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SYNTHESIS OF PYRRONE POLYMERS

by L. W. Frost and G. M. Bower

Prepared by

WESTINGHOUSE RESEARCH LABORATORIES
Pittsburgh, Pa.
for Langley Research Center

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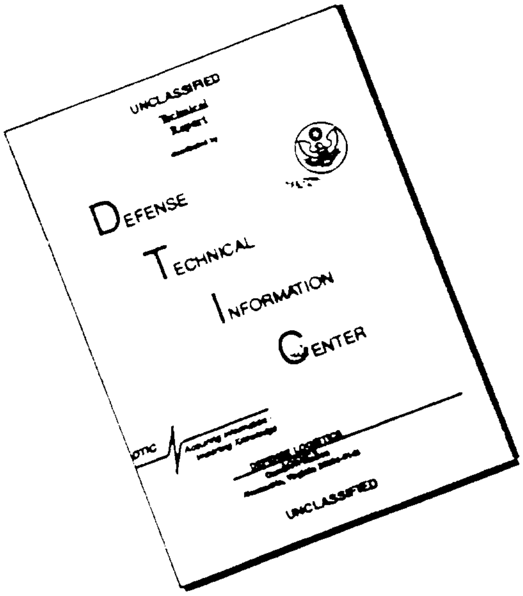

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SYNTHESIS OF PYRRONE POLYMERS

L. W. Frost and G. M. Bower
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SUMMARY

Several methods were found to control the gelation problem encountered in preparing pyrrones from dianhydrides and tetramines in polar solvents. Addition of a tertiary amine increased shelf life and attainable solids. Similar improvement was found when ortho chloro groups were used for steric deactivation of two amine groups. Complete elimination of the gel problem was achieved by blocking two amine groups with acetyl or carbethoxy groups. Low molecular weight "salt" intermediates made from diester diacids and tetramines were also relatively free from gelation problems. A two-solution system for preparing pyrrone-imide copolymers provided another way to avoid gelation.

Infrared and TGA studies showed that thermal curing gave good conversion to pyrrone only from dianhydride-tetramine polymers. Both blocked amine and salt types gave other structures, some of which were probably crosslinked.

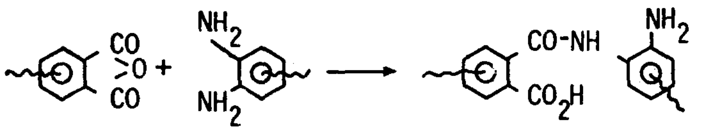
Some of the polymers gave partly cured films of good flexibility, but fully cured films had low strength. Laminates from several systems showed good but not outstanding properties. None of the polymers had a thermo-oxidative stability comparable to a good polyimide, although they compared favorably with other pyrrones.

Model compound experiments suggest that it may be possible to prepare polymers containing a 6-5 ladder structure from 2'-cyanoimide polymers. The final cure would produce no volatile by-products.

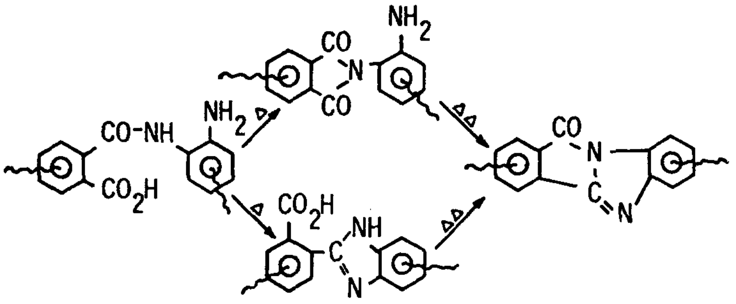
INTRODUCTION

Several investigators have reported the synthesis of pyrrone polymers by various procedures.[1-6]* A number of problems were encountered, and none of the methods has been entirely satisfactory. The method we have chosen to investigate is that of polymerization in aprotic polar solvents.[1,5] We have also done some work with ester and ester-salt syntheses.[4,6]

In the usual synthesis of pyrrones in aprotic solvents, a dianhydride is added gradually to a stirred solution of the equivalent quantity of an aromatic o,o-tetramine. A soluble poly (amino acid amide) is produced, which is converted to the pyrrone by heating. Ideally, the polymerization and cure reactions proceed as follows:



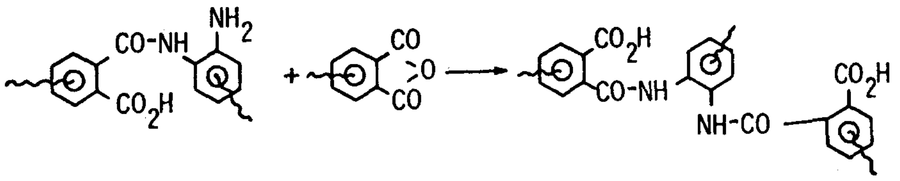
(1)



(2)

(3)

Eq. 1 shows the formation of the soluble poly (amino acid amide) at moderate temperatures. Eq. 2 and 3 show two routes by which the soluble intermediate can be converted by heat to the pyrrone structure. Apparently the actual reactions are more complex than this. One complication is the possibility of crosslinking in the soluble polymer:



(4)

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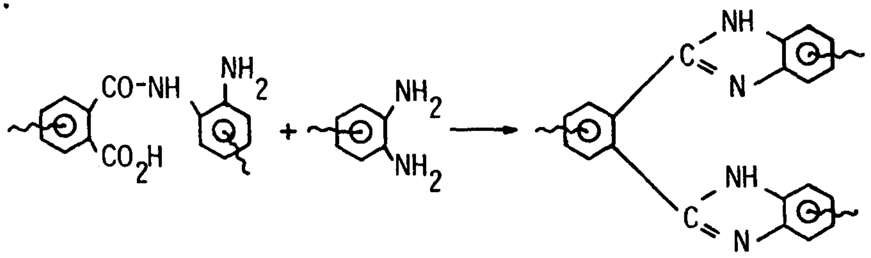
*Superscript numbers in text correspond to references, pp. 93, 94.

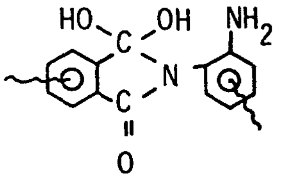
Although the amine groups of the poly (amino acid amide) are somewhat deactivated by the presence of an ortho acylamido group, they are still moderately reactive toward anhydrides. When reaction 1 nears completion, the concentration of the ortho diamino structure, which now occurs largely on chain ends, becomes very small relative to that of the ortho amino-amide structure. The latter then begins to compete successfully for anhydride groups, crosslinking occurs, and the polymer becomes insoluble. The presence of a slight excess of anhydride during the synthesis has been found to produce gelation by this mechanism.[5] Crosslinking may also occur during cure by a different mechanism if excess amino groups are present:

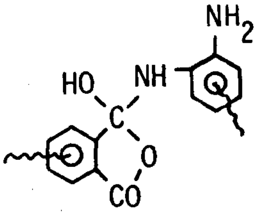


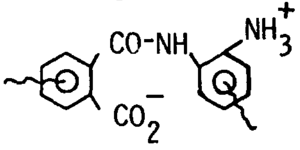
(5)

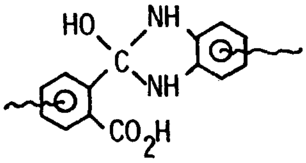
In addition to the problem of gelation, these crosslinking reactions introduce imide and benzimidazole linkages into the final polymer structure.

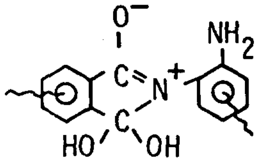
The soluble polymer is believed to be considerably more complex than the simple amino amide acid shown in eq. 1. Strong association with the solvent occurs, and cyclic and ionic forms, such as the following, probably occur in equilibrium:







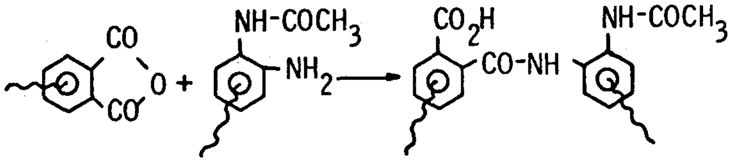




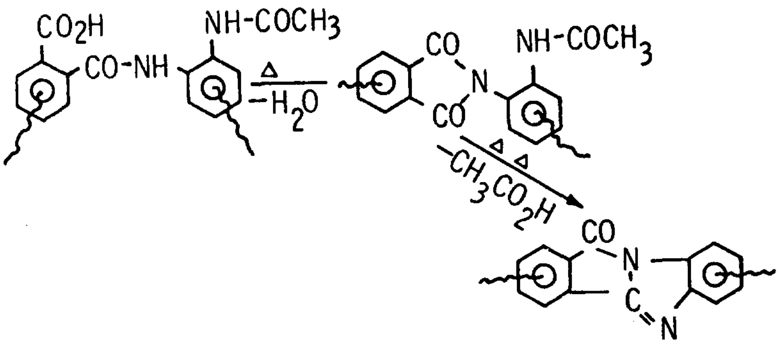
Experience with the closely related polyamide acids (polyimide precursors)[7-9] indicates that the various structural forms of the amino acid amide group react readily with anhydride or amino groups in an exchange reaction.[9] Polymer chains in solution, then, are continually breaking and reforming in a labile equilibrium, which probably includes a small concentration of crosslinked structures, such as the product of eq. 4, even when anhydride is not present in excess. As the concentration is increased, bimolecular reactions are favored, the equilibrium shifts toward crosslinked structures, and gelation occurs. Intermolecular association of the ionized forms also increases with concentration, giving apparent crosslinking. Another consequence of the ionic structures is an abnormally high viscosity due to polyelectrolyte effects.

As a result of these various reactions in solution it has been found quite difficult to obtain a soluble poly (amino acid amide) of high molecular weight by this method. Gelation occurs unless a dilute solution is used, with very rapid stirring and slow addition of a solution of dianhydride.[3,5] When these conditions are used, the solution viscosity increases steadily as dianhydride is added, with no sharp rise at equivalence,[4] although a slight excess of dianhydride produces sudden gelation. In contrast, the preparation of polyamide acids (polyimide precursors) by a similar procedure from diamines and dianhydrides occurs with a steep viscosity rise at equivalence and no gelation problems.[7,9]

The gelation and high viscosity resulting from crosslinked and ionized structures can be reduced or eliminated by blocking one of the amine groups in each of the ortho pairs. Since we are now dealing with the reaction of a diamine and a dianhydride, behavior typical of normal polyamide acids can be expected. For example, if one of the groups is acetylated the following reaction sequence is expected:



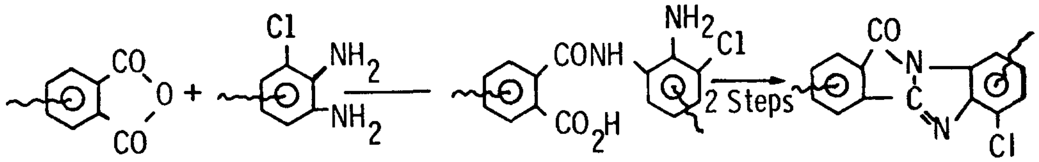
(6)



(7)

The acetamido group will not react with anhydrides at room temperature to give crosslinking as in eq. 4, nor is it basic enough to abstract a proton from a carboxyl group to give a polyelectrolyte. Therefore the polymerization reaction (eq. 6) is expected to proceed without gelation, at concentrations higher than can be used in the usual reaction (eq. 1). Other blocking groups, such as trimethylsilyl or carbethoxy can be expected to work in a similar way. Problems that might be encountered with the blocked systems are reduced reactivity of the remaining amino groups and difficulty in eliminating the blocking groups in the final step.

A second method of reducing the reactivity of one of the amine groups in an ortho pair is by steric hindrance. A bulky substituent ortho to one amine group will reduce its reactivity and minimize crosslinking, while permitting linear polymerization through the other amine group. For example, using a chlorine atom for hindrance, the following reaction course will be favored:



This method is less effective than acetylation in deactivating the amine group, so we may expect less freedom from gelation but more facile conversion to pyrrone during cure.

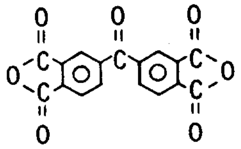
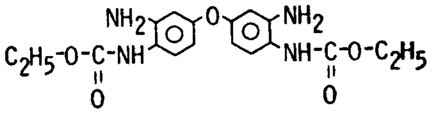
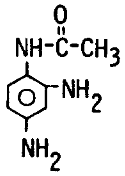
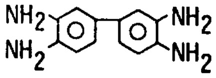
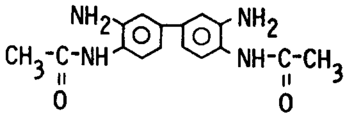
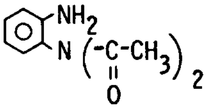
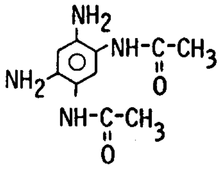
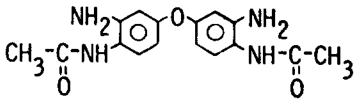
The use of protected or hindered amino groups avoids gelation by assuring that the soluble polymer is not crosslinked, although it is of high molecular weight. A third way to prevent gelation is to esterify the dianhydride component. This method gives a soluble intermediate of low molecular weight, which polymerizes further on curing.[4] A fourth approach is to modify the solvent system to minimize polymer-solvent interactions and ionization. Work on all four methods is reported here.

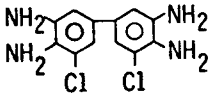
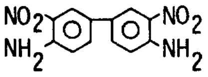
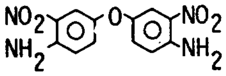
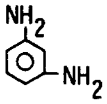
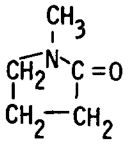
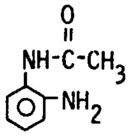
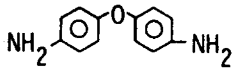
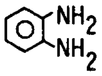
Imide-pyrrone copolymers may be expected to incorporate the desirable high modulus of pyrrones with the better thermal stability and processing properties of polyimides. In addition, gelation can be avoided by preparing a stable anhydride-rich polyimide precursor and a stable anhydride-poor pyrrone precursor, and blending these solutions just before use. Some work in this field was included in the project.

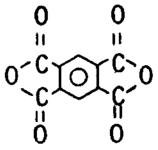
There is some evidence that the 5-5 ladder system of pyrrones is less stable than 6-5 or 6-6 systems. We have done some preliminary work with a 6-5 system closely related to pyrrones, which offers the additional possibility of undergoing the final cyclization reaction without eliminating volatile byproducts.

SYMBOLS

A considerable number of complex organic compounds have been used in this study. In order to keep the report from becoming too cumbersome, the following shorthand notation has been adopted, which is consistent with the notation used in previous NASA reports and papers.

BTDA	3,3',4,4'-benzophenonetetracarboxylic dianhydride	
CETADPO	N,N'-dicarbethoxy-3,3'-diamino-4,4'-oxydianiline	
DAA	2,4-diaminoacetanilide	
DAB	3,3'-diaminobenzidine	
DADAB	3,3'diamino-N,N'-diacetylbenzidine	
DAOPD	N,N diacetyl-o-phenylenediamine	
DATAB	1,3-diamino-4,6-diacetamidobenzene	
DATADPO	4,4'-diacetamido-3,3'-oxydianiline	

DCDAB	3,3'-dichloro-5,5'-diaminobenzidine	
DMAC	N,N-dimethylacetamide	
DMF	N,N-dimethylformamide	
DMSO	dimethyl sulfoxide	
DNB	3,3'-dinitrobenzidine	
DNODA	3,3'-dinitro-4,4'-oxydianiline	
HMP	hexamethylphosphoramide	$\left[(CH_3)_2N\right]_3$ PO
MPD	m-phenylenediamine	
NMP	N-methylpyrrolidone	
OAA	o-aminoacetanilide	
ODA	4,4'-oxydianiline	
OPD	o-phenylenediamine	
PA	phthalic anhydride	

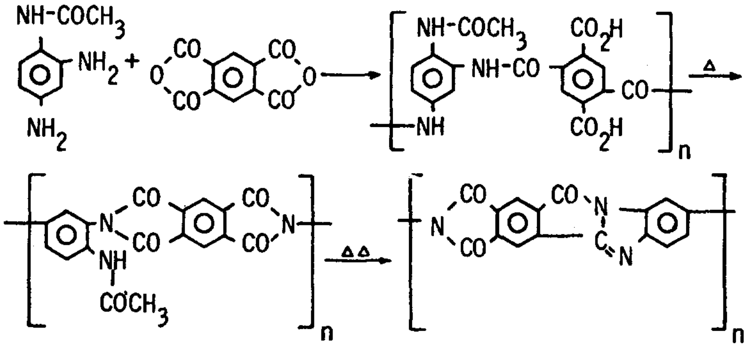
PMDA	pyromellitic dianhydride	
TEA	triethylamine	
THF	tetrahydrofuran	
TRAB	1,2,4-triaminobenzene	

The symbols are combined to indicate reaction products (simple or polymeric) of two or more of the compounds. For example $(OAA)_2$-PMDA represents the diimide obtained from the reaction of two moles of OAA and one mole of PMDA.

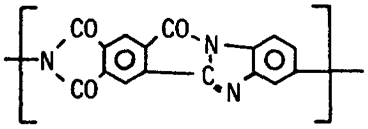
DIACETYL TETRAMINES AND THEIR POLYMERS

Polymers from 2,4-Diaminoacetanilide (DAA)

The most readily available diamine containing the desired o-acetamido amine structure is 2,4-diaminoacetanilide (DAA).[7] The following reactions with pyromellitic dianhydride are expected:



Two isomers are possible in the product of the first reaction, only one of which is shown. The cured product, which contains equal numbers of imide and pyrrone groups, is expected to be the same as the polymer previously prepared from 1,2,4-triaminobenzene (TRAB) and PMDA by Bell[10] and by Dunnavant,[11] except that the latter contains an additional isomeric configuration in the trisubstituted benzene ring:



In both polymers, in addition to the structures shown, some of the tetrasubstituted rings will be linked to two imide groups, with an equal number linked to two pyrrone groups. The latter structure occurs in two geometric isomers. The DAA polymers were studied primarily to compare the reactivity of an isolated amino group with that of an o-acetamido amine and to study the elimination of acetic acid to form a pyrrone linkage in the final step.

When PMDA was added in portions to a stirred solution of DAA in N,N-dimethylacetamide (DMAC) the viscosity behavior was the same as observed previously for simple diamines,[7] with a sharp viscosity peak at equivalence as the final increments of PMDA were added. The time required to reach maximum viscosity after each addition was less than one hour, which is about the same as that observed for m-phenylenediamine (MPD), and indicates comparable reactivity for both amine groups. Maximum viscosity was obtained with about a 1% excess of PMDA, and further addition gave a viscosity decline. The inherent viscosity of the polymer solution 28 hrs. after preparation was 0.69 dl/g. Attempts to cast films from the solution gave only brittle materials. Similar results were obtained when BTDA was substituted for PMDA.

Infrared spectra of DAA-PMDA and DAA-BTDA as a function of cure are discussed in a later section.

Polymers from 4,4'-Diacetamido-3,3'-oxydianiline(DATADPO)

Synthesis of DATADPO.-The compound 4,4'-diacetamido-3,3'-oxydianiline (DATADPO) was prepared from 4,4'-oxydianiline by acetylation, nitration, and reducton; and also from 3,3'-dinitro-4,4'-oxydianiline by acetylation and reduction.[12] The former method gave a better product.

Polymer solution preparation. - Polymer preparation from DATADPO proceeded smoothly with either PMDA or BTDA in DMAC, DMF, DMSO, NMP, or DMAC-xylene. Polymer solutions prepared in DMSO had the highest viscosity at 20-25% solids, although they did not have higher inherent viscosities. Table I summarizes viscosity data for several solvent systems. The inherent viscosities were not determined on the same batches of polymer as the Gardner viscosities, but the procedures and reactants were essentially the same. Although this polymer is expected to be relatively flexible, and the inherent viscosities are in the range expected to give good films, all efforts to cast films from DATADPO-BTDA failed to give a flexible cured product. Uncured films, plasticized with solvent, were very flexible, but as the cure progressed they became extremely fragile. Final cure at

300-325°C gave a somewhat tougher product, but we did not succeed in getting a film of reasonable size past the fragile stage without fragmentation.

Table I - Viscosities of DATADPO-BTDA Polymers

% Solids	Solvent	Viscosity		
		Gardner	cP	Inherent, dl/g., 35°C
23	21 g. DMSO	Z-6	14,800	0.62
25	19 g. DMF	V+	900	---
24	14 g. DMAC + 6.3 g. xylene	X-Y	1,500	---
25	19.3 g. NMP	X-Y	1,500	0.48
16	33.6 g. DMSO	W	1,070	---
26	11 g. DMAC + 7 g. xylene	W	1,070	---
25	DMAC	S	500	0.62

Fig. 1 shows a TGA curve in air for a sample of powdered cured DATADPO-BTDA film. If the polymer is in the imide form and free from solvent and adsorbed volatiles, loss of two moles of acetic acid would give a 20% weight loss. The plateaus at about 17 and 30% are in the right neighborhood, but the steady weight loss beginning at 50°C suggests that adventitious volatiles were also present.

Laminates. - Glass cloth laminates were made by methods similar to those used for laminates from polyimides prepared in aprotic solvents.[13] The system was not studied extensively, but the results shown in Table II indicate that initial strength and modulus values are at least as high as those of the polyimides. No aging studies were made.

Precipitated polymer. DATADPO reacted smoothly with PMDA in refluxing THF to give a precipitated powder. Infrared spectra, elemental analysis, and inherent viscosity indicate that this product was a low molecular weight polymer, largely in the form of the amide acid. On heating for 2 hrs. at 150°C, infrared spectra showed it to be converted largely to the imide.

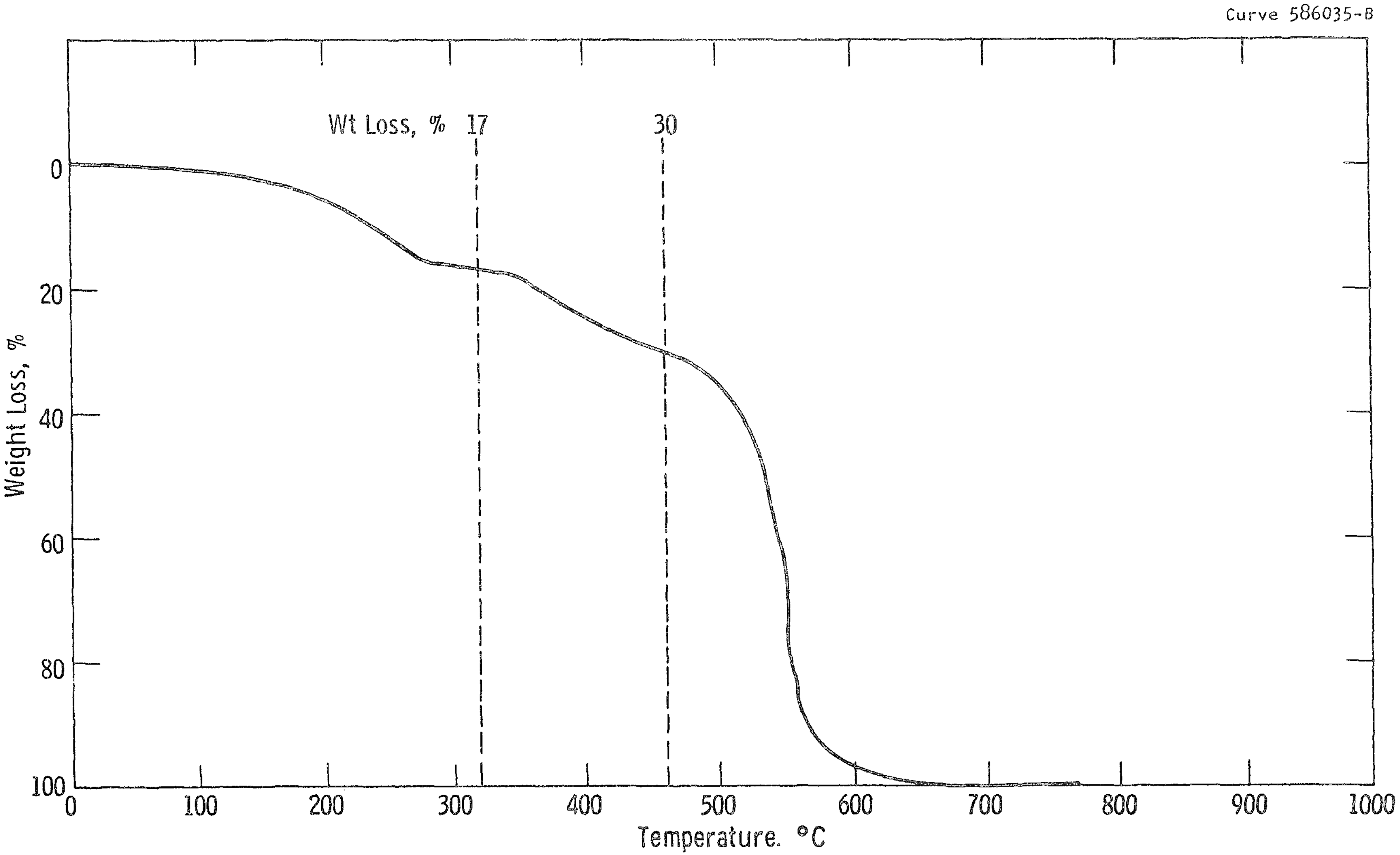


Fig. 1 – TGA of DATADPO - BTDA film in air at 5 °C/min.

Table II - Laminates from DATADPO-BTDA on 181 E Glass Cloth (A1100 soft finish)(a)

No. plies	Precure (b)		% Resin		Thickness, In.	Flex. Strength, (c) psi		Flex. Modulus, psi (c)	
	Time, min.	Temp., °C	Prepreg	Laminate		25°C	316°C (600°F)	25°C	316°C (600°F)
12	30	180	36.8	17	0.085	50,100	56,100	3.79×10^6	3.33×10^6
12	30	210	44.8	20	0.101	71,300	67,400	3.87×10^6	3.39×10^6
16	10	210	45	25	0.143	64,000	59,000	3.2×10^6	2.6×10^6

(a) Initial press temp. about 200°C. Temp. and press. raised gradually to 300°C and 500 psi. Held for 30 min.

(b) Warmed from 25°C to indicated temperature in 30 min. Held at temperature as shown.

(c) Average of three determinations.

Fig. 2 is a TGA curve for the polymer powder in nitrogen. Three rather poorly defined plateaus were found. If we assume the sample contains the polyamide acid plus nitrogen-free impurities, the nitrogen analysis indicates the presence of 8.5% of foreign matter, most of which (THF, water, etc.) is volatile. Weight loss due to two moles of water would be 6.2% and for two moles of acetic acid 20.6%. The 13% plateau at 280°C may be assumed to include the 6.2% water loss plus 6.8% of volatile impurities. Adding 20.6% for acetic acid gives 33.6%, which is in fair agreement with the 28% plateau at 470°C. If we assume loss of carbonyl groups to be the next step in the process, as indicated by Jewell,[14] an additional weight loss of 9.6% would be expected. The total of 43.2% is in good agreement with the third plateau at 44%. These TGA results are consistent with the proposed processes, but suggest that the reactions occur in an overlapping sequence, with rather poor separation between complete cure and incipient degradation.

A study of the curing reactions of DATADPO-PMDA by infrared spectroscopy is reported in a later section.

Polymers from 3,3'-Diamino-N,N'-diacetylbenzidine (DADAB)

Synthesis of DADAB. - 3,3'-Diamino-N,N'-diacetylbenzidine (DADAB) was synthesized from 3,3'-dinitrobenzidine by acetylation followed by reduction.[12]

DADAB and BTDA. - Although DADAB has a very low solubility in DMAC, a slurry of the two reacted with BTDA to give a clear solution, inherent viscosity 0.28 dl/g. A film cast from the solution was very brittle.

DADAB and PMDA. - The reaction of DADAB and PMDA is complicated by the fact that a portion of the product is insoluble in all organic solvents tested. A variety of solvent systems and mixing procedures were used, with similar results. The best procedure was to mix equimolar amounts of the dry ingredients and add the mixture to the solvent. This method gave clear solutions initially with DMAC, DMSO, and mixtures high in DMAC, but precipitation occurred on standing. DMAC is the best of the solvents tested.

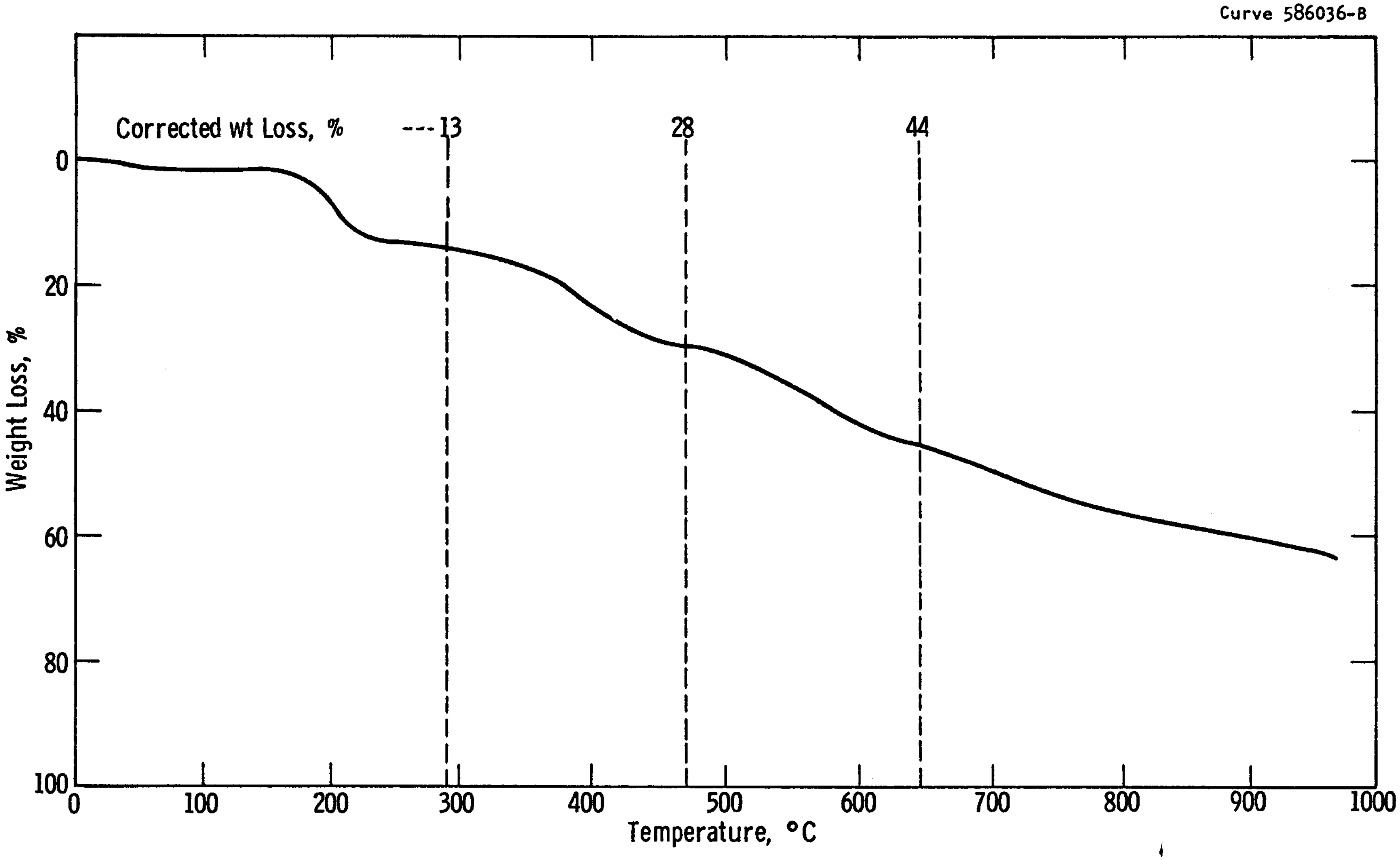


Fig. 2— TGA of DATADPO - PMDA powder in N_2 at 2.5 °C/min.

Some additional experiments were run to clarify the solubility behavior of this polymer. Several preparations were filtered, and the precipitates washed and dried. The amount of polymer left in solution was calculated from TGA data on the filtrate, by difference, or by precipitation with acetone and weighing. It was found that the amount of material dissolved was not proportional to the amount of solvent used, as would be expected if the solute were a single material. Rather, the soluble portion was a fairly constant fraction of the total solids, this fraction being almost independent of the ratio of solids to solvent.

Elemental analyses of several of the precipitates were fairly close to the calculated values for DADAB-PMDA, although C and N were consistently low, while H and O were high, suggesting contamination by water. Analysis of a sample prepared in DMSO corresponded to DADAB-PMDA plus 1.5 moles of DMSO per polymer unit.

In one case the soluble portion of the polymer was precipitated with acetone, washed and dried. This fraction analyzed closely for DADAB-PMDA plus one mole each of water and DMAC per polymer unit. In addition to having nearly the same analysis, the soluble and insoluble fractions from this run had nearly identical infrared spectra (Figs. 8, 9), which are consistent with the expected amide acid structure. However, in spite of these similarities, the insoluble fraction was found to have a solubility of less than 0.1% in DMAC, DMF, DMSO, or HMP, while the soluble fraction, after precipitation and drying, could be redissolved in DMAC to give a clear 40% solution. The only solvent found for the insoluble fraction was concentrated sulfuric acid.

Inherent viscosities, measured on fresh solutions before precipitation occurred, ranged from 0.56 dl/g. in DMSO to 0.32 dl/g. in DMAC. Films cast from the solutions were brittle.

The striking difference in solubility between the two DADAB-PMDA fractions presents an interesting problem. A difference in extent of imide formation is ruled out by infrared spectra. Differences in molecular weight, crystallinity, isomerism around the PMDA nucleus, or the presence of an impurity in the DADAB would be expected to produce a gradual distribution of solubilities rather than a sharp separation into a very soluble and a completely insoluble fraction. Let us assume, for example, that para linkage in the PMDA nucleus leads to a less soluble polymer. If these linkages are formed randomly and scattered throughout the polymer molecules, we should expect the solubilities of the molecules to be more or less inversely proportional to their para content, and to vary smoothly from high to low solubility. Since this does not occur, we might speculate that the fortuitous assembly of several para linkages in succession gives a configuration favoring further para linkage. The solvated polymer as formed is soluble, but solvent association is gradually replaced by thermodynamically favored self association, and precipitation occurs.

Polymer from 1,3-Diamino-4,6-diacetamidobenzene(DATAB)

Polymers from 1,3-diamino-4,6-diacetamidobenzene (DATAB) and PMDA are of particular interest because they would form complete ladders when fully cyclized. DATAB was synthesized from 4,6-dinitro-1,3-phenylenediamine by acetylation followed by reduction.[12] It turned out to be so insoluble and high-melting that purification was very difficult. A small amount of polymer prepared from crude DATAB and BTDA gave very poor films.

OTHER DEACTIVATION SYSTEMS

Trimethylsilyl Derivatives

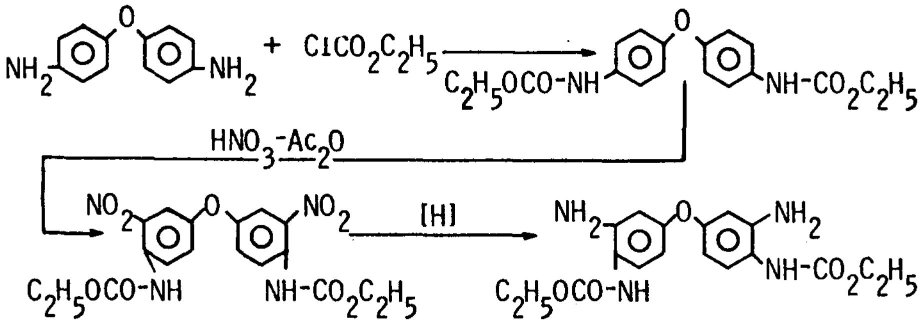
The trimethylsilyl group might also be used to deactivate one of a pair of ortho amino groups in pyrrone synthesis. It would have some advantages over an acetyl group in that 2-methylbenzimidazole formation would not be a problem, and the final cyclization to pyrrone would give the innocuous hexamethyldisiloxane rather than acetic acid as a byproduct.

Attempts were made to trimethylsilylate DAB; 3,3'-dinitrobenzidine (DNB); 4,4'-oxydianiline (ODA); and 3,3'-dinitro-4,4'-oxydianiline (DNODA). Both hexamethyldisilazane and trimethylchlorosilane were used as reagents, with pyridine, triethylamine, DMAC, and DMF as solvents. In addition to recovered starting materials, the following compounds were isolated: DAB·HCl, DNODA·pyridine·HCl, trimethylchlorosilane·pyridine·2 HCl, ODA·DMF·2 HCl, and triethylamine·HCl. Some of these complexes are rather interesting, but, since no trimethylsilylated amines were obtained, this approach was discontinued.

Carbethoxy Derivatives

The carbethoxy derivative is also useful in protecting an amine group. Elimination to give the pyrrone was expected to be easier in this case than with the acetyl derivative. The byproducts, ethanol and carbon dioxide, are also less objectionable than acetic acid in some applications.

N,N'-dicarbethoxy - 3,3'-diamino - 4,4'-oxydianiline (CETADPO) was prepared by the following reaction sequence:



Resin was prepared in the usual way in DMAC solution from CETADPO and BTDA. A thin film baked in steps was brittle after bakes of 135° and 190° and foamed at 300°C. A second film was heated in steps and then overnight at 217°C. Finally, the film was baked for 20 min. at 327°C. The film had shrunk but was still intact. Portions of the film could be bent double but not creased. One batch of resin prepared by adding powdered BTDA to a DMAC solution of the diamine had an inherent viscosity of 0.66 dl/g.

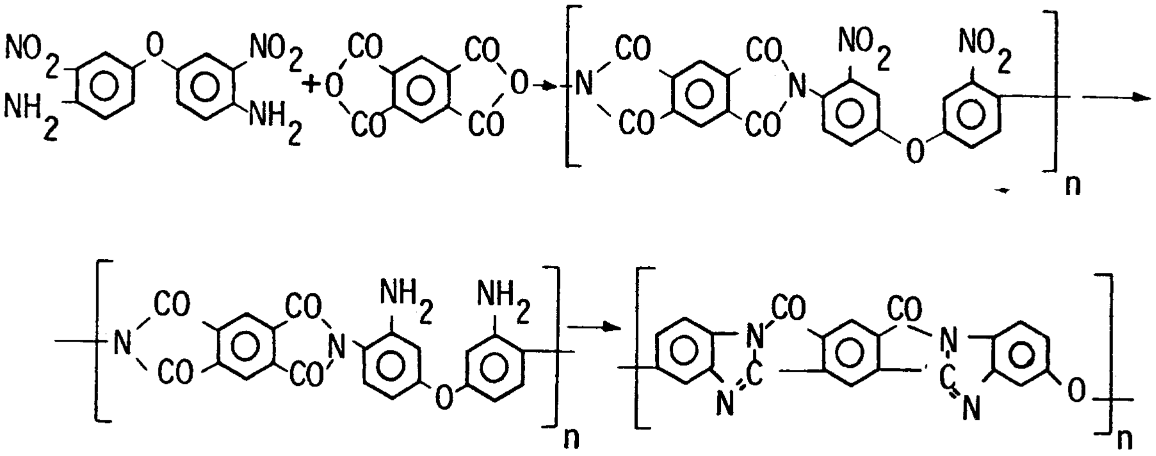
A laminate was prepared from the polymer using 181/A1100 glass cloth, with a precure of 2 hrs at 150°C and a press cure of 275°C and 500 psi for one hour. The laminate contained 32% resin and looked fairly good. When a specimen was heated to 316°C for testing, it softened and foamed. Apparently elimination of ethanol and carbon dioxide occurred rapidly at this temperature. A slow post-cure to 325°C was used on later samples. This treatment eliminated the foaming problem, and the following flexural properties were measured (average of three specimens):

Flex. Strength, K psi		Flex. Modulus, M psi	
25°C	316°C(600°F)	25°C	316°C(600°F)
57.4	17.1	1.9	0.74

Improved properties can probably be obtained by changing the cure schedules, and especially by increasing post-cure. The polymer shows some promise as a high-temperature foam.

Dinitro Diamine

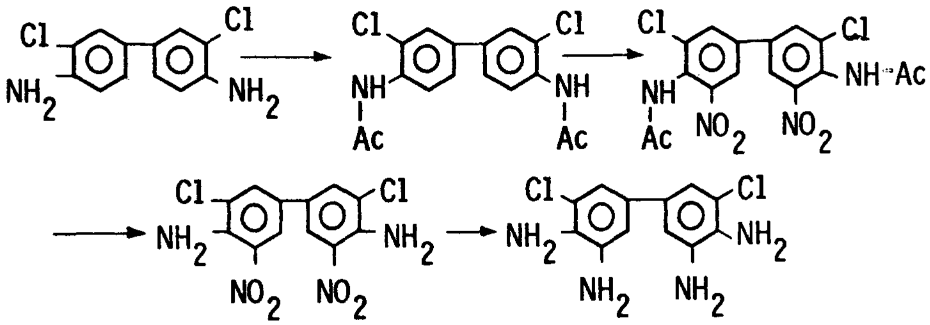
Another approach to the preparation of a linear polymer convertible to a pyrrone is as follows:



It was found that the amine group ortho to a nitro group was deactivated much more than one ortho to an acetamido group. In order to obtain a reasonable reaction rate with PMDA it was necessary to use a temperature that caused extensive dehydration to the imide. However, a soluble polymer was obtained, and the nitro groups hydrogenated readily to amine groups. Both the nitro imide and the amino imide polymer solutions gave continuous films of poor flexibility. On standing for three days at room temperature, the amino imide polymer solution gelled. The gelation is believed to be due to a redistribution reaction between free amine groups and amide acid linkages. The reaction between amine groups and amide acid linkages has been observed before in the case of linear polyimide precursors with a resultant decline in viscosity.[9] In the present case, however, the result of the redistribution is to change a linear polymer to a branched one with sufficient crosslinking to give a gel.

Synthesis of 3,3'-Dichloro-5,5'-Diaminobenzidine (DCDAB)

The synthesis of DCDAB was conducted according to the following scheme:



Considerable difficulty was encountered in the nitration step with incomplete nitration and with the formation of other isomers. Best results were obtained with fuming nitric acid at 5-10°C, but the yield of pure 5,5'-dinitro compound was only 32%. Concentrated sulfuric acid was the best reagent found for removing the acetyl group, and hydrazine proved superior to hydrogen in the final reduction.

Benzoyl and phthaloyl derivatives were also evaluated as amine protective groups in the nitration, but both gave very low yields of the desired isomer.

DCDAB Polymers

In general polymers prepared from DCDAB and dianhydrides showed the expected gelation and cure tendencies. Their solutions were more stable than those from unhindered tetramines but less stable than those from acetylated or carbethoxylated tetramines. Conversion to imide and pyrrone was similar to that of polymers from other tetramines (see "Curing Reactions" section, p. 35).

When solid PMDA was added to a DMAC solution of DCDAB, gel formed around the PMDA particles. Solutions of PMDA gave no gel, even up to 9% excess PMDA, although gelation could be induced by adding more PMDA after aging the solution for a few days. Solutions containing a slight excess of PMDA increased very slightly in viscosity on aging and did not gel in 54 days.

Polymers made with BTDA showed less tendency to gel during preparation, and powdered BTDA could be added to a well-stirred DCDAB solution without gelation in most cases. Solutions containing an excess of BTDA often gelled in about a day, but those with a 1% deficiency showed very little viscosity increase in 54 days.

Both types of polymer formed dark red films on baking in aluminum dishes. For the most part films thicker than 5 mils could be peeled easily from the dish. They were quite flexible but could not quite be creased without cracking. Thinner samples could be creased without cracking.

Weight loss data on films of these polymers are shown in Fig. 3 in comparison with MPD-BTDA polyimide aged concurrently in the same oven. Apparently BTDA gives better stability than PMDA in this system, but both are inferior to a good polyimide. Polymers containing an excess of tetramine were less stable than those in which the dianhydride was present in at least an equivalent amount.

Laminates were prepared from DCDAB-BTDA polymer containing about 2% excess BTDA. Glass cloth (181-A1100, E-glass) was hand dipped, precured and pressed at 325°C and 500 psi. Properties of the laminates are given in Table III. The strength and modulus values compare favorably with those of polyimide laminates,[14] but are inferior to the best pyrrones made by the ester method.[4] The quantity of material available was insufficient for a complete aging study, but, for a screening test, weight loss measurements at 325°C were made on pieces of laminates. Although the data are not strictly comparable, these results (Table III) suggest that, in thermal stability, DCDAB-BTDA polymers rank between polyimides[13] and pyrrones made by the ester method.[4]

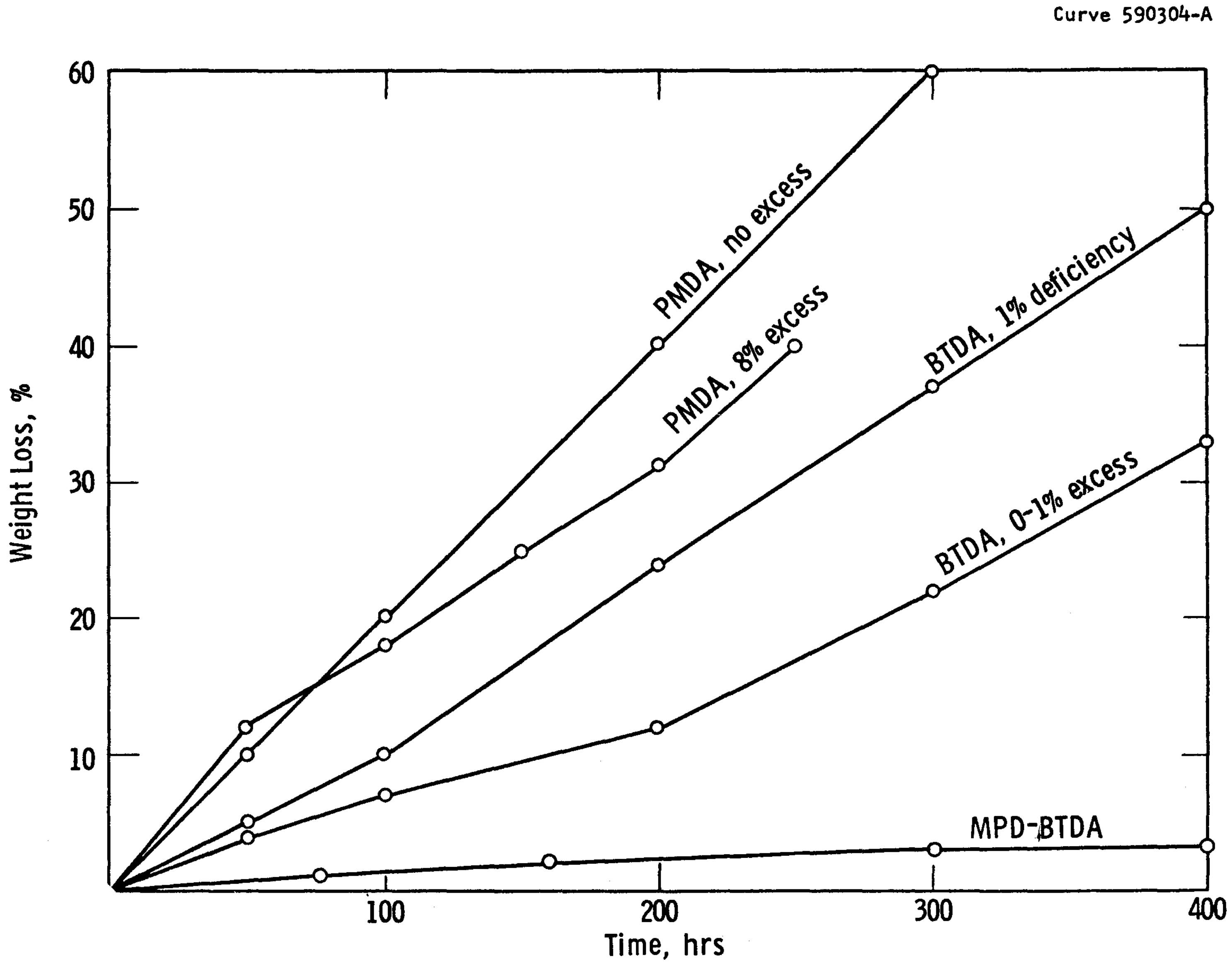


Fig. 3—Wt loss of DCDAB pyrrones at 325°C in air

TABLE III

Properties of DCDAB-BTDA Laminates

Laminate No.	E69-85-2	E69-87-2
Precure Temp., °C	125	150
Resin in Prepreg, %	38	42
Reins in Laminate, %	30	36
Flexural Strength, K psi[a]		
25°C	57.2	50.0
316°C(600°F)	42.9	49.4
Flexural Modulus, M psi[a]		
25°C	2.8	2.7
316°C(600°F)	2.5	2.7
Weight Loss at 325°C, % of Resin		
24 hrs	8.0	6.5
110 hrs	37.4	27.2

a-Average of three specimens.

POLYMERS FROM UNSUBSTITUTED TETRAMINES

Reaction with Dianhydrides

The gelation and high viscosity of amino acid amide polymer solutions are believed to be due partly to internal salt formation between the amino and carboxyl groups. Variations in basicity and dielectric properties of the solvent may be expected to change the degree of ionization of the polymer, and may lead to lower viscosity and decreased gelation tendencies. Therefore, mixtures of DMAC with various acids and bases were investigated as solvents for the reaction of DAB and BTDA. It was found that acids accelerated gelation, while bases retarded gelation and permitted the use of higher concentrations of polymer. For example, a 16% solution of polymer in DMAC containing two moles of triethylamine (TEA) per mole of DAB was stable for 8 days. Without the TEA, solutions containing more than 10% solids gelled during preparation. When both TEA and acetic acid were added, a slight increase in solids was possible, but TEA alone was more effective.

A laminate was pressed from glass cloth treated with resin from D36-40-1 (TEA) and another from D36-49-3 (lactic acid). Flexural strength and modulus values were low (Table IV). In both cases insufficient flow occurred in the press.

Reaction with Esters

The use of a diester diacid in place of a dianhydride in the synthesis of pyrrones leads to a soluble intermediate of low molecular weight,[4] which can sometimes be isolated as a crystalline salt.[6] This approach makes possible the preparation of solutions having high solids content and moderate viscosity. However, it is doubtful that the cured polymer contains much pyrrone structure (see "Curing Reactions" section).

TABLE IV

Laminates from DAB-BTDA Solutions Containing Additives

Resin Batch	% Resin		Thick-ness, In.	Flex. Strength, kpsi		Flex. Modulus, M psi	
	Prepreg	Laminate		25°C	316°C(600°F)	25°C	316°C(600°F)
D36-40-1[a]	39.8	31	0.139	47.3	31.7	2.98	2.16
D36-49-3[b]	42.5	40	0.133	23.7	16.0	2.71	1.79

No. plies. 12

Precure. . . . . .60 min/125°C

Press conditions . . . . . .500 psi, 350°C, 60 min.

a. Triethylamine added

b. Lactic acid added

The polymer of DAB and BTDA was prepared in DMAC and in NMP, using either ethylene glycol, methanol, isopropanol, or isobutanol to esterify the BTDA. Solutions of 30-40% solids were made without difficulty. Viscosity of the solutions increased with age, and one of them, made with Cellosolve (2-ethoxyethanol), gelled in 40 days. The use of less than the stoichiometric quantity of alcohol gave immediate gelation.

In no case were we able to isolate a crystalline salt from the reaction of DAB with a diester of BTDA. For example, when a solution of either the diisopropyl or the diisobutyl ester of BTDA in excess alcohol was poured into a hot aqueous solution of DAB, a soft, oily, dark-colored product was obtained. When the product from the isopropyl ester was heated it gave a solid foam.

Only the polymer from diisobutyl ester gave a continuous thin film, although thick fragments of the other cured polymers were quite tough. Weight loss in air at 325°C of films of polymers from Cellosolve and from ethylene glycol esters were high, reaching 35-50% in 314 hrs. A good polyimide with the same treatment would lose 6-8%.[7] The polymers made with Cellosolve appeared slightly more stable than those made with ethylene glycol.

Laminates were made on 181(A1100) E-glass cloth from resins prepared from DAB and BTDA esters with ethylene glycol, Cellosolve, and isobutanol. Their properties are shown in Table V.

A somewhat different approach to the ester-salt synthesis was attempted by the reaction of DAB with a solvent-free linear polyester acid derived from PMDA and ethylene glycol. If the solvent-free salt could be isolated, and would melt before curing, the need for exotic solvents would be eliminated and the release of volatiles during cure would be minimized.

The polyester was prepared by the method of Elwell and McGowan,[15] using tetrahydrofuran as reaction solvent. It was a tan granular solid, N.E. 119.3 (corresponding to a PMDA/glycol ratio of 1.188). Reaction with DAB (1 mole/mole PMDA) in a water-tetrahydrofuran medium gave the polymeric salt as a yellow powder. Unfortunately, the

TABLE V

Laminates from Esterified BTDA-DAB Resins

Alcohol Used	Ethylene Glycol	Cellosolve	Isobutanol
Precure			
Time, min	20	60	30
Temp., °C	150	85	100
Press Conditions			
Time, min.	60	60	30
Temp., °C	400	325	300
Press., psi	1500	1000	1000
Resin Content, %			
Prepreg	---	38	29
Laminate	30	---	24
Flexural Strength, K psi[a]			
25°C	51.1	58	37
316°C(600°F)	8.2[b]	37	25.5
Flexural Modulus, M psi[a]			
25°C	2.9	2.92	3.3
316°C(600°F)	1.5[b]	2.22	2.7

a-Average of 3 specimens.

b-After 100 hrs at 316°C.

product did not melt on heating and was soluble only in such solvents as DMAC and NMP. Films cast from a DMAC solution were red-brown and fairly flexible. Weight loss at 325°C in air was very high, reaching about 50% in 150 hrs.

PYRRONE-IMIDE COPOLYMERS

From Tetramines

Pyrrone precursor solutions prepared from unsubstituted tetramines in polar solvents are stable only if dianhydride is used in less than the equivalent quantity. On the other hand, polyimide precursor solutions containing excess anhydride are quite stable. Thus it is possible to prepare two stable solutions of low viscosity and blend them just before use to give a pyrrone-imide block copolymer. In addition to its convenience of preparation, this type of polymer may, to some extent, combine the superior thermal-oxidative resistance of polyimides with the high modulus of pyrrones.

We have used this approach with limited success. For example, an imide precursor solution was prepared in DMAC from MPD and BTDA, containing a 10% excess of BTDA. This was stirred into a DAB-BTDA solution that contained a 10% deficiency of BTDA, so that the final stoichiometry balanced. The viscosity of the solution at 24% solids was about 450 centistokes. A sample left at room temperature gelled in 3 days. A refrigerated sample was used to treat glass cloth for a laminate, properties of which are given in Table VI. Additional preparations were made in a similar way, using a DMF-xylene solvent system to facilitate solvent removal. Three more laminates were made, using 181 (A1100) E-glass cloth. Conditions were worked out that gave satisfactory flow in the press, and laminates of good appearance, but flexural properties were not outstanding (Table VI).

Table VI

Laminates from Pyrrone-Imide Copolymers

Polymer Composition	DAB-MPD-BTDA$_2$							DCDAB-MPD$_2$-BTDA$_3$	
Solvent System	DMAC	DMF-xylene						DMAC	
Precure									
Time, min.	15	60		60		60		60	
Temp., °C.	80	100		100		125		150	
Press Conditions[a]									
Time, min.	20	60		60		60		60	
Temp., °C	325	325		325		325		300	
Press., psi	500	500		500		500		500	
Resin Content, %									
Prepreg	46	42		45.5		48		33	
Laminate	33.5	34		---		42		31	
Flexural Strength, K psi[b]		(c)	(d)	(c)	(d)	(c)	(d)	(c)	(d)
25°C	47.0	45.9	45.2	33.1	38.5	47.6	39.3	---	---
316°C (600°F)	27.1	25.6	35.5	29.7	30.6	40.5	36.4	27.7	36.8
Flexural Modulus, M psi[b]									
25°C	4.0	2.9	2.8	2.4	2.5	2.6	2.6	---	---
316°C (600°F)	2.3	1.1	1.9	1.8	1.5	2.2	1.8	1.6	1.8

a. Initial 100°C, 55 psi; raised to 325°C, 500 psi in 55 min
b. Average of 2 specimens
c. No post-cure
d. Post-cured in oven 20 min at 300-325°C

When DCDAB was used as the tetramine, the two-solution method was not necessary. A copolymer containing one mole DCDAB, two moles MPD, and 3 moles BTDA was prepared as a 20% solution in DMAC by adding powdered BTDA to a stirred solution of the amines. One laminate worth testing was made from the polymer. Properties (Table VI) were similar to those of the copolymers derived from DAB.

From Diacetyl Tetramines

Evidence is presented in the section on "Curing Reactions" suggesting that polymers derived from diacetyl tetramines do not cure smoothly to pyrrones, but undergo other reactions leading to crosslinking. Therefore, copolymers obtained by the reaction of dianhydrides with mixtures of diamines and diacetyl tetramines, when fully cured, are expected to consist of some kind of crosslinked structure containing imide, pyrrone, and other linkages. Crosslinked polyimides derived from somewhat similar structures have been reported by Bower, et al.[16]

We have evaluated two polymers of this type. The first was prepared from two moles DADAB, 8 moles MPD, and 10 moles BTDA. The second was made from one mole DATADPO, two moles MPD, and 3 moles BTDA. Both were prepared by the addition of solid BTDA to the amines in DMAC. In the former case, a slurry of DADAB in DMAC was first reacted with sufficient BTDA to give a solution. The MPD was then added, followed by the remainder of the BTDA. Stable solutions were obtained.

Laminate data are given in Table VII. Although initial values are low compared with pyrrones made by the ester method,[4] retention of properties is probably better and is comparable to reported values for polyimides.[13,16]

TABLE VII

Laminates from Acetamidoimide Copolymers

Polymer Composition	$DADAB_2$-MPD_8-$BTDA_{10}$										$DATADPO$-MPD_2-$BTDA_3$			
Precure														
Time, min.	20		20				20		20		110		110	
Temp, °C	150		150				150		150		250		250	
Press Conditions														
Time, min.	15		30				60		60		60		60	
Temp, °C	470		400				350		350		325		350	
Press., psi	1000		1000				1000		1000		500		500	
Resin Content, %														
Prepreg	---		---				---		---		38		38	
Laminate	24		22				27		27		36		33.5	
Flexural Strength, K psi[a]	(b)	(e)	(b)	(c)	(e)	(f)	(b)	(e)	(b)	(d)	(b,g)	(b,h)	(b,g)	(b,h)
25°C	35		36.4				33.6		11.8					
316°C (600°F)		9.4	27.1	22.2	19.1	14.3		26.1	7.6	8.5	38.0	40.7	41.3	45.0
Flexural Modulus, M psi[a]														
25°C	3.4		3.4				2.7		2.2					
316°C (600°F)		2.5	2.8	2.7	2.4	2.5		2.3	1.7	2.0	2.5	2.6	2.6	2.6

a. Average of three specimens
b. Initial values
c. Aged 24 hrs at 316°C
d. Aged 48 hrs at 316°C
e. Aged 100 hrs at 316°C
f. Aged 250 hrs at 316°C
g. Not post-cured
h. Post-cured 30 min at 325°C

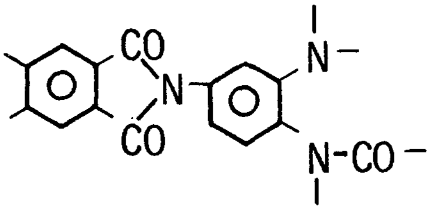
CURING REACTIONS

We have studied the mechanism of cure and the nature of cured and pyrolyzed products for polymers and model compounds representing the dianhydride-tetramine, dianhydride-diacetyltetramine, and diester-tetramine types. The chief methods used were thermogravimetry and infrared analysis.

A consideration of published and unpublished spectra of various polymers and model compounds has led to the following tentative infrared absorption correlations:

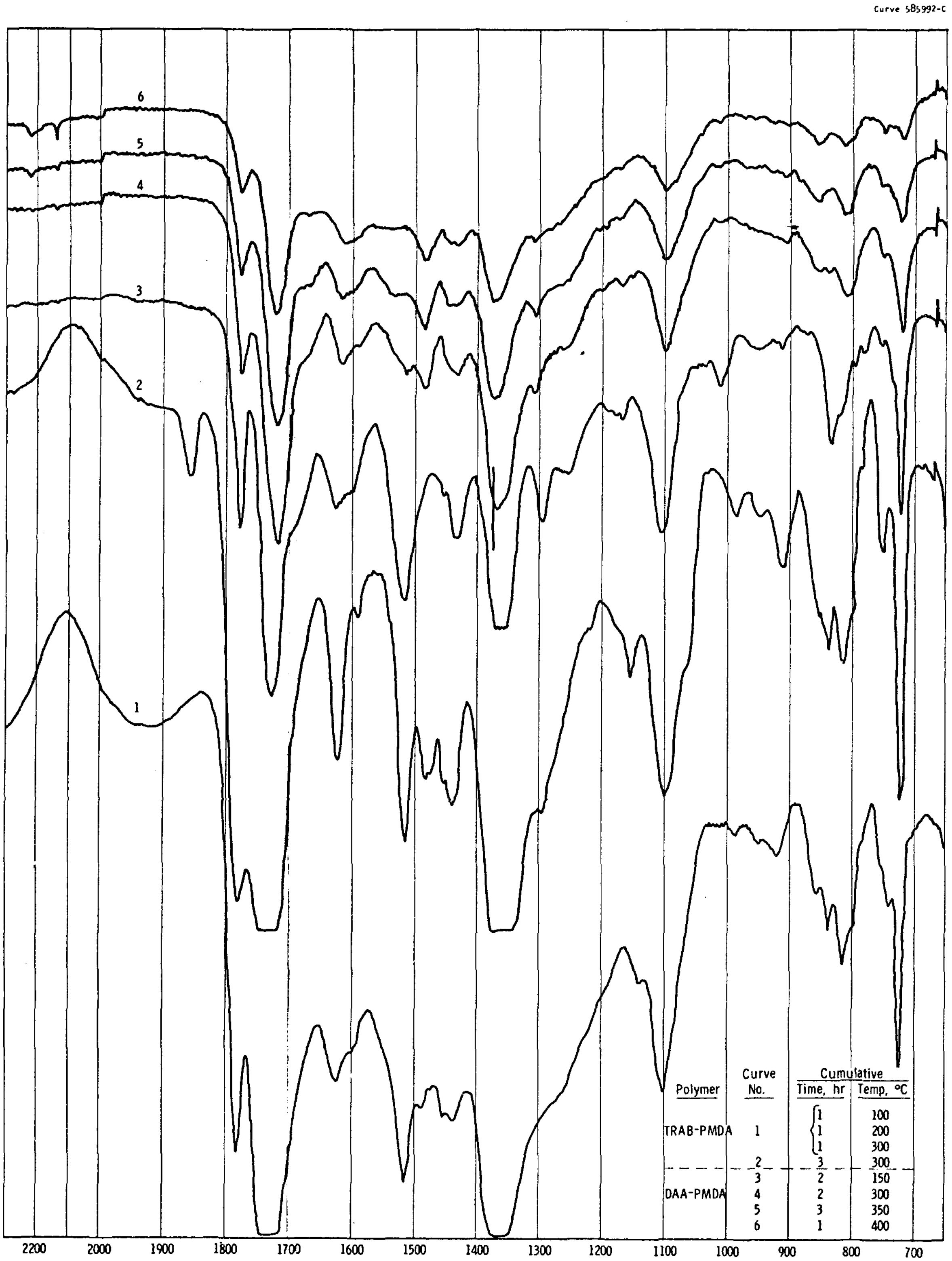
Wave Number, cm^{-1} (approximate)		
Polyimide	Polybenzimidazole[17]	Pyrrone
1780		1760
1720		1730
	1630	1610
		1560-1590
	1460	1470
		1430
1370		1370
	1290	
		1170
		1060
		930-960
		850
	800	820
720		720

Figure 4 shows successive spectra of a film of DAA-PMDA as it was cured. Curve 3 (2 hrs., 150°C) is a typical polyimide spectrum, with characteristic bands at 1780, 1725, 1370, and 725 cm^{-1}. After further heating, these bands remained, although the 725 band appeared to weaken relative to the others. Bands at 1515, 1290, 1010, and 840 cm^{-1} weakened or disappeared. The most noticeable of these is the strong 1515 band, which disappeared completely after the 300°C bake. An increase in relative intensity was found at the pyrrone frequencies of 1480, 860, and 810 cm^{-1}. For comparison, the spectrum of a film of cured TRAB-PMDA (obtained from Dr. V. L. Bell, NASA-Langley) is included (Curve 1). The spectrum is considerably heavier than those derived from DAA-PMDA, but corresponds very closely to curves 4 and 5 except that it still contains the band at 1515 cm^{-1}. Since a 300°C bake eliminated this band from the DAA-PMDA polymer, the TRAB-PMDA film was baked for 3 hrs. at 300°C and re-examined. The spectrum of the baked film (curve 2) still contained a band at 1515 cm^{-1}. The source of this band is not clear, although it is probably associated with a substitution pattern in the benzene ring or a vibration mode of a segment of the polymer chain. For example, the structure



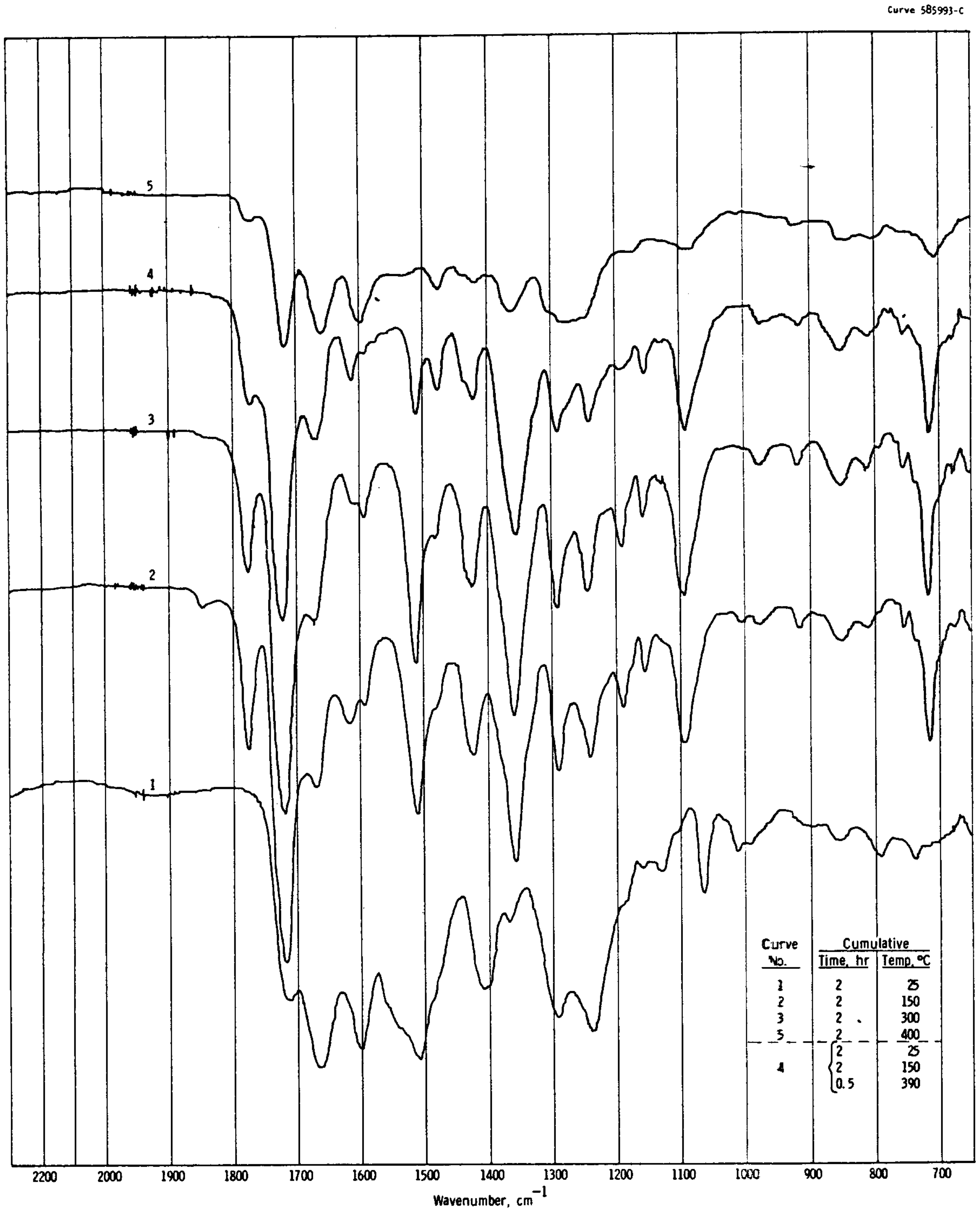
is present in both the imide and the pyrrone forms of the TRAB-PMDA polymer, but is present only in the imide form of the DAA-PMDA polymer. The most noticeable change on heating TRAB-PMDA was the appearance of a band at 1855 cm^{-1}, probably due to anhydride produced by cyclodehydration of terminal carboxyl groups.

Figure 5 shows a similar set of curves for DAA-BTDA. In this case the first curve is for an air-dried sample, still in the amide-acid stage, which lacks the four characteristic imide bands. A bake of 2 hrs. at 150°C converted it to imide (curve 2). The most significant change from curve 2 (imide) to curve 4 (390°C) was the growth of a band at



Polymer	Curve No.	Cumulative Time, hr	Cumulative Temp, °C
TRAB-PMDA	1	1 1 1	100 200 300
	2	3	300
DAA-PMDA	3	2	150
	4	2	300
	5	3	350
	6	1	400

Fig. 4—Infrared spectra of DAA-FMDA and TRAB-PMDA as a function of cure. DAA-PMDA film cast on CsI plate. TRAB-PMDA free film. Cure times cumulative



Curve No.	Cumulative Time, hr	Cumulative Temp, °C
1	2	25
2	2	150
3	2	300
5	2	400
4	2 2 0.5	25 150 390

Fig. 5—Infrared spectra of DAA-BTDA as a function of cure. Film cast on CsI plate. Cure times cumulative

1480 cm^{-1}. As in the preceding case, all four imide bands persisted through the 400°C cure, the 1725 carbonyl band remaining the strongest in the spectrum. Again, the band at 1515 cm^{-1} decreased with heating, but required 400°C for complete removal.

Although some of the spectral changes shown in Figs. 4 and 5 are consistent with pyrrone formation, absence of the strong pyrrone band at 1760 cm^{-1} indicates that very little pyrrone was formed from either TRAB or DAA polymers.

Figures 6 and 7 present a comparison of the spectra of DATADPO-PMDA and TADPO-PMDA during cure. A typical polyimide spectrum was obtained in the former case after 2 hrs. at 200°C. Further heating caused gradual elimination of one imide carbonyl at 1780 cm^{-1}, the amide carbonyl at 1680 cm^{-1}, the ring vibration at 1505 cm^{-1}, and bands at 1290, 1210, 1100, 1010, and 840 cm^{-1}. A relative increase was observed at the pyrrone frequencies of 1620, 1470, 1170, 960, 850, and 820 cm^{-1}. At the higher temperatures, a band at 2220 appeared, which has been identified tentatively as nitrile. In the case of TADPO-PMDA, the reaction apparently followed a somewhat different course. The polyimide spectrum in curve 2 is not very well-defined. The 1780 and 720 bands are weak, while pyrrone or benzimidazole bands have begun to appear. The spectrum of the cured polymer corresponds closely to that reported by Bell and Pezdirtz.[1] Essentially the same bands appeared on curing both the TADPO and DATADPO polymers (Fig. 6, curve 5 vs Fig. 7, curve 3), but the intensities were considerably different. For example the bands at 1760, 1330, and 1070 cm^{-1} in the TADPO-PMDA polymer were present only as shoulders in the DATADPO polymer. Substantial absence of the strong 1760 cm^{-1} pyrrone band from the spectra of DATADPO polymers indicates a low degree of pyrrone formation.

In Figs. 8 and 9, the soluble and insoluble fractions of DADAB-PMDA are compared, using polymer powder in a KBr disc. The two polymers gave very similar spectra, and the changes on heating were similar to those noted for DATADPO-PMDA, although the band at 1470 cm^{-1} did not develop as strongly. The spectrum of the fully cured material resembles that reported by Dawans and Marvel[2] for DAB-PMDA. The small differences

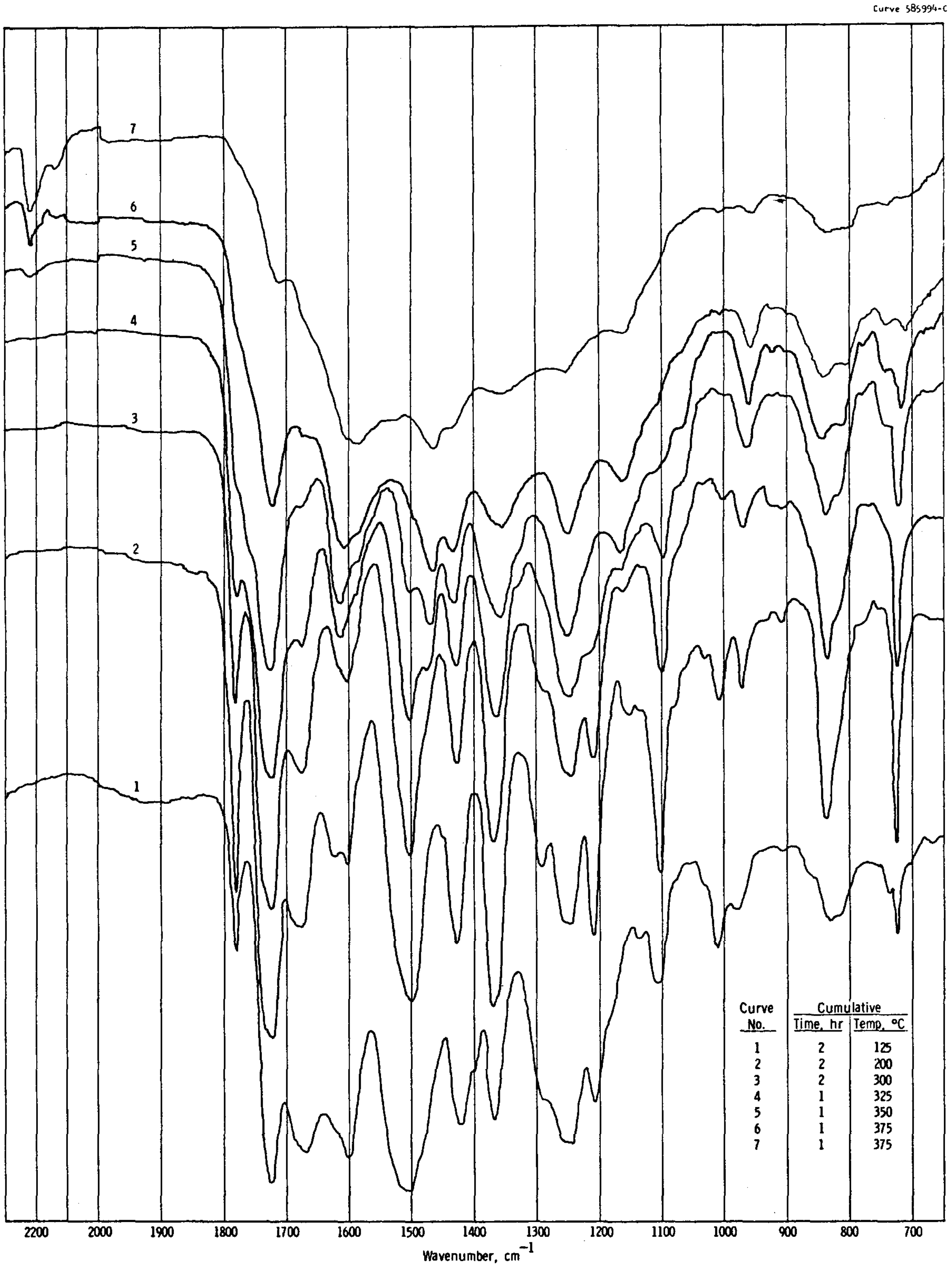


Fig. 6—Infrared spectra of DATADPO-PMDA as a function of cure. Film cast on CsI plate. Cure times cumulative

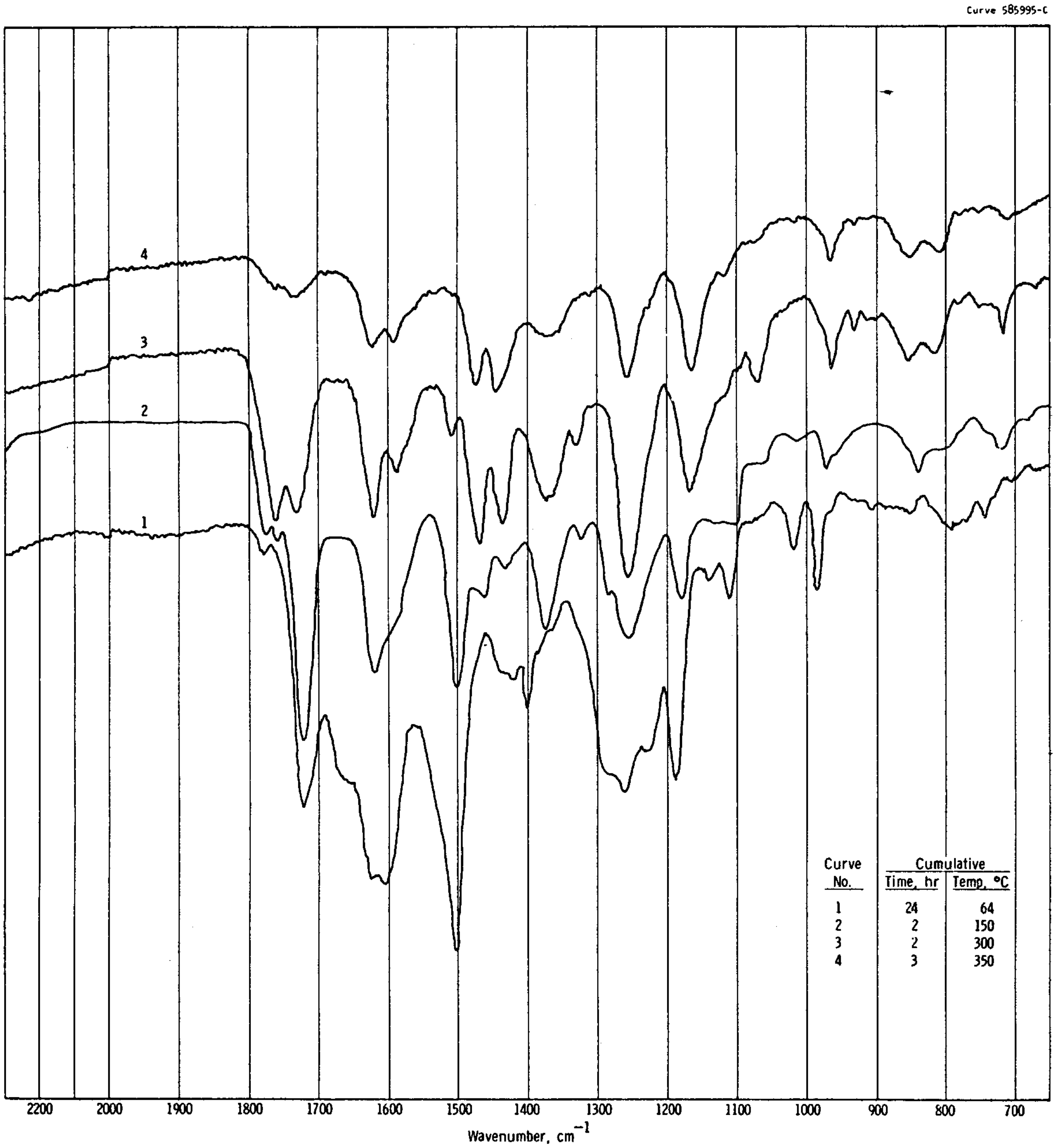


Fig. 7—Infrared spectra of TADPO-PMDA as a function of cure. Film cast on CsI plate. Cure times cumulative

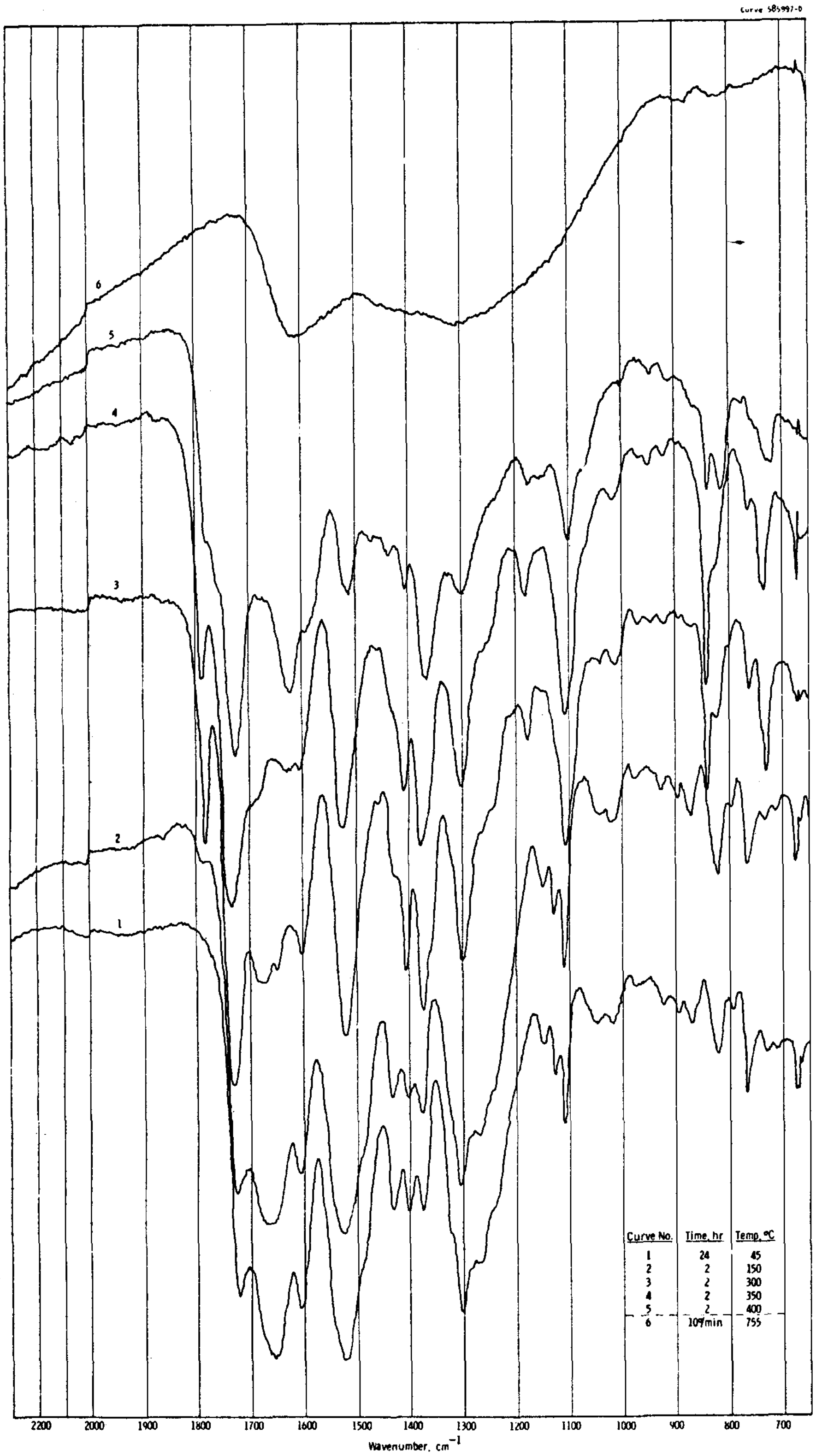


Fig. 8—Infrared spectra of DADAB·PMDA (DMAC insol fract) as a function of cure. Powder in KBr disc. Cure times not cumulative

Curve No.	Time, hr	Temp, °C
1	24	45
2	2	150
3	2	300
4	2	350
5	2	400
6	10°/min	755

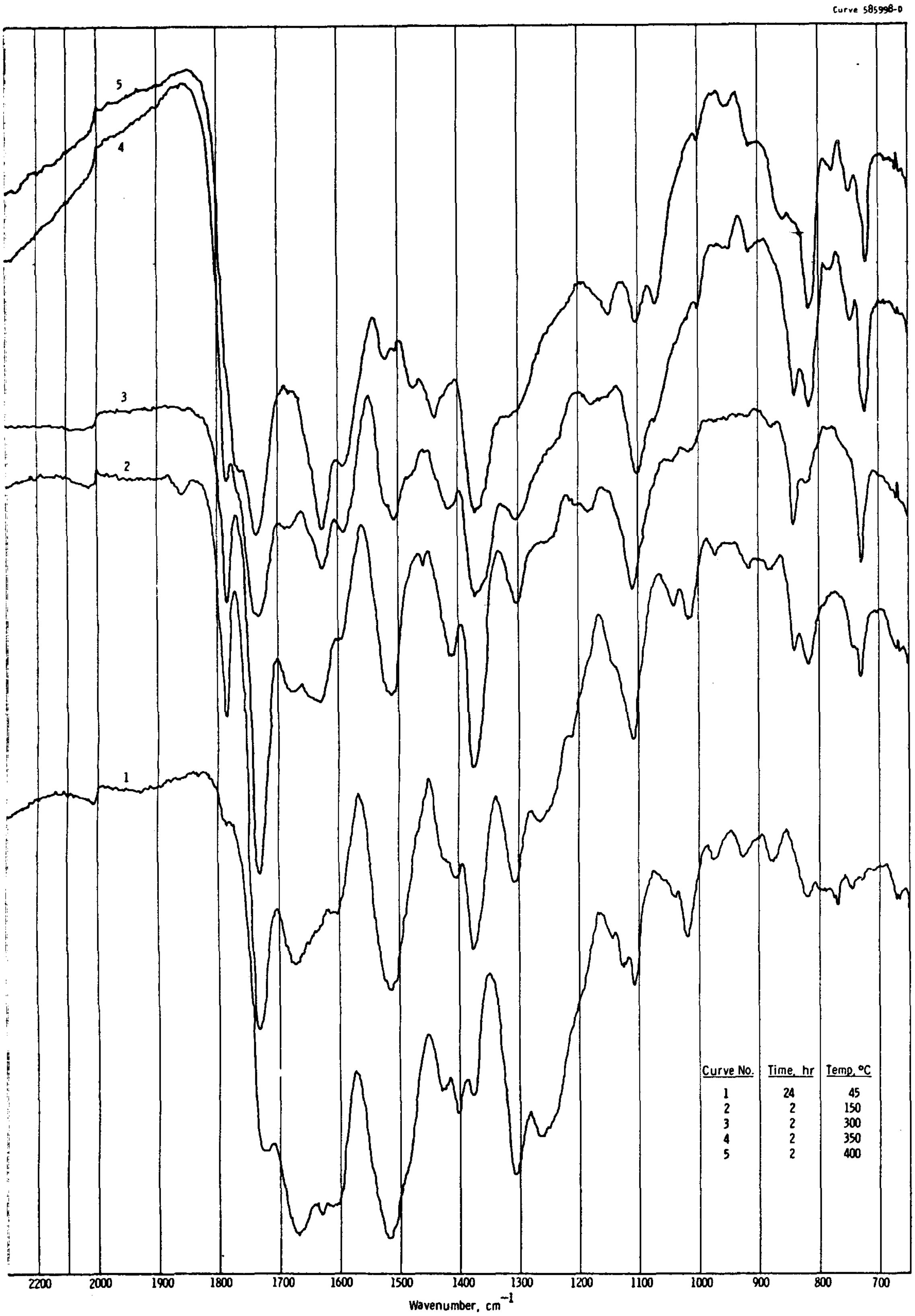


Fig. 9—Infrared spectra of DADAB-PMDA (DMAC sol fract) as a function of cure. Powder in KBr disc. Cure times not cumulative

which appear in the spectra of the soluble and insoluble fractions may be associated with isomerism. For example, variations at 780 cm^{-1} and in the 800-900 cm^{-1} region may be from this source. The soluble fraction appears to be more easily converted to imide and also to pyrrone. The imide bands appeared earlier in the baking cycle, and the pyrrone bands at 1760, 1590, 1470, 1440, 1060, and 820 cm^{-1} were somewhat better developed in the fully cured material, although none of these spectra shows a degree of pyrrone formation approaching that found for TADPO-PMDA.

Additional information on the cure mechanism of DADAB-PMDA is provided by vacuum pyrolysis experiments in which the volatile products were trapped and analyzed. A sample of the polymer under test was sealed in a glass apparatus which was evacuated to about 10^{-6} torr. The sample was then heated while volatiles were trapped in a liquid nitrogen trap. After a heating period the trap was removed and its contents analyzed. The trap was cleaned and replaced, and the cycle repeated. Several successive heating cycles were applied to each polymer sample, using various times and temperatures. For the insoluble fraction, the condensates were also titrated, to obtain a quantitative measure of the acetic acid produced. Results from the two samples are summarized in Table VIII. The observation that the acetyl group is not eliminated below 350°C agrees with the infrared spectral data. CO_2 elimination suggests that decarboxylation may be a side reaction. If some of the linkages are converted to benzimidazole groups through reaction with the acetamido group in the initial ring closure, an isolated carboxyl group would be left, which could easily lose CO_2. There is some indication of the formation of a volatile nitrile or isonitrile.

Infrared spectra of CETADPO-BTDA on curing were very similar to those of DATADPO polymers. A well-defined imide spectrum developed at 150°C, persisted to about 350°C, and gradually changed at 350°C to a spectrum closely resembling Fig. 6, curve 5.

Table VIII

Pyrolysis Products from DADAB-PMDA

Treatments, Successive				
Time. Hrs.	Temp.,°C	Wt. Loss, %	Volatile Products	Acid, % of Calc.
Insol. fraction (D92-143-1)				
14	150	13.0	CO_2, H_2O, THF[a]	1.18
2	300	7.4	CO_2, H_2O[b]	2.88
2	350	1.9	CO_2, H_2O, HOAc, Ac_2O[b]	6.28
18	350	2.9	CO_2, H_2O, HOAc, Ac_2O	6.66
TOTAL		25.2 (Calc. 35%)		17.00
Sol. fraction (D93-1-7)				
2	105	7.8	H_2O, DMAC	
2	150	5.0	H_2O, DMAC	
2	300	8.8	H_2O, CO_2[c]	
2	350	5.6	H_2O, HOAc, Ac_2O[d]	
TOTAL		27.2 (Calc. 42%)		

[a] Tetrahydrofuran used to wash sample was not completely removed. Probably aliphatic ester or ketone also (1735, 1460, 1370 cm^{-1}).

[b] Probably triple bond also (2160, 3070 cm^{-1}).

[c] Bleached indicator paper. NMR showed no aromatic protons. "Odor of cooked cabbage."

[d] Vapor absorbed also at 1135, 1100 cm^{-1}; liquid at 1370, 1133 cm^{-1}.

Figures 10-15 show representative infrared spectra of polymers prepared from DCDAB-BTDA and DCDAB-PMDA as films on cesium iodide plates. The samples were air dried and then baked at 153°C for 90 min. These spectra show well-developed imide bands at 1780, 1730 and 725 cm^{-1}. After a further bake at 300°C the band at 1780 shifts to 1770-1775 cm^{-1} and increases in relative intensity compared to the band at 1730 cm^{-1}. After a further 1 hour cure at 350°C the band at 1770 is stronger than the band

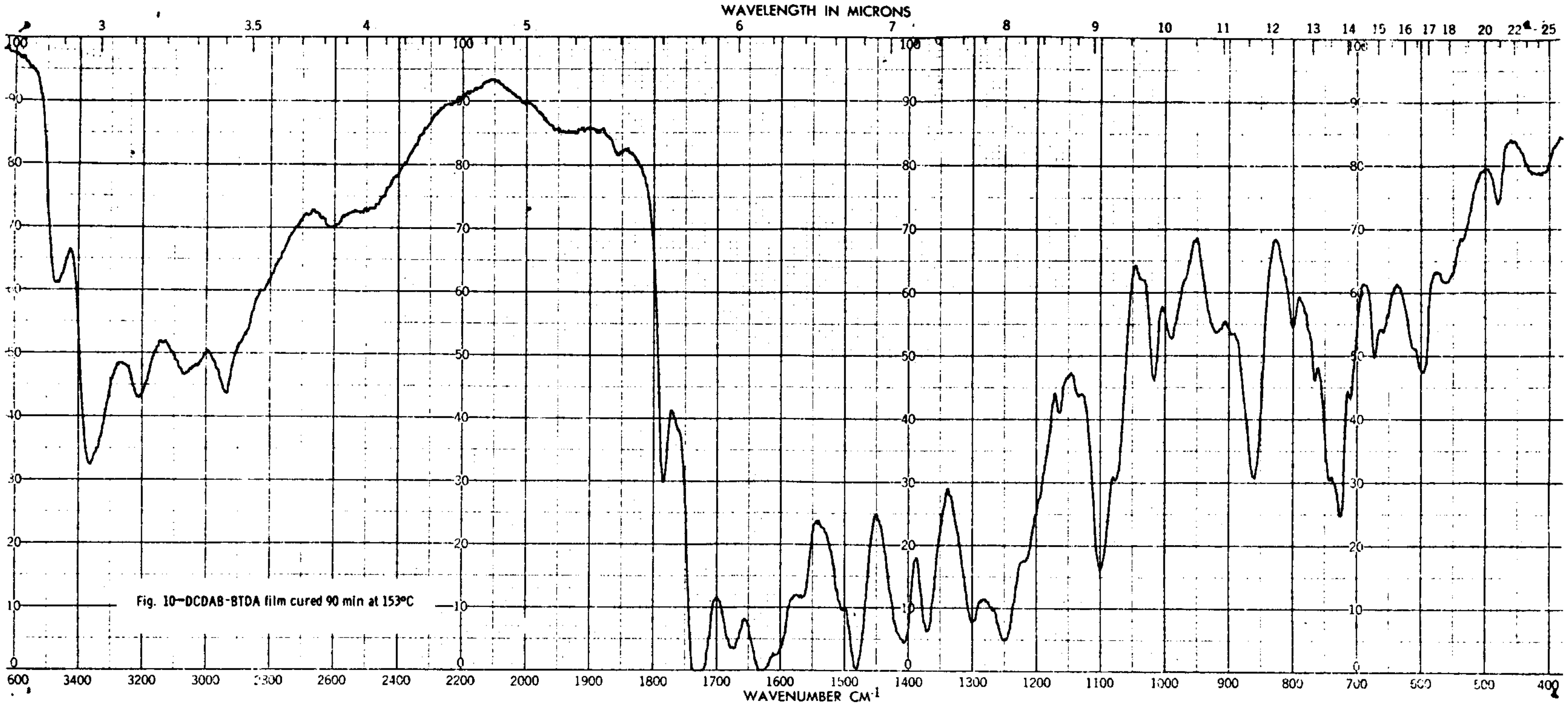


Fig. 10—DCDAB-BTDA film cured 90 min at 153°C

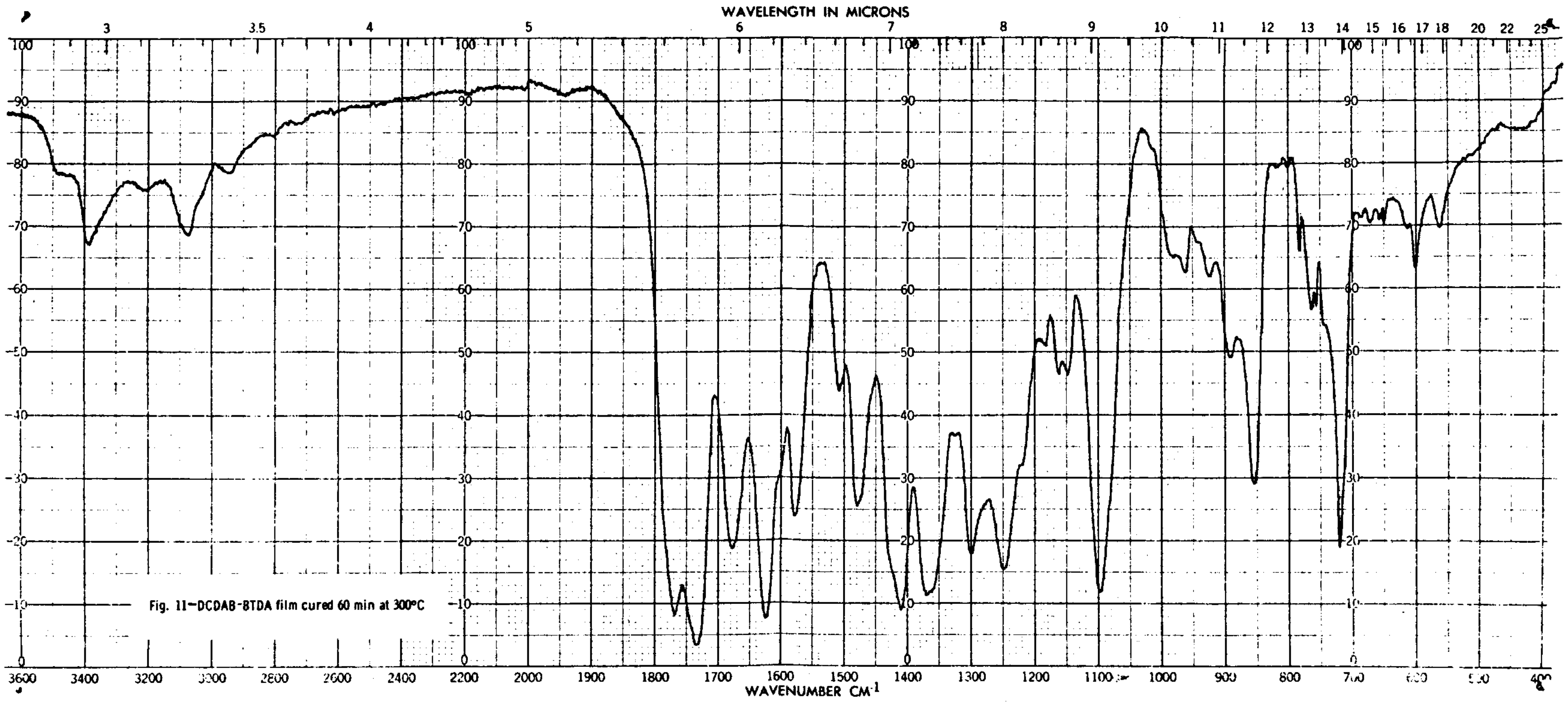


Fig. 11—DCDAB-BTDA film cured 60 min at 300°C

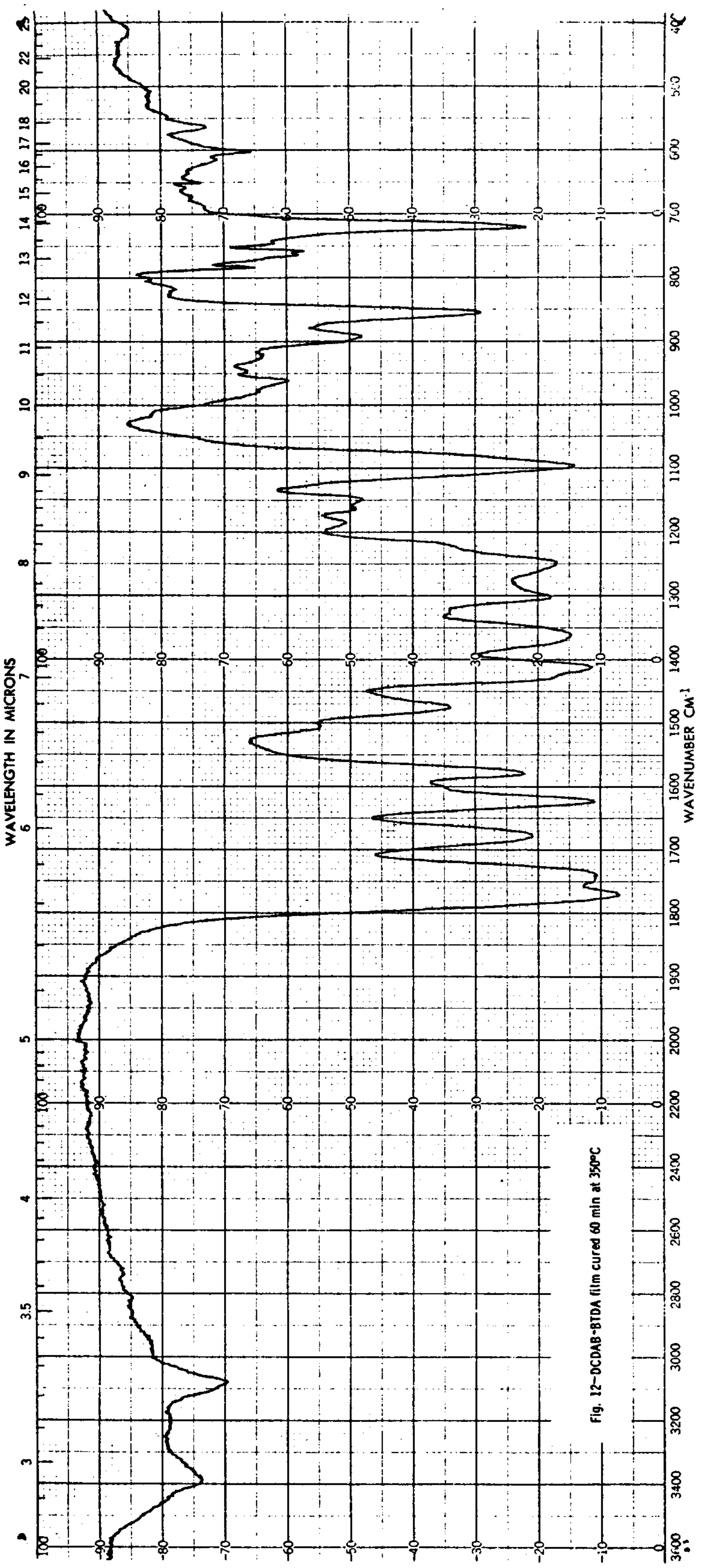


Fig. 12—DCDAB-BTDA film cured 60 min at 350°C

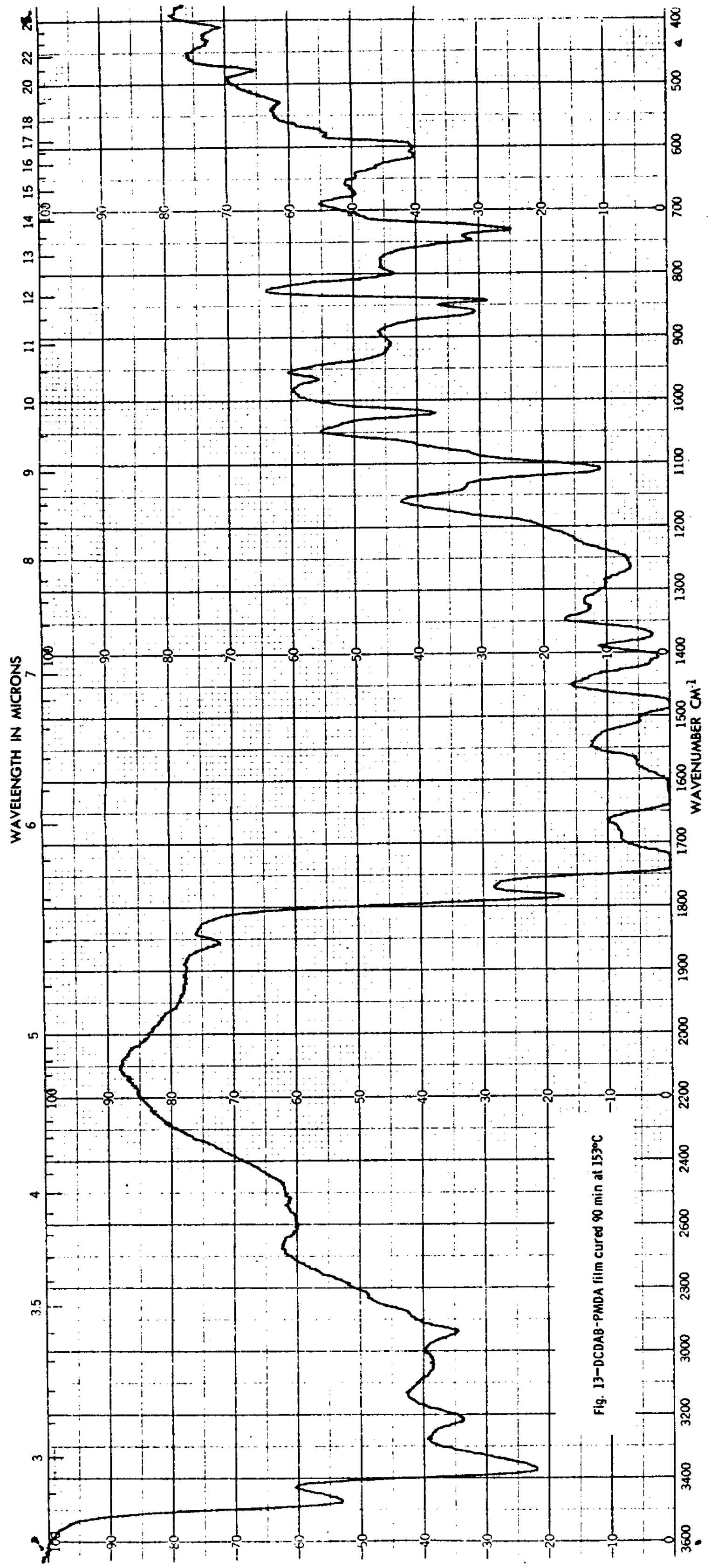


Fig. 13—DCDAB-PMDA film cured 90 min at 153°C

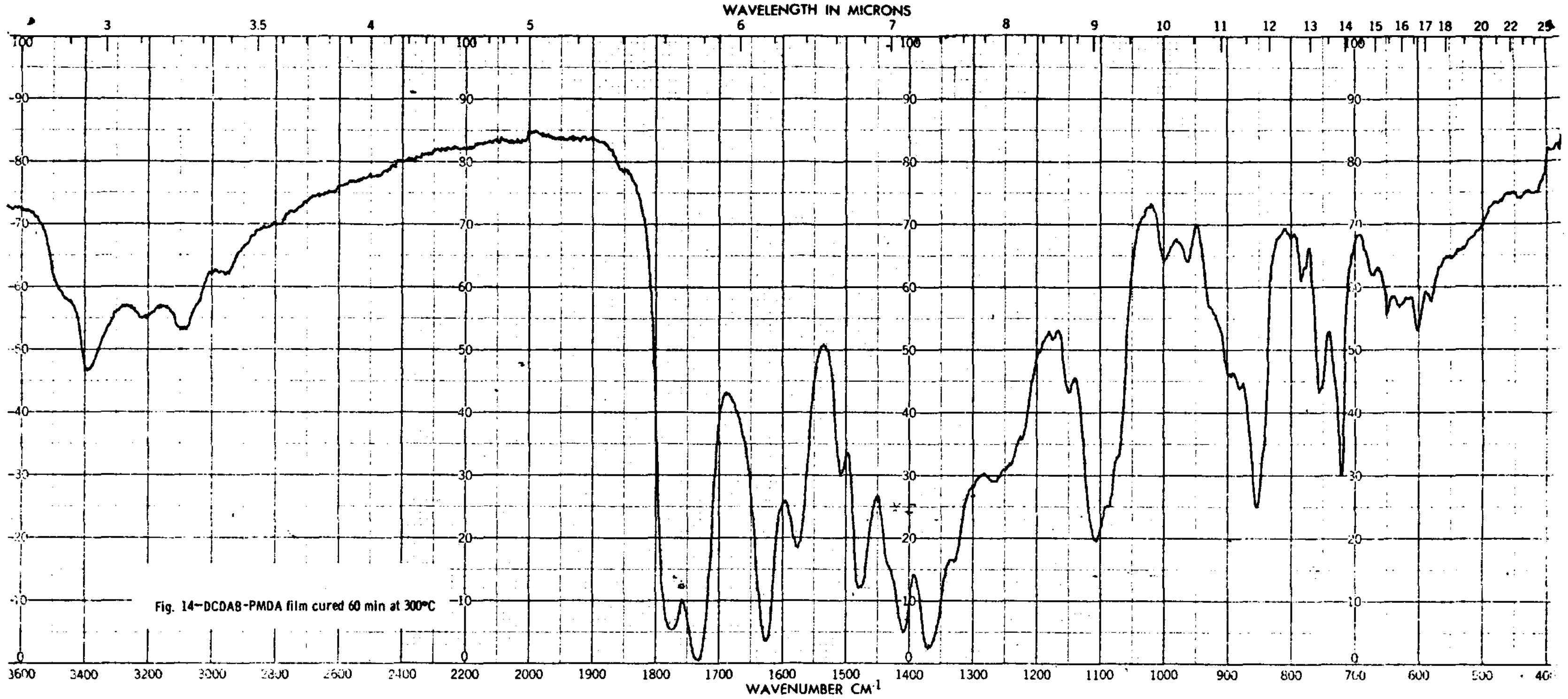


Fig. 14–DCDAB-PMDA film cured 60 min at 300°C

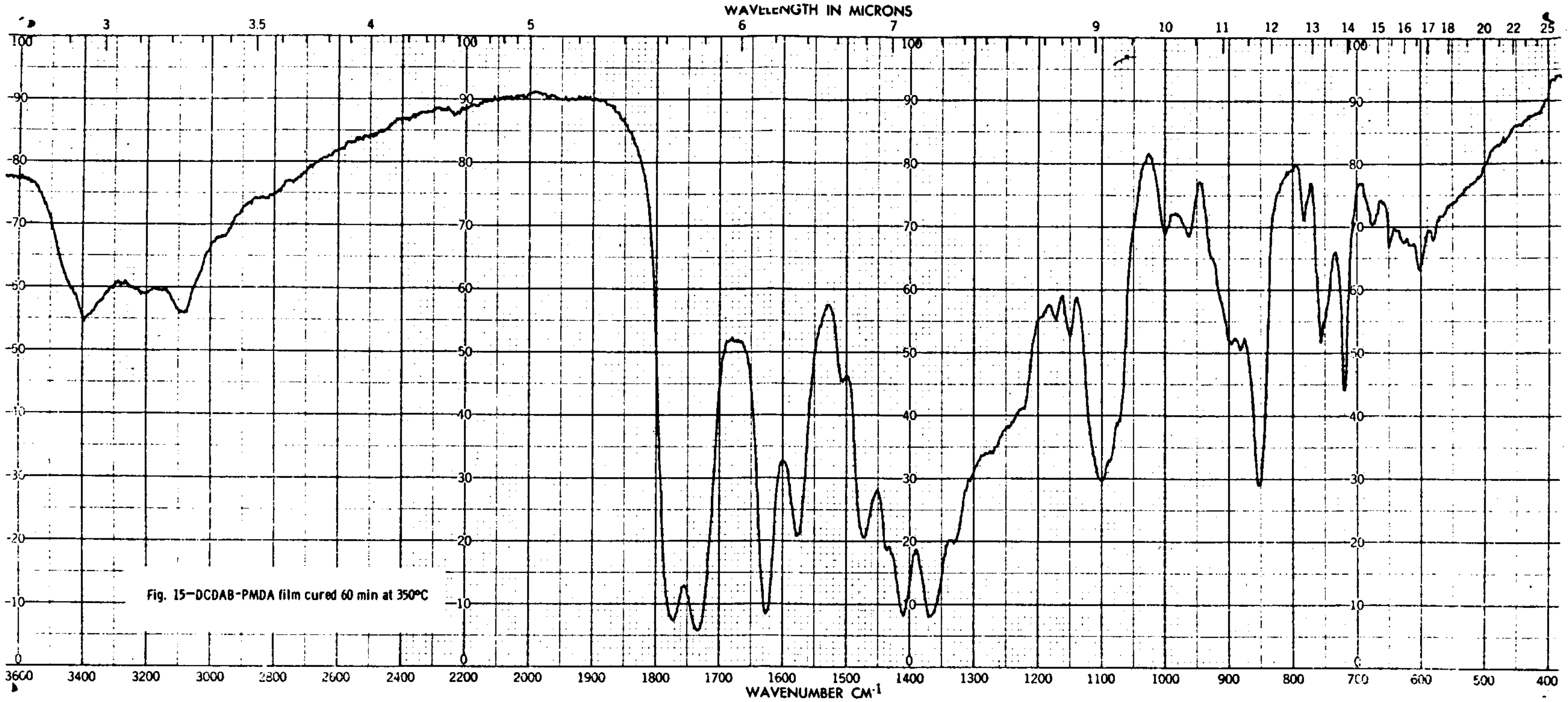


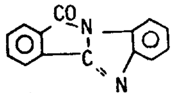
Fig. 15—DCDAB-PMDA film cured 60 min at 350°C

at 1730 cm^{-1} in the DCDAB-BTDA polymer and is almost as strong in the DCDAB-PMDA polymer. This behavior is indicative of pyrrone formation. In addition, in the DCDAB-BTDA polymer a band at 1580 cm^{-1} becomes much stronger after the bake at 300°C. This polymer also has a strong band at 1680 cm^{-1} which is absent in the spectra of the DCDAB-PMDA polymers. These bands may be due to the benzophenone ketone group. Apparently the presence of chlorine in these polymers did not inhibit pyrrone formation.

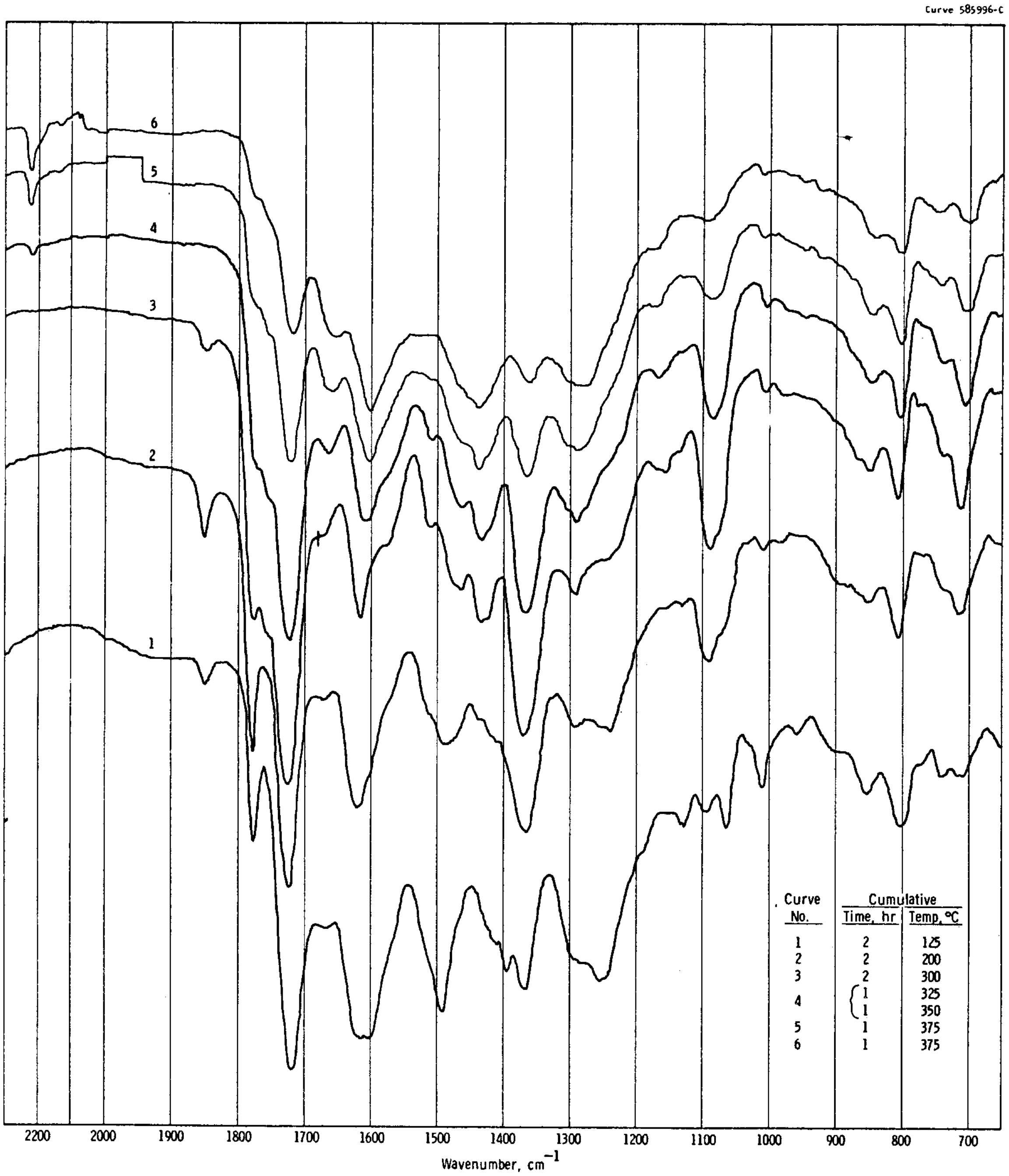
Figure 16 shows infrared curves for the salt prepared from DAB and the dimethyl ester of BTDA. A cure of 2 hrs. at 200°C gave a fairly good polyimide spectrum with a little anhydride at 1850 cm^{-1}. Additional baking eliminated the anhydride and also the 1780 imide band, while a nitrile band appeared at 2220 cm^{-1}. Ester bands at 1270 and 1130 cm^{-1} disappeared. Bands associated with a pyrrone structure developed to some extent, although many of them were very weak. For example, the 1760 cm^{-1} band is present only as a slight shoulder.

Similar results were obtained with the model compound derived from monoisopropyl phthalate and o-phenylenediamine, which was prepared and dried at 60°C in vacuo. When the solid was heated slowly, melting occurred at about 168°C, after which the material resolidified and turned green.

DTA gave strong endotherms at 132° and 170°, and a weak endotherm at 292°C. Infrared spectra, Figs. 17-19, were obtained of the dried product and of samples that were heated for 30 minutes at 135°, for 30 minutes at 180°, and for 30 minutes at 300°C. The samples cured at 60° and 135° gave essentially identical spectra. Absorption bands at 1580 and 1405 cm^{-1} may be attributed to a salt structure. These bands have mostly disappeared at 180° and entirely so after 30 minutes at 300°C. Figure 18 contains suggestions of polyimide, but the amount, if any, is small. Figure 19 shows some similarities to the spectrum of



but the weakness or absence of the strong bands at, e.g., 1765 and 715 cm^{-1} indicate that very little of this compound was formed.



Curve No.	Cumulative Time, hr	Cumulative Temp, °C
1	2	125
2	2	200
3	2	300
4	1 1	325 350
5	1	375
6	1	375

Fig. 16—Infrared spectra of Me_2-BTDA-DAB salt as a function of cure. Film cast on CsI plate. Cure times cumulative

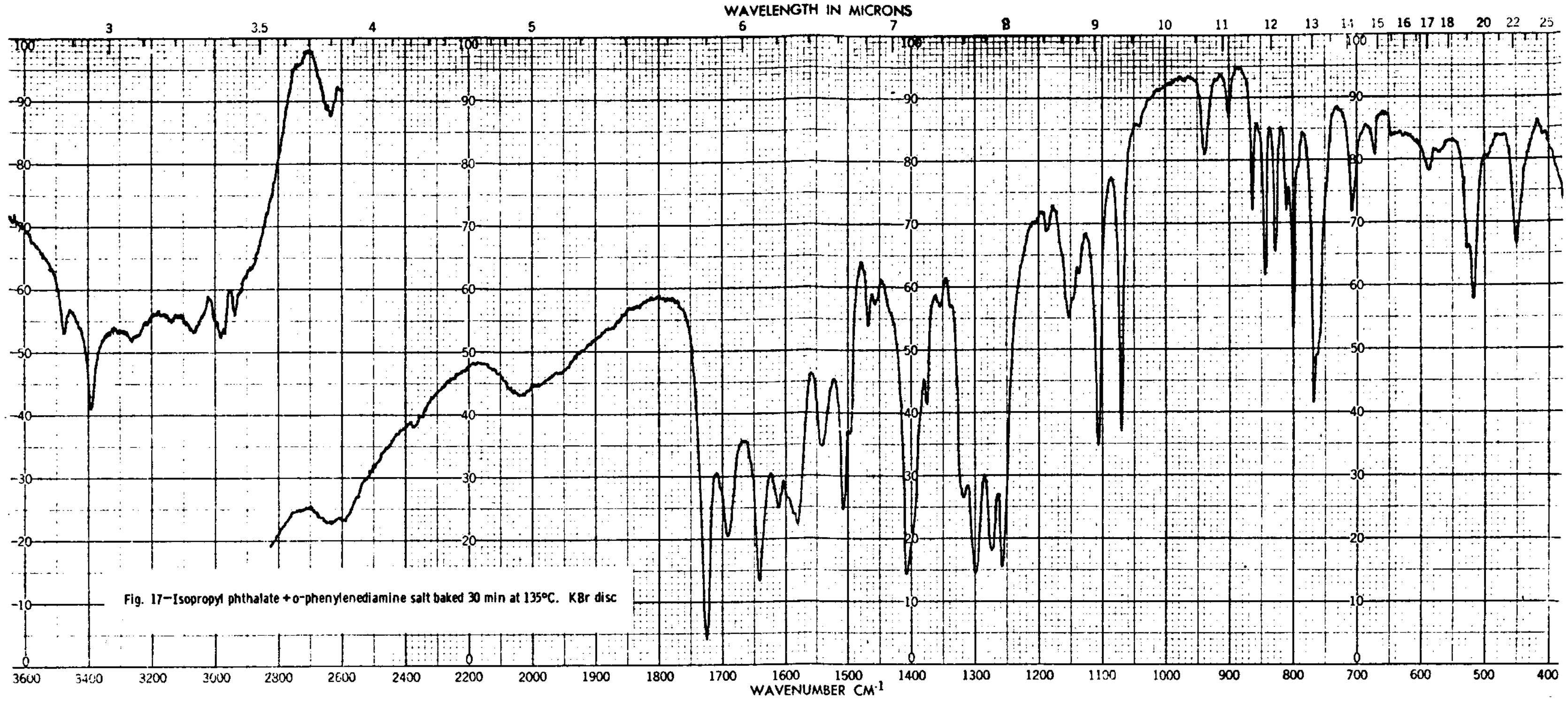


Fig. 17—Isopropyl phthalate + o-phenylenediamine salt baked 30 min at 135°C. KBr disc

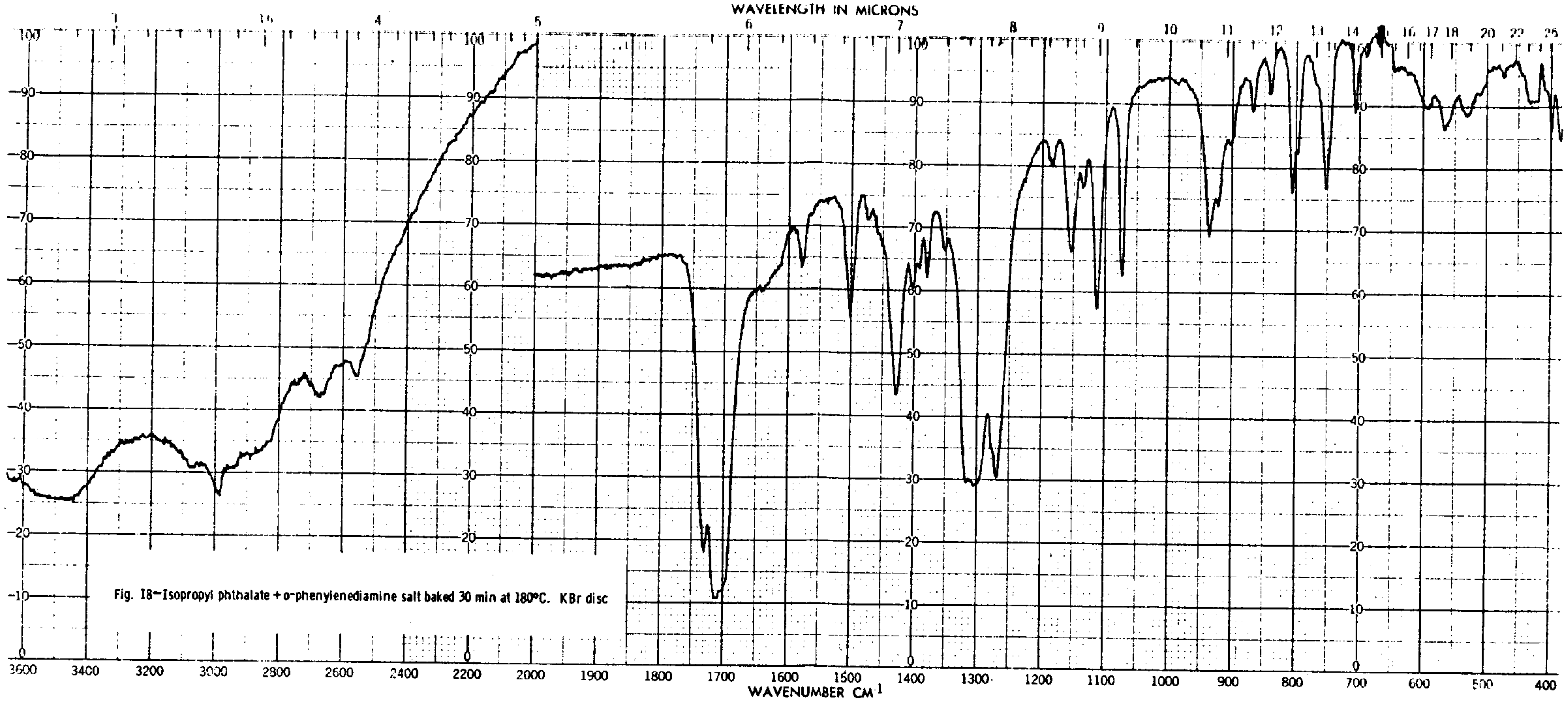


Fig. 18—Isopropyl phthalate + o-phenylenediamine salt baked 30 min at 180°C. KBr disc

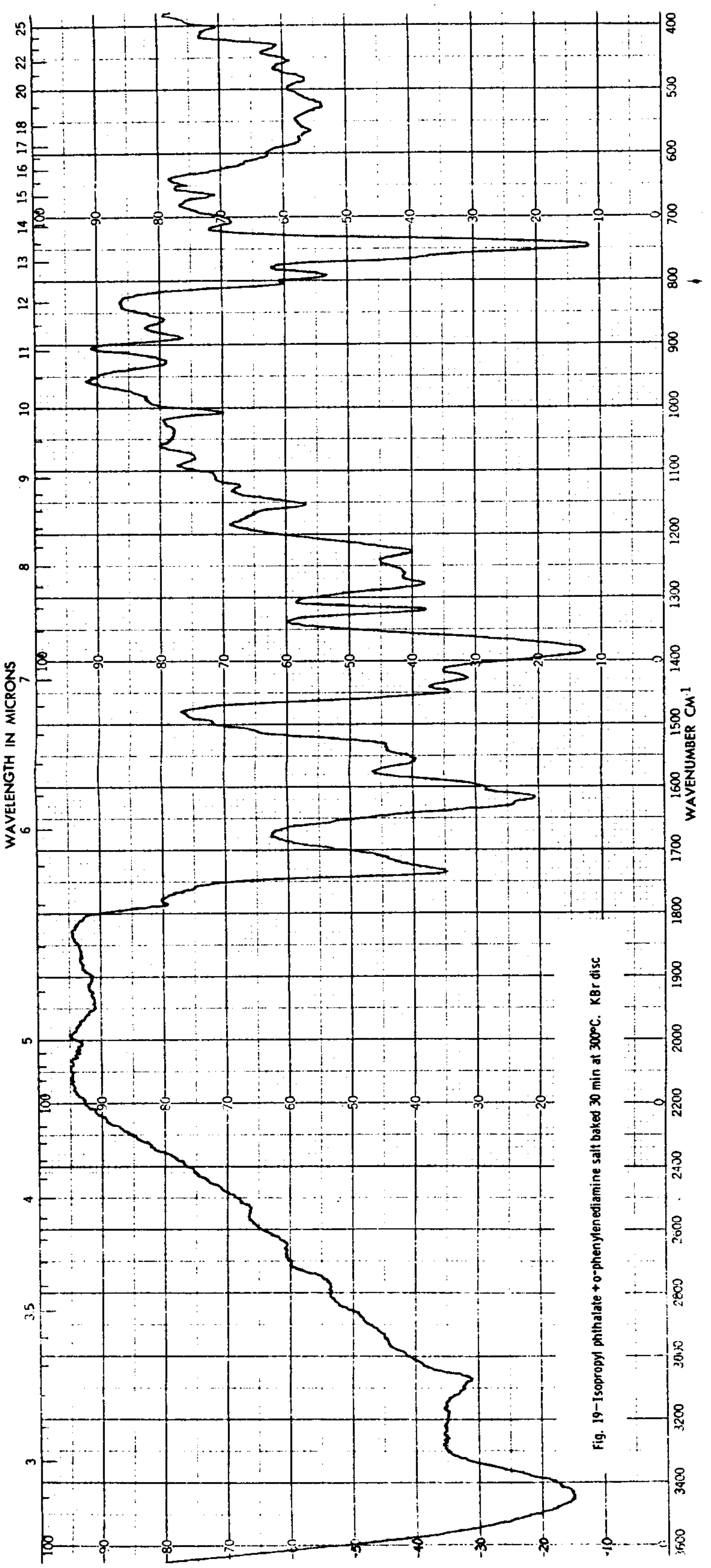
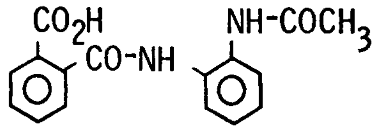
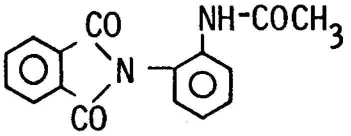


Fig. 19—Isopropyl phthalate + o-phenylenediamine salt baked 30 min at 300°C. KBr disc

A considerable amount of work was done with model compounds in an effort to clairfy the reactions occurring in the cure of polymers derived from diacetyl tetramines. Details of synthesis and properties of the model compounds are given in the Experimental Section.

The compound 

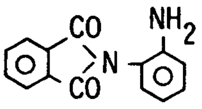
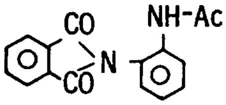
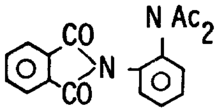
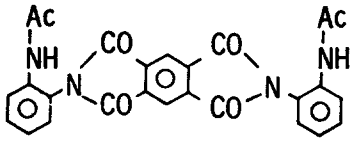
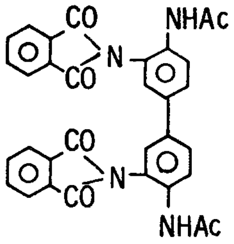
was heated in the DTA apparatus at 15°C/min to 200° C, held for 15 min at 200°, cooled to 50°C, and then reheated in the same way. In the first heating period a sharp endotherm occurred at 168°C, accompanied by melting. No crystallization occurred on cooling, and no endotherms were observed on reheating. These observations suggested that an amorphous polymer might have been formed. However, a second experiment, on a larger scale, led to a different conclusion. The compound was held at 200°C for 30 min in a slow stream of nitrogen. The weight loss was 90% of that calculated for simple dehydration, and recrystallization of the residue gave a 69% yield of 

(OAA-PA). Evaporation of the mother liquor gave a 23% yield (if pure OAA-PA) of a residue which showed no DTA endotherms. However, its infrared spectrum showed it to be almost entirely OAA-PA. These results agree with the infrared studies on polymers, which indicate that moderate heating of the acetamido amide acid structure gives nearly quantitative conversion to the imide.

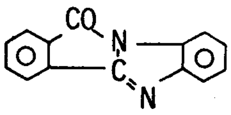
The next step in the cure was studied by pyrolyzing model compounds for 3 hrs. at 400°C in a slow stream of nitrogen. A horizontal glass tube was used, 25 mm in diameter, with a 30 cm hot zone. The sample was contained in a porcelain boat near one end of the hot zone, to provide for pyrolysis of vapors as well as residues. Results with five model imides of interest are summarized in Table IX. OPD-PA was converted almost quantitatively to the pyrrone, which sublimed.

Dwg. 7228091

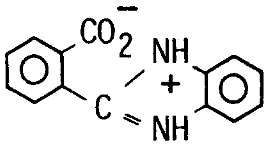
TABLE IX—PYROLYSIS OF MODEL COMPOUNDS AT 400°C IN N_2

Code Name	Structure	Sample Wt, g	Residue		Sublimate	
			g	% of Sample Wt	g	% of Sample Wt
OPD-PA		1.7757	0.0008	0.5	1.5849	89.3[a]
OAA-PA		0.6553	0.0248	3.78	0.4598	70.2
DAOPD-PA		1.0118	0.1684	16.64	0.3537	34.96
$(OAA)_2$-PMDA		3.3058	1.90	57.5	0.65	19.7
DADAB-$(PA)_2$		0.65	0.44	68.0	0.07	11.0

[a] 97% Yield of



In the case of OAA-PA, the infrared spectrum of the sublimate was almost identical to that of the starting material, indicating that most of the compound sublimed without change. Some minor spectral differences were observed, among them the appearance of a new band at 1570 cm^{-1}, an increase in a band at 1460, and a decrease in bands at 890 and 760 cm^{-1}. Figure 20 shows an infrared spectrum of the residue from this run. Five bands are present, at 1720, 1680, 1600, 1450, and 740 cm^{-1}. The material cannot be identified with certainty, but the spectrum is rather similar to that of



The compound DAOPD-PA incorporates a blocking structure that was not evaluated in polymers. It was studied briefly here to determine its suitability. The spectra of both sublimate and residue were essentially identical to the corresponding fractions from OAA-PA. The sublimate in this case was substantially different from the starting material. Apparently the second acetyl group is lost easily to give the monoacetyl compound.

Pyrolysis of $(OAA)_2$-PMDA gave sublimate and residue fractions having essentially identical spectra. Figure 21 shows the spectrum of the sublimate. The carbonyl region is more suggestive of an imide than a pyrrone. The spectrum as a whole resembles that of the other pyrolysis residues, with the addition of a strong band at 1380. Both imides and pyrrones absorb in this region. Pyrolyzed DADAB-PMDA polymer gave a spectrum (Fig. 9, curve 5) containing essentially the same bands, but with different intensity ratios.

In the case of DADAB-$(PA)_2$, both sublimate and residue gave typical pyrrone spectra. That of the sublimate is shown in Fig. 22. The residue spectrum was nearly identical but less sharp.

A programmed TGA run with OAA-PA gave sublimation only. Programmed TGA (2.5°/min in nitrogen) with the less volatile compounds $(OAA)_2$-PMDA (amide acid) and DADAB-$(PA)_2$ gave more interesting results, which are shown in Figs. 23 and 24. The two curves are very similar.

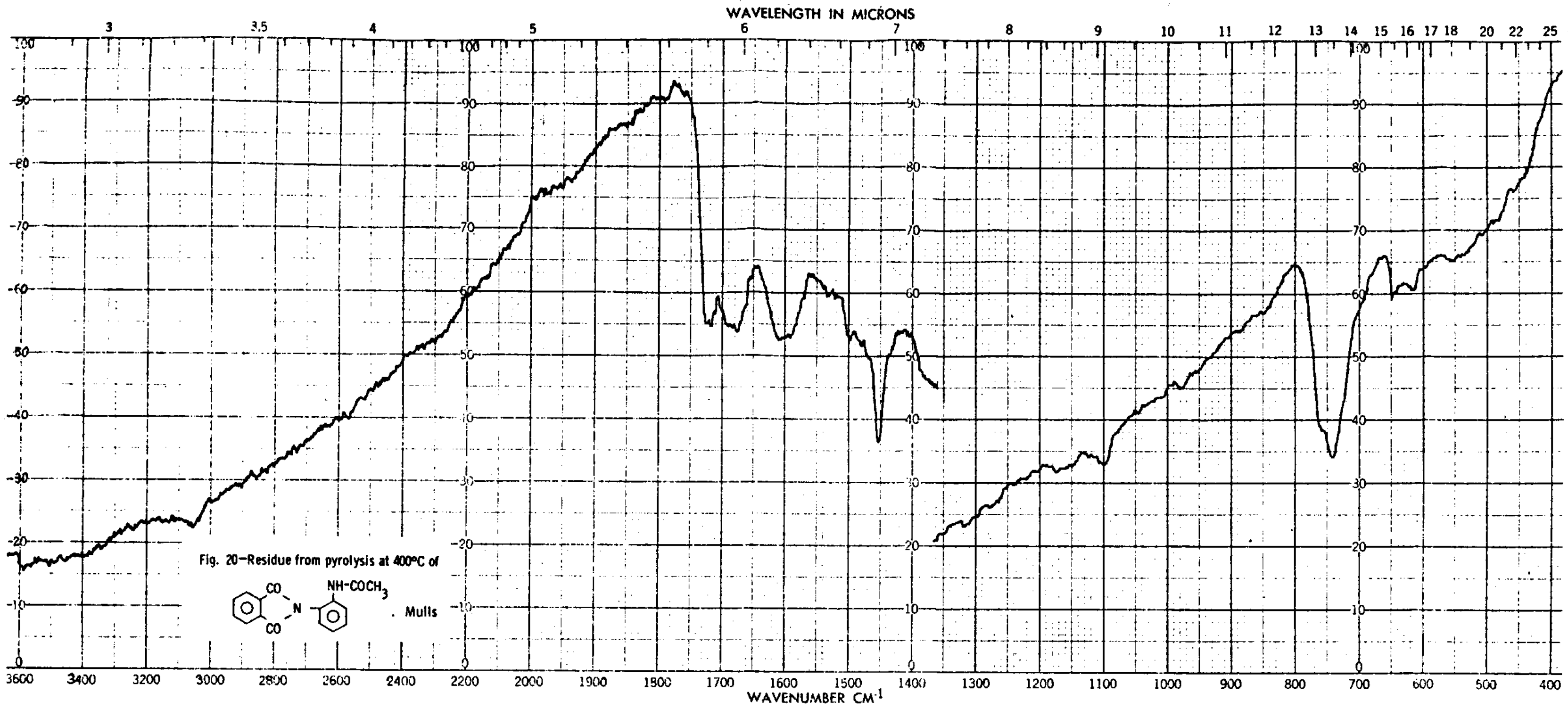


Fig. 20—Residue from pyrolysis at 400°C of . Mulls

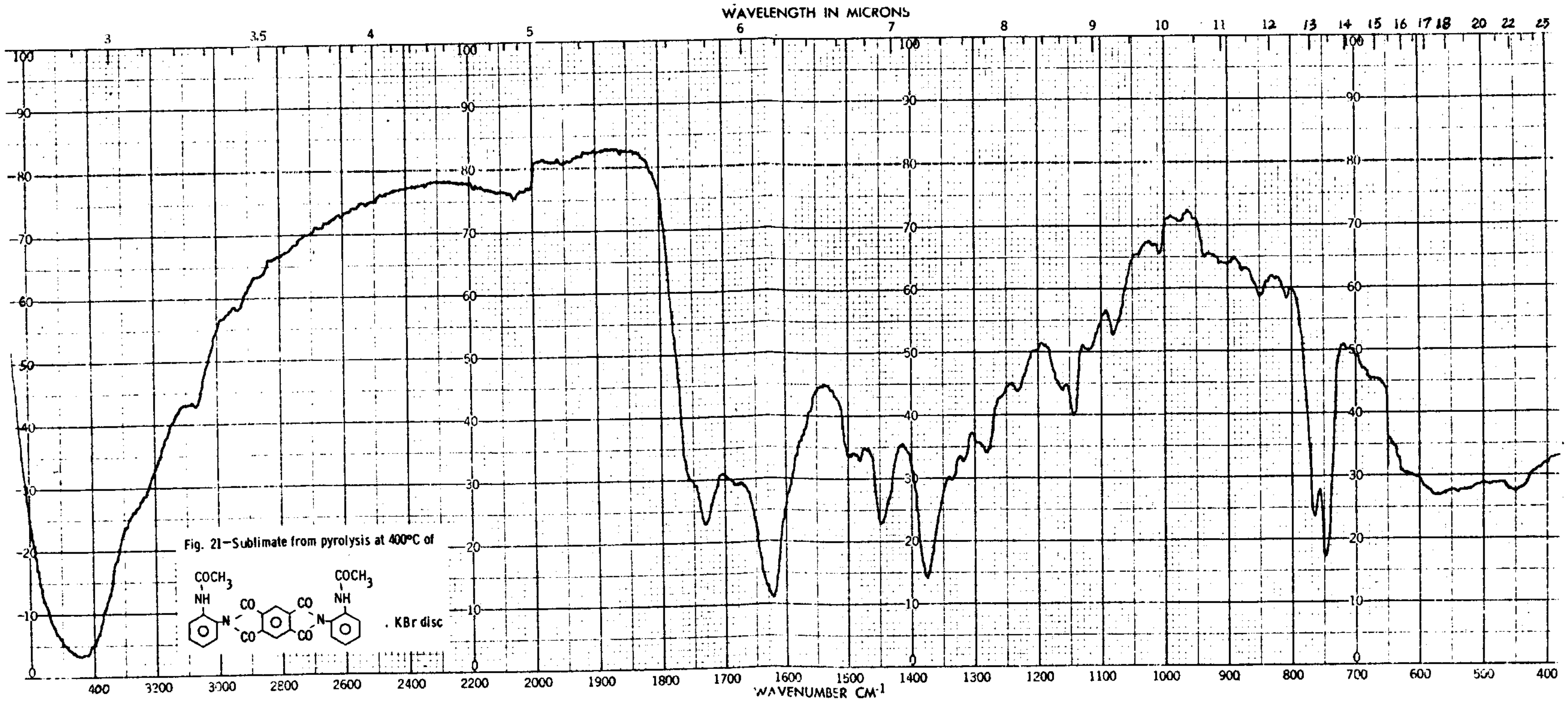


Fig. 21—Sublimate from pyrolysis at 400°C of [structure], KBr disc

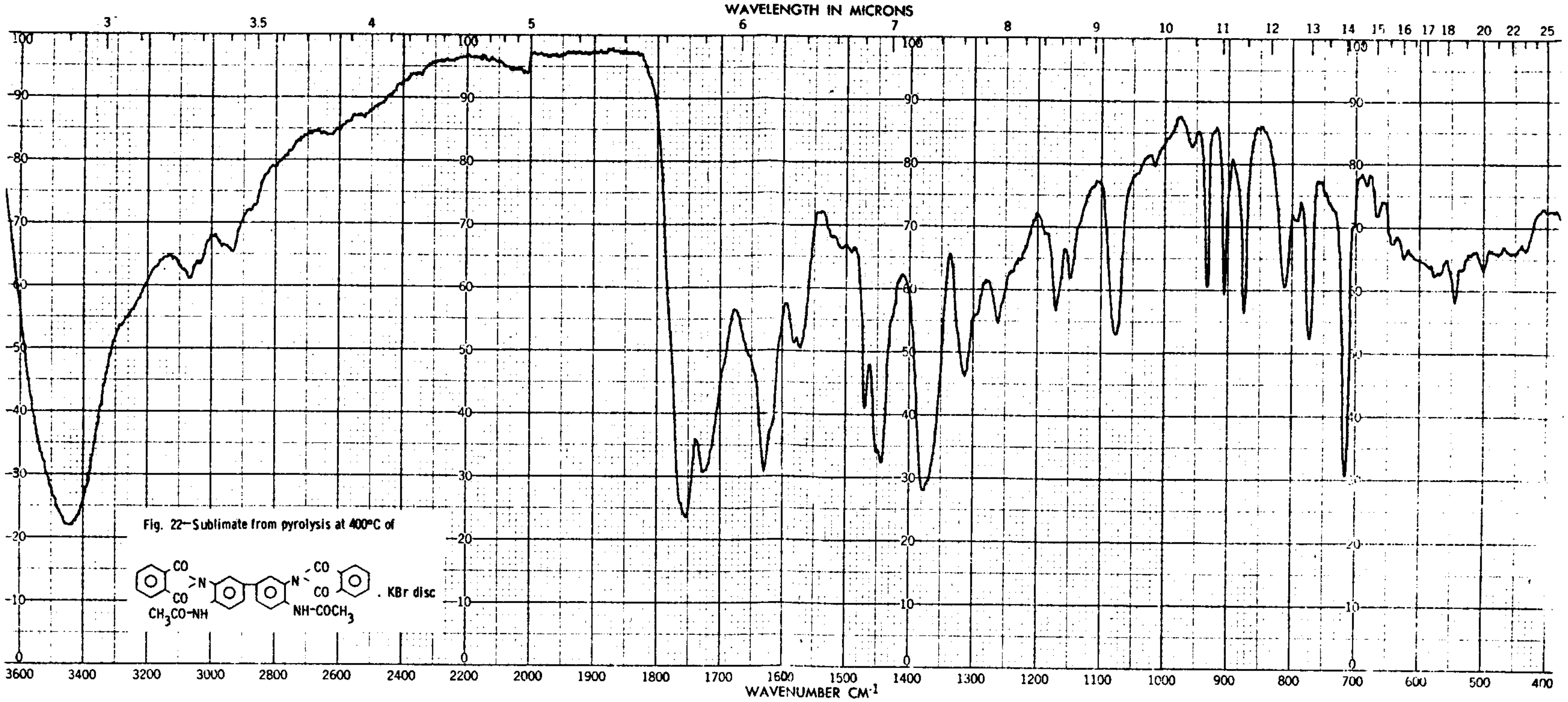


Fig. 22—Sublimate from pyrolysis at 400°C of . KBr disc

Curve 591421-B

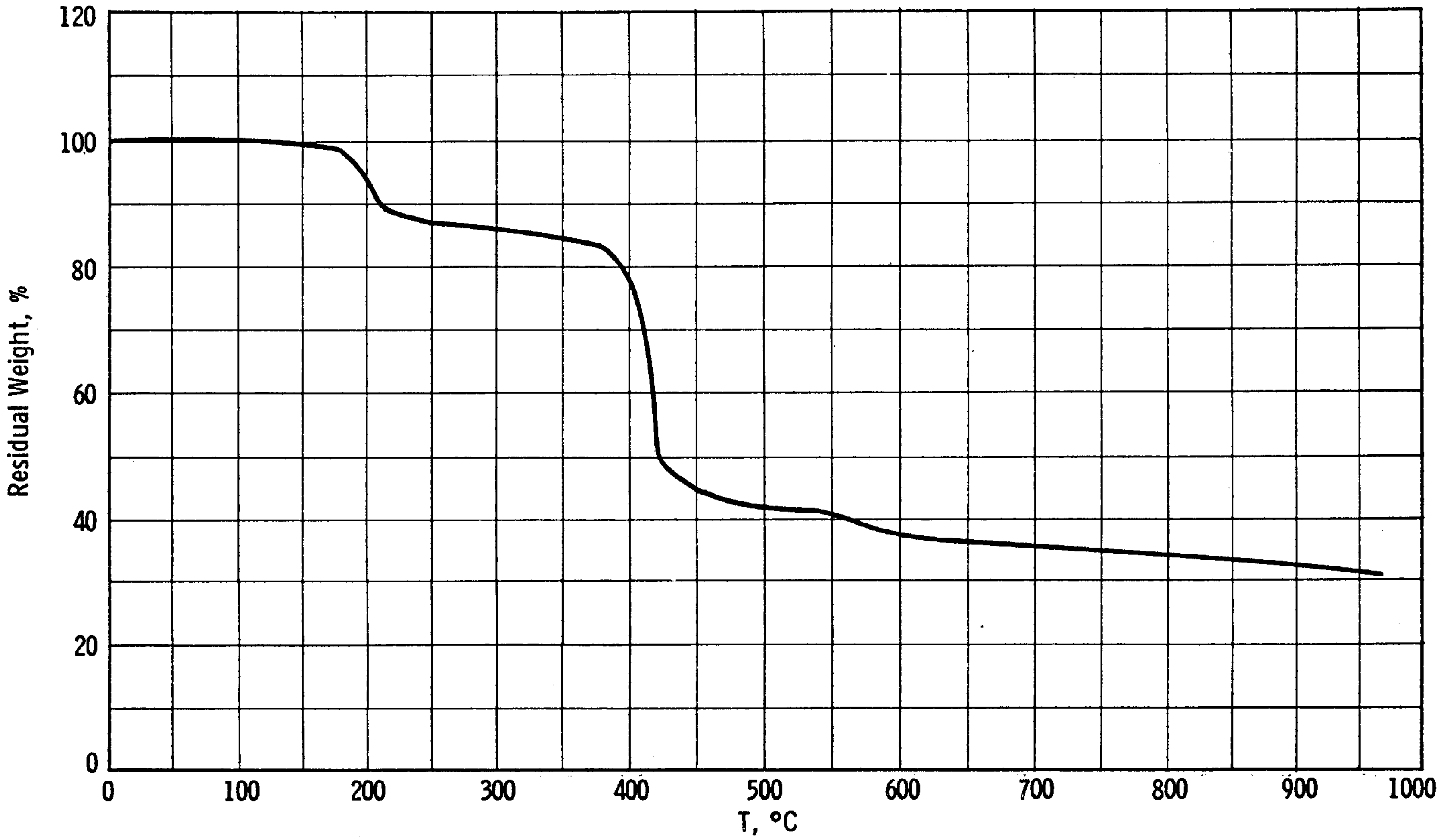


Fig. 23—Programmed TGA of $(OAA)_2$-PMDA (amide acid), 2.5°C per.min in N_2

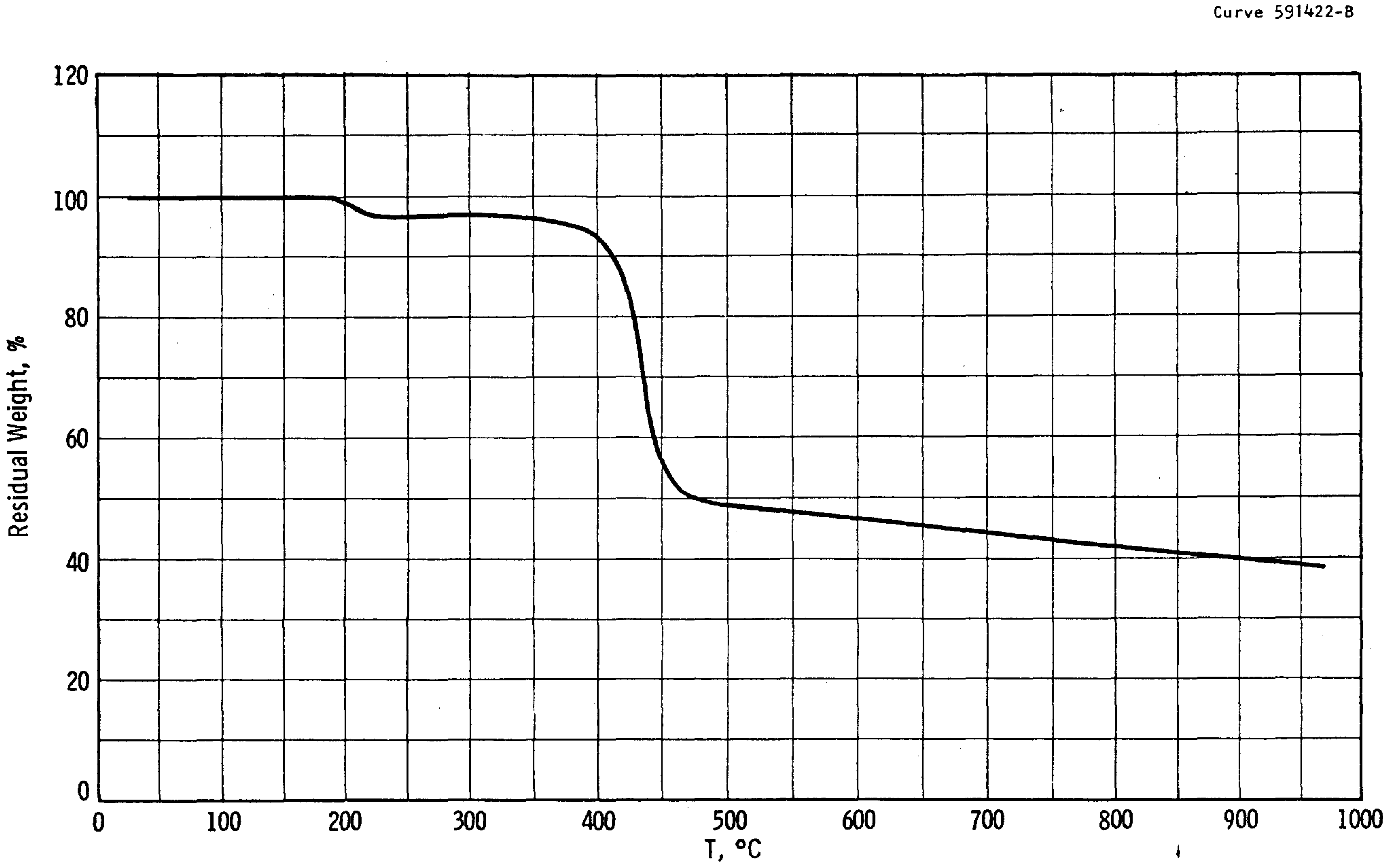


Fig. 24—Programmed TGA of DADAB-$(PA)_2$ (imide), 2.5°C per min in N_2

Two clear-cut steps are apparent in each of the weight loss curves, one at 200°C and one at 410° - 430°C. These are about the temperatures at which the loss of water and of acetic acid are expected to occur in $(OAA)_2$-PMDA(amide acid). The small drop at 200°C may be due to residual NMP in DADAB-$(PA)_2$. However, the magnitude of the steps is entirely wrong. For $(OAA)_2$-PMDA(amide acid), two moles of water would correspond to 8.0% loss, and two moles of acetic acid would add another 23.2%. Observed values were about 14% for the first step, 44% for the second. A third small step at 560°C added 4% more to the weight loss. In the case of DADAB-$(PA)_2$, if we assume that the 3.5% drop at 200°C was due to loss of NMP, the other step should add another 20.75% loss if due to acetic acid elimination. The actual loss in the second step was about 48%. An interesting feature of both curves is the retention of 32-38% of the sample weight at 970°C. A considerable amount of yellow sublimate was observed in both runs, and there was a brown residue.

Results of isothermal TGA at 400°C are shown in Fig. 25 for the imide forms of $(OAA)_2$-PMDA and DADAB-$(PA)_2$. The curves are quite different. For DADAB-$(PA)_2$ there was a rapid drop of about 6%, followed by gradual loss for the rest of the run. If the elimination of acetic acid were the only process, a loss of 21.5% would be expected. It was necessary to discontinue the determination before that value was reached. However, since sublimation was observed, weight loss cannot be equated with acetic acid loss. $(OAA)_2$-PMDA lost weight much more rapidly, and reached essentially constant weight in 80 minutes, but the residual weight was much lower than the value of 69.9% calculated for acetic acid loss. Some sublimation occurred in this case also, and a non-volatile resinous residue was formed. Of possible significance is the fact that the weight loss of $(OAA)_2$-PMDA at 400°C corresponds almost exactly to the loss of PMDA.

The results of cure and pyrolysis experiments are not entirely free from ambiguities, but the following statements are reasonably consistent with observations.

Curve 590305-A

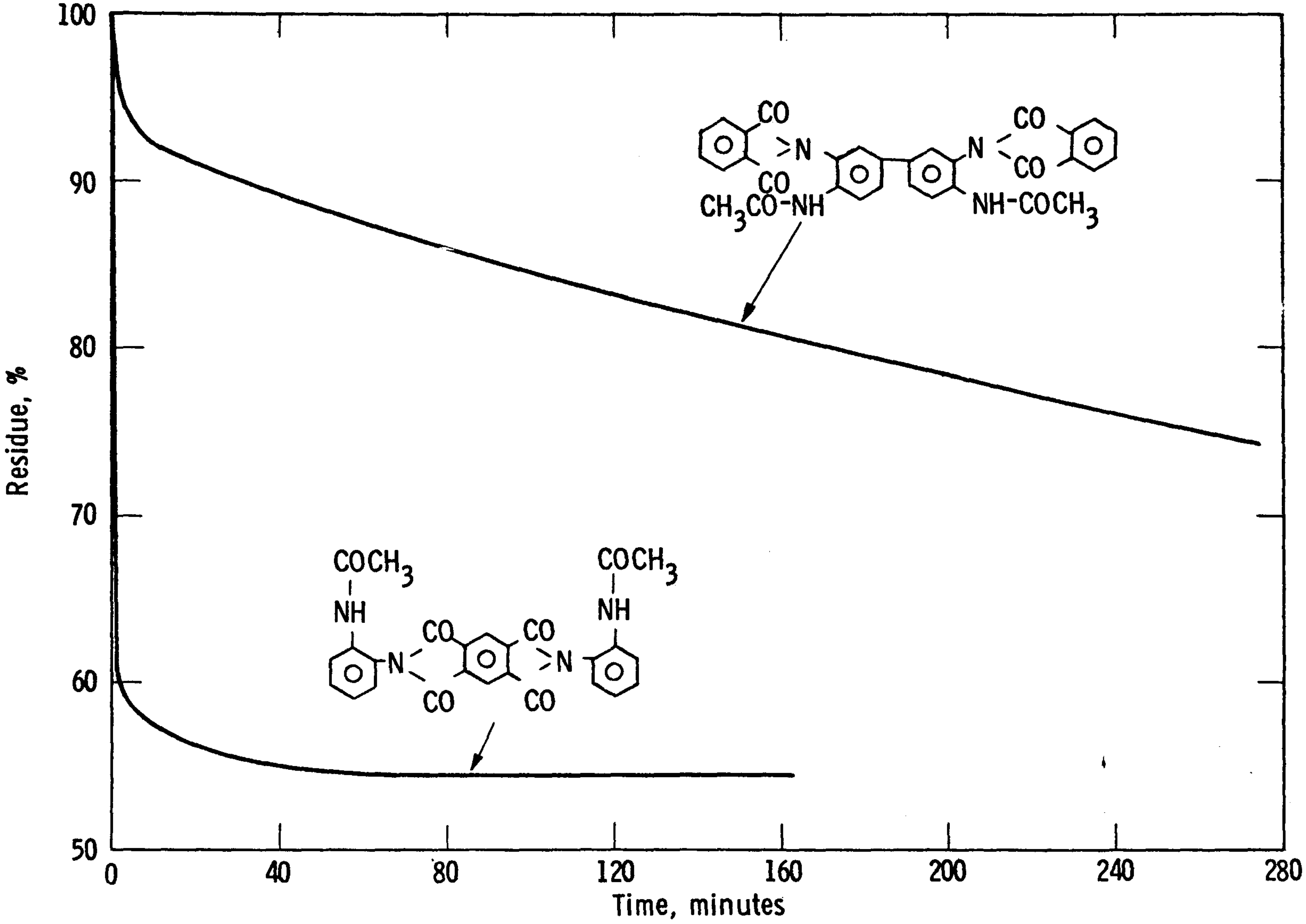


Fig. 25—Isothermal TGA for model compounds at 400°C in N_2

1. Polymers derived from tetramines and dianhydrides cure by more than one mechanism. Most of the linkages pass through an aminoimide structure, which is converted almost completely to pyrrone. However, a fairly substantial portion of them follow other pathways, which lead to branching and crosslinking in the uncured polymer and to the formation of other linkages (e.g., imide, benzimidazole) in the cured polymer.

2. Polymers derived from diacetyl tetramines and dianhydrides are converted almost quantitatively to a linear acetamido imide intermediate. A high temperature (350°C) is required for further cure. Both acetic acid and carbon dioxide are eliminated in the latter stages, with the formation of small amounts of pyrrone, together with benzimidazole and other structures, and some crosslinking.

3. Polymers derived from the hindered tetramine DCDAB are converted rather cleanly to amino imides and then to pyrrones. This system gives fewer side reactions in the first step than unhindered tetramines and fewer side reactions in the second step than diacetyl tetramines.

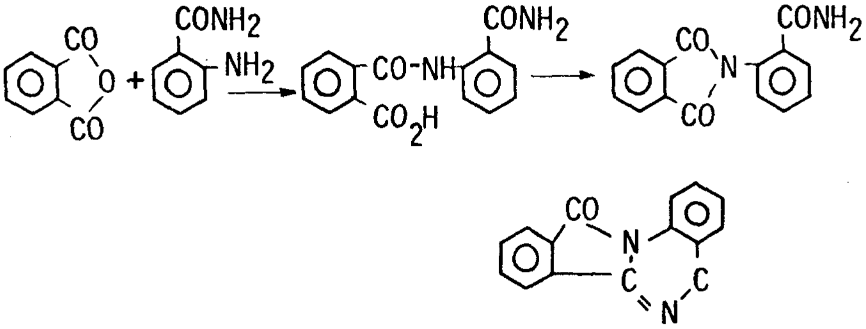
4. Salts from diester diacids and tetramines cure by several mechanisms, and the cured polymer contains very little pyrrone structure.

5. Details of structure play an important part in determining cure mechanism and final products. For example, DADAB-$(PA)_2$ cures readily to a pyrrone, whereas $(OAA)_2$-PMDA does not, and the o-diamino grouping in TRAB is not as cleanly converted to pyrrone as the corresponding structures in tetramines.

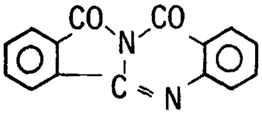
A 6-5 RING SYSTEM

A considerable amount of information, accumulated in the past few years, suggests that the thermal-oxidative stability of pyrrones is much lower than had been predicted for this heterocyclic ladder system. One possible explanation is that the 5-5 fused ring system is too highly strained to be very stable. Less strain would be expected in 6-5 or 6-6 fused rings. We have done a few experiments with a 6-5 system closely related to pyrrones.

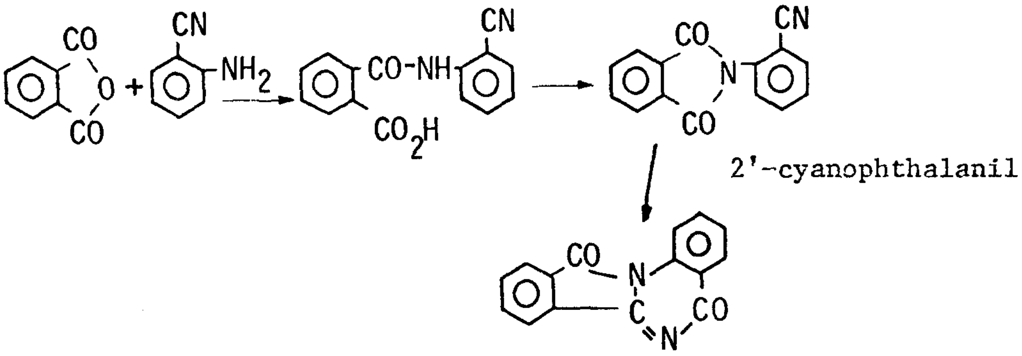
Polymers and model compounds containing the isoindoloquinazolinedione ring system have been synthesized by de Gaudemaris and others[18] by the following reaction sequence:



Later work by Kurihara and Yoda[19] indicates that a rearrangement may occur during cure to give the final structure



Work by Bogert and Hand[20] suggests the possibility of the following variation in the synthesis:

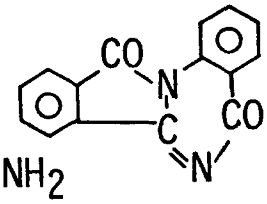
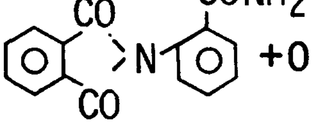


If successful, this approach would provide a final cure reaction with no elimination of volatiles, which would be very helpful in the preparation of films, laminates, molded objects, etc., with a minimum of voids, bubbles, and shrinkage.

We have prepared for reference purposes the amide-acid and the fully condensed model compounds, using a modification of published methods. We have also synthesized 2'-cyanophthalanil by the reaction shown and have briefly investigated methods of closing the second heterocyclic ring. The treatments used and the results obtained are shown in Table X.

The results with KOH-H_2O_2 are sufficiently promising that more work in this area seems justified. The next step would be synthesis of monomers containing two o-cyano amine groupings. We have done some work with this objective but have not yet succeeded in making a pure monomer. Preparation of a polyimide from the dicyano diamine should present no serious problems. It may be possible to effect the final cyclization by heat alone, or some catalyst system may be necessary. A possibility suggested by the model compound work is a combination of an organic peroxide and a fugitive strong base, such as benzyltrimethylammonium hydroxide.

TABLE X—REACTIONS OF 2'-CYANOPHTHALANIL

Treatment	Results
Heat	Sublimed Unchanged
H_2SO_4 (trace), Boiling Dioxane	No Reaction
KOH (trace), Boiling Dioxane	No Reaction
HCl, Boiling Ethanol	No Products Isolated; Odor of Ethyl Anthranilate
KOH, H_2O_2, Boiling H_2O	36% Yield of 
Conc. H_2SO_4, 65°C	 +Other Products

EXPERIMENTAL*

Preparation of CETADPO

Two hundred g. (1 mole) of 4,4'-oxdianiline was dissolved in 500 ml of DMAC and 200 ml of pyridine and warmed to 63°C. To this solution was added 239 g. (2.2 moles) of ethyl chloroformate in portions. The temperature rose to about 105°C. After cooling, the solution was poured into ice-water, giving a white precipitate, which was washed with water and dried at 100°C. Yield was 250 g. of a product with an endotherm at 149°C. After recrystallization from ethanol,a m.p. of 152°C was observed. Anal. Calc. for $C_{18}H_{20}N_2O_5$: C, 62.79; H, 5.85; N, 8.13; O, 23.23. Found: C, 62.68, 62.47; H, 5.88, 5.86; N, 7.94, 7.90; O, 23.83 and 23.96.

Nitration of N,N-bis(carbethoxy) oxydianiline was effected in acetic anhydride-nitric acid. A nitration solution was prepared by addition of 30 g. of 70% nitric acid to 180 ml of acetic anhydride cooled in an ice-salt bath. The solution was cooled further and 34.4 g. (0.1 mole) of N,N'-bis(carbethoxy) oxydianiline was added at such a rate that the temperature did not go above 3°C. A yellow precipitate separated, which was collected on the filter, washed with acetic acid and dried. Yield was 32.8 g. of material with a sharp endotherm at 120°C. A further yield of 7.5 g. (endotherm 118°C) was obtained by diluting the mother liquor with water. Total yield was 40.3 g. (95%). Anal. Calc. for $C_{18}H_{18}N_4O_9$: C, 49.78; H, 4.17; N, 12.90; O, 33.15. Found: C, 50.67, 50.81; H, 4.32, 4.39; N, 13.05, 13.23; O, 30.26, 30.09.

A slurry composed of 30 g of N,N'-bis(carbethoxy)-3,3'-dinitrooxydianiline, 1 g of 5% Pd-on-C, and 200 ml of 95% ethanol was

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*Reference 12 contains additional experimental work.

hydrogenated in a Parr hydrogenation apparatus at a maximum temperature of 72°C. After hydrogen uptake had stopped, the catalyst was removed by filtration. A white precipitate separated immediately upon cooling the filtrate. After filtration and drying, 22.4 g (87%) of material with a sharp endotherm at 168°C was obtained (D37-147-1). Subsequent hydrogenations under slightly different conditions gave material with two endotherms, a comparatively small one at 123° and a larger one at 182°C. Recrystallization of 5 g of D38-147-1 from 150 ml of 95% ethanol gave a material with 2 similar endotherms at 125° and 183°C. Anal. Calc. for $C_{18}H_{22}N_4O_5$: C, 57.75; H, 5.92; N, 14.97; O, 21.38. Found: C, 57.47, 57.60; H, 5.91, 5.98; N, 14.99, 15.03; O, 21.56, 21.32.

CETADPO-BTDA Polymer

A solution of 22.44 g (0.06 mole) of CETADPO in 98 g of DMAC was stirred while solid BTDA was added in portions, with periodic viscosity measurements of the solution. The viscosity reached an apparent maximum after the addition of 19.4 g (0.0603 mole) of BTDA. An additional 33 g of DMAC was added to give a 24.2% solution, viscosity X-Y (Gardner). Inherent viscosity of a 0.5% solution was 0.66 dl/g.

Preparation of DCDAB

3,3'-Dichlorobenzidine was acetylated with acetic anhydride to give a quantitative yield of the diacetyl derivative, m.p. 305-311°C. Recrystallization from DMAC-acetic acid gave a product m.p. 311°C (DTA), [J. C. Cain and P. May, J. Chem. Soc. 97, 723, report 302°.]

Dry ice was added with stirring to 5 pints of fuming nitric acid until the temperature reached 5°C. Over a period of 15 minutes 362 g of diacetyldichlorobenzidine was added, together with enough dry ice to maintain a temperature of 5-10°C. The dark solution was stirred for 15 minutes at 5-10°C and then poured into an ice-water mixture. The yellow precipitate was filtered off, washed thoroughly with water, and dried at 140°C. Three such batches were combined to give 1233 g of crude product. Recrystallization from 12 l. of DMAC gave 437 g (32% yield) of N,N'-diacetyl-3,3'-dichloro-5,5'-dinitrobenzidine. This compound does not have a melting point, but decomposes vigorously (DTA exotherm) at about 390°C. Anal. Calc. for $C_{16}H_{12}Cl_2N_4O_6$: C, 44.98; H, 2.83; N, 13.12; Cl, 16.60. Found: C, 45.10, 45.26; H, 2.84, 2.77; N, 13.15, 13.29; Cl, 16.63, 16.53.

Two liters of conc. sulfuric acid was stirred while 254 g of the above product was added. The mixture was warmed to 60°C and poured into ice-water. The precipitate was filtered off, washed with sodium bicarbonate solution and water and dried to give 201 g of 3,3'-dichloro-5,5'-dinitrobenzidine, m.p. (DTA) 315°C. Anal. Calc. for $C_{12}H_8Cl_2N_4O_4$: C, 42.00; H, 2.35; Cl, 20.67; N, 16.33. Found: C, 42.16, 42.35; H, 2.69, 2.82; Cl, 20.44, 20.66; N, 16.18, 16.21.

A slurry of 125 g of 3,3'-dichloro-5,5'-dinitrobenzidine, 2 pints of 95% ethanol, 12 g of 5% palladium-on-charcoal, and 110 ml of 85% hydrazine hydrate was stirred. The mixture gradually warmed spontaneously to reflux temperature and maintained reflux for about 15 minutes. Heating was then used to maintain reflux for another 27 minutes. The catalyst was removed by filtration, and 500 ml of deionized water containing a pinch of sodium hydrosulfite was added. A white precipitate formed as the solution was cooled and concentrated under nitrogen. After filtration and drying 35.3 g (34%) of DCDAB was obtained, m.p. (DTA) 175°C. Further concentration of the mother liquor gave about 17 g of material with an endotherm of 152°C. Recrystallization from ethanol-water raised the m.p. to 178°C. Anal. Calc. for $C_{12}H_{12}Cl_2N_4$: C, 50.90; H, 4.27; Cl, 25.04; N, 19.79. Found: C, 51.79, 51.59; H, 4.39, 4.35; Cl, 24.34, 24.47; N, 19.44, 19.55.

Polymers from DCDAB

Table XI summarizes polymers made with DCDAB and PMDA in DMAC. In run D36-104-1 all of the PMDA was added as a solid. In D36-106-1, part of the PMDA was added to the amine solution as a solid, followed by the remainder in DMAC solution. In both cases gel particles formed around the undissolved portions of PMDA. The gel particles were removed by filtration through cheese cloth. The runs D36-104-2, D36-106-2, and D36-127-1 all of the PMDA was added in solution, and no gel particles formed.

Table XI

Preparation of DCDAB-PMDA

Resin No.	DCDAB(g)	DMAC(g)	PMDA(g)	DMAC(g)	% Solids	Remarks
D36-104-1	2.83	15	2.18	none	25.0	gel particles
D36-104-2	2.83	5	2.18	15	20.0	very thin liq.
D36-106-1	5.66	10	4.72 (9% excess)	19	26.3	gel particles
D36-106-2	5.66	10	4.66 (8% excess)	22	24.4	2.75 stokes
D36-127-1	5.6632	12	4.3626	18	25.0	5.5 stokes

The excess of PMDA used in polymer solutions D36-106-1 and D36-106-2 did not gel the solutions. After 3 days the remaining portion of D36-106-2 (1/2 to 3/4 of original amount) was treated with 0.3 g PMDA dissolved in 2 ml DMAC. The viscosity of this solution rose rapidly and gelation occurred in about 40 minutes (D36-106-3). D36-127-1 solution viscosity increased to about 600 centistokes in 22 days, with no further change in 54 days.

DCDAB-BTDA polymers were prepared as follows.

D36-120-1,2,3,4 - To a solution of 4.2504 g (0.015 mole) DCDAB (twice recrystallized from aqueous alcohol) in 8 g DMAC was added 4.8310 g (0.015 mole) BTDA in 12 g DMAC. This formed a light yellow solution, D36-120-1. About 0.8 g solution was removed for weight loss measurements. Successively 0.0105 g BTDA in 3 g DMAC, 0.0119 g BTDA in 3 g DMAC, and 0.0117 g BTDA in 1.5 g DMAC were added to the solution. After each addition of BTDA, weight loss samples were removed, D36-120-2, 3, and 4. At the finish about 1% excess BTDA had been added. Film samples were cast from D36-120-4 and cured at 150° overnight. The thinnest samples, 1-2 mils, had check spots and were too fragile to be removed from the aluminum dishes. Thicker samples could be removed and were moderately flexible, though stiff. They were a characteristic deep-red color. The remainder of D36-120-4 gelled on standing overnight.

D36-125-1 - A second DCDAB-BTDA polymer was prepared in the same manner but with a 1% deficiency of BTDA. This resin at 25% solids had an initial viscosity of about 100 centistokes, which increased to 320 centistokes in 24 hours, 340 in 22 days, and the same after 54 days.

The weight loss of samples D36-120-1,2,3,4, D36-125-1 and D36-127-1 are given in Table XII and Fig. 3. Samples D36-120-1,2,3,4, placed together because of close similarity, showed the lowest rate of weight loss, expecially for the first 200 hours. After 200 hours the rate of loss became nearly constant at about 0.1% hr, which is almost the same as that of D36-125-1 through its aging period.

Table XII

Weight Loss of DCDAB-BTDA and DCDAB-PMDA Polymers at 325°C (%)

	50 hrs.	100 hrs.	200 hrs.	300 hrs.	400 hrs.
D36-120-1,2,3,4	4	7	12	22	33
D36-125-1	5	10	24	37	50
D36-127-1	10	20	40	60 (extrapolated)	
D36-106-2	12	18	31	39 (250 hrs.)	

The DCDAB-BTDA polymers, both D36-125-1 and the D36-120-1,2,3,4 group show a lower weight loss than the DCDAB-PMDA polymers D36-127-1 and D36-106-3.

A check on the weight loss data was made by concurrently running samples of polyimide prepared from m-phenylene diamine and BTDA (I-8). Samples of this material lost 3-4% and then remained at a nearly constant weight at 325°C. Also, some samples of I-8 as well as some of the pyrrone samples were aged in closed dishes and some in the open. There was no significant difference in the weight loss of samples whether aged in the open or in closed dishes.

Polymers from Ester-Salts

A solution prepared by refluxing 16.1 g (0.05 mole) of BTDA in 160 ml of isopropanol for 5 hours was poured into a solution of 10.7 g (0.05 mole) of DAB in 550 ml of water at 98°C. A red solution resulted. On cooling, an oil separated, which became solid on addition of ice. The mixture was filtered, but the solid was very soft at room temperature. A small amount of the solid was dissolved in DMAC. A typical brittle red film was obtained from this solution. On heating the original oily solid a foam was obtained.

The diisobutyl ester of BTDA was prepared by refluxing 2200 ml of isobutanol with 322 g (1 mole) of BTDA until a clear solution was obtained. This hot solution was then poured into a boiling slurry containing 214 g (1 mole) DAB in 2 l. of distilled water. The resulting solution was evaporated under nitrogen for 90 hours, leaving an oily residue. This residue was dried at < 125°C for about 24 hours. The final dark, dry product weighed 678 g. The theoretical yield of the diisobutyl ester salt with DAB is 684 g.

A moderately viscous solution was prepared with 625 g of the above material and 940 g DMAC by warming to 50-55°C and stirring for several hours (E69-60-1). A fairly good film was obtained from this resin. Glass cloth was impregnated with the resin solution, precured for one hour at 100°C, and pressed at 1000 psi and 300°C. The laminate was of very poor quality, and could be broken by hand. A second laminate was prepared with a much lower solids content. The prepreg sheets of the first laminate had 49.5% solids after a 30-minute bake at 100°C. For the second laminate the solids content of the resin was cut to 26%. On dipping the glass cloth followed by a bake for 30 minutes at 100°C, a resin content of 29% was obtained. The laminate was prepared by putting the stacked sheets in the press, preheated to 100°C, and immediately applying 1000 psi. The temperature was then raised to 300°C over a

50-minute period and held there for 30 minutes. The final laminate (E69-62-1) contained 24% resin and was 0.105" thick (12 plies). Flexural strength and modulus at room temperature were 37 kpsi and 3.3 Mpsi. At 316°C they were 25.5 kpsi and 2.7 Mpsi, respectively.

A mixture of 1500 ml of tetrahydrofuran (dried over CaH_2) and 218.1 g (1 mole) of purified PMDA was heated to 60-65°C and stirred under reflux in a slow stream of dry nitrogen while a solution of 62.1 g (1 mole) of ethylene glycol (dried over $CaSO_4$) in 250 ml of tetrahydrofuran was added slowly (6 hrs). A clear solution was obtained. Solvent was removed under vacuum, and the residual solid was washed several times with benzene and dried for 12 days at 50°C under vacuum. The product was a dry, granular tan solid weighing 290 g (calc. 280 g), which still had an odor of benzene. Apparently the last of the benzene is removable only with great difficulty. Titration of an acetone solution of the polymer with NaOH gave a neutral equivalent of 119.3, which corresponds to a PMDA/glycol ratio of 1.188, an average MW of 1757, and 276 g of polymer per mole of PMDA present.

A solution of 13.80 g (0.05 mole PMDA) of the glycol-PMDA polymer in a mixture of 100 ml THF and 100 ml water was added, under nitrogen, to a hot, stirred solution of 10.72 g (0.05 mole) recrystallized DAB in 1000 ml water. The mixture was allowed to cool to room temperature and then evaporated to dryness in a stream of nitrogen. The residue was ground to give a yellow powder (D94-8-4), weighing 25.3 g (calc. 24.5 g). This product was found to be essentially insoluble in THF or water, slightly soluble in acetone or Cellosolve, partially soluble in DMF, and very soluble in DMAC or NMP.

A solution of 15.00 g of D94-8-4 in 27.90 g of DMAC (25.0% solids, based on cured pyrrone) was clear brown, with a viscosity of about 50 cstks. Films cast in aluminum dishes were continuous, red-brown, and fairly flexible. Determinations of percent solids and weight loss were made on two such films in circulating air ovens, with the following results:

Sample wt., g			0.7038	0.3433
			Residue, %	
Baking schedule,	hrs.	°C		
	1	150	31.4	31.0
	18	150	29.2	28.7
	1	300	26.6	26.5
	2	300	25.8	25.2
	7	300	25.4	25.1
	1	325	25.0	24.8
			Wt. loss of residue, %	
	4.5	325	1.8	3.5
	7	325	2.8	4.1
	8.5	325	2.6	3.5
	26.5	325	7.2	14.0
	33.5	325	11.0	16.7
	51.5	325	16.6	25.4
	75.0	325	23.1	32.9
	147.5	325	46.5	58.8

The residue weight agrees well with the calculated solids content and indicates that the cure is largely complete after 2 hours at 300°C. Weight loss of the thinner sample was considerably more rapid than that of the thick one, but both are rather high.

A mixture of 322.2 g (1 mole) of BTDA and 500 ml of DMAC was stirred at 60-65°C while a solution of 62.07 g (1 mole) of ethylene glycol in 196 g of DMAC was added over a 6 hour period. A clear viscous solution of the linear polyester was obtained, to which was added 214.3 g (1 mole) of DAB. A very viscous solution was obtained, which was diluted with 150 ml of DMAC to give a workable viscosity. When stored overnight in a refrigerator, the solution gelled. The gel was stirred vigorously with 1200 ml of DMAC to give a clear 20% solution, viscosity M-N (Gardner). A second night in the refrigerator produced a gel which could not be liquified. The preparation was repeated to give a resin solution (34% solids) having an initial viscosity of G (Gardner), which increased to T-U in eight hours.

Soon after polymer preparation, 181 A1100 E-glass cloth was coated with the solution, using two dips and a cure of 20 minutes at 150°C after each dip. This precure was probably too severe, since very little flow occurred in the press. Four 6" x 6" laminates were made. Flexural properties were measured at room temperature before aging and at 600°F after 100 hours at 600°F. Results for the best laminate are given in Table V. Fairly respectable initial values were obtained, but strength retention on aging was poor. Better results could probably be obtained with milder precure conditions.

Pyrrone-Imide Copolymers

An imide-pyrrone copolymer was prepared from MPD, DAB and BTDA. An imide precursor solution was first prepared from MPD and BTDA, containing a 10% excess of BTDA. This was stirred into a DAB-BTDA solution that contained a 10% deficiency of BTDA, so that the final stoichiometry balanced. The viscosity of the solution at 24% solids was about 450 centistokes. A sample left at room temperature gelled in 3 days. A refrigerated sample was used to treat glass cloth (A1100-181) for a laminate. Two coats were brushed on, and each coat was baked at 80°C for 15 minutes. This treatment gave a sheet that contained 46% resin. A laminate was prepared from 13 6" x 6" sheets. The sheets were placed in the press at 100°C. Initial pressure was 55 psi. The pressure and temperature were increased to 500 psi and 325°C over 55 minutes and kept there for 20 minutes. Some beads appeared at 200°, indicating flow. The final laminate had a resin content of 33.5% and was 1/8" thick. Two strips tested at 315°C had an average flexural strength of 27,100 psi and a modulus of 2.3 x 10^6. Average of 2 samples tested at room temperature was flexural, 47,000 psi, and modulus 4.02 x 10^6 psi. All samples failed by delamination, indicating that a strong bond was not formed.

In order to facilitate solvent removal, additional runs were made in which the DMAC was replaced with an 80-20 DMF-xylene mixture.

A large quantity of imide polymer was prepared as follows: To a solution prepared from 86.2 g (0.8 mole) of MPD in 733 g DMF and 183 g xylene was added 308 g (0.96 mole) of solid BTDA. This mixture was stirred about 1 hour (D36-148-1).

Two batches of pyrrone solution were prepared by adding to 51.4 g (0.24 mole) of DAB in 80 g DMF and 20 g xylene 61.8 g (.192 mole) of BTDA dissolved in 280 g of DMF and 70 g of xylene. (D36-148-2 and D36-149-1.) To each of these solutions, while still in the Waring blender, was added 393 g of D36-148-1 to give the imide-pyrrone precursor solutions D36-148-3 and D36-149-2.

Sheets of glass cloth (181 A1100) were impregnated with the resins. Glass cloth impregnated with D36-148-3 and precured for one hour at 100°C was used to make laminate E69-10-2. Two laminates were prepared from resin D36-149-2. For E68-12-1 the treated glass cloth was precured at 100°C and for E68-13-1 precure was at 125°C. The prepreg was put into a press preheated to 325°C, the pressure immediately raised to 500 psi and pressed for one hour after the temperature returned to 325°C. All three laminates looked good. The flow was adequate but not excessive. Four test strips (1 x 4 x 1/8") were cut from each laminate. Two strips from each laminate were post cured at 300-325°C for 20 minutes and two were not cured further. Laminate properties are summarized in Table VI.

A suspension of 5.97 g (0.02 mole) of DADAB in 140.5 g DMAC was stirred while 6.44 g (0.02 mole) of BTDA was added. A clear solution was obtained, in which was dissolved 8.65 g (0.08 mole) of MPD. To this solution was added 25.78 g (0.08 mole) of BTDA, with stirring. A clear amber solution was obtained, viscosity X (Gardner). A thin film was baked in an aluminum dish, with the following results:

Baking Schedule (Cumulative)	% Residue
3 hrs. 150° + 1 hr. 175° + 1.5 hrs. 200°C	24.3
16 hrs. 250°C	23.3
2 hrs. 300° + 1 hr. 350°C	23.0
1.5 hrs. 400°C	22.9

Since the calculated residue for imidization is 23.1%, and that for imidization plus loss of acetic acid is 21.8%, it seems apparent that the baking schedule used gave primarily polyimide.

Additional batches of polymer prepared on a larger scale by the same procedure gave solutions with viscosities of S-X (Gardner) at 23-24% solids.

A 6 x 6" 10-ply laminate was made, using 181 A-1100 E-glass cloth. The coated cloth was air-dried for 45 minutes and then precured for 20 minutes at 150°C. The laminate was pressed at 1000 psi and a temperature that rose from 300 to 490°C in 30 minutes and was held at 450 to 490°C for 15 minutes. A smooth black board was obtained, 0.09" thick, containing 24% resin. Flexural strength and modulus values were 35 kpsi and 3.4 Mpsi at room temperature and 9.4 kpsi and 2.5 Mpsi at 316°C. A 12-ply 12 x 12" laminate was made from the same prepreg, at 1000 psi and 400°C for 30 minutes. The pressure was released momentarily to release volatiles (bumped) in the early part of the pressing, and some resin blew out of the board at that time. The final laminate was 0.106" thick, contained 22% resin, and did not appear as uniform as the small board. Flexural strength and modulus values were 36.4 kpsi and 3.4 Mpsi at room temperature and 27.1 kpsi and 2.8 Mpsi at 316°C.

The strength values are not impressive, but the modulus is somewhat higher than that of laminates from the unmodified polyimide, which is in the range of 2.5-2.8 Mpsi at room temperature. Two additional laminates, made under other conditions, are included in Table VII. Their properties are similar.

Model Compound Syntheses

Isopropyl phthalate - OPD Salt. - A solution prepared from 10.4 g (0.05 mole) isopropyl phthalate and 100 ml isopropanol was poured into a hot solution of 5.4 g of o-phenylene diamine in 50 ml of water. There was no precipitate or color change. On cooling, a solid precipitated, which was dried at 60°C in vacuo to give 10 g of solid. In the melting point apparatus melting occurred at about 168°C, after which the material resolidified and turned green. DTA gave strong endotherms at 132° and 170°, and a weak endotherm at 292°C.

2'-Nitrophthalanil. - A mixture of 27.63 g (0.2 mole) of o-nitroaniline, 29.62 g (0.2 mole) of sublimed phthalic anhydride, 150 ml of DMAC, and 50 ml of xylene was refluxed with stirring under a Dean-Stark trap. During an 18 hour period, 5.9 ml of aqueous layer collected in the trap, after which no additional material was obtained. The cooled product was mixed with 200 ml of water, stirred for 2 hours, and filtered. The resulting precipitate was filtered off, washed with water, and dried at 140°C under vacuum to give 36.5 g (68% yield) of crude 2'-nitrophthalanil. Recrystallization from 350 ml of glacial acetic acid gave 34.1 g of yellow needles, m.p. (DTA) 203°C. Anal. Calc. for $C_{14}H_8N_2O_4$: C, 62.75; H, 3.01; N, 10.45; O, 23.87. Found: C, 62.60, 62.71; H, 3.07, 2.93; N, 10.34, 10.50; O, 24.05, 23.81.

2'-Aminophthalanil. - A mixture of 34.0 g of 2'-nitrophthalanil, 1700 ml of ethanol, and 2 g of 5% Pd-on-C catalyst was hydrogenated at 150 psi and 75-95°C. The product was filtered hot. The filtrate was cooled, and the resulting yellow crystals were filtered off and dried to give 19.0 g (63% yield) of 2'-aminophthalanil, m.p. (DTA) 193°C. The DTA curve also had a small endotherm at 164°C. A second recrystallization from ethanol removed the second endotherm and raised the m.p. to 194°C. Anal. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76; O, 13.43. Found: C, 70.84, 70.85; H, 4.13, 4.24; N, 11.60, 11.53; O, 13.23, 13.47.

This compound was also prepared from phthalic anhydride and o-phenylenediamine (see below).

Products from phthalic anhydride and o-phenylenediamine. - A solution of 14.8 g (0.1 mole) of sublimed phthalic anhydride in 200 ml of chloroform was added slowly to a stirred solution of 10.8 g (0.1 mole) of o-phenylenediamine in 250 ml of chloroform. A precipitate formed during the addition. When addition was complete the mixture was refluxed for an hour and filtered hot. The solid product was washed with hot chloroform and dried to give 24.3 g (95% yield) of crude product. A series of recrystallizations from ethanol and from chloroform yielded two fractions of interest. D93-28-2, m.p. (DTA) 194°C, was identified as 2'-aminophthalanil. D93-27-10, m.p. (DTA) 272°C, agrees in m.p. and analysis with 2'-carboxybenzimidazole. Anal. Calc. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23; N, 11.76; O, 13.43. Found: C, 70.24, 70.18; H, 4.03, 4.17; N, 11.22, 11.32; O, 14.77, 14.68. Reaction of the former with acetic anhydride gave 2'-acetamidophthalanil, while the latter gave 1,2-benzoylenebenzimidazole.

A mixture of 0.50 g of D93-28-2 and 2.5 ml of acetic anhydride was heated to boiling to give a clear solution. On cooling, a granular solid separated. An equal volume of water was added to the mixture, which was warmed for a few minutes and filtered. The solid was washed with water and dried to give 0.49 g of a tan granular solid product (D93-29-4), m.p. (DTA) 203°C. Anal. Calc. for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 10.00; O, 17.12. Found: C, 67.66, 67.87; H, 4.16, 4.26; N, 9.64, 9.80; O, 18.33, 18.45. The infrared spectrum contained the features expected for 2'-acetamidophthalanil. (See below for another synthesis.)

The DTA behavior of 2'-acetamidophthalanil is interesting. Samples dried at high temperatures gave a single sharp endotherm at 203-205°C. If the product was recrystallized from chloroform and dried at a moderate temperature, fluffy white needles were obtained which gave a short, sharp endotherm at about 185°, followed immediately by an exotherm, peaking at about 188°, and then a deep, sharp endotherm at 203 to 205°C. When the melted sample was allowed to cool and was then reheated, only the upper endotherm was observed.

A mixture of 1.0 g of D93-27-10 and 5 ml of acetic anhydride was boiled for 10 minutes. The solid slowly dissolved. On cooling a precipitate formed, which was filtered off, washed with water, and dried to give 0.81 g of yellow needles (D93-29-3), m.p. (DTA) 214°C. *Anal*. Calc. for $C_{14}H_8N_2O$: C, 76.35; H, 3.66; N, 12.72; O, 7.27. Found: C, 76.92, 76.70; H, 3.63, 3.66; N, 12.95, 12.75; O, 6.86, 6.96. The infrared spectrum agreed in every respect with a spectrum of authentic 1,2-benzoylenebenzimidazole supplied by Dr. Norman Johnston, NASA.

2'-Acetamidophthalanilic Acid. - A mixture of 136 g (0.92 mole) of sublimed phthalic anhydride, 136 g (0.91 mole) of 2-aminoacetanilide and 1050 ml of chloroform was refluxed with stirring for 2 hours, and allowed to cool. The precipitate was filtered off and dried at 50°C under vacuum to give 260 g (96% yield) of 2'-acetamidophthalanilic acid as a white powder m.p. 164°C (DTA). Recrystallization from ethanol gave white needles (D93-44-1) m.p. 168°C (DTA, 15°/min). *Anal*. Calc. for $C_{16}H_{14}N_2O_4$: C, 64.42; H, 4.73; N, 9.39; O, 21.45. Found: C. 64.37, 64.41; H, 4.70, 4.69; N, 9.31, 9.29; O, 21.51, 21.66.

2'-Acetamidophthalanil, 2'-(diacetylamino)-phthalanil, and $C_{16}H_{10}N_2O_2$. - A mixture of 29.6 g (0.2 mole) of phthalic anhydride (sublimed), 29.9 g (0.2 mole) of o-aminoacetanilide, and 225 ml of chloroform was refluxed with stirring for 3 hours. Acetic anhydride (200 ml) was added and solvent was distilled until a vapor temperature of 130°C was reached. The residual clear yellow solution (212 g) was evaporated nearly to dryness at room temperature in a stream of nitrogen. The resulting moist solid was recrystallized twice from methanol to give 22.1 g of white crystals (D93-15-4). An additional 6.2 g was recovered from the filtrate from the second crystallization.

Evaporation of the filtrate from the first crystallization, followed by drying for 4 days at 135°C under vacuum, gave 20.9 g of a yellow-brown solid. Extraction of this material with 200 ml of boiling methanol gave a solution and a yellow solid. The latter was filtered off and dried to give 2.2 g of tan powder. A 0.5 g sample of this residue was recrystallized twice from 50 ml of DMSO to give 0.3 g of fine yellow crystals (D93-25-3). Anal. Calc. for $C_{16}H_{10}N_2O_2$: C, 73.27; H, 3.85; N, 10.69; O, 12.20. Found: C, 72.42, 72.19; H, 3.82, 3.78; N, 10.56, 10.36; O, 13.29, 13.40. The DTA curve gave only poorly defined endotherms, the major one being at about 440°C. The IR spectrum showed no absorption bands in the imide carbonyl region, but absorbed strongly at 3200 (broad), 1620, 1590, 1570, 1470, 1410, 1370, 1350, 1340, 1280, 1190, 1150, 740, 530, and 480 cm^{-1}. The mass spectrum showed the presence of two compounds, MW 262 (corresponding to analysis $C_{16}H_{10}N_2O_2$) and 276. The former lost two units of m/e = 28 in steps, giving 234^{+} and 206^{+} (206^{++} and 206^{+++} also observed). The latter also lost a 28 unit to give 248^{+}. The nmr spectrum was inconclusive because of partial solubility problems. The structure of this by-product has not been established.

D93-15-4 was recrystallized several times from methanol and from chloroform. Two major fractions were obtained and identified. D93-40-7, m.p. (DTA) 205°C, gave an infrared spectrum matching that of D93-29-4 and was identified as 2'-acetamidophthalanil. Anal. Calc. for $C_{16}H_{12}N_2O_3$: C, 68.56; H, 4.32; N, 10.00, O, 17.12. Found: C, 68.45, 68.70; H, 4.46, 4.46; N, 9.85, 10.06; O, 17.30, 17.20.

D93-28-4, m.p. (DTA) 182°C, was identified as 2'-(diacetylamino) phthalanil. Anal. Calc. for $C_{18}H_{14}N_2O_4$: C, 67.07; H, 4.38; N, 8.69; O, 19.86. Found: C, 66.87, 67.10; H, 4.30, 4.37; N, 8.89, 8.69; O, 20.06, 19.90.

Pyromellitic diacid bis (o-acetamido-anilide). - A solution of 21.8 g (0.1 mole) of sublimed PMDA in 225 ml of THF was added to a warm stirred mixture of 30.0 g (0.2 mole) of 2-aminoacetanilide and 150 ml of THF. A brick red color appeared where the solutions first mixed, but faded rapidly. A heavy white precipitate formed. The mixture was refluxed gently for 30 minutes, cooled, and filtered. The solid product was dried at 65°C under vacuum to give 52.0 g (100% yield) of pyromellitic diacid bis (o-acetamidoanilide), probably a mixture of the two expected isomers. Anal. Calc. for $C_{26}H_{22}N_4O_8$: C, 60.23; H, 4.28; N, 10.80; O, 24.69. Found: C, 60.20, 60.05; H, 4.83, 4.74; N, 10.03, 9.92;

O, 24.95, 25.12. DTA gave a rather broad endotherm at 187°C (m.p. and dehydration of amic acid) and a sharp one at 384°C (m.p. of imide).

Pyromellitic bis (o-acetamidoanil). - A mixture of 25.9 g (0.05 mole) of the preceeding product and 100 ml of xylene was refluxed with stirring, using a Dean-Stark trap to remove water. After 7 hours of reflux, 1.7 ml (calc. 1.8 ml) of water had collected. The solid product was filtered off and dried at 130°C under vacuum to give 23.8 g (99% yield) of crude product. A 10 g sample was recrystallized from 250 ml of DMF to give 4.1 g of purified pyromellitic bis (o-acetamidoanil), m.p. (DTA) 390°C. Anal. Calc. for $C_{26}H_{18}N_4O_6$: C, 64.73; H, 3.76; N, 11.61; O. 19.90. Found: C, 64.79, 64.68; H, 3.90, 3.77; N, 11.50, 11.53; O, 19.82, 19.99.

N,N'-Diacetyl-3,3'bis(N",N"'-phthalimido)benzidine. - A mixture of 14.9 g (0.05 mole) of N,N'-diacetyl-3,3'-diaminobenzidine, 14.8 g (0.10 mole) of sublimed phthalic anhydride, and 50 ml of DMSO (dried over Molecular Sieve) was heated slowly. A clear solution was obtained at 70°C. The solution was held at 80°C for 2 hours and at 115-120°C for one hour. During the latter period a heavy precipitate slowly formed. The mixture was cooled and filtered. The solid product was washed with acetone and dried at 130°C under vacuum to give 12.0 g of pale yellow powder. An additional 7.4 g of product was recovered by diluting the filtrate with water (70% total yield). A 10 g sample of the first crop was recrystallized from NMP to give 8.8 g of purified N,N'-diacetyl-3,3'-bis (N",N"'-phthalimido) benzidine, m.p. (DTA) 415°C. Anal. Calc. for $C_{32}H_{22}N_4O_6$: C, 68.81; H, 3.97; N, 10.04; O, 17.19. Found: C, 68.05, 68.19; H, 4.08, 4.11; N, 10.07, 10.09; O, 17.99, 17.85.

2'-Carbamoylphthalanilic acid and isoindoloquinazolinedione. - A mixture of 68 g (0.5 mole) of anthranilic amide, 350 g of chloroform, 450 g of ethyl acetate, and 74 g (0.5 mole) of phthalic anhydride was allowed to stand for 4 days at room temperature. The mixture was filtered, and the solid product dried at 100°C under vacuum to give 147 g of solids. Recrystallization of 100 g of this product from 500 ml of glacial acetic acid gave 48.7 g (50% yield) of purified

2'-carbamoylphthalanilic acid, m.p. (DTA) 182°C. Anal. Calc. for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.26; N, 9.86; O, 22.52. Found: C, 62.71, 62.95; H, 4.14, 4.18; N, 9.91, 9.84; O, 23.05, 23.23.

A solution of 25 g of the crude product above in 200 ml of DMAC was held at 160°C for one hour and allowed to cool. Addition of 200 ml of water gave a precipitate, which was filtered off, washed with water, and recrystallized from Cellosolve-water to give 4.65 g (21% yield) of isoindolo [2,1-a] quinazoline-5,11-dione, m.p. (DTA) 239°C. Anal. Calc. for $C_{15}H_8N_2O_2$: C, 72.58; H, 3.25; N, 11.29; O, 12.89. Found: C, 72.84, 72.86; H, 3.13, 3.25; N, 11.24, 11.08; O, 12.76, 12.88.

2'-Cyanophthalanil. - A warm solution of 14.8 g (0.1 mole) of sublimed phthalic anhydride in 75 ml of ethyl acetate was added to a solution of 11.8 g (0.1 mole) of anthranilonitrile in 25 ml of ethyl acetate. The mixture was boiled for 5 minutes and allowed to cool. No precipitate formed, so the solution was evaporated to dryness in a stream of nitrogen. The residue was boiled for 2 minutes with 100 ml of acetic anhydride to give a clear solution, which crystallized on cooling. Recrystallization from ethanol gave two crops of crystals, weighing 8.90 and 2.90 g, m.p. (DTA) 183 and 181°C, respectively. Anal. Calc. for $C_{15}H_8N_2O_2$: C, 72.58; H, 3.25; N, 11.29; O, 12.89. Found: C, 72.30, 72.17; H, 3.27, 3.32; N, 11.19, 11.20; O, 13.30, 13.41 (excellent agreement for 0.6% water). The infrared spectrum shows nitrile at 2240 and imide at 1790, 1755, 1740, 1720, 1375, and 720 cm^{-1}.

Bergmann and Bentov[21] report a melting point of 144-5° for this compound, but the analysis and spectrum leave little doubt that our product is 2'-cyanophthalanil.

Cyclization of 2'-cyanophthalanil. - A sample (0.50 g) of 2'-cyanophthalanil was held at 275°C for one hour. It melted to an amber liquid, which solidified on cooling. The infrared spectrum of this product was identical with that of the starting material. A second sample was baked for 2 hours at 400°C. It evaporated completely and was not recovered.

A small sample of 2'-cyanophthalanil was placed in a horizontal glass tube, and a very slow stream of nitrogen was passed over it while the tube was heated with a burner. The sample sublimed at atmospheric pressure to give fluffy white crystals, which were identified by infrared spectroscopy as starting material.

A 1.00 g sample of 2'-cyanophthalanil was dissolved in 20 ml of dioxane. A trace of sulfuric acid was added and the solution boiled for one hour. The product was recovered by dilution with water, filtration and drying to give 0.95 g of starting material, m.p. 180°C.

The preceding procedure was repeated, using 1 ml of 10% KOH in methanol in place of the sulfuric acid. The recovered product consisted of 0.59 g of starting material, m.p. 180°C.

A solution of 0.50 g of 2'-cyanophthalanil, 20 ml of ethanol, and 5 ml of conc. HCl was boiled for one hour. Dilution with water gave no precipitate. Neutralization of the aqueous solution with ammonia gave no precipitate. A definite odor similar to grapes suggests that ethyl anthranilate may have been present, but no products were isolated.

The procedure in this run was similar to that used by Bogert and Hand[20] for the preparation of 2-methyl-4-ketodihydroquinazoline from N-acetylanthranilonitrile. A mixture of 5 ml of 10% KOH, 2 ml of 30% hydrogen peroxide, 18 ml of water, and 1.00 g of 2'-cyanophthalanil was heated to boiling to give a clear solution. No precipitation occurred on cooling, but neutralization with HCl gave a white precipitate, which was filtered off, washed, and dried to give 0.36 g of crude isoindoloquinazolinedione, m.p. (DTA) 210°C. Recrystallization from ethanol gave fluffy white needles, giving DTA endotherms at 220 and 232°C. Sublimation of the crude product in vacuum gave yellow crystals giving a single sharp endotherm at 233°C. Both gave infrared spectra essentially identical to that of authentic isoindolo [2,1-a] quinazoline-5,11-dione.

A solution of 1.00 g of 2'-cyanophthalanil in 5 ml of conc. sulfuric acid was held at 60-70°C for 10 minutes and then poured into water. The resulting precipitate was filtered off, washed with water, and recrystallized from ethanol to give 0.36 g of tan flakes, m.p. (DTA)

218°C. Anal. Calc. for $C_{15}H_{10}N_2O_3$: C, 67.66; H, 3.79; N, 10.52; O, 18.03. Found: C, 68.77, 69.02; H, 3.71, 3.60; N, 10.38, 10.30; O, 17.24, 17.41. These data, together with the infrared spectrum, indicate that the product is primarily 2'-carbamoylphthalanil, with some impurities.

CONCLUSIONS

1. The presence of an ortho acetamido or carbethoxamido group does not greatly reduce the reactivity of an aromatic primary amino group toward an anhydride. Consequently, difunctional compounds, such as 2,4-diaminoacetanilide; 4,4'-diacetamido-3,3'-oxydianiline; and N,N'-dicarbethoxy-3,3'-diamino-4,4'-oxydianiline react readily with dianhydrides in polar aprotic solvents to give solutions of linear acylamido acid amide polymers. A slight reduction in reactivity is suggested by the fact that these polymers have somewhat lower inherent viscosities than those prepared from unsubstituted diamines.

2. The acylamido acid amide polymers are stable in solution and show no tendency to crosslink or gel.

3. The acylamido acid amide polymers are converted cleanly to acylamido imide polymers by heating for about 2 hrs. at 150°C. Further heating at 300°C for several hours produces no change in structure. At 350-400°C the blocking group is eliminated, with, however, only slight conversion to pyrrone. Other structures containing a cyclic carbonyl group are apparently formed, and crosslinking probably occurs. Pyrrone formation is far less complete than for polymers derived from tetramines and dianhydrides.

4. Extremely brittle films were cast from the acylamido acid amide polymers that have been prepared (inherent viscosity 0.5-0.6).

5. Laminates with good initial properties can be made from the acetamido acid amide polymers.

6. Polymers containing the carbethoxy group retain some thermoplasticity unless very fully cured. Consequently, films and laminates tend to blister and foam unless cured slowly. Even after a post-cure to 325°C, laminates have low hot strength and modulus.

7. Reaction of pyromellitic dianhydride and 3,3'-diamino-N,N'-diacetylbenzidine gives a polymer 85-95% of which has a solubility in dimethylacetamide of greater than 40%. The remaining 5-15% of the product has a solubility of less than 0.1%. The two fractions have nearly the same infrared spectra and elemental analysis.

8. The presence of an ortho nitro group greatly reduces the reactivity of an aromatic primary amine group toward an anhydride. Consequently, the reaction of 3,3'-dinitro-4,4'-oxydianiline with pyromellitic dianhydride requires such a high temperature that a nitro imide polymer is obtained. The nitro groups can be reduced, giving an amino imide polymer. Solutions of this polymer gel in a few days.

9. The reaction of a tetramine and 3,3', 4,4'-benzophenone-tetracarboxylic dianhydride in a polar aprotic solvent gives a soluble amino acid amide polymer, which ordinarily gels at concentrations above 10%. Addition of a base such as triethylamine retards gelation and permits the preparation of solutions up to about 16%. Acids accelerate gelation.

10. Reaction of tetramines with a diester diacid from 3,3' 4,4'-benzophenonetetracarboxylic dianhydride gives low molecular weight polymers, which can be prepared up to at least 30% solids. On heating, these polymers apparently cure by a mechanism involving both amino imide and ester amide intermediates. Conversion to pyrrone is less complete than for polymers derived from diacetamido diamines or from tetramines.

11. Polymers prepared from dianhydrides and 3,3'-dichloro-5,5'-diaminobenzidine have less tendency to gel than those from 3,3'-diaminobenzidine because of steric deactivation of amine groups by the ortho chlorine. These polymers cure readily to pyrrones. Laminates prepared from them are similar in properties to laminates from polyimides. Their thermal stability is a little better than that of "pyrrones" made from esters and tetramines.

12. Pyrrone-imide block copolymers are conveniently prepared by blending solutions of anhydride-rich polyimimide precursor and

anhydride-poor pyrrone precursor. The individual solutions are stable indefinitely, and the mixed solution has a shelf life of a few days. Laminates from these copolymers have properties similar to those of polyimides.

13. Copolymers derived from a dianhydride and a mixture of diamine and diacetyl tetramine are probably crosslinked polyimides when fully cured. They give laminates with moderately good flexural strength and retention of properties at 600°F.

14. Under proper conditions, a 2'-cyanoimide group is converted to an isoindoloquinazolinedione. It may be possible to prepare 6-5 ladder polymers by this route without producing by-products in the final cure.

15. Pyrrone polymers prepared from dianhydrides and tetramines, and related polymers prepared from dianhydrides and diacetyl tetramines or from esters and tetramines, have lower thermo-oxidative stability than the better polyimides.

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