INFORMATION NOT TO BE
RELEASED OUTSIDE NASA
UNTIL PAPER PRESENTED

SYNTHESIS AND THERMAL STABILITY
OF BENZIMIDAZOLE-AROMATIC IMIDE COPOLYMERS

Toshikazu Kurosaki and Philip R. Young

NASA Langley Research Center
Langley Station, Hampton, Va., USA

Presented at the IUPAC International Symposium
on Macromolecular Chemistry

FACILITY FORM 602

N68-27171 (ACCESSION NUMBER)	(THRU)
22 (PAGES)	1 (CODE)
TMX-59061 (NASA CR OR TMX OR AD NUMBER)	06 (CATEGORY)

Tokyo-Kyoto, Japan
September 28 - October 4, 1966

GPO PRICE $

CFSTI PRICE(S) $

Hard copy (HC) 1

Microfiche (MF)

ff 653 July 65

[redacted]

Synthesis and Thermal Stability of Benzimidazole-Aromatic Imide Copolymers

Toshikazu Kurosaki* and Philip R. Young
National Aeronautics and Space Administration, Langley Research Center,
Spacecraft Materials Section, Hampton, Virginia

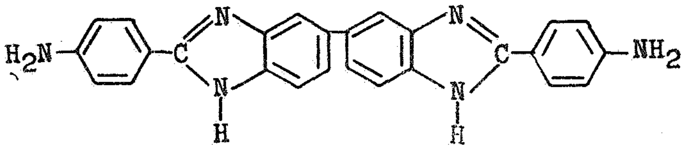
Introduction

Polybenzimidazoles(1-3) and aromatic polyimides(4-7) are well known for their high thermal stability. Recently Iwakura (8) et al. tried to prepare thermally stable benzimidazole-amide copolymers from 2,2'-amino-phenyl-5,5'-dibenzimidazole and dicarboxylic acid dichlorides. The approach in this laboratory was to synthesize benzimidazole-aromatic imide copolymers from diaminophenylbenzimidazoles and aromatic dianhydrides. This approach established that by choosing appropriate polymerization methods and curing processes, polymer films of high strength and excellent thermal stability were obtained. Recently Preston and Black(9) independently reported the results of their preparation of a series of copolymers, including one containing aromatic imide linkages contributed by one of the constituents.

This paper deals with the synthesis of various types of benzimidazole-aromatic imide copolymers, and the measurement of their mechanical and thermal properties.

Results and Discussion

The following discussion is related to the synthesis and evaluation of four types of diaminophenylbenzimidazoles as diamine monomers. Each of the four diamines results from the reaction of either para- or meta-aminobenzoic acid with an aromatic tetraamine, such as 1,2,4,5-tetraaminobenzene (TAB) or 3,3'-diaminobenzidine (DAB):

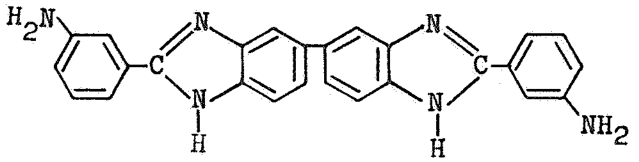


2,2'-di-p-aminophenyl-5,5'-dibenzimidazole (DAB-p-AB)

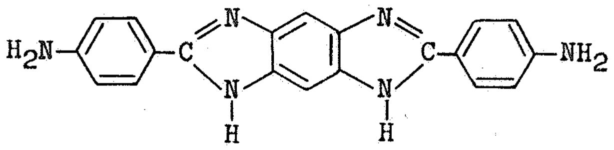
---

*NAS-NRC Resident Research Associate on leave of absence from the Tokyo Institute of Technology.

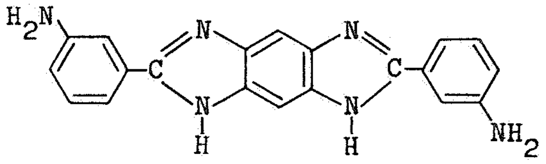
[redacted]



2,2'-di-m-aminophenyl-5,5'-dibenzimidazole (DAB-m-AB)

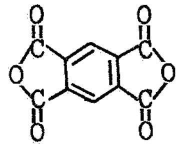


2,2'-di-p-aminophenyl-2,6-imidazobenzimidazole (TAB-p-AB)

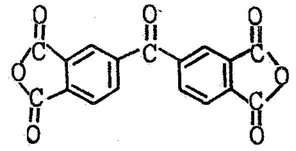


2,2'-di-m-aminophenyl-2,6-imidazobenzimidazole (TAB-m-AB)

These four diamines were then reacted with either of the two dianhydrides:

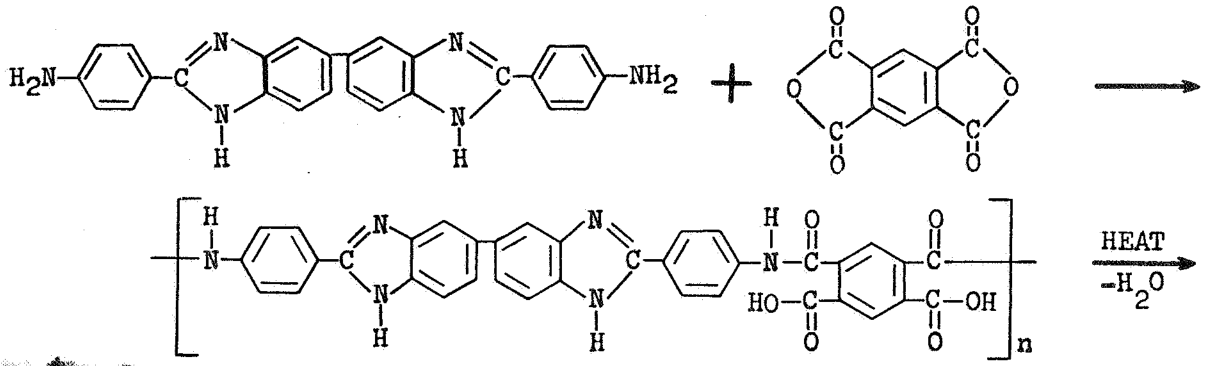


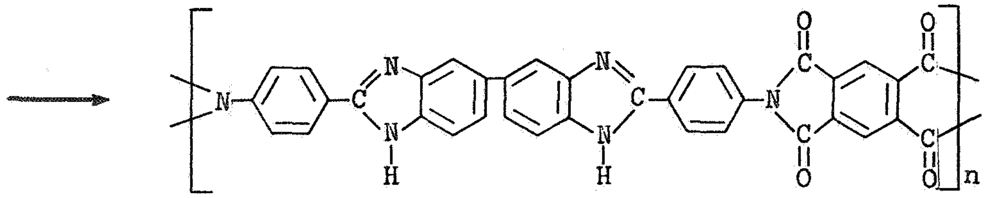
Pyromellitic dianhydride (PMDA), and



3,3'4,4'-benzophenone tetracarboxylic dianhydride (BPDA)

As a result of these reactions, eight types of polymers were synthesized from which films were prepared. The general reaction route is illustrated below by the combination of DAB-p-AB and PMDA in a typical polyimide synthesis.





The above mechanism was substantiated through the use of model compounds.

Monomers

The four monomers were prepared by Iwakura's method(8) of heating the appropriate aminobenzoic acids and tetraamines in polyphosphoric acid at 150°-170°C for ten hours. All of the monomers prepared in this manner were highly complexed(8) with solvent and drying was accomplished only after heating at 280°-300°C. Although the specific nature of the complex could not be confirmed from the infrared spectra of the undried and dried products (Figs. 1 and 2), it was assumed that complexing had occurred with alcohol and/or water, as indicated by the virtual disappearance of the -OH absorption peak in the 3400 cm^{-1} region on drying.

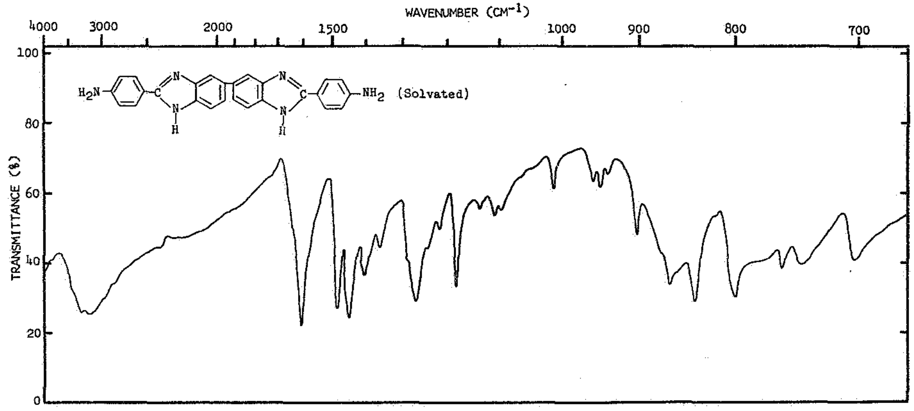


Figure 1. - I. R. spectrum of undried DAB-p-AB. (KBr pellet)

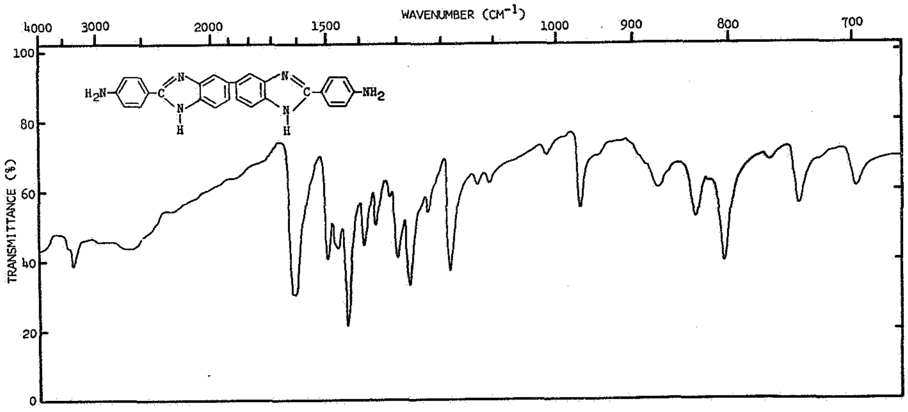


Figure 2. - I. R. spectrum of dried DAB-p-AB. (KBr pellet)

The differential thermal analysis (DTA) curves of undried DAB-p-AB and TAB-p-AB (Figs. 3 and 4) suggest strong solvent complexing of these compounds with loss of solvent occurring around 200°C.

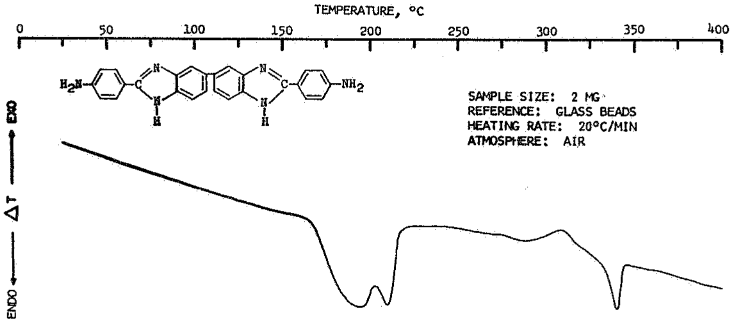


Figure 3. - DTA thermogram of undried DAB-p-AB, showing desolvation near 200°C and melting near 334°C.

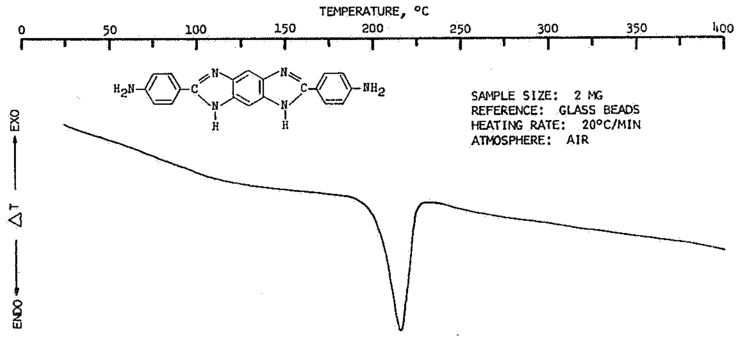


Figure 4. - DTA thermogram of undried TAB-p-AB, showing desolvation near 200°C.

The infrared spectra of the model compound, 2-aminophenylbenzimidazole, and each of the diamine monomers DAB-m-AB, TAB-p-AB, and TAB-m-AB are shown in Figures 5,6,7, and 8, respectively. Elemental analyses for each of the undried and dried monomers are summarized in Table I. These results are in good agreement with the proposed monomer structures.

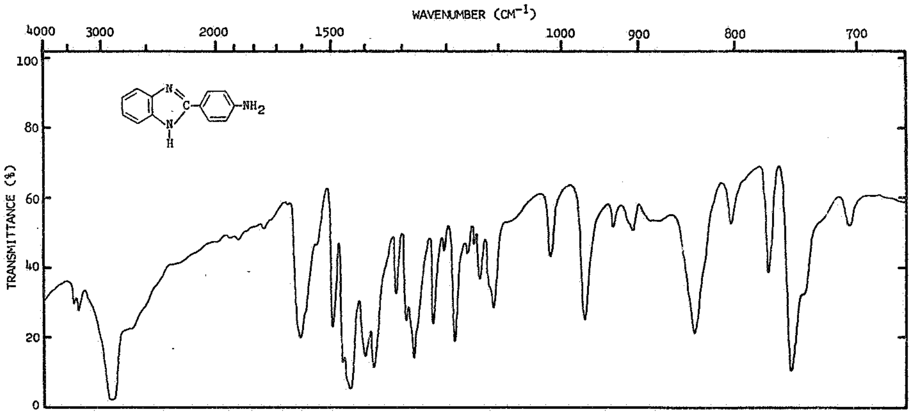


Figure 5. - I. R. spectrum of 2-aminophenyl benzimidazole, a model compound for the monomers.

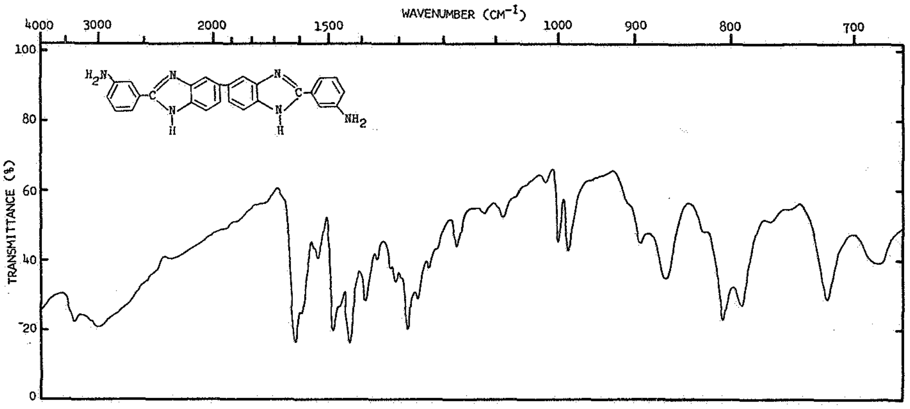


Figure 6. - I. R. spectrum of dried DAB-m-AB. (KBr pellet)

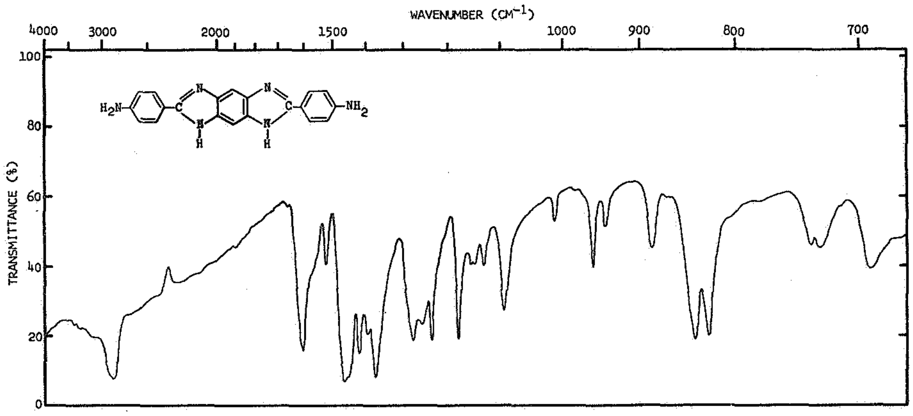


Figure 7. - I. R. spectrum of dried TAB-p-AB. (Nujol mull)

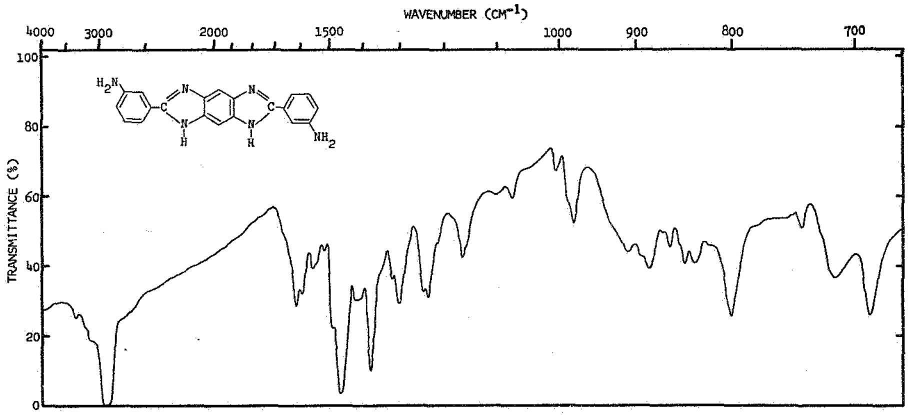


Figure 8. - I. R. spectrum of dried TAB-m-AB. (Nujol mull)

Table I

Elemental Analyses of Monomers

		Carbon %		Hydrogen %		Nitrogen %	
Compound	Condition	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
DAB-p-AB	Undried	74.98	68.48	4.84	5.39	20.18	17.61
	Dried	74.98	74.90	4.84	4.63	20.18	20.05
DAB-m-AB	Undried	74.98	71.53	4.84	4.90	20.18	19.12
	Dried	74.98	74.62	4.84	4.64	20.18	19.78
TAB-p-AB	Undried	70.60	68.16	4.70	4.94	24.70	22.59
	Dried	70.60	70.47	4.70	4.74	24.70	24.66
TAB-m-AB	Undried	70.60	68.58	4.70	4.73	24.70	23.05
	Dried	70.60	70.52	4.70	4.70	24.70	24.57

Polymerizations

Polymerization procedures were studied thoroughly in order to obtain high molecular weight aromatic polyamic acids. All solution polymerization methods, in which the aromatic dianhydride solution was added to a solution or slurry of monomer and solvent, failed to yield high molecular weight polymers. The solution polymerization in dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), and N-methylpyrrolidone at room temperature provided only low molecular weight polyamic acid prepolymers. The films from these prepolymers were found to be quite brittle even after only superficial drying at 80°-100°C.

High molecular weight polymers were obtained by the addition of theoretical amounts of solid dianhydride to mixtures of monomers and solvent. Dimethylsulfoxide was found to be the most suitable solvent of those examined. The effects of solvent on the intrinsic viscosities of the polymers are summarized in Table II.

Table II

Solvent Effect on Viscosity

Prepolymer	DMSO	DMAC
DAB-p-AB + PMDA	3.3 dl/g	1.45 dl/g
DAB-p-AB + BPDA	1.12	0.59
DAB-m-AB + PMDA	0.95	0.48
DAB-m-AB + BPDA	0.80	----
TAB-m-AB + PPDA	0.80	----

In the polymerization of DAB-p-AB and TAB-p-AB the entire reaction mixture formed a "gel" after the addition of the theoretical amount of anhydride. This was believed to be due to electrostatic interaction between polymer chains. However, these "gels" could be broken down by stirring vigorously in a Waring Blendor at temperatures below 80°C.

The polyamic acid prepolymers were cast on glass plates and dried superfically at 85°-100°C in air for 45-60 minutes. They were then cured at 280°-320°C in air for periods ranging from 15 minutes to ten hours to bring about ring closure. Lower curing temperatures (e.g. 175°-220°C) which have been previously reported (8) invariably led to "flaking" films.

A number of model compounds were prepared and examined to study the spectral changes which accompany the formation of the intermediate acid-amide and subsequent ring closure. These compounds and their respective infrared spectra are given below:

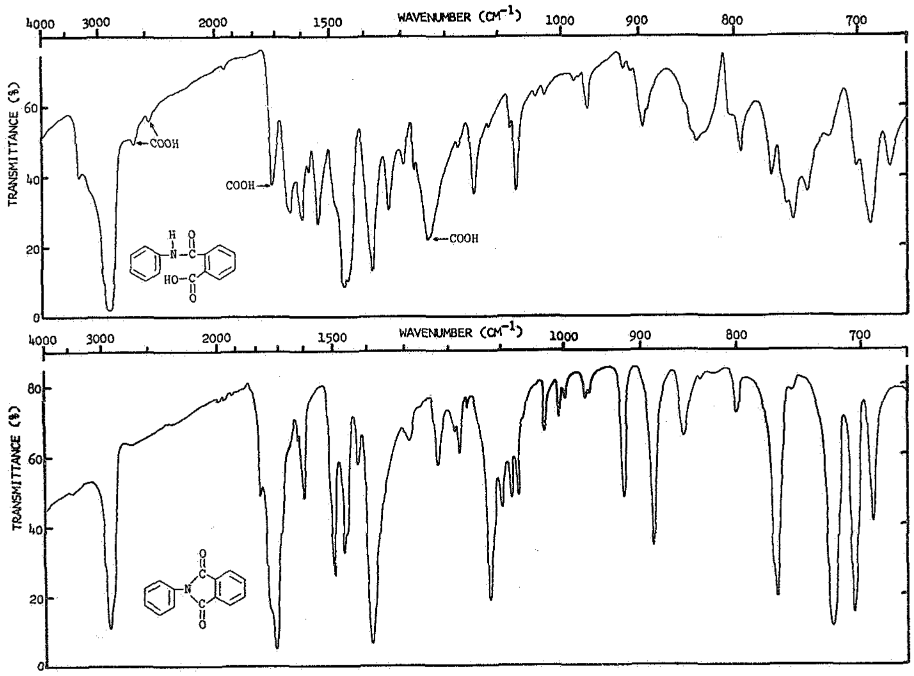


Figure 9. - Above: Phthalo-mono-anilide. (Nujol mull)

Below: N-phenyl phthalimide. (Nujol mull)

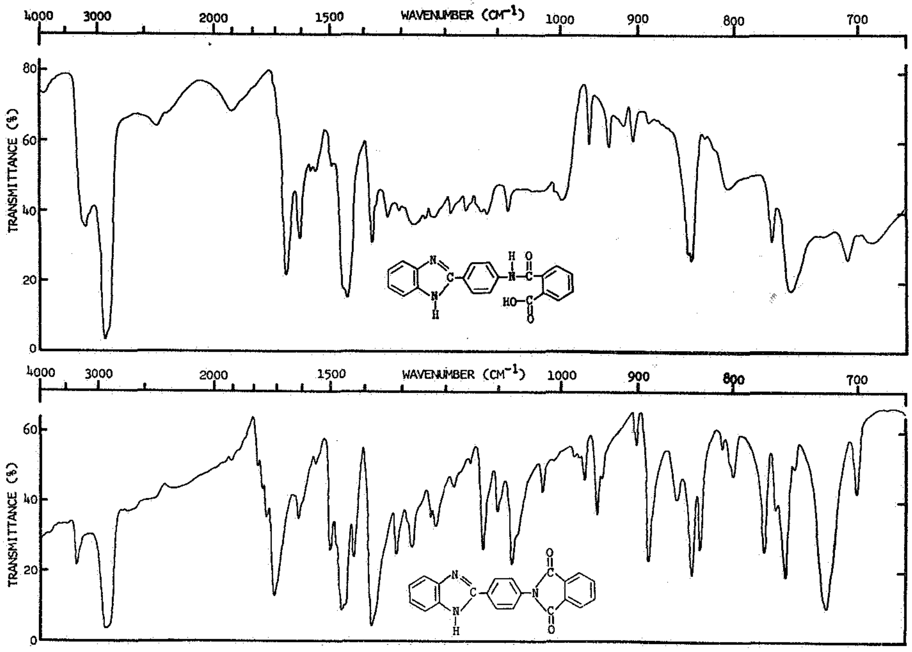


Figure 10. - Above: 2-N-phthaloyl-p-aminophenyl benzimidazole. (Nujol mull)

Below: 2-p-Phthaliminophenyl benzimidazole. (Nujol mull)

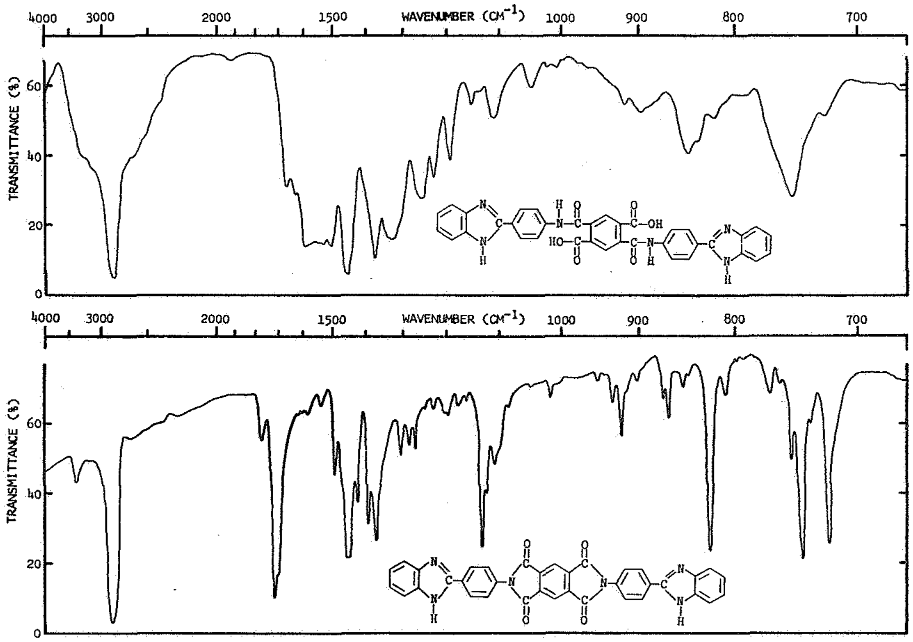


Figure 11. - Above: 1,4, Pyromellito-bis-p-2-benzimidazolylanilide. (Nujol mull)

Below: N,N'-p-2-Benzimidazole-phenylpyromellito-imide. (Nujol mull)

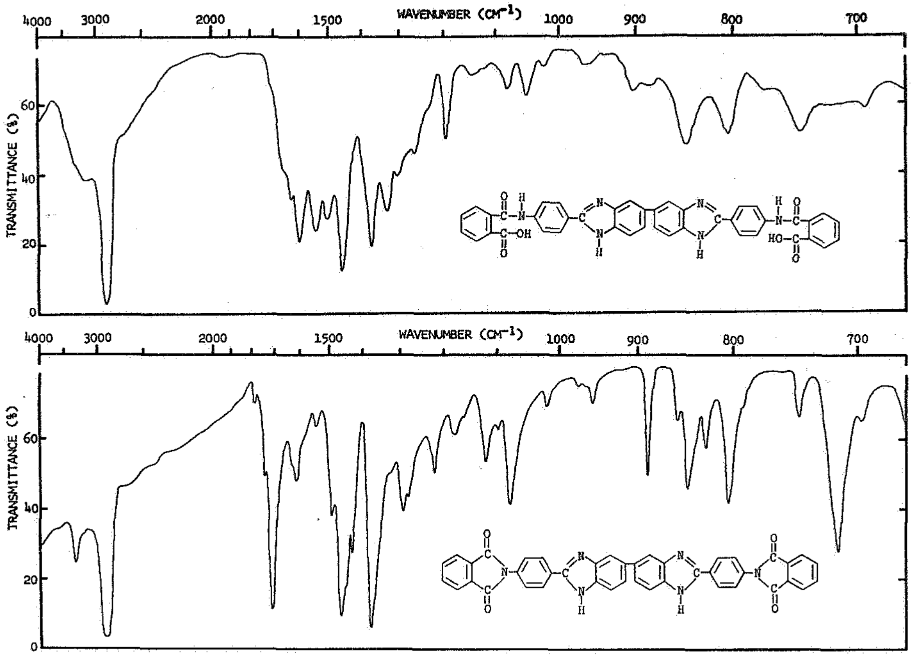


Figure 12. - Above: 2,2'-Di-p-phthalamidophenyl-5,5'-benzimidazole. (Nujol mull)

Below: 2,2'-Di-p-phthaliminophenyl-5,5'-bibenzimidazole (Nujol mull)

In some instances, ring closure was accomplished by refluxing in a mixture of Pyridine and acetic anhydride. It was observed that the infrared spectra of the products, obtained either by direct heating or from a refluxing solution, were identical. The infrared spectra of the polyamic-acid prepolymer I and the completely cyclized and cured product II are shown in Figure 13.

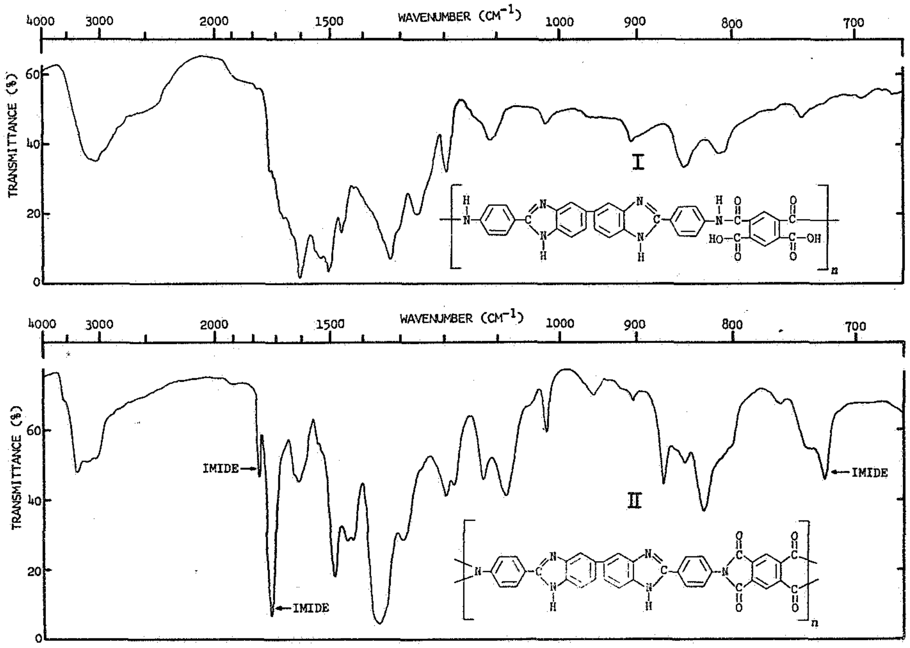


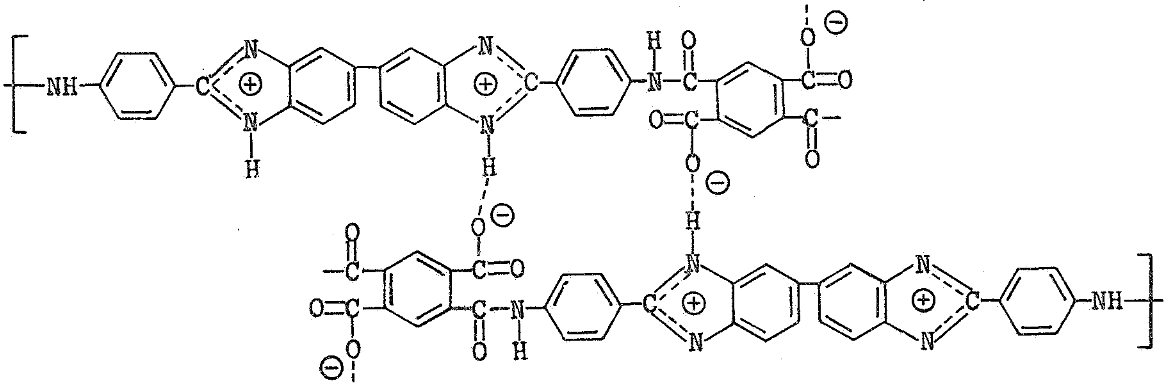
Figure 13. - Above: I. R. spectrum of polyamic acid prepolymer (I).

Below: I. R. spectrum of benzimidazole-aromatic imide copolymer (II) from DAB-p-AB and PMDA, formed by ring closure.

An examination of the infrared spectrum of phthalo-mono-anilide (Fig. 9) discloses that the simplest amide-acid moiety can be characterized by absorption peaks at 2400-2700 cm^{-1}, 1720 cm^{-1}, and 1230 cm^{-1}, attributable to the carboxyl group. In the more complicated model compounds, which contain the benzimidazole ring, the characteristic carboxyl absorption has been apparently replaced by absorption due to carboxylate ion near 1500 cm^{-1}. Similar peaks are observed for the amide-acids shown in Figures 10, 11, and 12.

These observations suggest the possibility of salt formation between the carboxylic acid group and the basic benzimidazole ring. The spectra of compounds before ring closure shown in Figures 11 and 12 exhibit a broadening of the absorption in the region of 1700-1500 cm^{-1}. This is due presumably to the combined effects of the un-ionized acid, the carboxylate ion, and the amide groups; however, the carboxylate ion apparently predominates over the un-ionized acid.

These observations suggest that the polyamic-acid prepolymer structure might be more adequately interpreted as the ionized form shown below, rather than the non-ionized structure previously depicted as I.



Ionized Form of Structure of Polyamic-Acid Prepolymer

Interpretation of these results in terms of the polar structure shown above would then account for the observed formation of "gel" on addition of an anhydride. It would also be expected that the tendence of carboxylic acid groups to participate in ring closure would be inhibited by salt formation with the benzimidazole ring, and relatively higher temperatures would be necessary to bring about the proper ring closure. Consequently, one might anticipate that curing at lower temperatures would lead to chain scission with subsequent "flaking" of the polymer films. Occurrence of flaking after curing at 175-220°C supports this argument.

By heating these model compounds and the polyamic-acid prepolymers, typical imide-absorption peaks appeared in the infrared around 1790 cm^{-1}, 1710 cm^{-1}, and 720 cm^{-1} (Fig. 13). The infrared spectrum of each copolymer film was recorded and found to support the proposed benzimidazole and aromatic imide structures. No substantial changes in the spectra were observed by extending heating times up to at least 7 hours at 300°C. Elemental analyses for the various polymer films are shown in Table III.

Table III

Elemental Analysis of Benzimidazole-Aromatic Copolymers Dried at 80°C Under Vacuum for 10 Hours

	%	Obs.	Calc.	Obs. (corr.)	Obs. H_2O wt.%
DAB-p-AB-PMDA 0.5 hr/300°C	C	65.52	72.34	71.46	8.32 (8)
	H	3.52	2.87	2.59	
	N	12.86	14.07	14.03	
	O	18.10	10.71	10.71	
DAB-m-AB-PMDA 1 hr/300°C	C	64.85	72.34	72.43	9.27 (6)
	H	3.63	2.87	2.59	
	N	12.59	14.07	13.88	
	O	18.94	10.71	10.71	
DAB-p-AB-BPDA 2 hrs/300°C	C	68.66	73.60	73.10	6.07 (4 and 6*)
	H	3.63	3.02	2.94	
	N	10.94	11.98	11.64	
	O	16.79	11.40	11.40	
DAB-m-AB-BPDA 3.5 hrs/300°C	C	69.31	73.60	73.32	5.47 (5)
	H	3.37	3.02	2.76	
	N	11.06	11.98	11.70	
	O	16.26	11.40	11.40	
TAB-p-AB-PMDA 0.5 hr/300°C	C	62.84	68.96	70.84	11.30 (9)
	H	3.84	2.71	2.07	
	N	11.45	16.09	12.96	
	O	22.28	12.25	12.25	
TAB-p-AB-BPDA 1 hr/300°C	C	66.05	70.92	70.67	6.54 (6)
	H	3.37	2.90	2.64	
	N	12.00	13.42	12.83	
	O	18.58	12.77	12.77	
TAB-m-AB-BPDA 3 hrs/300°C	C	65.34	70.92	70.75	7.65 (6)
	H	3.07	2.90	2.21	
	N	12.03	13.42	13.03	
	O	19.56	12.77	12.77	
DAB-m-AB-BPDA 0.25 hr/300°C	C	68.67	73.60	73.13	6.10 ——
	H	3.57	3.02	2.89	
	N	10.94	11.98	11.65	
	O	16.82	11.40	11.40	
TAB-m-AB-BPDA 0.25 hr/300°C	C	63.52	70.92	70.42	9.91 ——
	H	3.60	2.90	2.58	
	N	11.31	13.42	12.54	
	O	21.57	12.77	12.77	

Analyses for C, H (Dumas Method) and N (Kjeldahl Method) were conducted by Micro-Analysis, Inc., Wilmington, Delaware.

( ) indicates absorbed water loss up to 250°C from TGA data.

* TGA measurement extended to 350°C

Table III gives the results of elemental analyses for C, H, N, and O for seven of the copolymers investigated. Values in the "Calc." column should be compared with those in the column headed "Obs. (Corr.)." This comparison confirms the copolymer structures which are typified by the structure for the DAB-p-AB - PMDA copolymer given in Figure 13.

The experimental quantities in the "Obs." column were corrected for the presence of absorbed water to give the values in the column headed "Obs. (Corr.)." This was done by attributing any excess above the calculated percentage of oxygen to oxygen from absorbed water and calculating the effect which that quantity of absorbed water (listed in the "Absorbed Water" column) would have on the percentages of the other elements. The validity of this procedure is confirmed by the direct thermogravimetric measurement of the percentage of absorbed water in each copolymer, the results of which appear in parentheses in the column headed "Absorbed Water." The larger deviation of corrected values in the shorter cured samples is assumed to be due to the presence of unevaporated solvent and absorbed water. Similar water absorption behavior has been observed for polyimidazopyrrolones.(10).

The mechanical properties of the copolymers are summarized in Table IV. Those films containing the para-aminobenzoic acid unit exhibit tensile strengths of approximately 25,000 psi, while those containing the meta-aminobenzoic acid unit have tensile strengths around 17,500 psi. This difference in tensile strength between the two series may be due to the presence of some irregularity present in the main polymer chain due to the presence of the meta isomer.

Table IV

Mechanical Properties of Copolymer Films Cured for One Hour at 300°C

	Tensile Strength, psi	Elongation, %
DAB-p-AB-PMDA	24,750*	2.0
DAB-p-AB-BPDA	24,000+	3.8
DAB-m-AB-PMDA	17,600*	3.5
DAB-m-AB-BPDA	17,500**	3.5
TAB-p-AB-PMDA	25,600+	1.5
TAB-p-AB-BPDA	27,200+	3.3
TAB-m-AB-PMDA*	---+	---+
TAB-m-AB-BPDA	17,600*	3.3

* 1 hr. cure + 0.5 hrs. cure
** 2 hrs. cure

In Table V are given the results of a preliminary study of the effects of time at 300°C on the mechanical properties of the films. Some variation in these properties with film thickness was observed in certain cases. There were five instances in which casting was made from a concentrated polymer solution (15-18%).

Table V

Effect of Time at 300°C on Mechanical Properties of Copolymer Films

Copolymer Film	Strength, psi	Elongation, %	% of Maximum Tensile Strength
DAB-p-AB-PMDA			
15 min	21,000	2.5	85
2 hrs.	24,750	2.1	100
10 hrs.	24,000	2.0	97
DAB-p-AB-BPDA			
15 min.	22,000	3.8	91.5
1 hr.	24,000	3.8	100
2 hrs.	23,000	3.6	97.0
4 hrs.	23,800	3.1	98.7
30 min. } prepared from 15-18% solution	30,700	3.4	
10 hrs.	26,500	2.7	87.5
DAB-m-AB-PMDA			
10 min.	18,400	3.4	100
1 hr.	17,600	3.5	95.5
2 hrs.	17,900	3.6	97.5
30 min. } prepared from 15-18% solution	21,300	4.7	
4 hrs.	22,300	4.7	
10 hrs.	19,900	3.7	93.5
DAB-m-AB-BPDA			
15 min.	17,600	3.8	100
2 hrs.	17,500	3.5	99.5
3.5 hrs.	17,400	3.5	98.5
TAB-p-AB-PMDA			
15 min.	24,300	1.7	95
30 min.	25,600	1.7	100
1 hr.	24,000	1.7	94
6 hrs.	20,00	1.5	78.3
TAB-p-AB-BPDA			
30 min	27,200	3.3	100
1 hr.	23,000	2.8	84.5
2.5 hrs.	21,200	2.3	78.0
6.5 hrs.	21,500	2.2	79.0
10 hrs.	21,800	2.2	80.0
TAB-m-AB-BPDA			
15 min.	12,000	2.4	68.7
1 hr.	17,600	3.3	100
3 hrs.	18,000	2.9	102
10 hrs.	15,000	2.6	85.3

The fully cured copolymer films maintain their strength for at least 10 hours at 300°C in air. A minimum curing time of one hour is required to approach maximum tensile strength. Shorter cure times produce incomplete ring closure which results in increased sensitivity to hydrolysis at room temperature. Accordingly, incompletely cured polyamic-acid prepolymers that are exposed to the atmosphere for several months become very brittle, presumably due to hydrolysis of amide groups, acid-catalyzed by neighboring carboxylate groups.

Thermal Stability

The oxidation temperatures of the benzimidazole-aromatic imide copolymer films can be ascertained from their maximum exothermic peaks when evaluated using the DuPont DTA-900 Differential Thermal Analyzer. The results are summarized in Table VI and an example of a typical DTA curve is shown in Figure 14.

Table VI

Oxidation Temperature of Benzimidazole-Aromatic Imide Copolymers

Copolymer	Oxidation Temp., °C
DAB-p-AB-PMDA	568
DAB-p-AB-BPDA	586
DAB-m-AB-PMDA	577
DAB-m-AB-BPDA	590
TAB-p-AB-PMDA	568
TAB-p-AB-BPDA	590
TAB-m-AB-PMDA	577
TAB-m-AB-BPDA	590

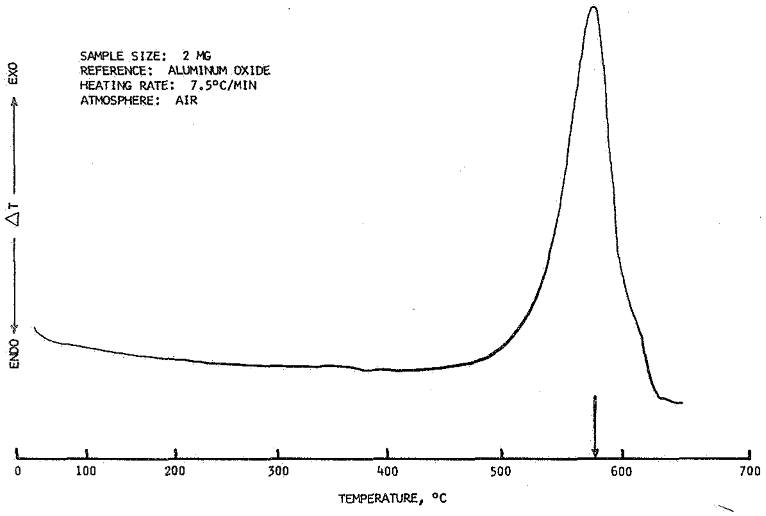


Figure 14. - DTA thermogram of DAB-m-AB-PMDA, run in air.

The DTA studies indicate that there is no significant difference between the thermal stability of the diaminobenzidine and tetraaminobenzene derivatives; however, the meta-aminobenzoic acid and benzophenone dianhydride units appear to increase the thermal stability of the polymers to a slight extent.

The thermogravimetric measurements were made both in air and <u>in vacuo</u> to evaluate the thermal stability of the copolymer. The thermograms, programmed at a heating rate of 5°C per minute, are summarized in figures 15, 16, 17, and 18.

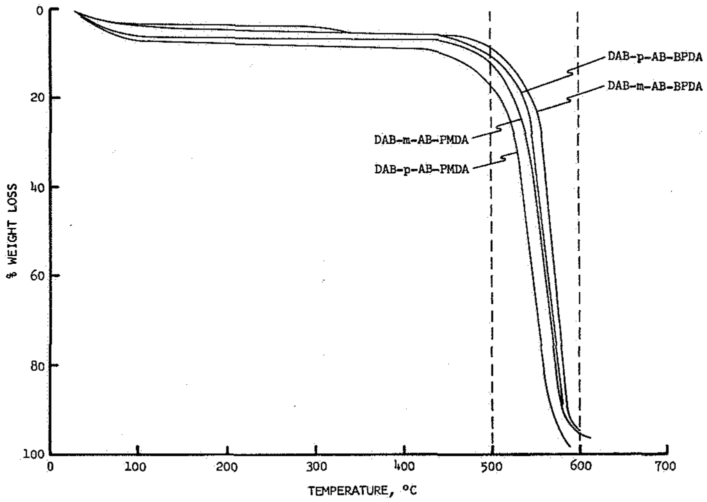


Figure 15. - TGA thermograms of DAB copolymers run in air at a 5°C/min heating rate.

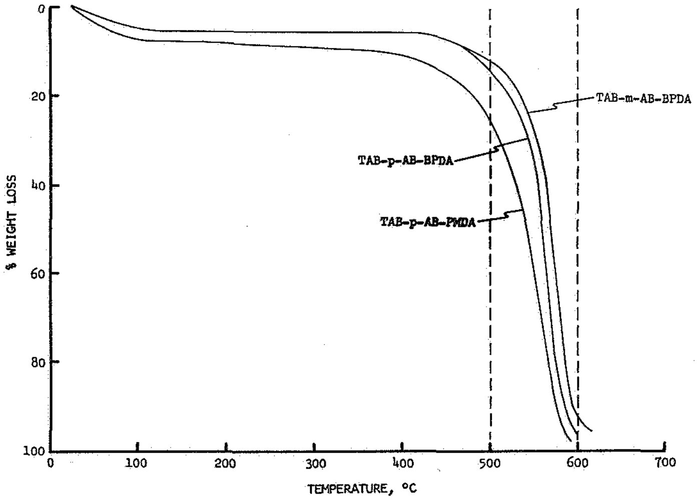


Figure 16. - TGA thermograms of TAB copolymers run in air at a 5°C/min heating rate.

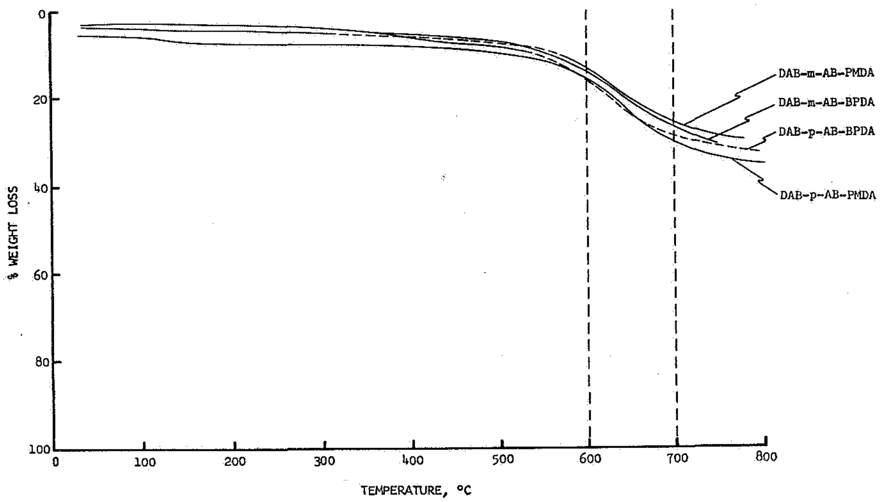


Figure 17. - TGA thermograms of DAB copolymers run *in vacuo* at a 5°C/min heating rate.

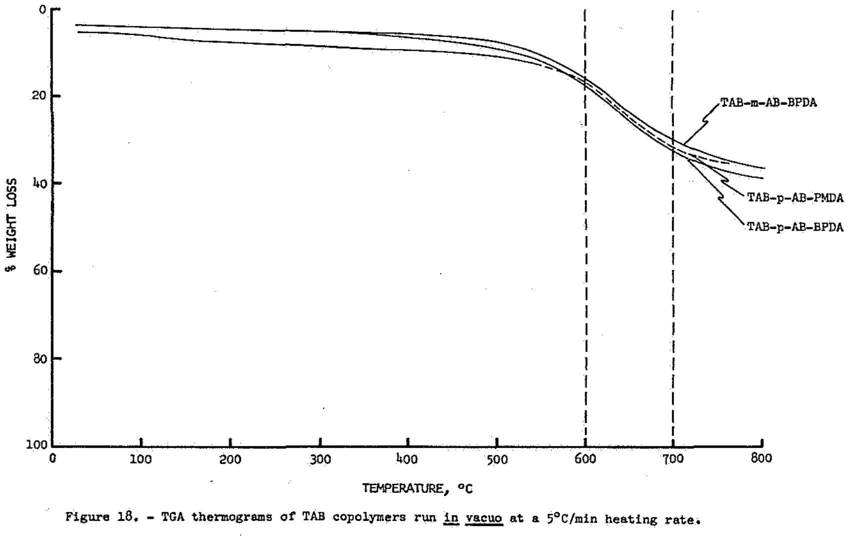


Figure 18. - TGA thermograms of TAB copolymers run *in vacuo* at a 5°C/min heating rate.

The results in Figures 15-18 show that in air, the 15% weight loss levels for diaminobenzidine-derived polymers lie in the 520°-550°C range, and 490°-535°C for tetraaminobenzine polymers. The recorded temperatures (corrected for absorbed water) for the diaminobenzidine and tetraaminobenzene polymers in a vacuum are 625°-630°C and 620°-625°C, respectively. The thermal stability values of the DAB-m-AB - PMDA imide copolymer are higher than those previously reported for similar copolymers of DAB-m-AB and PMDA.

This report of the excellent thermal stability of the benzimidazole-aromatic imide copolymer contrasts somewhat with the data reported previously for the copolymer of diaminobenzidine-meta-amino benzoic acid and pyromellitic dianhydride(8, 9). A more detailed study of these copolymers will be reported in a future publication(11).

Experimental

Properties

Intrinsic Viscosity. - Viscosity measurements were made in N,N-dimethylacetamide at 25°C using Ubbelohde viscometers. The solutions were prepared from polymers which had been precipitated and dried *in vacuo*, and intrinsic viscosity was measured by a four-point extrapolation to infinite dilution following Huggins' Equation.

Differential Thermal Analysis (DTA). - These measurements were performed on the polymers using a DuPont 900 Differential Thermal Analyzer. The conditions employed have been detailed in figures 3, 4, and 14.

Thermogravimetric Analysis (TGA). - These studies were performed using a null-balancing automatic recording electrobalance (Cahn RG Electrobalance) using polymer sample sizes of 2.05 ± 0.03 milligrams. Vacuum measurements were carried out at a pressure of 10^{-6} (Torr) which was maintained by an ion pump with a capacity of 250 liters per second.

Mechanical Properties. - The mechanical properties of the polymer films were measured on an Instron Tensile Tester, using film strips 0.5 inch wide with 3.0 inches gage length, and a cross-head speed of 3.0 inches (100% strain) per minute.

Infrared Spectra. - Infrared spectra were recorded using a Perkin-Elmer Model 137 Infrared Spectrometer.

Reagents

3,3'-Diaminobenzidine (DAB). - This starting material was obtained from Burdick and Jackson Laboratories, Inc., Muskegon, Michigan and used as received.

1,2,4,5-Tetraaminobenzene Tetrahydrochloride. - This material was obtained from Burdick and Jackson Laboratories, Inc. and was used without purification.

Aminobenzoic Acids. - Reagent grade m- and p-aminobenzoic acids were used as received from Fisher Scientific Company.

Pyromellitic Dianhydride (PMDA). - This dianhydride was obtained from Hexagon Laboratories, Inc., New York, N. Y., and Princeton Chemical Company, Princeton, New Jersey. The commercial material was sublimed at 220°C/0.5 mm before use.

Benzophenone Tetracarboxylic Acid Dianhydride (BPDA). - BPDA was obtained from Gulf Chemical Company, Pittsburgh, Pennsylvania and was recrystallized from acetic anhydride.

Model Compounds

Phthalomonoanilide. - Fifty grams (0.338 mole) of phthalic anhydride was added, with stirring to a solution of 30 g. (0.323 mole) of aniline in 300 ml. of benzene at 50°C. The reaction mixture was allowed to stand at room temperature for one hour. The crystals which precipitated were collected by filtration and recrystallized from ethanol. The yield of colorless crystals, m.p. 183-184°C, was 70 grams (88%).

Anal. Calcd. for $C_{14}H_{11}NO_3$: C, 69.69; H, 4.60; N, 5.81.
Obs.: C, 70.02; H, 4.51; N, 5.94.

N-Phenylphthalimide. - Ten grams of phthalomonoanilide was heated under a flow of nitrogen for three hours at 230-250°C. The resulting product, which was insoluble in benzene and ethanol, was recrystallized from tetrahydrofuran to give 7 g. (76%) of colorless crystals, m.p. 209-210°C.

Anal. Calcd. for $C_{14}H_9NO_2$: C, 75.32; H, 4.07; N, 6.27.
Obs.: C, 75.48; H, 4.10; N, 6.38.

2-(p-Aminophenyl) benzimidazole. - A solution of 15 g. (0.139 mole) of o-phenylenediamine and 22 g. (0.160 mole) of p-aminobenzoic acid in aqueous 4 N hydrochloric acid was refluxed for 70 hours. After the reaction mixture was neutralized with aqueous ammonium hydroxide, the product was collected by filtration and recrystallized from 1:1 ethanol:water. The yield of colorless crystals was 17 g. (59%), m.p. 252°C.

Anal. Calcd. for $C_{13}H_{11}N_3$: C, 74.60; H, 5.31; N, 20.08.
Obs.: C, 74.63; H, 5.41; N, 20.23.

2-(N-Phthaloyl-p-aminophenyl) benzimidazole. - Phthalic anhydride (1.4 g., 0.0095 mole) was added in small portions to a solution of 2.1 g. (0.01 mole) of 2-(p-aminophenyl) benzimidazole in 10 ml. of dimethylformamide at room temperature. The solution was then heated at 100°C for 15 minutes during which time a solid precipitated from solution. The yellow crystals which were collected by filtration weighed 3.3 g. (97%), m.p. 270°C.

Anal. Calcd. for $C_{21}H_{15}N_3O_3$: C, 70.37; H, 4.51; N, 11.73.
Obs.: C, 71.35; H, 4.50; N, 11.52.

2-(p-Phthaliminophenyl) benzimidazole. - 2-(N-Phthaloyl-p-aminophenyl) benzimidazole was heated at 300°C for one hour under vacuum. The resulting yellow solid was washed with ethanol to give a 95% yield of solid melting at 318-320°C.

Anal. Calcd. for $C_{21}H_{13}N_3O_2$: C, 74.26; H, 3.87; N, 12.45.
Obs.: C, 74.45; H, 3.79; N, 12.66.

1,4-Pyromellito-bis(p-2-benzimidazole) anilide. - Pyromellitic dianhydride (0.5 g., 0.0023 mole) was added with stirring at room temperature to a slurry of one gram (0.0048 mole) of 2-(p-aminophenyl) benzimidazole in 20 ml. of dimethylacetamide. The mixture became homogeneous after which precipitation of a solid occurred. The crude product was collected by filtration and washed with ethanol to give an 85% yield of a light yellow, infusible solid.

Anal. Calcd. for $C_{36}H_{24}N_6O_6$: C, 67.91; H, 3.81; N, 13.20.
Obs.: C, 65.01; H, 4.34; N, 12.35.
Obs. (Corr. as a complex with 5.58 wt. % of C_2H_5OH), C, 67.91; H, 3.61; N, 13.07.

N,N'-Di(p-2-benzimidazolyl phenyl) pyromellitimide. - The corresponding pyromellitobenzimidazolyl-anilide was heated in a tube under vacuum at 300°C for one hour. A golden, infusible solid was obtained which was washed with ethanol. The yield of product was 95%. The same imidization was carried out by boiling the carboxyanilide in a 1:1 solution of pyridine and acetic anhydride for three hours. The solid which precipitated was collected by filtration and washed with ethanol.

Anal. Calcd. for $C_{36}H_{20}N_6O_4$: C, 71.99; H, 3.36; N, 13.66.
Obs. (via heat): C, 71.13; H, 3.39; N, 13.72.
Obs. (pyridine and acetic anhydride): C, 71.21; H, 3.41; N, 13.92.
Obs. (Corr. as a complex with 1.65 wt. % of C_2H_5OH), C, 71.99; H, 3.10; N, 13.95 (via heat).
Obs. (Corr. as a complex with 1.46 wt. % of C_2H_5OH), C, 71.99; H, 3.22; N, 14.13 (pyridine and acetic anhydride).

2,2'-Di-(p-phthalamido phenyl)-5,5'-bibenzimidazole. - Phthalic anhydride (0.6 g., 4×10^{-3} mole) was added to a mixture of 0.8 g. (1.9×10^{-3} mole) of 2,2'-di-(p-amino phenyl)-5,5'-bibenzimidazole in 10 ml. dimethyl acetamide. The solid which precipitated was washed with alcohol to give a 100% yield of a light yellow, infusible powder.

Anal. Calcd. for $C_{42}H_{28}N_6O_6$: C, 70.77; H, 3.97; N, 11.79
Obs.: C, 68.43; H, 4.45; N, 11.60.
Obs. (Corr. as a complex with 4.49 wt. % of C_2H_5OH), C, 70.77; H, 3.86; N, 12.14.

2,2'-Bis-(p-phthaliminophenyl)-5,5'-bibenzimidazole. - One gram of the corresponding phthalamido-phenylbenzimidazole was heated at 300°C for three hours. A 95% yield of an infusible, yellow solid was obtained. The reaction was also performed by boiling the starting material in a 1:1 pyridine: acetic anhydride solution for three hours. After the mixture was cooled, the solid was collected by filtration and washed with ethanol to give a golden infusible powder.

Anal. Calcd. for $C_{42}H_{24}N_6O_4$: C, 74.54; H, 3.58; N, 12.42.
Obs. (via heat): C, 73.44; H, 3.75; N, 13.33.
Obs. (Pyridine and acetic anhydride), C, 73.13; H, 3.83; N, 12.30.
Obs. (Corr. as a complex with 2.11 wt. % of C_2H_5OH), c, 74.54; H, 3.47; N, 12.60 (via heat).
Obs. (Corr. as a complex with 2.86 wt. % of C_2H_5OH), c, 74.54; H, 3.35; N, 12.66.

Monomers

Diaminophenylbenzimidazoles. -

(a) Using 3,3'-Diaminobenzidine (DAB) - The tetraamines were dissolved in polyphosphoric acid as a 5% solution by weight and heated under a protective nitrogen atmosphere. Two molar quantities of the aminobenzoic acid were added at 170°C and heating was continued, with stirring, for 10 hours under nitrogen. After the polyphosphoric acid solution was cooled to room temperature, the reaction product was precipitated with water. The solid was collected by filtration, stirred in aqueous ammonium hydroxide solution, filtered and dried. The crude product was purified by dissolving in ethanol and treating with charcoal, followed by filtration and reprecipitation with water.

(b) Using 1,2,4,5-Tetraaminobenzene (TAB) - The tetrahydrochloride salt of TAB was used in the reaction rather than the free base, and the reaction procedure was the same as with DAB. However, the purification procedure for the crude monomers required the use of formic acid to dissolve the product in ethanol. Precipitation of the products was effected by addition of the formic acid-ethanol solution to dilute ammonium hydroxide after filtration.

Desolvation of all monomers was effected by heating for 3 to 4 hours under a pressure of 1 Torr. DTA investigation of melting point was made on all the monomers but only the DAB-p-AB compound exhibited a melting point, this occurring at about 334°C (see Figure 3).

Polymerization

The polymerization procedure involved the addition of the di(aminophenylbenzimidazole) to dimethylsulfoxide which resulted in a slurry or solution, depending on the type of monomer used.

Solid dianhydride powder was added slowly while stirring the mixture at room temperature under nitrogen. When monomers based on m-aminobenzoic acid were polymerized, a smooth, viscous polymer solution was obtained after the stoichiometric amount of dianhydride had been added. However, when the monomers based on p-aminobenzoic acid were used, a "gel" resulted after 85-95%

of the dianhydrides were added. This apparent "gel" could be converted to a smooth polymer solution by stirring the entire mass rapidly in a Waring Blendor, while the remaining dianhydride was added, together with amounts of solvent necessary to give a polymer solids concentration of 6-10% by weight. The vigorous stirring resulted in an increase in temperature of the solution and it was found that best results were achieved when the temperature was kept at 75-80°C for 15-20 minutes.

The polymer solutions, at room temperatures in the case of m-aminobenzoic acid-derived polymers or at elevated temperatures in the case of p-aminobenzoic acid-derived polymers, were cast onto glass plates and spread with doctor knives. The major part of the solvent was removed by heating in a forced-draft air oven at 85-100°C for 1-1.5 hours. The films were then cured by heating in an oven preheated to 300°C for periods ranging from 15 minutes to two hours. The infrared spectra of the films indicated that the imidization reaction was essentially complete within 30 minutes.

Acknowledgement

This work was carried out under a NASA NAS-NRC Resident Research Associateship.

The authors thank Mr. Howard L. Price for making the mechanical property measurements and Mr. Robert A. Jewell for making the TGA measurements.

Bibliography

1. H. Vogel and C. S. Marvel, J. Polymer Sci., <u>1</u>, 511, (1961).
2. H. Vogel and C. S. Marvel, J. Polymer Sci., <u>A1</u>, 1531 (1963).
3. L. Plummer and C. S. Marvel, J. Polymer Sci., <u>A2</u>, 2559, (1964).
4. W. M. Edward and I. M. Robinson, U. S. Patent 2,710,853 (1955), and U. S. Patent 2,867,609 (1959).
5. G. M. Bower and L. W. Frost, J. Polymer Sci., <u>A7</u>, 3135 (1963).
6. C. E. Sroog, A. L. Endrey, S. V. Abrano, C. E. Berr, W. M. Edwards, and K. L. Oliver, J. Polymer Sci., <u>A3</u>, 1373 (1965).
7. L. W. Frost and I. Kesse, J. Appl. Polymer Sci., <u>8</u>, 1039 (1964).
8. Y. Iwakura, K. Uno, Y. Imai, and M. Fukui, Makr. Mol. Chem., <u>72</u>, 41 (1964).
9. J. Preston and W. B. Black, Polymer Letter, <u>3</u>, 845 (1965).
10. R. A. Jewell, unpublished results.
11. T. Kurosaki and R. Jewell, "Thermal Behavior of Benzimidazole-Aromatic Imide Copolymers," to be published later.