (PMDA), 3,3',4,4'-tetraaminodiphenyl ether (TADPO), and *p,p'*-oxydianiline (ODA).

The two copolymer series were prepared by the reactions illustrated in eqs. (3) and (4). PMDA, ODA, and TADPO were the starting materials for the series of copolymers prepared by the reaction shown in eq. (3). This series of copolymers is referred to in this report as the PMDA-ODA/-TADPO series. The second group of copolymers, represented by eq. (4), was prepared by utilizing 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), 3,3'-diaminobenzidine (DAB), and ODA as the basic chemicals. This series is referred to as the BTDA-ODA/DAB series. The numerical ratios appearing in eqs. (3) and (4) indicate the relative molar amounts of diamines (ODA) and tetraamines (TADPO and DAB) used to prepare the copolymers.



(4)



## EXPERIMENTAL

## Reagents

Pyromellitic dianhydride was purified by vacuum sublimation at 225° to 240°C and 0.5 torr. 3,3',4,4'-Benzophenone tetracarboxylic dianhydride was purified by recrystallization from acetic anhydride. 3,3',4,4'-Tetraaminodiphenyl ether was synthesized and purified by a method described previously.<sup>7,11</sup> *p,p'*-Oxydianiline was purified by recrystallization from acetone, followed by sublimation at 185°C and 0.5 torr. 3,3'-Diaminobenzidine was used as received from Burdick and Jackson Laboratories, Inc., Muskegon, Mich. *N,N*-Dimethylacetamide was purified by distillation from pyromellitic dianhydride.

## Polymerizations

A summary of the polymerizations leading to the PMDA-ODA/TADPO copolymers is given in Table I, and a summary of the polymerizations for the BTDA-ODA/DAB copolymers is listed in Table II. Detailed procedures for the synthesis of the copolymers are given in the following sections.

TABLE II  
Summary of Polymerizations for BTDA-ODA/DAB Copolymers

ODA/- DAB ratio	Reactants			Solvent (DMAc), ml	Intrinsic viscosity, dl/g
	ODA, mmoles	DAB, mmoles	BTDA, mmoles		
100/0	20.0	—	20.5	60	1.05
75/25	15.0	5.0	20.2	60	1.18
50/50	10.0	10.0	20.2	60	1.28
25/75	5.0	15.0	20.1	60	0.85
0/100	—	20.0	20.1	60	0.83

**PMDA-ODA/TADPO (100/0).** The PDMA-ODA/TADPO (100/0) control polyimide was prepared by the addition of 4.00 g of solid PMDA to a stirred solution (high-speed household blender) of 4.00 g of ODA in 60 ml of *N,N*-dimethylacetamide (DMAc) under a nitrogen atmosphere. After 15 min, all the PMDA had dissolved and the temperature of the solution had increased to between 35° and 40°C. A solution of 0.55 g of PMDA in 14 ml of DMAc was added dropwise to the stirred polymer solution until the desired consistency was obtained. The measured viscosity of the resulting prepolymer is presented in Table I.

**PMDA-ODA/TADPO (90/10, 75/25, 50/50, 25/75, 0/100).** The PMDA-ODA/TADPO copolymers (90/10, 75/25, 50/50, 25/75) and the PMDA-ODA/TADPO (0/100) control Pyrrone were prepared by the following procedure which is illustrated for the 90/10 copolymer. A solution of 4.00 g of PMDA in 30 ml of DMAc was added to a rapidly stirred solution of 3.60 g of ODA and 0.46 g of TADPO in 35 ml of DMAc.

The reaction resulted in heating of the polymer solution to between 35° and 40°C. After the resulting solution had been stirred for 15 min, a solution of 0.55 g of PMDA in 10 ml of DMAc was added dropwise. This total addition of 4.55 g of PMDA resulted in a viscous polymer solution,  $[\eta] = 1.65$  dl/g, in DMAc at 25°.

**BTDA-ODA/DAB (100/0, 75/25, 50/50, 25/75, 0/100).** The BTDA-ODA/DAB (100/0) control polyimide was synthesized by the same method (addition of solid dianhydride) as that used to prepare the PMDA-ODA/TADPO (100/0) control polyimide, and the BTDA-ODA/DAB copolymers (75/25, 50/50, 25/75) and the BTDA-ODA/DAB (0/100) control Pyrrone were prepared by the same method (addition of dianhydride solution) as that used for preparation of the corresponding PMDA-derived copolymers.

### Film Preparation

Films were solvent-cast from the previously described polymer solutions onto glass plates, dried at 100°C for 2 hr, and cured at 175°C for 1 hr and then at 30°C for 1 additional hr. The cured films were easily stripped from the glass plates and used for characterization. The copolymer films were light yellow for the polyimides and progressed through orange shades with increasing Pyrrone content to the deep-red color of the pure Pyrrone. The infrared spectra (Perkin-Elmer Model 421) of the PMDA-ODA/TADPO copolymers, which were obtained to confirm the composition, appeared to be composites of the spectra of the two homopolymers: PMDA-ODA polyimide<sup>2</sup> and PMDA-TADPO Pyrrone.<sup>3</sup> The intensity of the absorption bands at 5.63  $\mu$ , 9.85  $\mu$ , and 16.6  $\mu$  in the copolymer spectra increased with increasing imide (ODA) content, while the intensity of the bands at 6.19  $\mu$  and 10.4  $\mu$  increased with increasing Pyrrone (TADPO) content.

### Measurement of Properties

Viscosity measurements were performed with Ubbelohde viscometers at 25°C in DMAc. The intrinsic viscosity was from a four-point extrapolation to infinite dilution. Thermogravimetric analyses were performed<sup>10</sup> by using a null-balancing automatic-recording electrobalance (Cahn RG electrobalance) with 1-mil film samples weighing  $2.05 \pm 0.03$  mg. The vacuum measurements were made at a pressure of  $1 \times 10^{-6}$  torr maintained by an ion pump with a capacity of 250 liters/sec. Differential thermal analyses were made with a du Pont 900 differential thermal analyzer.

The tensile stress-strain tests were performed with a Model TTC Instron Universal Tester on at least ten separate 0.5-in.-wide strips of film by utilizing a 3.0-in. grip separation and a crosshead speed of 0.2 in./min. From the stress-strain curve, it was possible to determine the initial tangent modulus, the 0.2% offset yield strength, and the tensile strength and elongation at break.

The moisture absorption was determined by exposing 2.0-mg samples of 1-mil film to alternate environments of 100% relative humidity (RH) at 25°C and 0% RH at 100°C. The following equation was used:

$$\% \text{ water} = \frac{(\text{wt at } 100\% \text{ RH, } 25^{\circ}\text{C}) - (\text{wt at } 0\% \text{ RH, } 100^{\circ}\text{C})}{\text{wt at } 0\% \text{ RH, } 100^{\circ}\text{C}} \times 100.$$

## RESULTS AND DISCUSSION

### Mechanical Properties

Mechanical properties of the two series of copolymer films are pictured in Figures 1 and 2. Thickness varied from about 0.80 to 1.30 mils, although the individual test specimens for each film composition were the same thickness to within 0.10 mil.

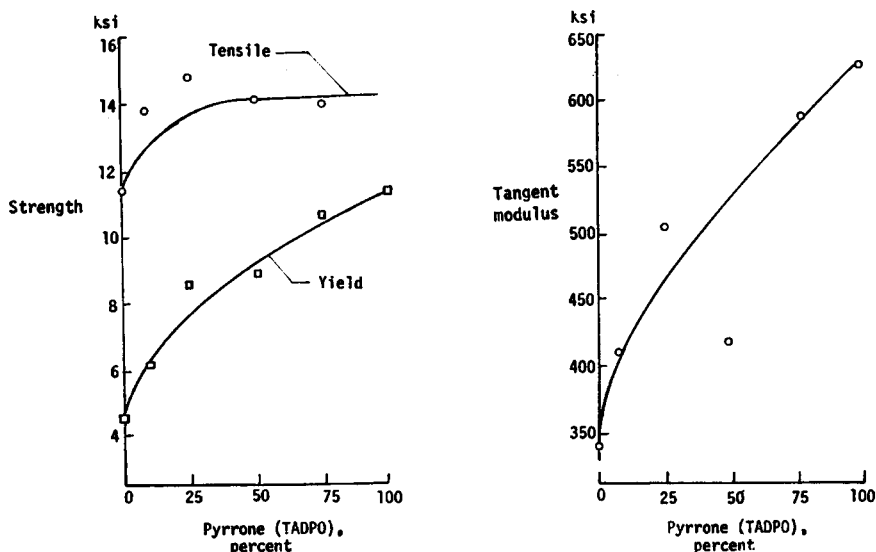


Fig. 1. Tensile properties of PMDA-ODA/TADPO copolymer films.

The properties of both series of films reflect the changes to be expected for a progressive stiffening of the polymer chains (increased film brittleness) with increasing Pyrrone (TADPO and DAB) content. The tangent moduli show a general increase and the elongations show a corresponding decrease. Although less consistent, the yield and tensile strengths of the two series of films increase with increasing Pyrrone content.

### Thermal Stability

The thermal stabilities of the two copolymer series were determined by heating the films under vacuum using the thermogravimetric analytical procedure. The results are shown in Figure 3 for the PMDA-ODA/-

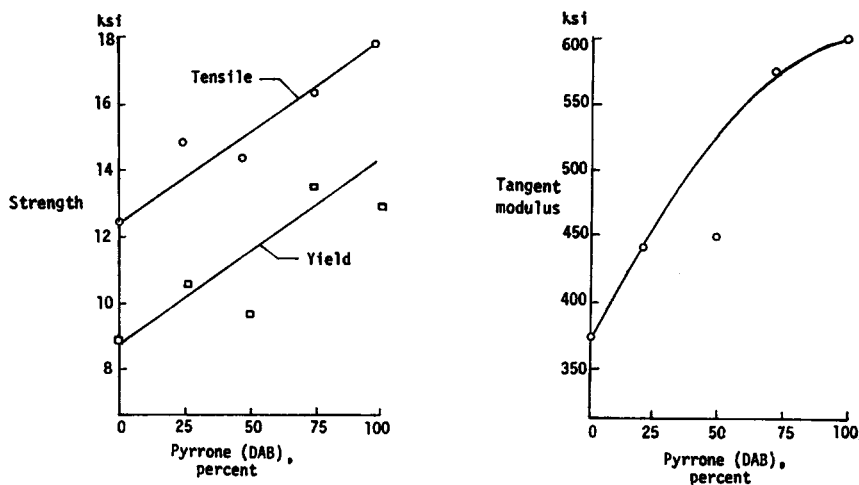


Fig. 2. Tensile properties of BTDA-ODA/DAB copolymer films.

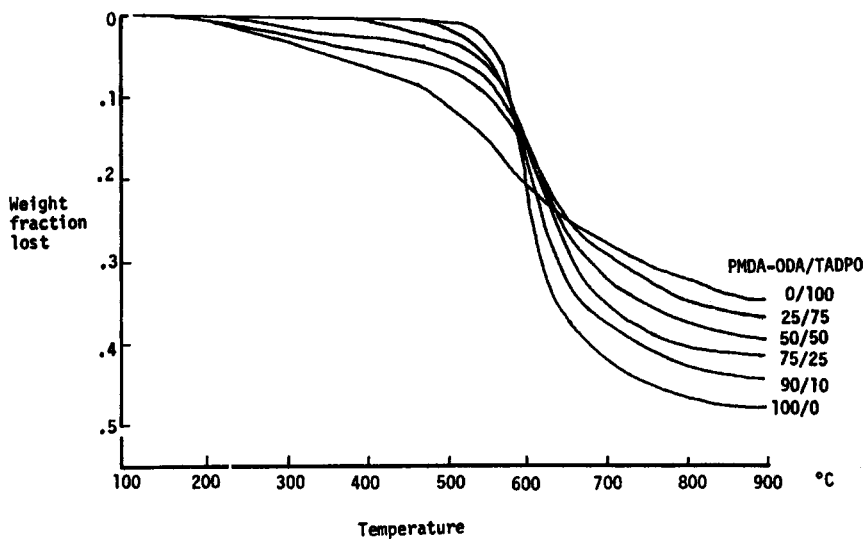


Fig. 3. Thermogravimetric analyses of PMDA-ODA/TADPO copolymer films under vacuum. Pressure,  $10^{-4}$  torr; heating rate,  $5^{\circ}\text{C}/\text{min}$ ; sample size, 2.0 mg; preconditioned for 30 min at  $100^{\circ}\text{C}$ .

TADPO films and in Figure 4 for the BTDA-ODA/DAB films. Copolymerization generally increased the thermal stability over that of the polyimides. For both series, the char yields at  $800^{\circ}\text{C}$  were greater for the copolymers containing more Pyrnone structure (higher percentages of TADPO and DAB).

The thermal stabilities of the copolymers were also measured by thermogravimetric analysis in air. The relative oxidative stabilities are pictured



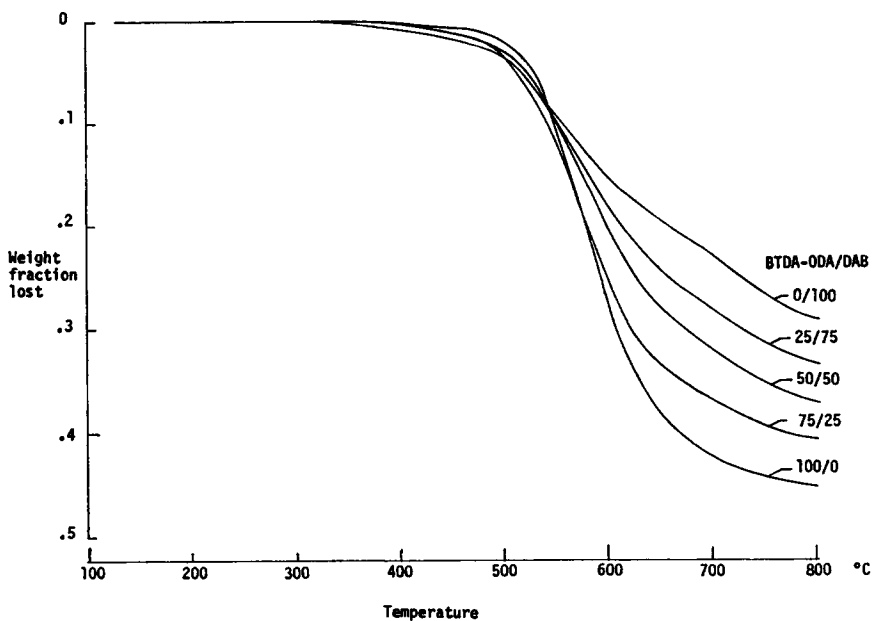


Fig. 4. Thermogravimetric analyses of BTDA-ODA/DAB copolymer films under vacuum. Pressure,  $10^{-6}$  torr; heating rate,  $5^{\circ}\text{C}/\text{min}$ ; sample size, 2.0 mg; preconditioned for 30 min at  $100^{\circ}\text{C}$ .

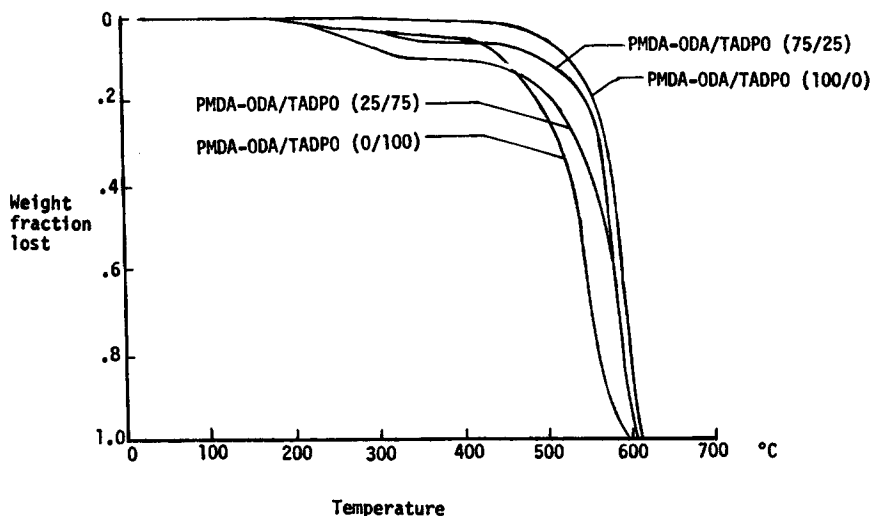


Fig. 5. Thermogravimetric analyses of PMDA-ODA/TADPO copolymer films in air. Atmosphere, air; heating rate,  $5^{\circ}\text{C}/\text{min}$ ; sample size, 2.0 mg; preconditioned for 30 min at  $100^{\circ}\text{C}$ .

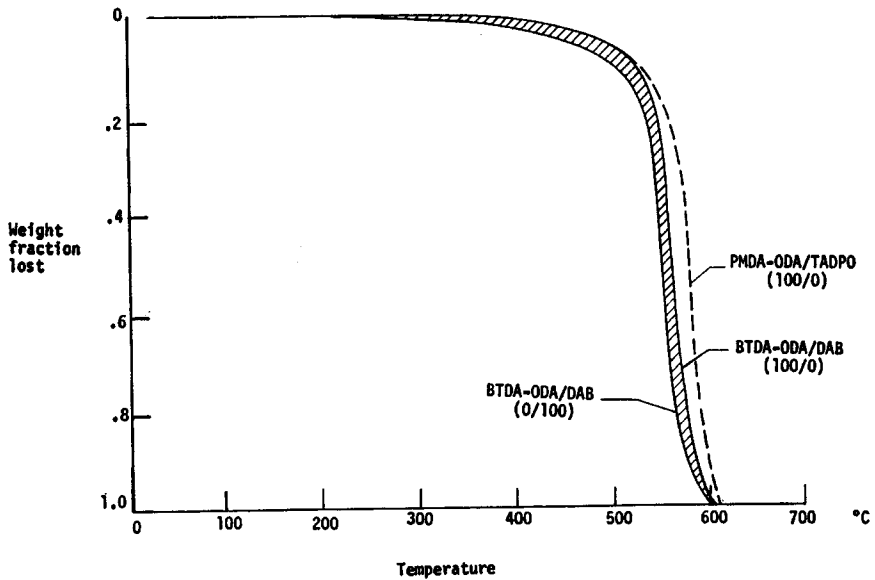


Fig. 6. Thermogravimetric analyses of BTDA-ODA/DAB copolymer films in air. Atmosphere, air; heating rate, 5°C/min; sample size, 2.0 mg; preconditioned for 30 min at 100°C.

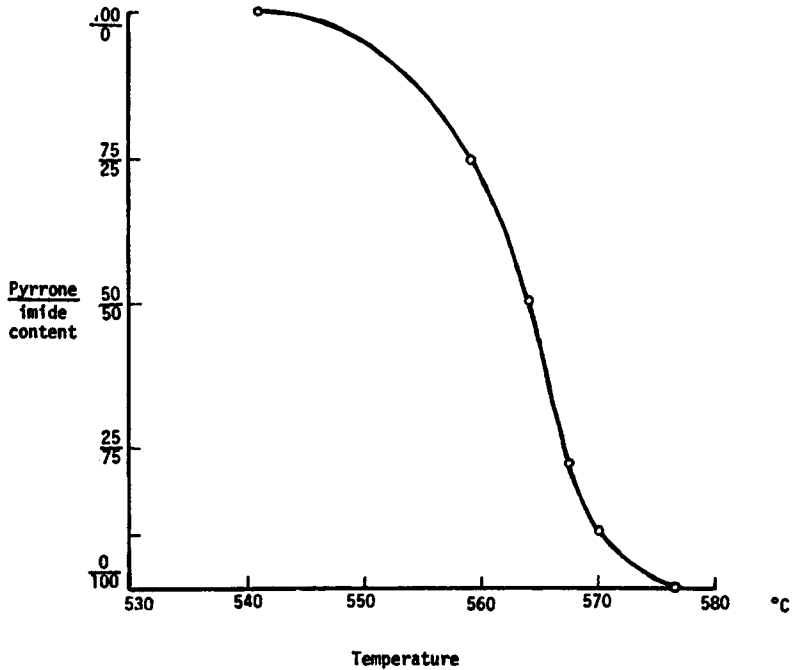


Fig. 7. Temperatures of maximum rates of decomposition in air of PMDA-ODA/TADPO copolymer films as a function of Pyrrone/imide content.

in Figure 5 for the PMDA-ODA/TADPO films and in Figure 6 for the BTDA-ODA/DAB films. The thermal stability of the PMDA series increases slightly with increasing imide content. Because of the close similarities of the thermogravimetric curves for the BTDA-derived copolymers they have all been represented within the shaded area of the curves for the BDTA-ODA/DAB (0/100) control polyimide and the BTDA-ODA/DAB (0/100) control Pyrrone films. For a comparison of the two series, the curve for the control polyimide of the PMDA-derived series has been indicated by a dashed line in Figure 6.

The effect of the copolymerization on the oxidative stability of the PMDA-ODA/TADPO copolymer series is pictured in a different manner in Figure 7. Here, the temperatures of maximum rates of decomposition of the copolymers, as determined by differential thermal analysis, are plotted as a function of Pyrrone/imide (TADPO/ODA) content, and it is apparent that the temperatures of the maximum rates of decomposition for the copolymers increase with increasing imide content. A corresponding evaluation of the BTDA-ODA/DAB series was not made.

Thus, it can be concluded that even though the thermal stabilities of the imide-Pyrrone copolymers in a vacuum are greater with increasing Pyrrone content, the effect of copolymerization on the oxidative stabilities is quite the opposite; that is, the copolymers with the higher imide content are superior in a thermal air environment.

### Chemical Stability

The resistance of the imide-Pyrrone copolymers to strong caustic and acidic reagents was more similar to that of the pure Pyrrones<sup>7</sup> than to that of the polyimides.<sup>2</sup> The presence of as little as 10% of the Pyrrone structure resulted in a marked change in chemical resistance, as shown in Table III for the PMDA-ODA/TADPO series. The reason for such an enhancement of the chemical resistance by the inclusion of Pyrrone structures has not been determined with certainty. The suggestion is strong that cross-linking is the main factor. However, while as little as 10% Pyrrone struc-

TABLE III  
Effect of Caustic and Acidic Reagents on PDMA-ODA/TADPO Copolymer Films\*

Copolymer composition	2 <i>N</i> NaOH	96% H <sub>2</sub> SO <sub>4</sub>	Fuming HNO <sub>3</sub>
PMDA-ODA/TADPO (100/0)	gelled mass in 0.5 hr	gelled mass in 1.0 hr	dissolved in 0.5 hr
PMDA-ODA/TADPO (90/10)	film intact for over hr	film intact for over hr	dissolved in 24 to 48 hr
PMDA-ODA/TADPO (75/25, 50/50, 25/75)	"	"	film intact for over 48 hr
PMDA-ODA/TADPO (0/100)	"	"	"

\* Tests performed on 1-mil films at room temperature.

ture in the PMDA-ODA/TADPO series resulted in a marked change in solubility, the mechanical properties of the film were not markedly changed from those of the pure polyimide film (PMDA-ODA/TADPO (100/0)), as would have been expected from a large amount of crosslinking. Therefore, some doubt is cast on the validity of the crosslinking explanation.

An experiment that not only emphasized the chemical stability of the imide-Pyrone copolymers, but also substantiated their copolymeric nature involved soaking 1-mil films of the PMDA-ODA/TADPO (75/25, 25/75) copolymers in yellow fuming nitric acid at room temperature. After 24 hr, the 75/25 and 25/75 copolymers had lost only 5% and 2% of their weights, respectively. In contrast, a film prepared from a simple mixture of 75% PMDA-ODA polyimide and 25% PMDA-TADPO Pyrrone prepolymers lost 57% of its weight after identical treatment. This result proves that the copolymers were not mere physical mixtures.

### Water Absorption

Regular variation of copolymer properties with respect to the constituent groups (Pyrone and imide) was further exemplified by the amounts of water absorbed readily by thin films of the two copolymer series. The weight percent of water absorbed at 25°C and 100% RH are plotted as a function of the amount of Pyrrone content (TADPO and DAB) for the

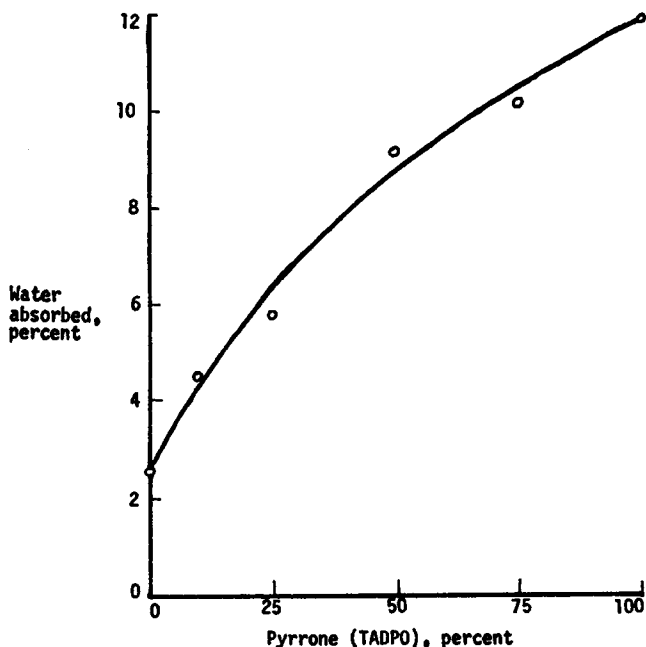


Fig. 8. Percentage water absorption by PMDA-ODA/TADPO copolymer films.

PMDA-ODA/TADPO series in Figure 8 and for the BTDA-ODA/DAB series in Figure 9. Though the increased water absorption caused by copolymerization would be less than desirable for such end uses as electrical insulation, uses can be imagined where the hydrophilic nature would be

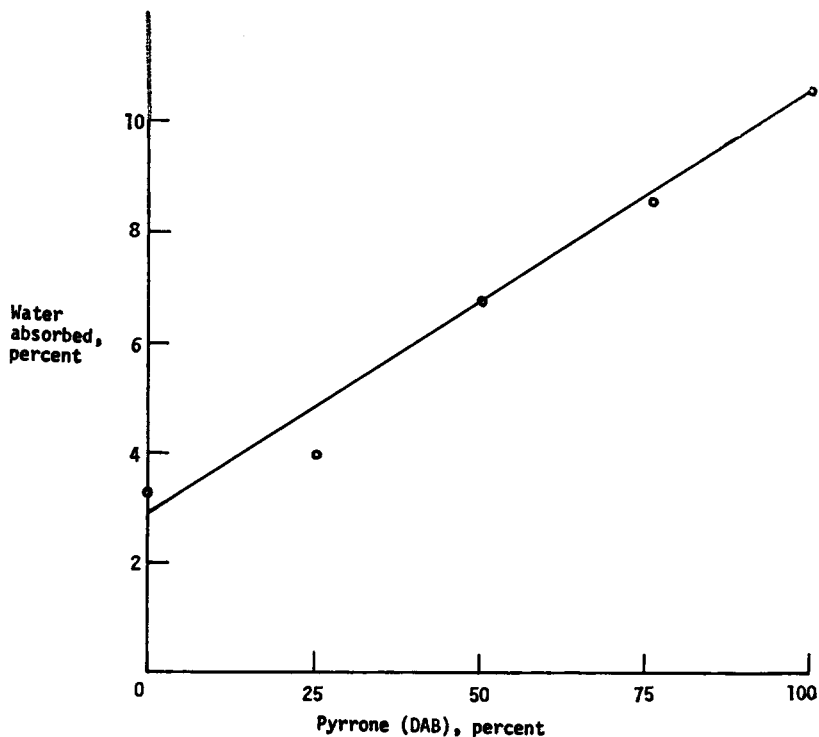


Fig. 9. Percentage water absorption by BTDA-ODA/DAB copolymer films.

desirable, such as in membranes for desalination or alkaline battery separators.

### CONCLUSIONS

Monomers for the synthesis of polyimides and pyrrone polymers can be copolymerized to give materials of potential use in aerospace applications. The compositions of these copolymers can be easily varied to give a versatile selection of properties. The properties vary in a regular manner with the compositions of the copolymers. The value of this property variation was demonstrated by the moderation of the inherent brittleness of pyrrone films by the incorporation of imide groups into the polymer.

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