NASA CR-66693

SYNTHESIS OF PYRRONE POLYMERS

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

Westinghouse Research Laboratories

Contract No. NAS1-7354

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SUMMARY

When pyrrone prepolymers are prepared by the reaction of a dianhydride and a tetramine in a polar aprotic solvent, some chain branching occurs, and gelation is difficult to avoid. In this study stable solutions of linear prepolymers have been prepared by substituting various diacetamido diamines for the tetramines. Satisfactory laminates were prepared from one of these polymers, although film casting attempts failed. Infrared and TGA studies showed that a 150°C cure converts the prepolymer to a polyimide, which is quite stable at 300°C. Some conversion to the pyrrone occurs at 350-400°C, although it is far less complete than for polymers derived from tetramines. Other unidentified structures are also produced.

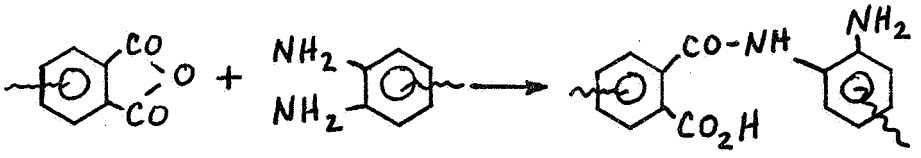
When preparing prepolymer from a dianhydride and a tetramine, it was found that addition of triethylamine or other bases reduced the gelation tendency and permitted an increase of polymer concentration from 10 to 16%. Acids accelerated gelation. Poor laminates were obtained from these solutions.

Solutions of low molecular weight polymers up to 30% solids were obtained by the reaction of tetramines with diester diacids. Fairly good laminates were obtained. Cure of these polymers apparently goes through a stage containing both imide and amide ester linkages, which is very poorly converted to pyrrone.

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:



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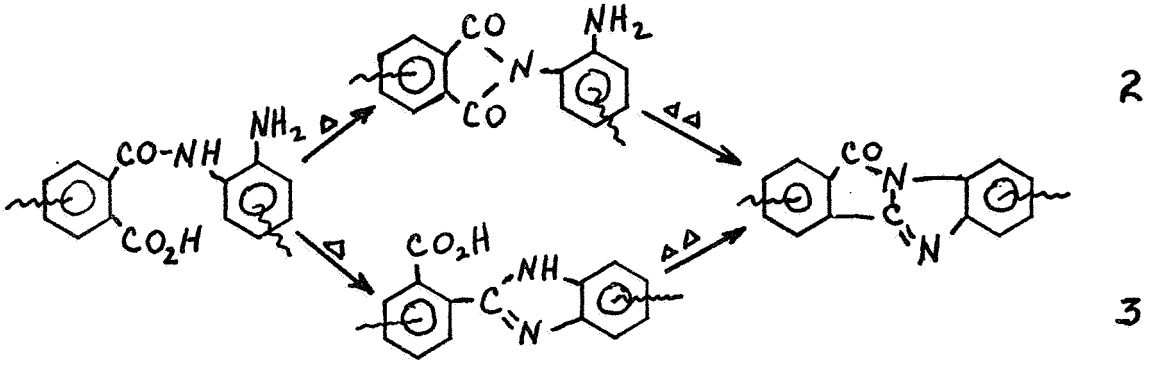

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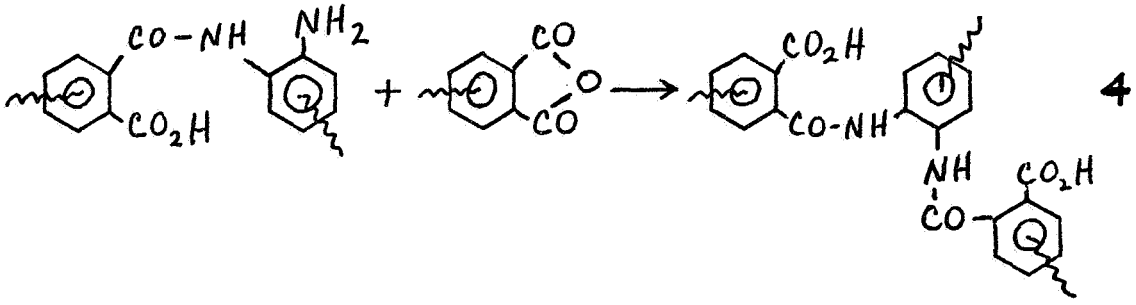
Eq. 1 shows the formation of the soluble poly (amino acid amide) at moderate temperatures. Eq. 2 and 3 show two routes by which the soluble intermediate can be converted by heat to the pyrrone structure. Apparently the actual reactions are more complex than this. One complication is the possibility of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



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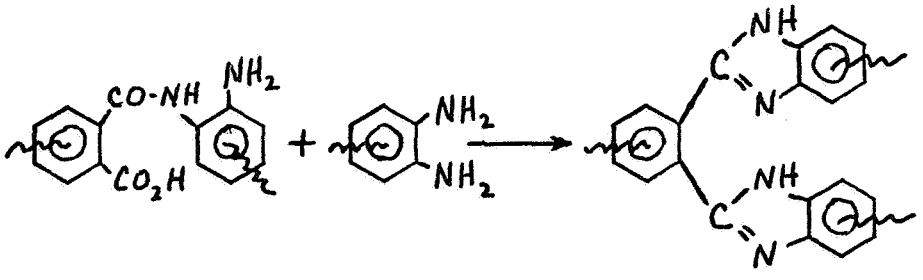
Although the amine groups of the poly (amino acid amide) are somewhat deactivated by the presence of an ortho acylamido group, they are still moderately reactive toward anhydrides. When reaction 1 nears completion, the concentration of the ortho diamino structure, which now occurs largely on chain ends, becomes very small relative to that of the ortho aminoamide 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:



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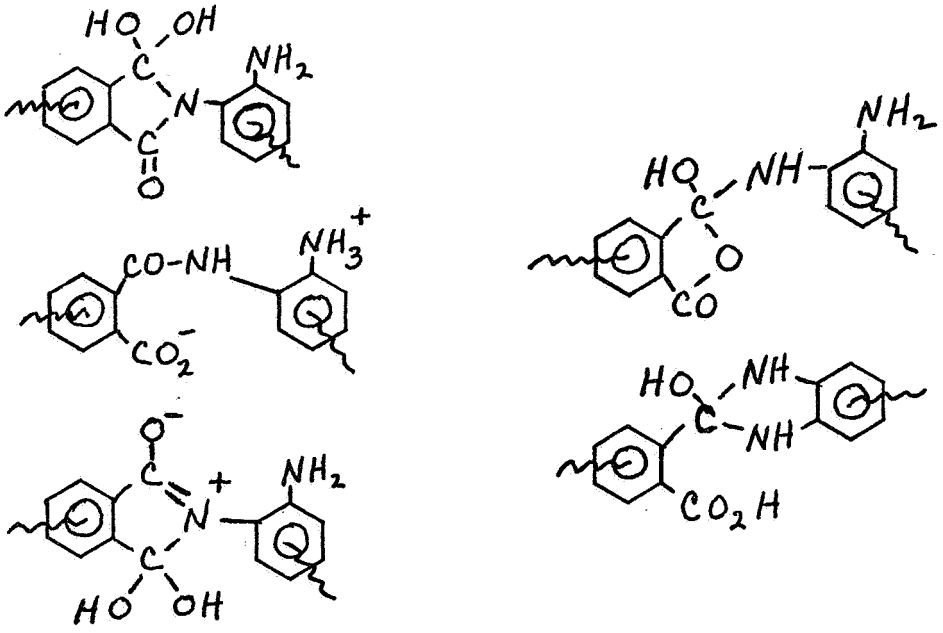
In addition to the problem of gelation, these crosslinking reactions introduce imide and benzimidazole linkages into the final polymer structure.

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:

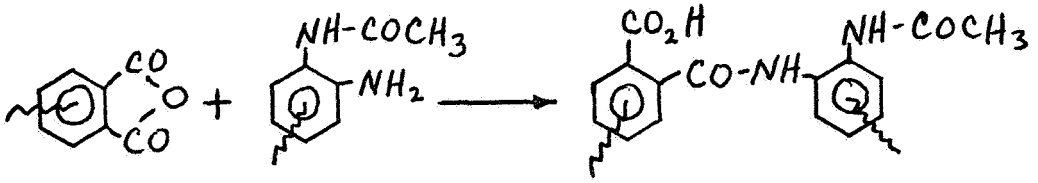


Experience with the closely related polyamide acids (polyimide precursors)[7-9] indicates that the various structural forms of the amino acid amide group react readily with anhydride or amino groups in an exchange reaction.[9] Polymer chains in solution, then, are continually breaking and reforming in 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:



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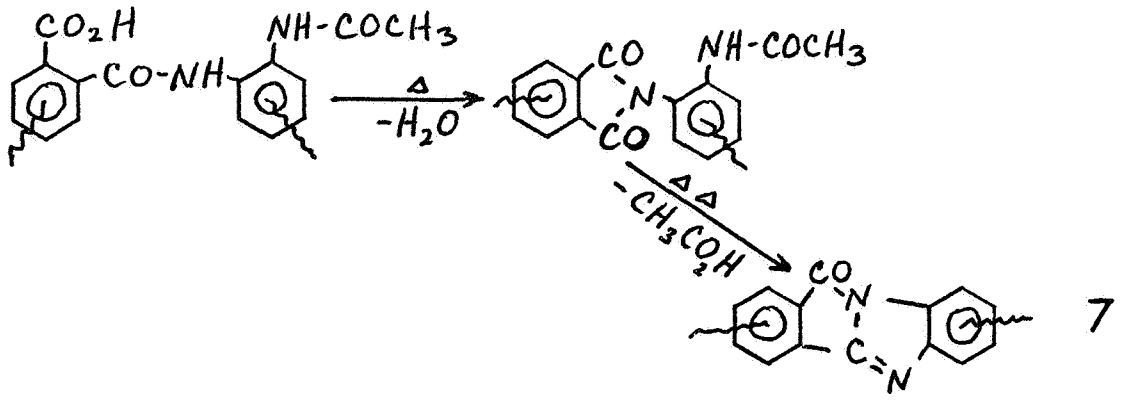

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The acetamido group will not react with anhydrides at room temperature to give crosslinking as in eq. 4, nor is it basic enough to abstract a proton from a carboxyl group to give a polyelectrolyte. Therefore the polymerization reaction (eq. 6) is expected to proceed without gelation, at concentrations higher than can be used in the usual reaction (eq. 1). Other blocking groups, such as trimethylsilyl, 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.

The use of protected amino groups avoids gelation by assuring that the soluble polymer is not crosslinked, although it is of high molecular weight. A second 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 third approach is to modify the solvent system to minimize polymer-solvent interactions and ionization. Most of the work reported here is related to the first method, with lesser amounts on the second and third.

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
DAA	2,4-diaminoacetanilide
DAB	3,3'-diaminobenzidine
DADAB	3,3'-diamino-N,N'-diacetylbenzidine
DATAB	1,3-diamino-4,6-diacetamidobenzene
DATADPO	4,4'-diacetamido-3,3'-oxydianiline
DMAC	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
DNB	3,3'-dinitrobenzidine
DNODA	3,3'-dinitro-4,4'-oxydianiline
HMP	hexamethylphosphoramide
MPD	m-phenylenediamine
NMP	N-methylpyrrolidone
ODA	4,4'-oxydianiline
PMDA	pyromellitic dianhydride
TEA	triethylamine
THF	tetrahydrofuran
TRAB	1,2,4-triaminobenzene

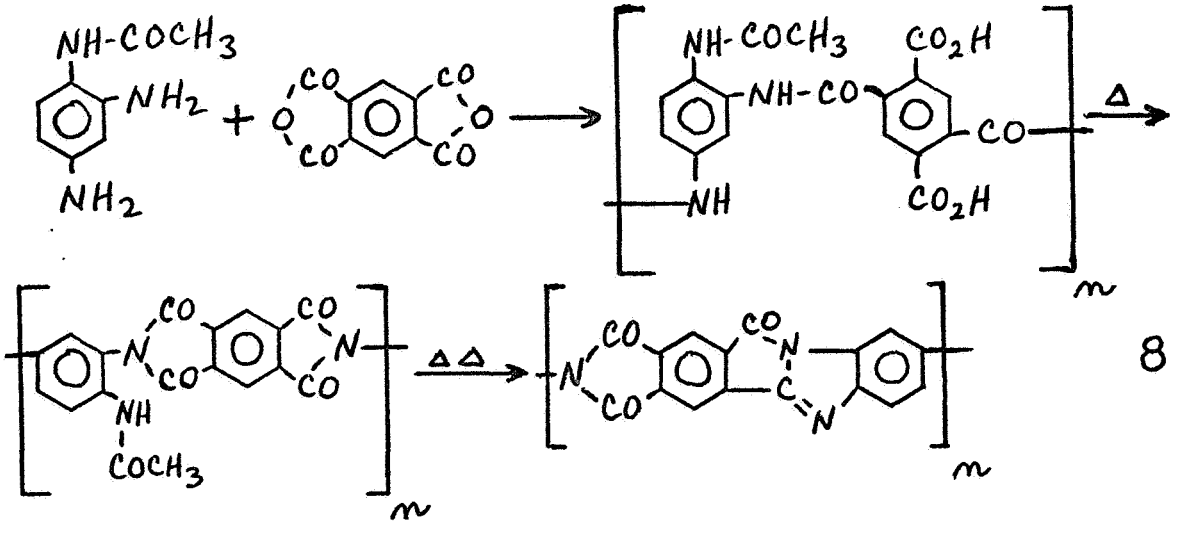
DIACETYL TETRAMINES AND THEIR POLYMERS

Model Compound

The model compound 2'-acetamido-N-phenylphthalimide was prepared and purified. It was heated in a TGA apparatus to determine if it would cyclize to a pyrrone with loss of acetic acid. Under the conditions used (10°C/min. in nitrogen) it sublimed without appreciable decomposition at 200-360°C. No further work was done with the model compound, since it appeared that work with polymers would be more productive.

Polymers from 2,4-Diaminoacetanilide (DAA)

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



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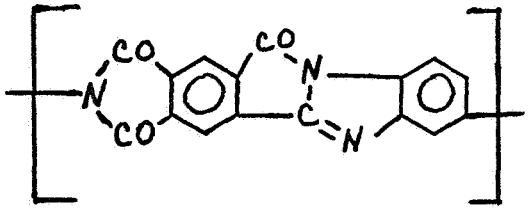
Two isomers are possible in the product of the first reaction, only one of which is shown. The cured product, which contains equal numbers of imide and pyrrone groups, is expected to be the same as the polymer previously prepared from 1,2,4-triaminobenzene (TRAB) and PMDA by Bell[10] and by Dunnavant,[11] 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] Fig. 1 shows the typical viscosity peak at equivalence as the last three 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). 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.

An attempt was made to obtain a solvent-free uncured polymer sample by reaction in tetrahydrofuran (THF). Such a sample would be useful in the study of curing reactions by TGA and infrared. However, even after refluxing an equimolar mixture for 3 hrs., a considerable amount of DAA was recovered. The reaction product had an inherent viscosity of only 0.044 dl/g., and was shown by infrared analysis to contain anhydride and imide groups. TGA and elemental analysis were also inconsistent with the desired product.

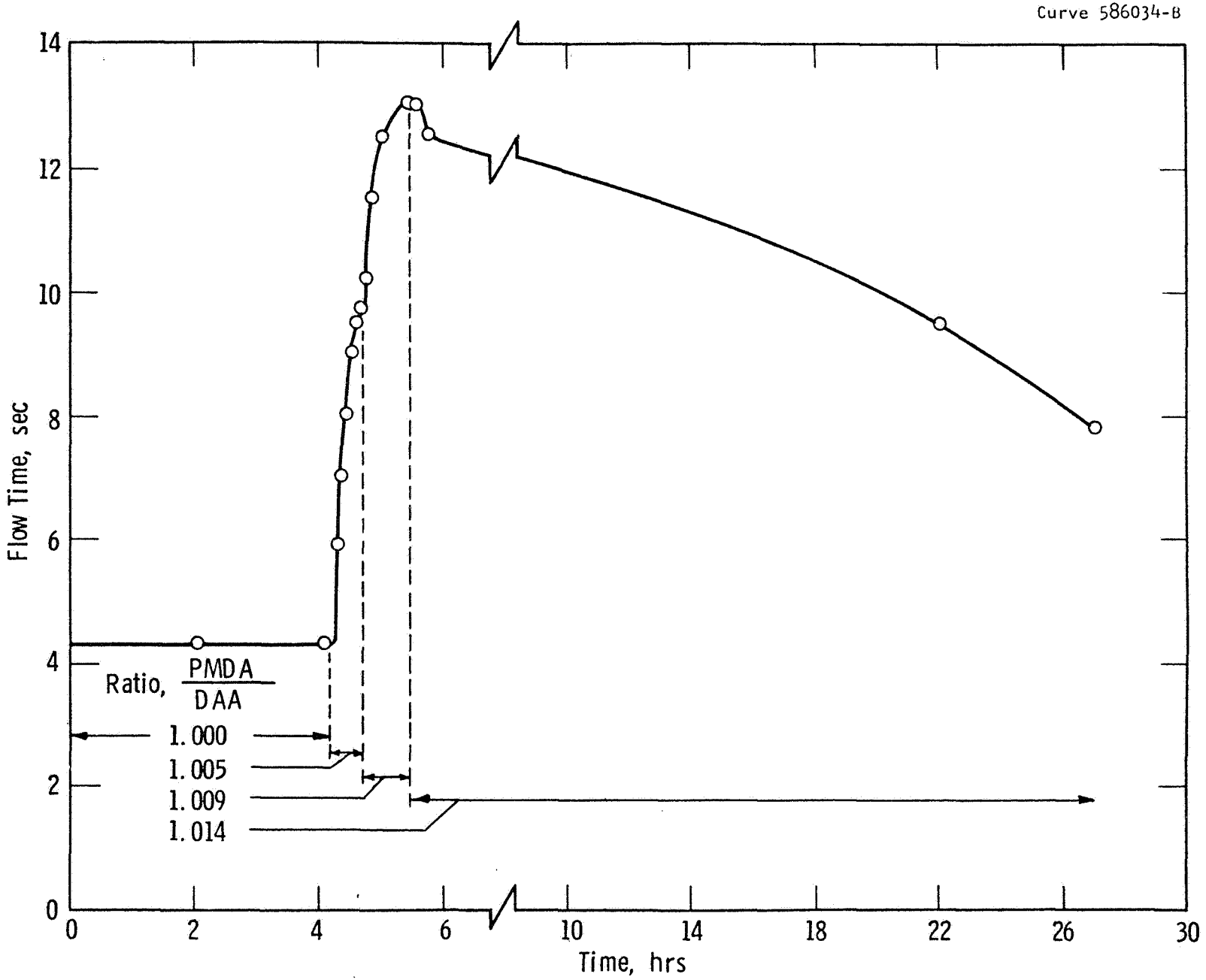
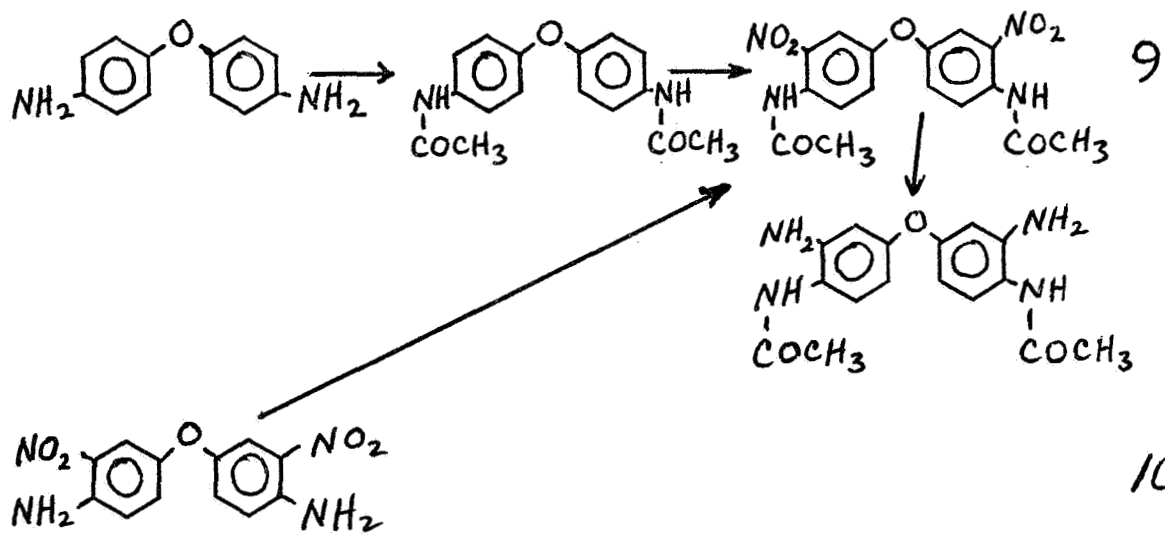


Fig. 1— Reaction of PMDA and DAA in DMAC at 25 °C.

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 by the following two methods:



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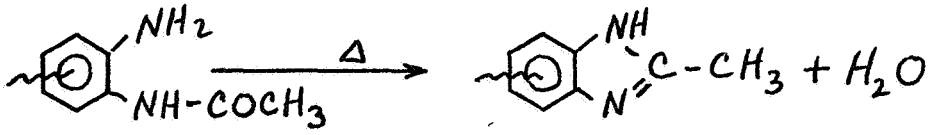
The product from eq. 9 was of higher purity, probably because of a greater tendency toward polyacetylation in the other method. Another problem in the synthesis of compounds of this type is their ability to cyclize to a 2-methylbenzimidazole:



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If this reaction should occur at both ends of the molecule, the product would be relatively innocuous, but reaction at one end only would give a monofunctional chain stopper. It was found possible to avoid this side reaction by recrystallizing and drying the product at a low temperature.

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

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

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.

Fig. 2 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 poorly defined 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. 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. - The reaction of DAA and PMDA in THF was not very successful, probably because of the low solubility of DAA. DATADPO is considerably more soluble, and 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

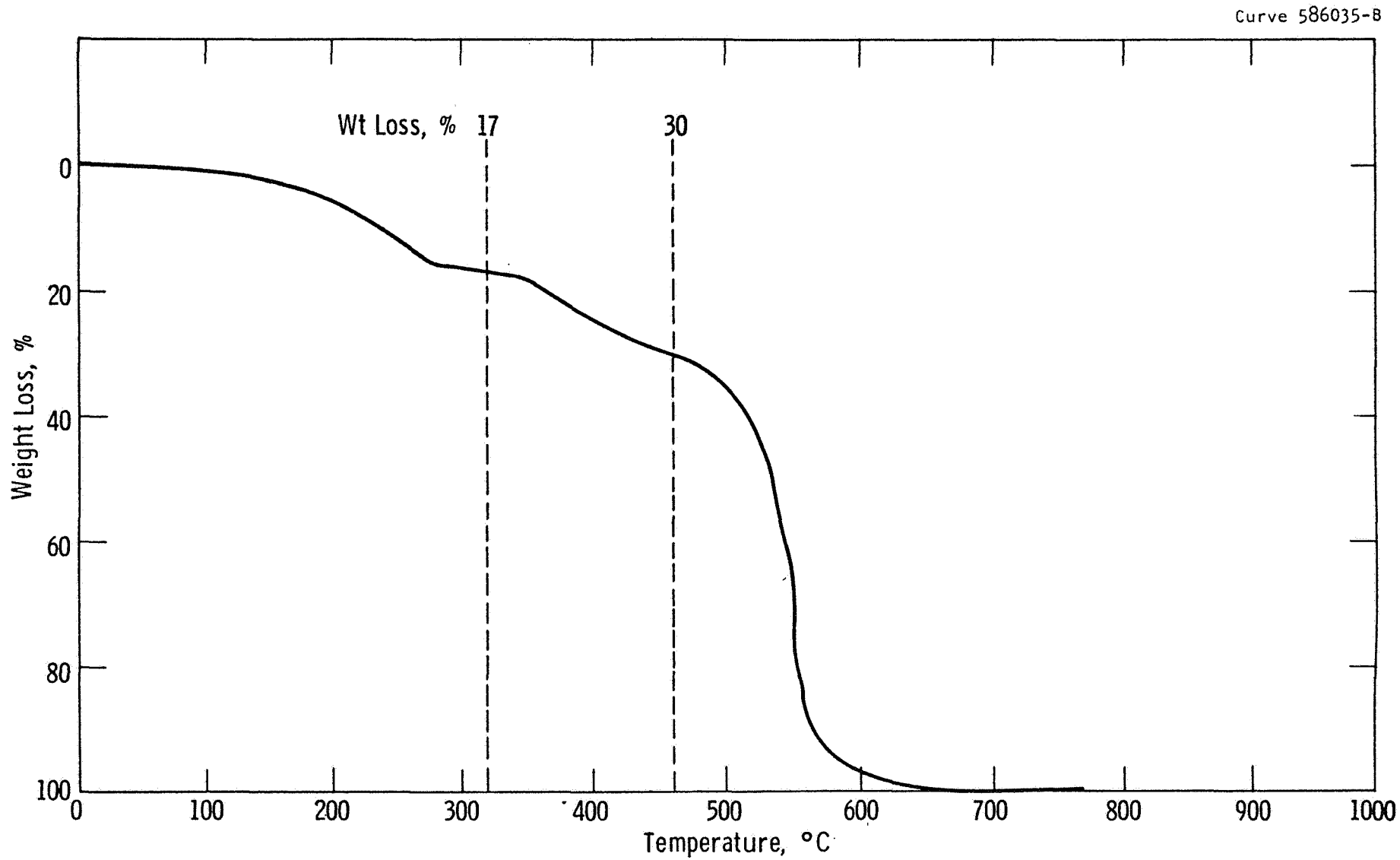


Fig. 2— TGA of DATADPO - BTDA film in air at 5 °C/min.

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

No. plies	Precure[b] Time, min.	Precure[b] Temp., °C	% Resin Prepreg	% Resin Laminate	Thickness, In.	Flex. Strength, psi[c] 70°F	Flex. Strength, psi[c] 600°F	Flex. Modulus, psi[c] 70°F	Flex. Modulus, psi[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.

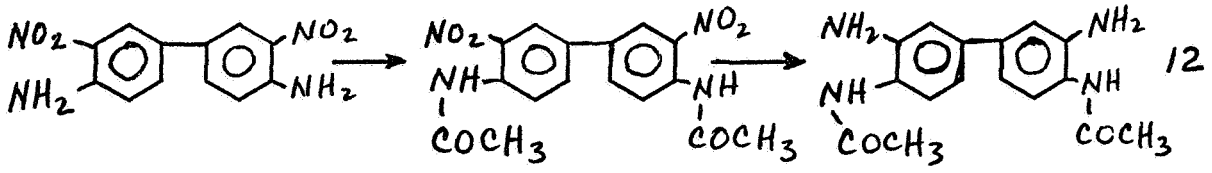
2 hrs. at 150°C, infrared spectra showed it to be converted largely to the imide.

Fig. 3 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,[13] 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. - The synthesis of 3,3'-diamino-N,N'-diacetylbenzidine (DADAB) was conducted as follows:



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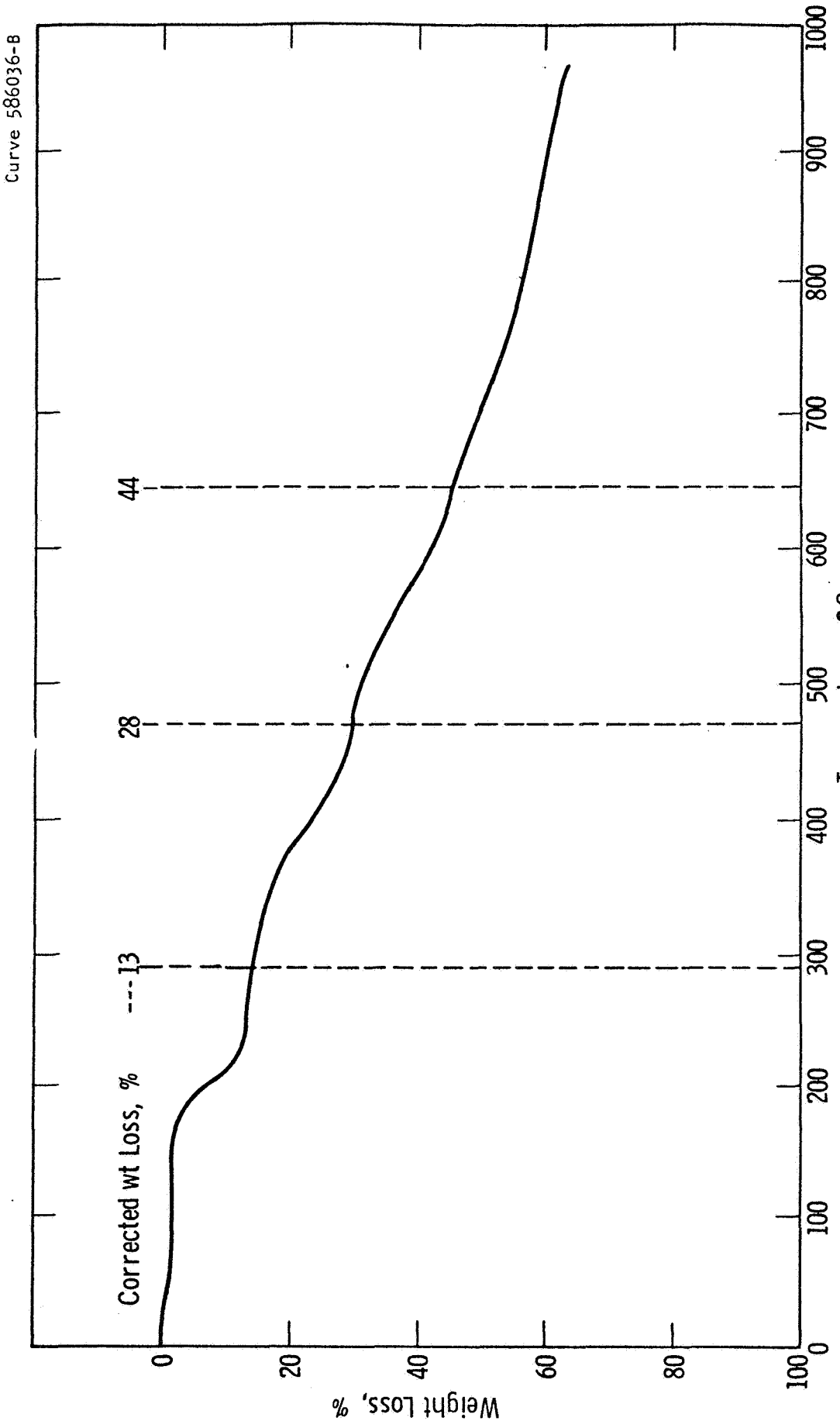

Fig. 3— TGA of DATADPO - PMDA powder in N_2 at 2.5 °C/min.

The acetylation reaction, with acetic anhydride and sulfuric acid, gave both the diacetyl derivative shown and the triacetyl compound. Separation by crystallization was necessary. Later in the program a supply of dinitrodiacetylbenzidine was obtained from American Aniline, so the first step was eliminated. The only good solvent found for DADAB at room temperature was DMSO, although warm DMF turned out to be a more satisfactory hydrogenation solvent. The product was purified by passing a solution in DMSO through a column of alumina, adding water to the effluent, and allowing the DADAB to crystallize. Elemental analysis of the resulting product indicated a high degree of purity.

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.

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 checked very well for 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 contained slightly more nitrogen than the insoluble fractions, and 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, NMP, 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.

A sample of the soluble fraction was heated under vacuum, and the volatile products were collected and analyzed by infrared spectroscopy. Products obtained in 2 hrs. at 100°C plus 2 hrs. at 150°C were water and DMAC only. An additional 2 hrs. at 300°C gave water, carbon dioxide, and an aliphatic material, which appeared to be an acetate. In 2 hrs. at 350°C acetic acid, acetic anhydride, and additional water were obtained. Apparently, curing above 300°C is necessary to eliminate the acetyl group from these polymers. The same conclusion is reached from consideration of infrared spectra of the polymer itself, which are discussed in a later section.

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.

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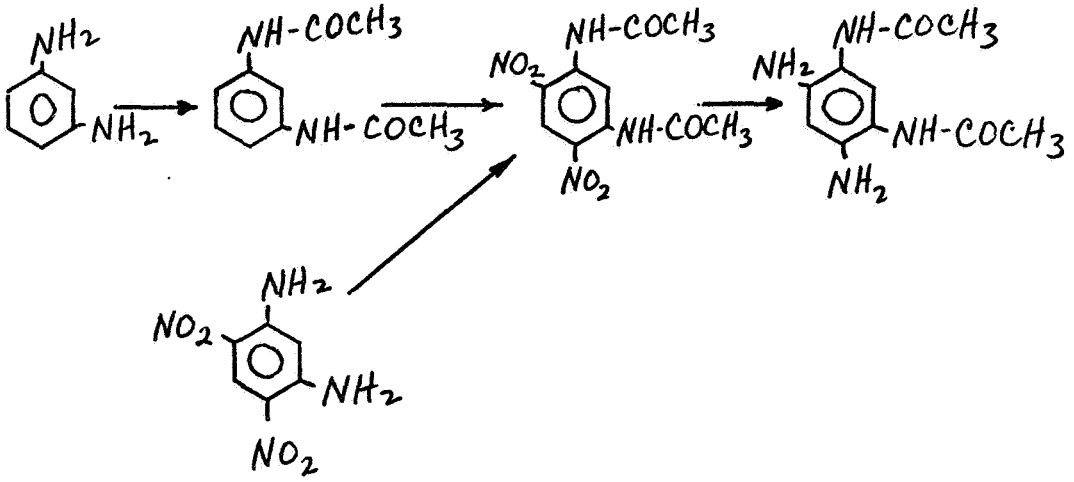


In the first method (eq. 13) the nitration step turned out to be very difficult. Several methods were tried, but only the mononitro derivative was obtained in good yield. The second method (eq. 14) was more successful, although acetylation gave some triacetyl compound along with the desired diacetyl derivative. DATAB was prepared in this way, but turned out to be so insoluble and high melting that purification was very difficult. A small amount of polymer was prepared from crude DATAB and BTDA. It gave very poor films.

TRIMETHYLSILYL DERIVATIVES OF TETRAMINES

The trimethylsilyl group could 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.

OTHER DEACTIVATION SYSTEMS

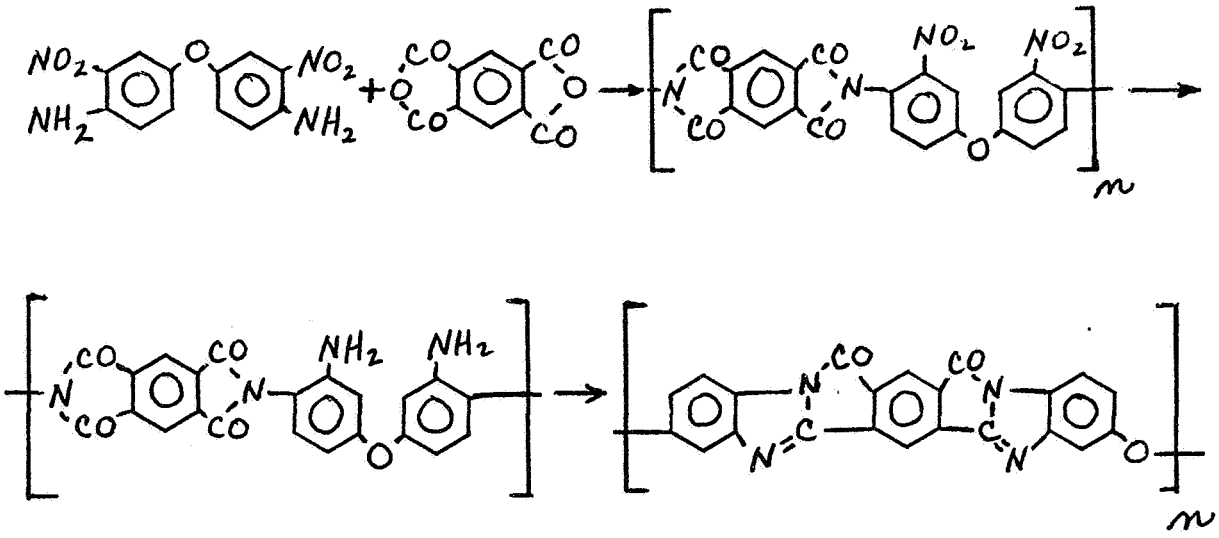
Tosylate

The tosyl (p-toluenesulfonyl) group was investigated briefly as an additional blocking group for amines. The chief advantages of this approach are the ease of preparation and purification of the amine derivative and the absence of side reactions, which are a problem with acetyl and trimethylsilyl derivatives. Disadvantages are low volatility of by-products in the final cure and possible difficulty in breaking the N-S bond to form the pyrrone.

The bis (p-toluenesulfonamide) of ODA was prepared as described by Ray & Soffer.[14] It was nitrated with nitric acid and acetic anhydride to give a compound believed to be the dinitro compound, but reduction to the diamine has not been carried out.

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.

POLYMERS FROM TETRAMINES

Reaction with Dianhydrides

A few experiments performed on the reaction of tetramines and dianhydrides in aprotic solvents were in agreement with the results of Bell,[1] Colson,[3] and others. When a dry mixture of DAB and BTDA was added to stirred DMAC, gelation occurred at 7.6% solids. Addition of more DMAC did not dissolve the gel immediately, but at 4.9% solids it dissolved on standing for 3 days. Films cast from the solution were continuous but brittle.

The gelation and high viscosity of amino acid amide polymer solutions are believed to be associated in part with 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 III). In both cases insufficient flow occurred in the press.

One additional approach to the problem of gelation is the preparation of pyrrone-imide copolymers. Since solutions of imide precursors tend to decline in viscosity on storage,[9] while those of pyrrones tend to become more viscous and gel, a combination of the two might reasonably be expected to be stable. Cured copolymers of this type have been shown by Bell[10] to have desirable properties. Several preparations of the copolymer MPD-DAB-$BTDA_2$ were made. The tendency to gel seemed to be about the same as that of unmodified pyrrones. A 10.9% solution was stable, but a 21% solution gelled quickly.

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.

The polymer of DAB and BTDA was prepared in DMAC and in NMP, using either ethylene glycol or Cellosolve to esterify the BTDA. Solutions of about 30% solids were made without difficulty. Viscosity of the solutions increased with age, and one of them gelled in 40 days. The use of less than the stoichiometric quantity of alcohol gave immediate gelation. The preparation of these solutions is summarized in Table IV.

Table III

Laminates from DAB-BTDA on E Glass Cloth (A1100 soft finish)

Resin Batch	% Resin		Thick-ness, In.	Flex. Strength, psi		Flex. Modulus, psi	
	Prepreg	Laminate		70°F	600°F	70°F	600°F
D36-40-1	39.8	31	0.139	47,250	31,700	2.98×10^6	2.16×10^6
D36-49-3	42.5	40	0.133	23,700	16,000	2.71×10^6	1.79×10^6

No. plies.....12

Precure..... 60 min/125°C

Press conditions... 500 psi, 350°C

Table IV

Preparation of Esterified DAB-BTDA Solutions

Run No.	BTDA		DAB		Alcohol		Solvent		Calc.[a]	Viscosity, cstk.[b]			
	moles	g.	moles	g.	moles	g.	Name	g.	% solids	Initial	3 days	6 days	40 days
					Ethylene Glycol								
D35-122-2	0.01	3.22	0.01	2.14	0.01	0.62	DMAC	17	23.3				
D35-122-3	0.01	3.22	0.01	2.14	0.008	0.50	NMP	16	24.5	Gel			
D35-124-1	0.01	3.22	0.01	2.14	0.016	1.00	NMP	17	23.0				
D35-124-2	0.01	3.22	0.01	2.14	0.016	1.00	NMP	10	32.7				
					Cellosolve								
D34-125-1	0.02	6.44	0.02	4.28	0.04	3.6	NMP	22	29.6	275	880	1500	7500
D35-125-2	0.022	7.08	0.02	4.28	0.044	4.0	NMP	22	30.5	500	1500	3000	gel
D35-125-3	0.024	7.73	0.02	4.28	0.049	4.4	DMAC	26.4	28.1	(c)	50	90	165

a. Calc. by dividing the weight of the DAB + BTDA by the total weight.

b. Viscosities were measured in Gardner tubes and are approximate. Aged at room temperature (about 25°C).

c. Less than the Gardner "A" (50 ctsks).

None of these polymer solutions gave a continuous thin film, although thick fragments of the cured polymer were quite tough. Weight loss of films of the polymers on aging at 325°C in air is shown in Table V. The values are high, reaching 35-50% in 314 hrs. A good polyimide with the same treatment would lose 6-8%.[7] The polymers made with Cellosolve appear slightly more stable than those made with ethylene glycol.

A laminate prepared from the Cellosolve ester of DAB-BTDA gave the following values of flexural strength and modulus:

Flex. strength, psi		Flex. modulus, psi	
70°F	600°F	70°F	600°F
58,000	37,000	2.92×10^6	2.22×10^6

Polymers prepared from DAB and the dimethyl ester of BTDA were tried unsuccessfully as laminating resins. Their infrared spectra on curing are discussed in a later section.

Table V

Weight Loss of DAB-BTDA Polymers at 325°C

Run Number	Weight Loss, %[a]			
	50 hours	100 hours	150 hours	314 hours
D35-124-1	11.5	20.2	28.5	49.5
D35-124-2	9.6	19.0	25.7	47.5
D34-125-1	8.9	15.5	23.3	44.5
D35-125-2	8.1	14.0	20.1	34.8
D35-125-3	9.6	15.0	22.4	44.5

a. average of two samples

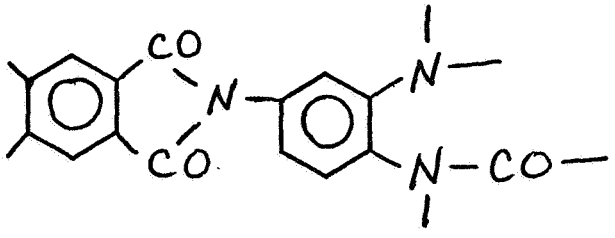
INFRARED SPECTRA AND CURING REACTIONS

Infrared spectroscopy is a convenient method for studying the structure of these polymers and the course of their curing reactions. Two general methods have been used. In one method a solution of polymer is applied as a thin film to the surface of a CsI plate. The coated plate is then subjected to a series of baking cycles, with an infrared scan following each heating period. This method has the advantage that the same specimen is used for each spectrum, so that sample preparation is constant. Disadvantages are possible interaction between sample and substrate, and a general weakening of spectra and loss of detail as baking progresses. In the second method, polymer powder is subjected to various heat treatments, and the product of each is pressed into a KBr pellet, which is used for the determination. In this method the absorbance for each determination can be adjusted to a convenient level by varying the amount of sample used in the pellet. However, variations in preparation of the pellets may affect the spectra somewhat. All of the spectra reported here were run on a Beckman IR 12 grating spectrophotometer.

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[15]	Pyrrone
1780		1760
1720		1730
	1630	1610
		1560-1590
	1460	1470
		1430
1370		1370
	1290	
		1170
		1060
		930-960
		850
	800	820
720		720

Fig. 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.

Fig. 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 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 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.

Figs. 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 very low degree of pyrrone formulation.

In Figs. 8 and 9, the soluble and insoluble fractions of DADAB-PMDA are compared, using the KBr disc method. 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} does 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 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 the imide and also to the 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 PMDA-TADPO.

Fig. 10 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 well developed 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.

If the assignment of infrared absorption bands is essentially correct as indicated, it appears that polymers derived from o-acetamido amines are converted, with moderate heating, to acetamido imides. Evidently this structure is rather stable. Infrared study of both the residue and the volatiles indicates that elimination of acetic acid does not occur at an appreciable rate below about 350°C. When it does occur, there is little to no conversion to pyrrone. Some of the bands associated with pyrrones develop on heating, but the characteristic strong band at 1760 cm^{-1} appears very weakly or not at all. Since the imide band at 1780 cm^{-1} is eliminated on heating, it is apparent that some new structure is formed from the imide linkage. Further work is needed to establish the nature of this change. Polymers derived from o-diamino compounds apparently form some pyrrone structures before imide formation is complete, and their conversion to pyrrone is both easier and much more nearly complete than that of the acetylated derivatives. The salt synthesis,

from a diester diacid and a tetramine, appears to lead to an intermediate stage in which both imide and ester-amide linkages are present. Conversion to pyrrone is probably less complete than in either of the other systems.

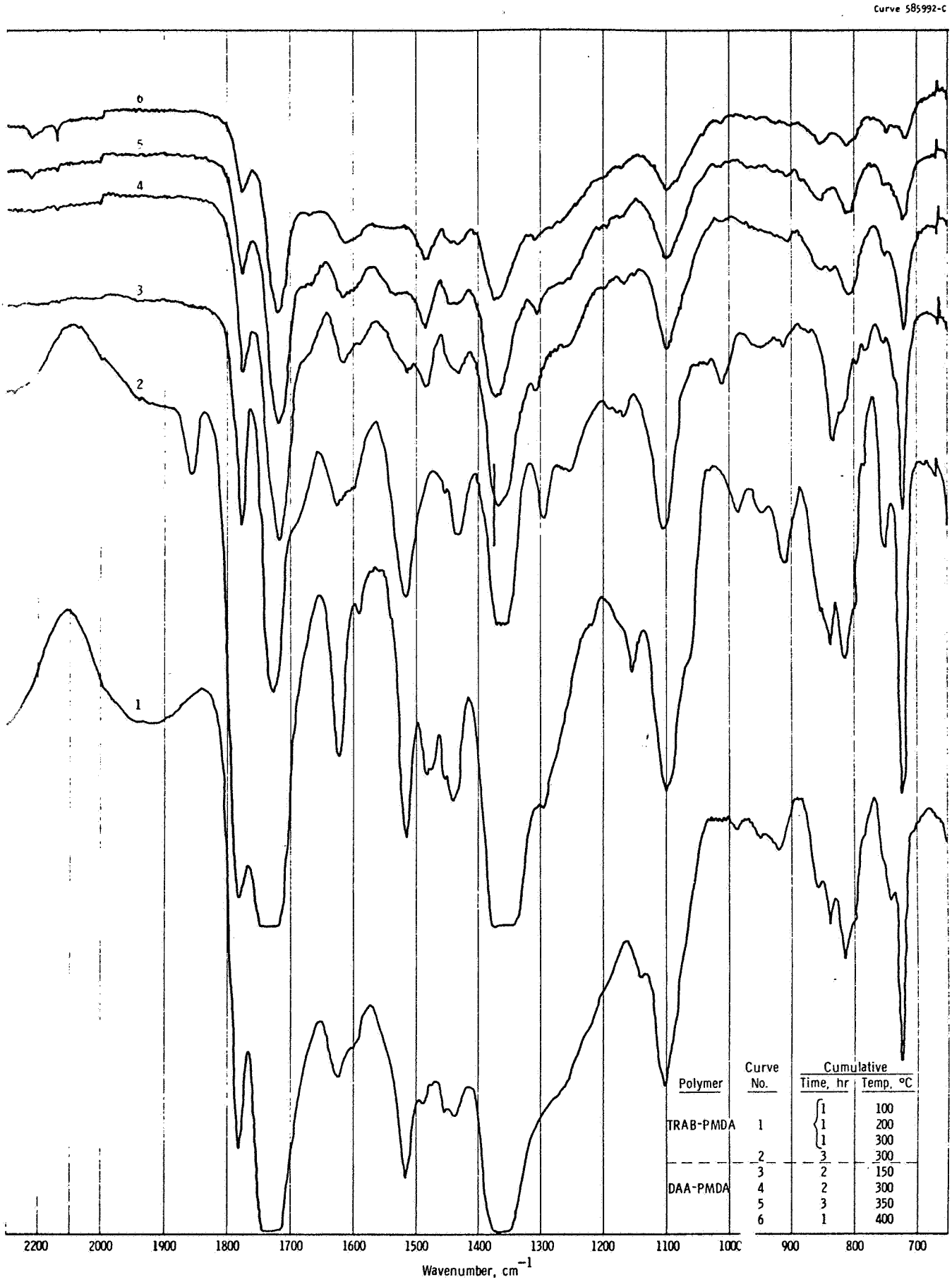


Fig. 4—Infrared spectra of DAA-PMDA and TRAB-PMDA as a function of cure. DAA-PMDA film cast on CsI plate. TRAB-PMDA free film. Cure times cumulative

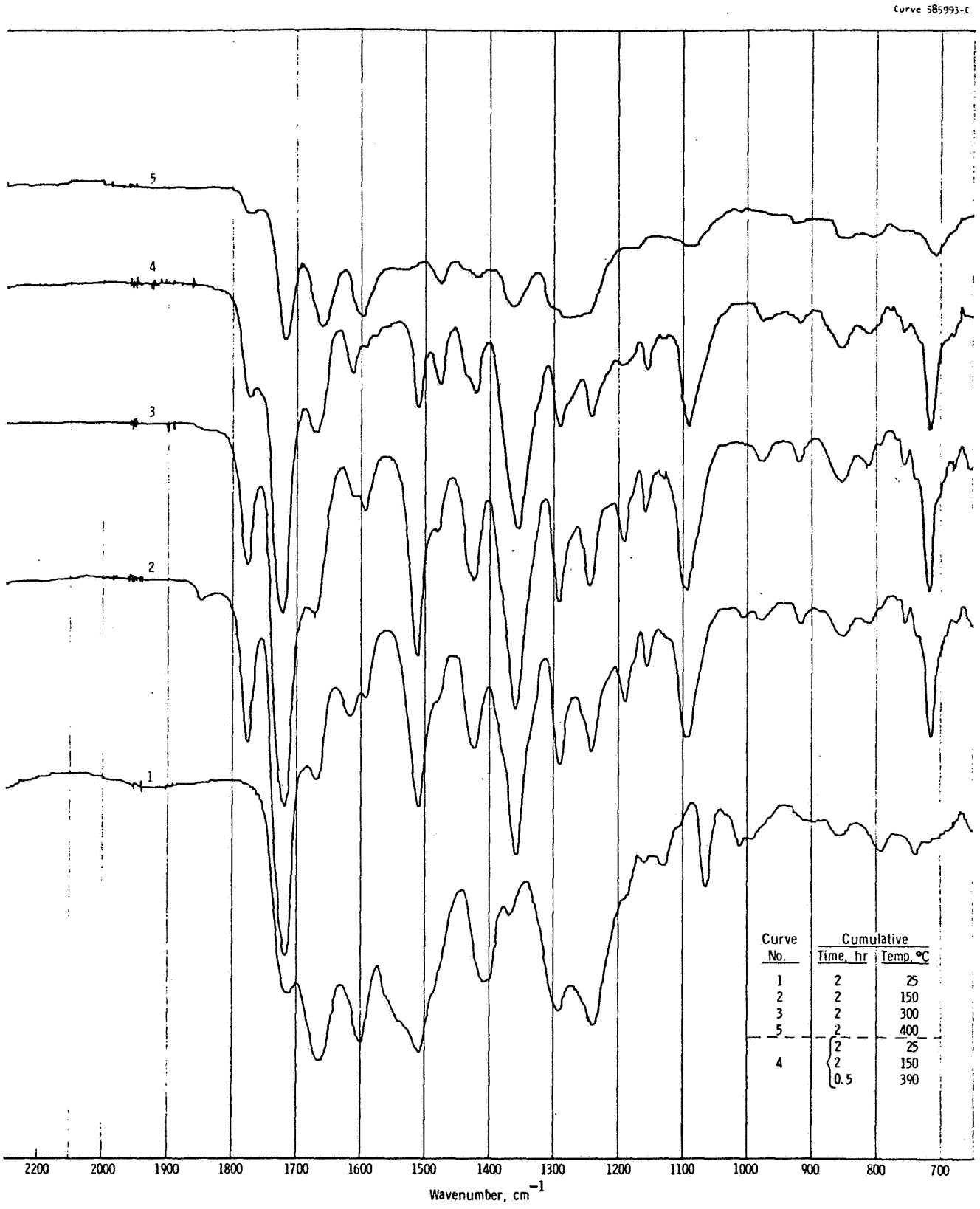


Fig. 5—Infrared spectra of DAA-BTDA as a function of cure. Film cast on CsI plate. Cure times cumulative.

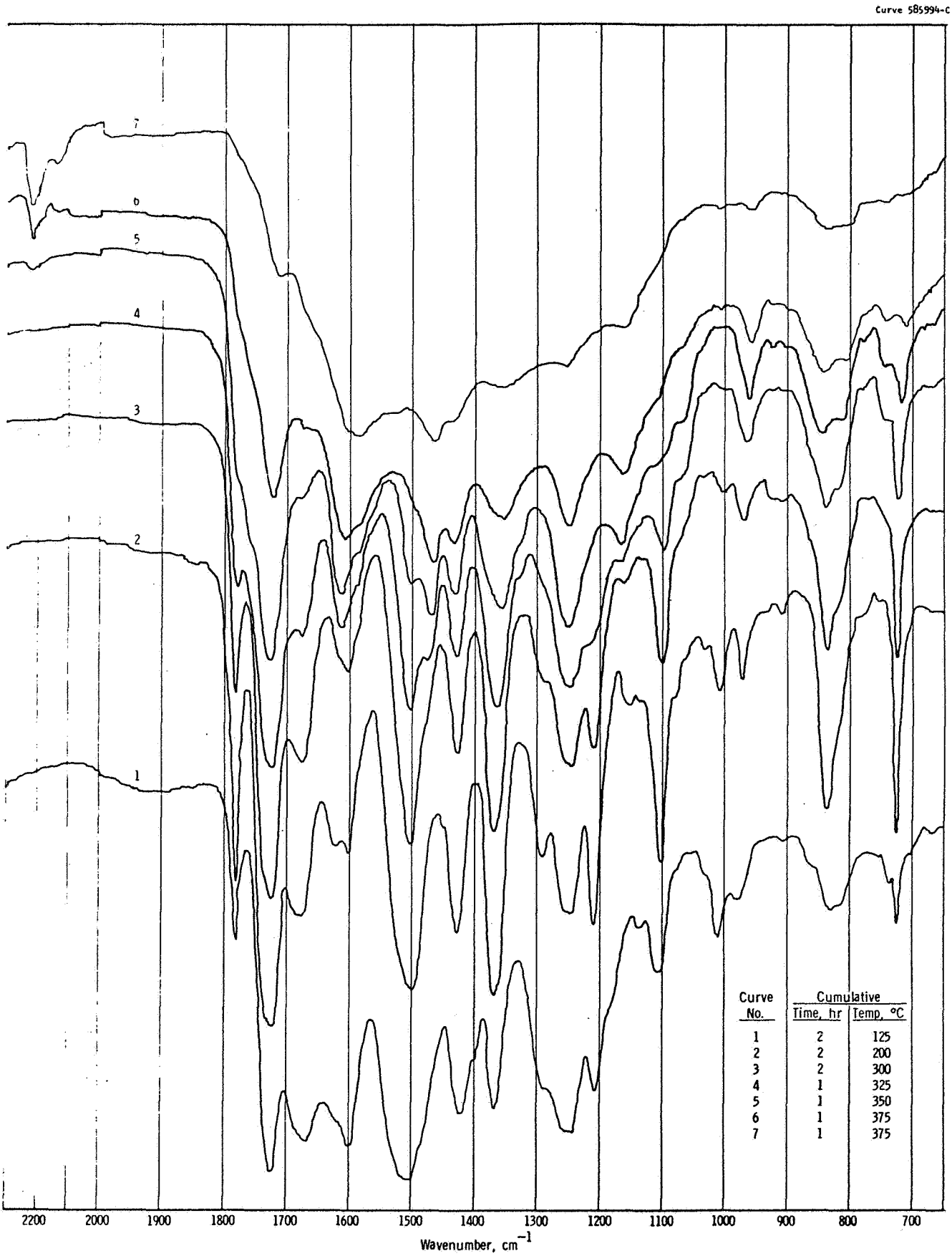


Fig. 6—Infrared spectra of DATADPO-PMDA as a function of cure. Film cast on CsI plate. Cure times cumulative

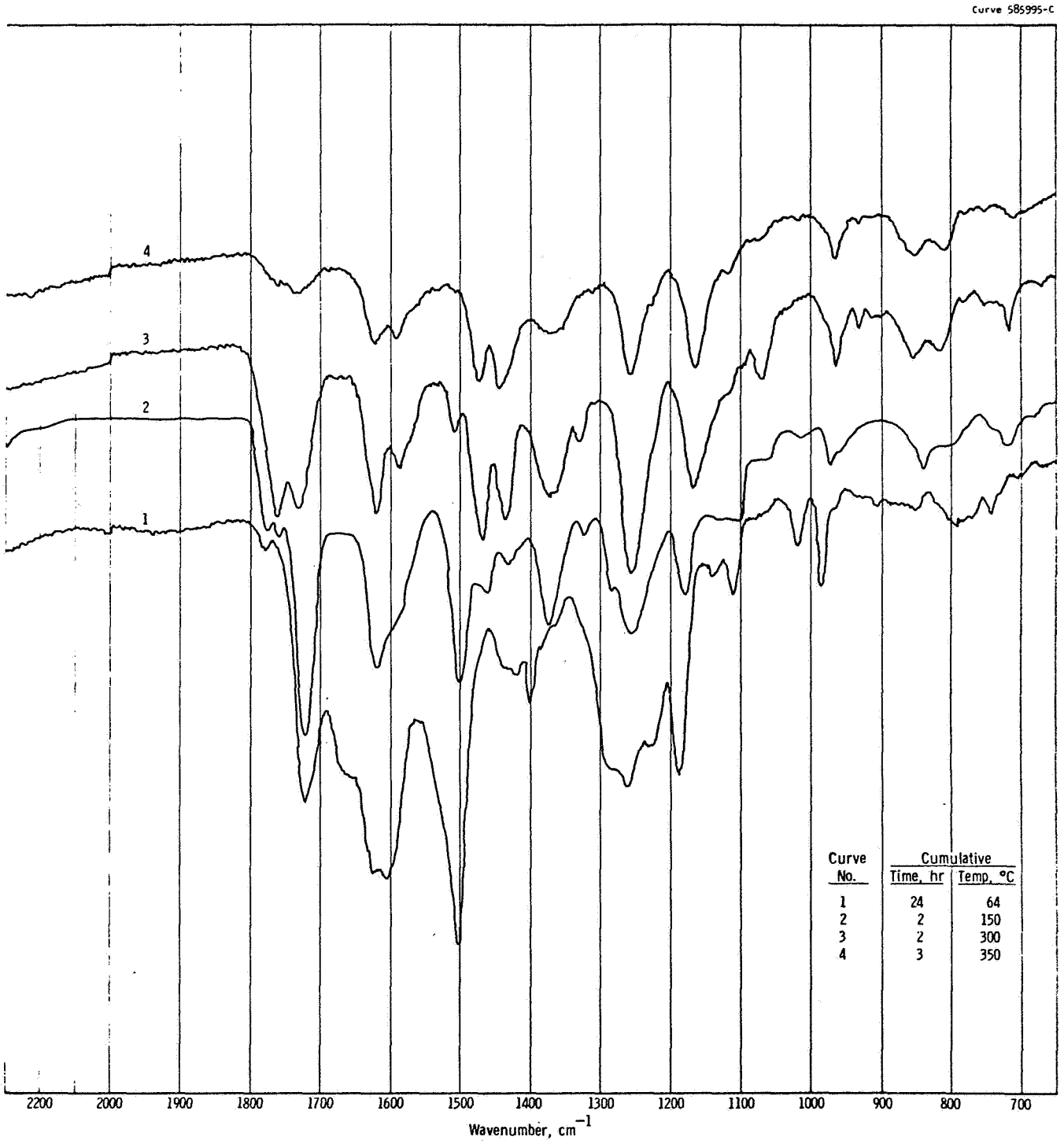


Fig. 7—Infrared spectra of TADPO-PMDA as a function of cure. Film cast on CsI plate. Cure times cumulative

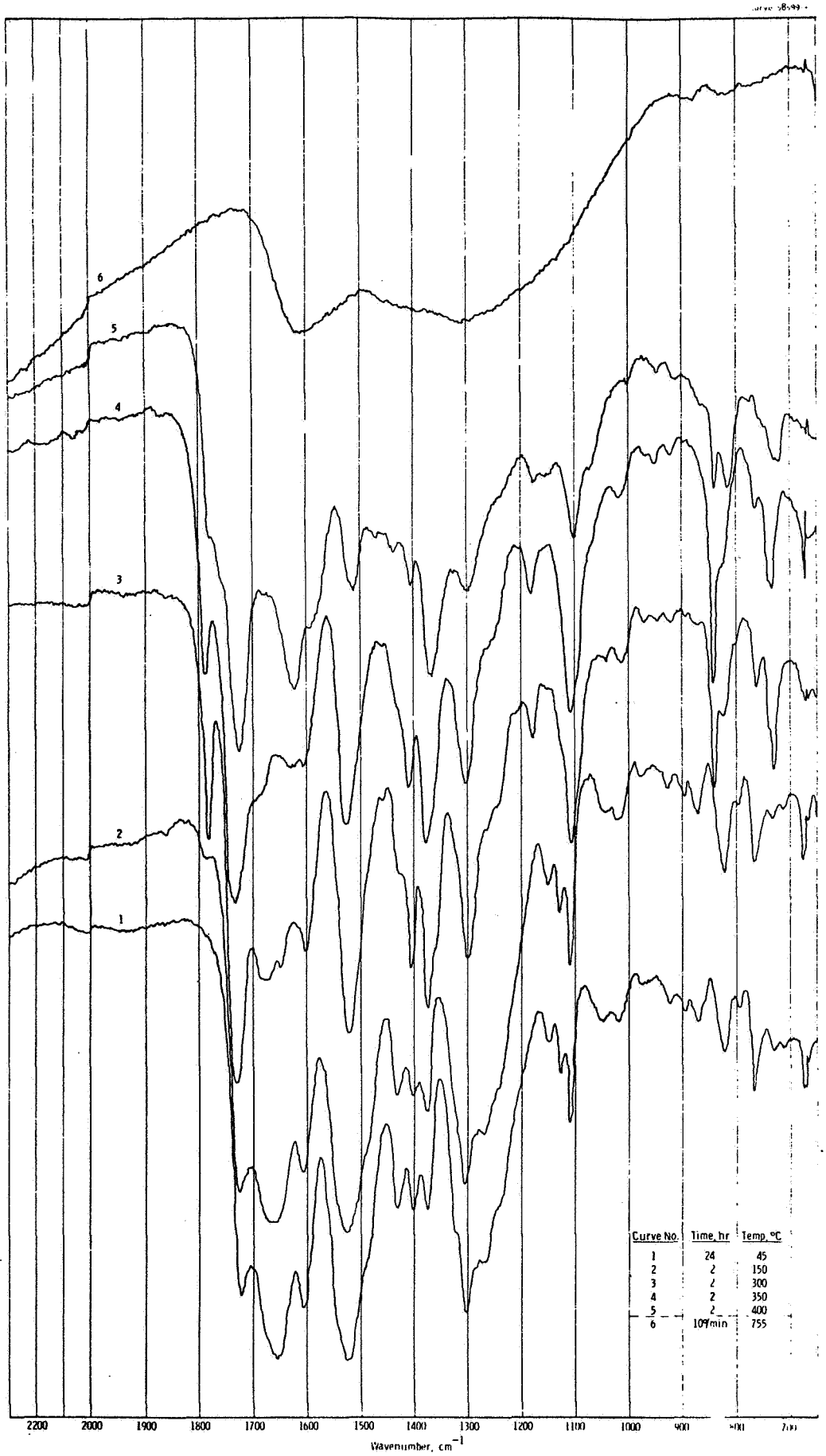


Fig. 8—Infrared spectra of DADAB-PMDA (DMAC insol fract) as a function of cure. Powder in KBr disc. Cur[illegible] times not [illegible]

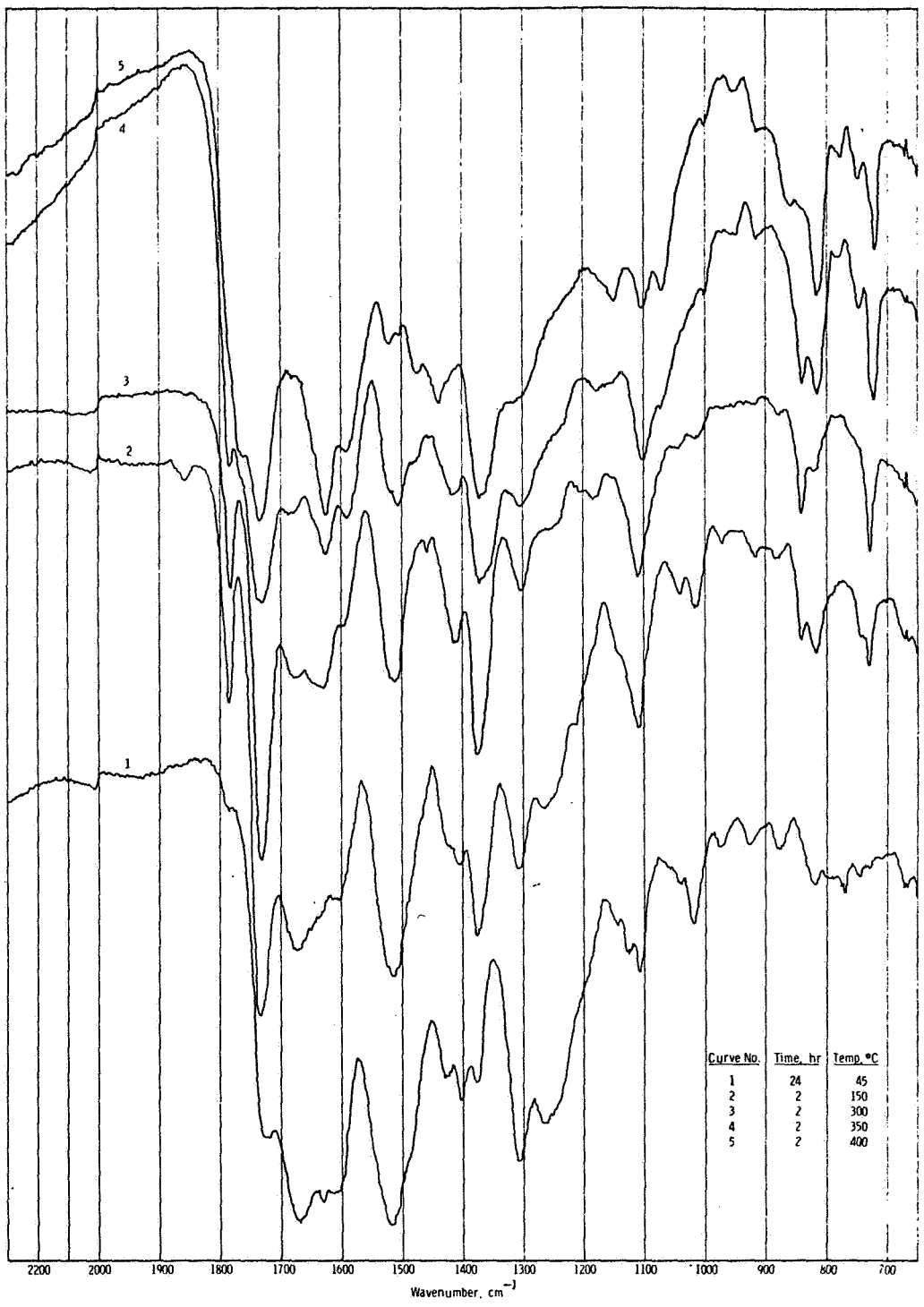


Fig. 9—Infrared spectra of DADAB-PMDA (DMAC sol fract) as a function of cure. Powder in KBr disc. Cure times not cumulative

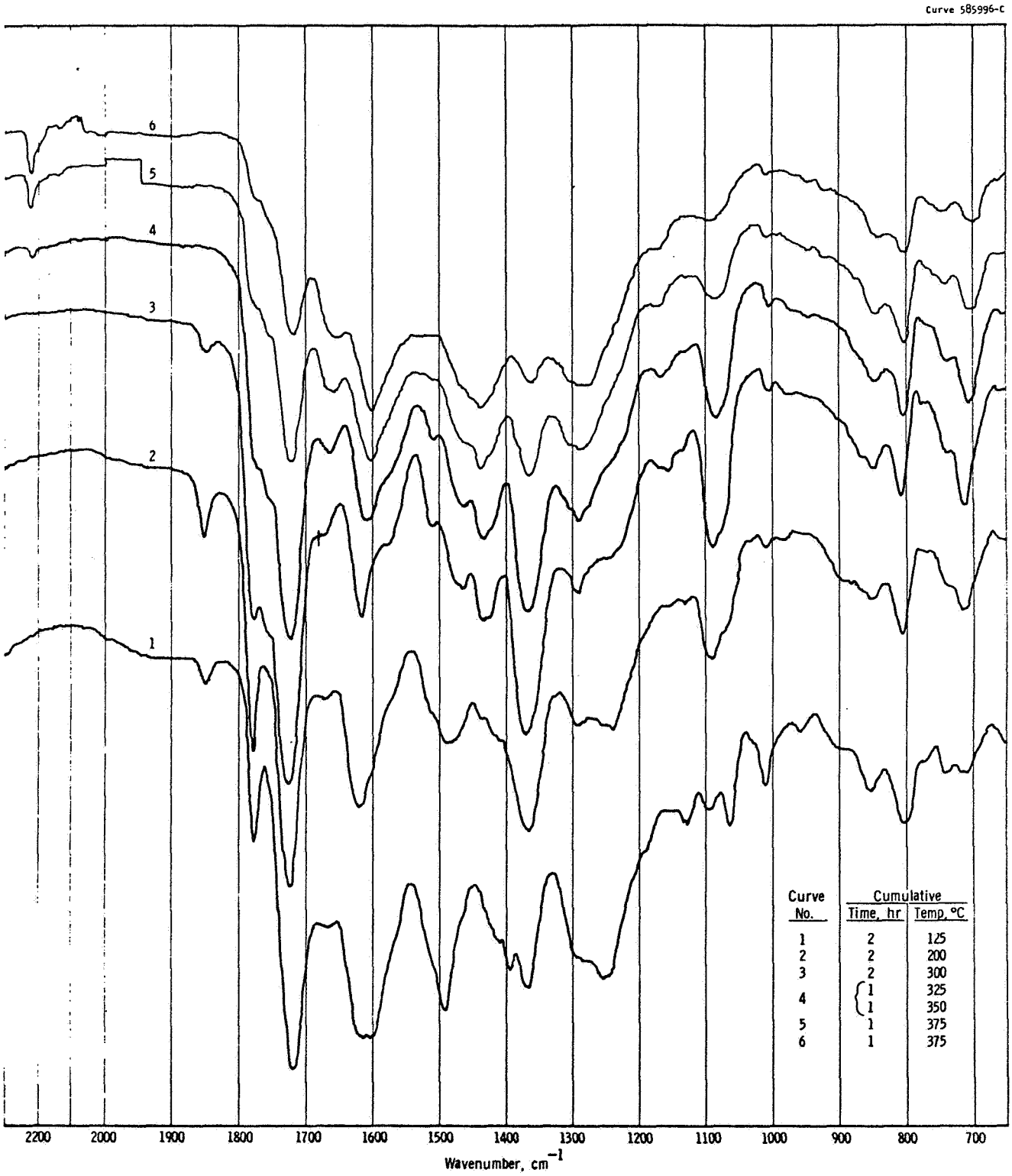


Fig. 10—Infrared spectra of Me_2-BTDA-DAB salt as a function of cure. Film cast on CsI plate. Cure times cumulative

EXPERIMENTAL

Purification of Materials

Purification methods for specially synthesized compounds are included individually in the appropriate sections. More generally used materials are considered here.

The most-used solvent in this study was DMAC. As received from duPont it is of excellent purity, but it is quite hygroscopic and tends to pick up moisture from the atmosphere during handling. Several drying methods were compared, using Karl Fischer titrations. In each case, about 300 ml. of DMAC was allowed to stand in contact with about 30 g. of the drying agent for one week. The azeotroped samples were prepared by mixing DMAC with half its volume of the second solvent and distilling to a vapor temperature of about 150°C. The residue from distillation was used as the sample.

The following results were obtained:

Drying Agent	H_2O content, ppm
None	20
4A Molecular Sieve, as received	10-20
5A Molecular Sieve, as received	7.0-7.5
4A Molecular Sieve, dried 16 hrs. at 325°C	20
5A Molecular Sieve, dried 16 hrs. at 325°C	8.8-10
Calcium hydride	7.5-8.5
Calcium sulfate (Drierite)	10-20
Azeotroped with benzene	20-30
Azeotroped with toluene	7.5

A separate experiment was run, using a sample of DMAC containing 120-150 ppm of water. After 3 weeks of treatment, 4A Molecular Sieve gave 20-30 ppm, and P_2O_5 gave 10-15 ppm of water. The precision of the determination is about ± 15 ppm. We are probably justified in saying that 5A Molecular Sieve, P_2O_5, calcium hydride, and azeotroping with toluene are more effective than the other methods, and that DMAC dried by any of the three contains < 20 ppm of water. Of the three, 5A Molecular Sieve is the most convenient to use.

The two dianhydrides, PMDA and BTDA, usually contain some colored impurities as received and also pick up moisture in handling. Recrystallization from acetone, various washing methods, and sublimation, have been used to purify these materials.

A batch of PMDA which was recrystallized from acetone was titrated by a slight modification of the duPont method. In this procedure one sample of the material is esterified by boiling for 20 min. with 75 ml of anhydrous methanol and is then titrated with 0.5 N NaOH to a phenolphthalein endpoint. A second sample is hydrolyzed by boiling for 20 min. with 75 ml of water and 30 ml of pyridine and is titrated in the same way. The two titrations provide data to calculate the percentage of PMDA, PMA, and inert material. Actually, the acid is probably present largely as monoanhydride diacid,[12] but is reported conveniently as PMA. Duplicate results for this sample were:

% PMDA:	98.61, 98.72
% PMA:	1.36, 1.32
% Inert:	.03, - .04

The sample was then baked for 26 hrs. at 160°C under vacuum, with a slow sweep of dried air. The resulting product was brownish in color, but gave the following results on titration:

% PMDA:	100.0, 100.5
% PMA:	0.15, 0.21

Apparently this baking schedule is effective in converting the acid quantitatively to the anhydride.

A sample of BTDA was purified by washing with dry isopropanol, as recommended by Gulf Oil Corp. A second sample was recrystallized from cyclohexanone, washed with dry acetone, and dried for 24 hrs. at 160°C under vacuum, with a slow sweep of dry air. Both samples were titrated, with the following results:

Isopropanol wash.	% BTDA:	98.4, 98.8
	% BTA:	1.4, 1.2
	% Inert:	0.2, 0.04
Recryst. from cyclohexanone (D92-136-2).		
	% BTDA:	99.4, 99.8
	% BTA:	0.7, 0.6
	% Inert:	0, 0

The cyclohexanone recrystallization gives a better product.

DAB, as obtained from Burdick and Jackson, was tan to brown and contained darker particles. It was purified by the following method. Thirty grams of DAB was dissolved in 1500 ml.of boiling water, and the solution filtered hot. A considerable amount of black, tarry material was removed on the filter. Sodium hydrosulfite was sprinkled slowly

into the hot, red solution, which immediately became colorless. The amount required was less than 0.5 g. As the solution cooled, DAB crystallized as long, colorless plates. The product was filtered off and dried at 100°C under vacuum, with a slow nitrogen sweep, to give 25 g. of pale tan plates, melting sharply at 178°C.

Anal. Calc. for $C_{12}H_{14}N_4$: C, 67.26; H, 6.06; N, 26.10. Found: C, 67.11, 67.11; H, 7.08, 6.95; N, 26.08, 26.30.

Model Compound

N-(o-aminophenyl) phthalamic acid was prepared in 90% yield by the method of Colson, Michel and Paufler (J. Polymer Sci. A-1, 4, 67 (1966). Ten grams of the crude product was dissolved in 50 g. of boiling acetic anhydride. Upon cooling, crystals separated and were filtered off. Additional product was obtained by diluting the filtrate with water. The combined solids were recrystallized twice from toluene and dried under vacuum at 110°C to give 5.4 g. (49% yield) of 2'-acetamido-N-phenylphthalimide as white needles, m.p. 204.5 - 205.5°C. Anal. Calc. for $C_{16}H_{12}O_3N_2$: C, 68.6; H, 4.32; N, 10.0. Found: C, 69.14, 69.02; H, 4.47, 4.56; N, 10.27, 10.07. To investigate the elimination of acetic acid from this compound, a 20 mg. sample was heated in a duPont 950 TGA apparatus in a slow stream of nitrogen at a heating rate of 10°C/min. Unfortunately, the compound was too volatile, and sublimed without decomposition, the weight loss reaching 50% at 330°C and 100% at 360°C. A sample of sublimate from the exit tube had a m.p. of 204-204.5°C.

Polymers from DAA

Purification of DAA. - Rough solubility tests were made on a fairly pure sample of 2,4-diaminoacetanilide (DAA), with the following results:

Water dissolves 10% at 32-35°C

Methanol dissolves 6-7% at 40°C

95% Ethanol dissolves 7% at 78°C

A sample of DAA was then purified by the following series of steps:

1. A sample of fairly pure DAA was recrystallized twice from 95% ethanol.

2. The recrystallized product was dissolved in water at room temperature. The nearly saturated solution was treated with activated charcoal (Darco G) and filtered. The resulting colorless solution was evaporated at room temperature in a stream of nitrogen to about 25% of its original volume. Unfortunately a reddish color developed during the evaporation, and the crystals which separated retained some of the color. They were filtered off.

3. The product from step 2 was recrystallized from water containing a trace of sodium hydrosulfite. The decolorizing action of sodium hydrosulfite in this application is quite dramatic. A pinch of sodium hydrosulfite was sprinkled slowly into the hot red solution, which faded within seconds to a very pale pink. Upon cooling, DAA crystallized as nearly colorless prisms, which were dried for 3 days at 100°C under vacuum. Nearly white DAA melting sharply at 163°C was obtained in this way.

Anal. Calc. for $C_8H_{11}ON_3$: C, 58.16; H, 6.71; N, 25.44. Found: C, 58.16, 58.35; H, 6.78, 6.58; N, 25.39, 25.61.

Reaction of PMDA and DAA in DMAC. - A solution of 16.520 g. (0.1 mole) of purified DAA in 217 ml. of DMAC (dried over 5 A Molecular Sieve) was stirred in flame-dried apparatus under dry nitrogen while 21.813 g. (0.1 mole) of PMDA was added rapidly. Complete solution occurred exothermically in a few minutes. The solution was stirred for about 3 hrs. to be sure reaction was complete. A solution of PMDA in DMAC (0.100 g/ml) was then added in 1.00 ml. increments to the stirred polymer solution. Viscosity was measured by drawing the solution up into a 7 mm tube and measuring the flow time between two marks about 10 cm apart, at a head of about 25 cm. After each addition the flow time was checked periodically until it began to level off. At this point another increment was added and the process repeated until no further increase occurred. The final addition of PMDA gave a characteristic decline in viscosity, which has been observed before in polyamic acid solutions to which excess anhydride was added.[7] The results are summarized in Figure 1. Apparently the optimum amount of PMDA would have been about 1% more than the calculated quantity. The final solution was light amber, and had an inherent viscosity (0.5% in DMAC, 25°C) of 0.69 dl/g 28 hrs. after the initial PMDA addition. Films cast from it were brittle.

A film of the solution was cast on a CsI plate and infrared spectra of the sample were determined initially and after the following successive heating periods in a circulating air oven: 2 hrs, 150°C; 2 hrs, 300°C; 3 hrs, 350°C; 1 hr, 400°C. The resulting spectra are shown in Fig. 4.

A cured film of TRAB-PMDA, about 0.3 mil thick, was obtained from Dr. V. L. Bell (NASA Langley). Spectra of this free film, as received and after baking 3 hrs. at 300°C, were also run, and are included for comparison.

Reaction of PMDA and DAA in THF. - A mixture of 8.260 g. (0.05 mole) of purified DAA (D92-118-11) and 200 ml. of THF (dried over calcium hydride) was stirred while a solution of 10.9065 g. (0.05 mole) of PMDA (recrystallized from acetone) in 125 ml. of THF was added rapidly. Unexpectedly, the DAA turned out to be almost insoluble in THF. The addition of the PMDA solution produced a brown color, which gradually faded to yellow. After stirring for 45 min. at room temperature the mixture was a yellow solution containing a small amount of white precipitate. It was refluxed for 3 hrs., with no change in appearance. About 2/3 of the solvent was distilled off, and the residue cooled and filtered. The solid product was dried at 100°C under vacuum to give 6.5 g. of yellow, granular material (D92-119-4). The filtrate was evaporated to near dryness at room temperature in a stream of nitrogen. The sticky residue was dried for 16 hrs. at 100°C under vacuum. A dry foam was obtained, which was ground to a powder and dried for 7 hrs. at 100°C under vacuum to give 13.4 g. of yellow powder (D92-120-1). The precipitated product (D92-119-4) was found to consist of a mixture of yellow powder and pale tan translucent particles. A quantity of the latter were separated mechanically under a microscope and analyzed by DTA. A single sharp endotherm at 158°C, corresponding to the melting point, indicates that this material is probably DAA, and that the reaction was incomplete. The yellow powder (D92-120-1) obtained by evaporating

the filtrate appears to be a low polymer with anhydride endgroups. The inherent viscosity in DMAC at 28°C was 0.044 dl/g, and the IR spectrum showed strong anhydride absorption peaks at 1860 and 910 cm^{-1}. Strong imide bands were also present at 1790, 1715, 1370, and 710 cm^{-1}. Apparently refluxing in THF, followed by drying at 100°C, converted most of the amic acid to imide in this case. Elemental analysis corresponded roughly to $PMDA_{3.74}$ - DAA (imidized). Calc. for $C_{45.4}H_{14.5}N_3O_{21.4}$: C, 57.6; H, 1.55; N, 4.45. Found: C, 57.30, 57.27; H, 3.00, 3.08; N, 4.48, 4.41. Apparently a considerable amount of free PMDA is mixed with a condensation product of very low molecular weight.

A TGA curve was run on D92-120-1 in nitrogen at 2.5°C/min. This experiment was done before the elemental analysis and infrared spectra were received, and was intended to show weight-loss plateaus corresponding to the loss of water and acetic acid from the polymer. In view of the apparently heterogeneous and non-polymeric nature of the sample, the results are not very significant, but it is interesting that the sample did not sublime, as might have been expected. The weight loss occurred in four fairly well-defined steps, with minimum slopes as follows:

Temp., °C	Wt. Loss, %
220	14
360	32
470	41
750	70

It seems likely that the first step may be simply loss of adsorbed water and THF. Loss of acetic acid should give a loss of about 6.4% of the initial weight. This may be the chief process occurring from 360 to 470°C.

Reaction of BTDA and DAA in DMAC. - An equimolar amount of BTDA was added to a solution of DAA in DMAC. At 20% solids a viscosity of "U" (6.27 poises) was obtained. Films of this polymer prepared in aluminum dishes are very brittle after treatment up to 150°C, and crack spontaneously upon cooling. When baked out to higher temperature they become less brittle, but blister very badly, indicating loss of volatile material. On further heating above 300°C they become darker and redder but do not develop the deep red color of a DAB-BTDA pyrrone polymer cured in a similar manner.

Preparation of DATADPO

Nitration of 4,4'-diacetamidodiphenyl ether. - To a slurry prepared from 40 g. (.13 mole) of 4,4'-diacetamidodiphenyl ether and 200 ml. acetic acid was added a solution composed of 50 ml. of acetic acid and 50 ml. of fuming nitric acid. The temperature rose from 25° to 65°. On cooling a heavy precipitate formed, which stopped the stirrer. Water and ice were added. The yellow precipitate was collected and dried. Yield, 52 g.; m.p. 213-215°C. A sample recrystallized from DMAC had a m.p. of 214-215°C.

Acetylation of 3,3'-dinitro - 4,4'-oxydianiline. - Five g. of 3,3'-dinitro - 4,4'-oxydianiline obtained from Dr. Bell of NASA was dissolved in 100 ml. of warm acetic anhydride. A drop of concentrated

sulfuric acid was added. A yellow precipitate separated almost immediately. The excess acetic anhydride was decomposed with water and the solid was collected and dried. A yield of 5.9 g., m.p. 202-204°C was obtained. Apparently this is less pure than the product obtained by nitration of 4,4'-diacetamidodiphenyl ether.

Purification of 3,3'-dinitro-4,4'-diacetamidodiphenyl ether. - Small samples of 4,4'-diacetamido-3,3'-dinitrodiphenyl ether were recrystallized from 5 different solvents. Acetic acid, butyrolactone, cyclohexanone, butanone-DMAC, and Cellosolve-DMAC were used. All of these recrystallizations raised the melting point of the material from around 214° to 215°C or slightly better. The material recrystallized from Cellosolve-DMAC gave the highest endotherm at about 217°C. However it had a second, smaller endotherm at 204°C, which persisted on further drying (4 hrs. at 150°C under vacuum).

Multiple recrystallizations did not raise the melting points. Several of the systems were scaled up.

Fifty g. of 4,4'-diacetamido-3,3'-dinitrodiphenyl ether (Batch D35-156-1) was dissolved in a mixture of 1000 ml. of Cellosolve and 100 ml. of DMAC at reflux, treated with charcoal and filtered. After cooling, filtering and drying 42 g. product was obtained, which was dissolved in 600 ml. of hot acetic acid. After treatment with charcoal, filtering, cooling, refiltering and drying, 36 g. of product was obtained. Another batch was recrystallized twice from acetic acid. A third batch was recrystallized first from acetic acid and then from Cellosolve-DMAC. All of these products gave essentially the same results on hydrogenation.

Hydrogenation of 4,4'-diacetamido-3,3'-dinitrodiphenyl ether. - Hydrogenation was performed in a Parr shaker apparatus at 50-70°C. Several runs were made with different proportions of dinitro compound to solvent. Solvents used were methanol and absolute ethanol. About 0.2 g. of 5% Pd-on-C catalyst was used in each run except D35-83-2, in which 1 g. catalyst was used. Results were as follows.

Run No.	g. Dinitro Compound	Solvent	Yield, g.	DTA Behavior*
D35-81-2	10	150 ml. EtOH	5.1	Endo 165° weak 185° very weak 229° strong, sharp Exo 190° medium
D35-82-2	20	200 ml. EtOH	7.2	Endo 186° medium 225° medium Exo 190° strong
D35-82-3	10	150 ml. MeOH	2.6	Endo 184° very weak 229° strong, sharp Exo 190° medium
D35-83-1	15	200 ml. MeOH	8.5	Endo 192° very weak 230° strong, sharp Exo 195° weak
D35-83-2	20	200 ml. MeOH	10.1	Endo 193° very weak 232° strong, sharp Exo 195° very weak

*duPont 900 DTA apparatus, heating rate 20°/min for D35-81-2, D35-83-1, and D35-83-2; 50°/min for D35-82-2, D35-82-3.

The DTA curves suggest that partial conversion to the benzimidazole occurred in the hydrogenation and separation steps. Elemental analyses were obtained for two of the products. D35-82-2 (hydrogenated in ethanol) was believed to be mostly in the acetamido form. D32-83-2 (hydrogenated in methanol) was believed to be mostly in the benzimidazole form.

Analysis, %	C	H	N
D35-82-2	60.93, 60.91	5.85, 5.71	17.85, 17.62
D35-83-2	61.05, 61.28	5.81, 5.86	17.75, 17.99
Calc. for $C_{16}H_{18}N_4O_3$ (acetamido)	61.62	5.70	17.60
Calc. for $C_{16}H_{14}N_4O$ (benzimidazole)	69.10	5.08	20.12

It is apparent that both samples are essentially pure 4,4'-diacetamido-3,3'-oxydianiline. Additional evidence is supplied by spectral analyses. Infrared spectra of the two samples were identical. N-H stretching bands were found at 3260 and 3420 cm^{-1}, which are typical of amino and acetamido groups. The benzimidazole N-H, on the other hand, absorbs below 3150 cm^{-1}, as shown by spectra of 5-ethoxybenzimidazole (Sadtler #25,484) and 2-methylbenzimidazole (Sadtler #11,516). An NMR spectrum of D35-83-2 in dimethyl sulfoxide showed six types of protons, two of which were eliminated by deuteration with D_2O. These results are also consistent with the acetamido amine structure, whereas the benzimidazole structure would require five types of protons, only one of which would be deuterated.

There can be no doubt that both samples, in spite of differences in their DTA curves, are essentially pure 4,4'-diacetamido-3,3'-oxydianiline.

Further purification was carried out, however. A 20 g. portion of the product was dissolved in 700 ml. of methanol at 40°C. The solution was stirred with 30 g. of charcoal and filtered warm. On cooling, a precipitate formed, which was filtered off and dried at 60°C under vacuum to give 8 g. of a white solid (D35-110-1), m.p. 222-5°C. This material did not appear noticeably better.

Polymers from DATADPO

DATADPO and BTDA. - A solution of 6.28 g. (.020 mole) of D35-110-1 in 36 g. of DMAC was stirred while 5.0 g. of BTDA was added. When solution was complete, additional BTDA was added in small increments until a total of 6.7 g. (.021 mole) had been added. The viscosity rose after each addition, and the final solution had a viscosity of about 500 cstk at 25% solids.

Similar preparations in other solvents gave the viscosities shown in Table I.

DATADPO and PMDA. - This polymer was prepared by the preceding procedure and also in THF, as follows.

A mixture (partial solution) of 15.717 g. (0.05 mole) of DATADPO and 250 ml. of THF (dried over calcium hydride) was refluxed in flame-dried apparatus under dry nitrogen while a solution of 10.9065 g. (0.05 mole) of PMDA in 125 ml. of THF was added rapidly. The mixture was refluxed for four hours, during which time the undissolved solid became more finely divided and bulky. After cooling to room temperature the mixture was filtered, and the solid product was dried for 20 hrs. at 100°C under vacuum to give a pale yellow powder (D92-121-2) weighing

26.1 g. (98% yield, if in the amide acid form). The inherent viscosity (0.5% in DMAC, 28°C) was 0.092 dl/g. Elemental analysis agrees reasonably well with values calculated for DATADPO-PMDA (amide acid). Calc. for $C_{26}H_{20}O_9N_4$:C, 58.66; H, 3.79; N, 10.52. Found: C, 58.43, 58.60; H, 4.10, 4.19; N, 9.60, 9.68.

Film casting attempts. - Films cast on aluminum dishes, glass, and copper foil adhered very strongly to the substrate. In only one example was a creasable film obtained. This was a small sample cast on an aluminum dish and removed by soaking in water. The film could not be removed from the glass except in shreds. The samples on copper foil blistered in spite of a very cautious cure cycle. When the copper was removed by dissolving in ferric chloride the film was in shreds.

Additional film casting experiments were done, using a 25% solids solution, which was spread on matte-finished aluminum plates. Cure schedules and results were as follows.

D92-97-2: 2 hrs/100°C + 17 hrs/175°C + 24 hrs/200°C + 5 hrs/225°C + 1 hr/300°C. The product was dark red-brown, clear, adherent, glossy. It cracked spontaneously into many pieces. Individual fragments were moderately flexible.

D92-97-3: 19 hrs/100°C + 24 hrs/200°C + 5 hrs/225°C + 1 hr/300°C. The product was red-brown, opaque, with many fine cracks. It was very fragile.

D92-97-5: 19 hrs/25°C; peeled from substrate; 1 hr/100°C (vac.) + 23 hrs/200°C + 5 hrs/225°C + 1 hr/300°C. The product was a dark red-brown film which had melted and adhered very strongly to the glass dish during the 200° bake. Areas that had not stuck were moderately flexible.

D97-99-2: 24 hrs/25°C; peeled from substrate; 20 hrs/25°C (vac.) + 3.5 hrs/150°C + 1 hr/300°C. The product was a light brown mass of bubbles. It had melted and adhered strongly to the glass dish during the 300° bake. Fairly tough.

D97-99-3: 24 hrs/25°C; peeled from substrate; 20 hrs/25°C (vac.) + 3.5 hrs/225°C + 1 hr/300°C. The product was dark red-brown, with a rough surface, but little bubbling. It adhered to the glass dish and was rather weak.

D97-99-5: 24 hrs/25°C; peeled from substrate; 20 hrs/25°C (vac.); soaked 30 min. in 80:20 acetic anhydride-pyridine; 3 hrs/150°C + 1 hr/300°C. The product was light brown, curled, bubbly, fairly strong.

D97-99-6: 24 hrs/25°C; peeled from substrate; 20 hrs/25°C (vac.); soaked 30 min. in 80:20 acetic anhydride-pyridine; 3 hrs/225°C + 1 hr/300°C. The product was dark red-brown, rough surface, few bubbles, weak.

The films which were peeled from the substrate after 24 hrs of air-drying were clear, pale yellow, and very flexible. When these films were baked, even at 100°C (vac.) for one hour, or imidized at room temperature with acetic anhydride-pyridine, they became very brittle. Some improvement in strength occurred after the 300°C bake, but none of the films remained intact that long.

Laminate preparation. - A polymer solution was prepared from 51 g. diacetyl TADPO, 310 g. DMAC, and 52.4 g. BTDA (D35-138-1). This solution was used to impregnate glass cloth (E glass, 181-A1100, soft finish). This cloth was placed in a cold oven which was then warmed to 180° and kept there for 30 min. The cloth was cut into 7" squares, and 12 sheets were stacked and pressed between 6" square platens at 300-330°C and 500 psi

for 30 min. Around all four sides were large portions of foamed resin, indicating good flow and also evolution of volatiles. The laminate was dark brown, glossy, well-filled, and gave a good ring when struck. In a second preparation, the final precure temperature was raised from 180° to 210°C. This resulted in a prepeg that was quite brittle and flaky. The amount of squeeze-out on pressing was still high, but apparently less than before because the finished laminate was thicker. In a third preparation, the treated cloth was cured by raising the temperature over a 30 min. period to 210°C and holding the temperature for 10 minutes. The cloth contained 45% resin and was flaky and brittle.

Sixteen sheets were put in a press, preheated to 200°C. Initial pressure was 55 psi. In ten minutes the press temperature was raised to 240°C, and slight beading of resin was observed at the edges. The pressure was increased to 110 psi and at 250°C considerable flow occurred.

After flow had stopped the pressure was increased to 500 psi and temperature to 300°C. These conditions were held for 30 minutes. Flexural strength and modulus values for the three laminates are given in Table II.

TGA results. - A film of DATADPO-BTDA solution in DMAC in an aluminum dish was baked at 180°C for about 2 hours. The crumbly film obtained was ground into a powder, and a TGA curve was run at 5°C/min in air. Figure 2 shows the result. The polymer began to lose weight almost immediately, and at 500°C had lost about 35% of its initial weight. The weight loss then became faster, with 90% being gone by 565°.

If the polymer were completely solvent free and completely in the acetamido-imide form, the loss of acetic acid and conversion to pyrrone would give a 20% weight loss. It was hoped than an inflection in the TGA curve would occur at about that value. Rather poorly resolved minima in slope occurred at 17% and at about 29% loss, but it is apparent that solvent loss, acetic acid loss and thermal degradation of the polymer occurred in an overlapping sequence that prevented an effective resolution of the processes.

A TGA curve was determined in nitrogen at 2.5°C/min for the DATADPO-PMDA sample prepared in THF. The results are shown in Fig. 3. An initial loss of about 1.4% (0.28 mg) was apparently due to mechanical loss or to an instrumental problem. This amount was subtracted from the recorded loss values to get the corrected weight losses.

Preparation of DADAB

In Run D92-76-3, 27.4 g. (0.1 mole) of 3,3'-dinitrobenzidine (Burdick and Jackson) was refluxed in 650 ml. of acetic anhydride for one hour. The solid changed from dark red to yellow but did not dissolve. The mixture was cooled and filtered to give a solid product, which was recrystallized from 500 ml. of DMAC to give 8.3 g. of a dark yellow powder (D92-77-1). The mother liquor was diluted with 1,000 ml. of water. The resulting precipitate was dried to give 20.1 g. of a product which gave sharp DTA endotherms at 196 and 324°C. This material was extracted with boiling acetic anhydride to give a solution (D92-77-3) and a solid residue. The residue was boiled for 30 min. with 100 ml. of acetic anhydride containing a drop of concentrated sulfuric acid. A clear solution was obtained from which crystals separated on cooling.

They were filtered off, washed and dried to give 1.75 g. of solid product (D92-79-4).

The acetic anhydride extract, D92-77-3, was cooled, giving a precipitate, which was filtered off and dried to give 0.77 g. of solids (D92-79-2). The filtrate was boiled down in a stream of nitrogen and cooled. The resulting crystals were filtered off, washed and dried to give 10.35 g. of bright yellow powder (D92-79-3). The mother liquor was boiled down further, mixed with that from D92-79-4, and diluted with water. A precipitate formed, which was filtered off and dried to give 6.95 g. of yellow-gray powder (D92-79-5).

A summary of the products obtained in this run, together with their DTA behavior follows.

Product No.	Wt., g.	DTA* Endotherms, °C
D92-77-1	8.30	330 (sharp, strong)
D92-79-4	1.75	231 (sharp) ca 330 (broad)
D92-79-2	0.77	217 (sharp, medium) 238 (sharp, strong)
D92-79-3	10.35	204 (sharp, strong) ca 330 (broad, weak)
D92-79-5	6.95	199 (fairly sharp, medium) 228 (fairly sharp, medium)

* duPont 900 DTA apparatus, heating rate 20°C/min.

A sample of D92-77-1 was recrystallized from DMF to give a dark yellow product, m.p. 330°C. The IR spectrum shows a single carbonyl peak at 1705 cm^{-1}, indicating a single acetamido group. A sample of D92-79-3 was recrystallized from acetic anhydride. A bright yellow product was obtained, m.p. 217°C. The IR spectrum has a doublet at 1700-1720 cm^{-1}, indicating the presence of two acetamido groups.

Analysis, %	C	H	N	O	Total
D92-80-9 (recrystallized D92-77-1)	53.74	4.10	15.63	26.89	100.36
	53.60	4.01	15.66	26.75	100.02
Calc. for $C_{16}H_{14}O_6N_4$	53.7	3.94	15.66	26.8	--
D92-80-7 (recrystallized D92-79-3)	54.17	4.25	13.63	27.90	99.95
	54.10	4.19	13.64	27.97	99.90
Calc. for $C_{18}H_{16}N_4O_7$	54.0	4.03	14.00	28.0	--

Another run was made as follows. A mixture of 23.7 g. (.0865 mole) of 3,3'-dinitrobenzidine, 500 ml. of acetic anhydride, and one drop of concentrated sulfuric acid was refluxed for two hours. During the heating a clear solution was obtained for a short time, followed by precipitation. After the reflux period, 180 ml. of distillate was removed, after which the pot residue was cooled to 15°C and filtered. The solid product was washed with acetic acid and dried at 130°C under vacuum, to give 23.5 g. (76% yield) of 3,3'-dinitro-N,N'-diacetylbenzidine, m.p. (DTA) 328°C. An additional 2.5 g. of crude material (endotherms at 215, 238, 322°C) was recovered from the filtrate.

Later in the program, an 8 lb. sample of 3,3'-dinitro-N,N'-diacetylbenzidine was obtained from American Aniline. The material was rather impure, and so several solvents were tested for recrystallization.

The following dissolved less than 1% of the compound at their boiling points: xylene, ethanol, acetone, 2-ethoxyethanol, and acetic acid. DMF, DMAC, DMSO, and NMP all dissolved about 8% at 150°C. Of these, DMF appeared slightly the best, giving a 58% recovery of a bright yellow product, m.p. 320-3°C.

Five 150 g. batches of 3,3'-dinitro-N,N'-diacetylbenzidine (American Aniline) were recrystallized, using 1800 ml. of DMF for each batch. The products were washed with water and with acetone and were dried at 100°C in vacuum to give 301 g. of light yellow powder, melting sharply at 329°C. This material was hydrogenated in 16 batches, using about 20 g. per batch, together with 200 ml. of DMF and 2 g. of 5% Pd-on-C catalyst. A pressure of 40-50 psi and a temperature of 50-70°C were used. The product in each case was filtered while warm, and the filtrate mixed with 250 ml. of water. After standing overnight in a refrigerator, the mixture was filtered and the solid product washed with water followed by acetone, and dried at 100°C under vacuum. The combined hydrogenated product weighed 206.5 g. (83% yield).

This compound (DADAB) has surprising low solubility in common solvents. The following rough tests of solubility were made as a guide for recrystallization:

	25°C	80°C
Acetic acid	<10%	20%
DMAC	<10%	<10%
DMF	<10%	>10%
NMP	<10%	<10%
DMSO	23%	---
Hexamethylphosphoramide	<10%	>10%
Pyridine	<10%	<10%

The following experiments were run to explore methods of purification of DADAB.

Crude DADAB (2.0 g.) was dissolved in 9.2 g. of warm DMF. After cooling overnight, the mixture was filtered. The solid was washed with water and with acetone and was air-dried to give 1.2 g. of pale yellow crystals.

Crude DADAB (1.00 g.) was dissolved in 3.50 g. of DMSO. The solution was mixed with 3.50 g. of water, cooled to room temperature, and filtered. The solid was washed with water and with acetone and dried at 100°C under vacuum to give 0.97 g. of product. The procedure was repeated two more times, using different quantities of water, with the following results.

DMSO - H_2O Mixture			DADAB		Solubility, %
DMSO, g.	H_2O, g.	% DMSO	Initial, g.	Recovered, g.	
3.50	3.50	50	1.00	0.97	0.4
3.50	1.00	78	1.00	0.90	2.2
3.50	0.50	87	1.00	0.68	7.4

A solution of 1.00 g. of crude DADAB in 4 g. of DMSO was passed through a 1 x 25 cm. column of adsorption alumina (dried at 300°C). Additional DMSO was used to wash the product through the column. Five successive fractions of eluate were collected. Each was diluted with twice its volume of water, cooled to room temperature, and filtered. The solid products were washed with water and with acetone and were dried for 2 hrs. at 90°C under vacuum. Results are shown below. At the

top of the column was a layer of black powder (catalyst) and a greenish sludge. The three fractions obtained were pale yellow powders.

Fraction No.	Volume, ml.	Product, g.	Conc., g./ml.
D92-107-1	5.0	0.34	.068
" " 2	7.0	0.27	.039
" " 3	7.0	0.07	.01
" " 4	10.0	0	0
" " 5	20.0	0	0

A solution of 1.00 g. of crude DADAB in 4 g. of DMSO was mixed with 0.5 g. of decolorizing charcoal (Norit-A). After standing for five hours the mixture was filtered, giving a brown filtrate. It was not worked up further, since the alumina treatment gave a much better looking product. A solution of 205 g. of the crude hydrogenation product in 800 g. of DMSO was allowed to flow through a 1 3/4" x 22" column of adsorption alumina (activated by heating overnight at 325°C). Additional DMSO was added immediately thereafter, and the column was kept filled with liquid as long as product was being collected. The first 1800 ml. of solution to come through was diluted with 3600 ml. of water and allowed to stand overnight in the refrigerator. The resulting precipitate was filtered off, washed with water and with acetone, and dried at 100°C under vacuum to give 175 g. of pale yellow powder (sharp DTA endotherms at 263 and 348°C). A second fraction of 700 ml. was collected and worked up similarly. It yielded only 5 g. of inferior r terial.

A DTA curve (20°/min) showed a sharp endotherm at 260°C followed by an exotherm peaking at 290° and a sharp endotherm at 349°C. Visually, a sample put in a block at 250° and heated at 3°/min. melted sharply at 255°, changed to a red solid at about 265° and then became so dark that the second melting point could not be seen. Apparently the compound melts at 255-260 and then dehydrates to the benzimidazole (eq. 11), the latter melting at 344°C. The IR spectrum of the unheated compound shows carbonyl peaks at 1585 and 1650 cm^{-1}, corresponding to the two acetamido groups. Anal. Calc. for $C_{16}H_{18}O_2N_4$: C, 64.41; H, 6.08; N, 18.78. Found: C, 64.19, 64.40; H, 6.06, 6.18; N, 18.79, 18.55.

Polymers from DADAB

DADAB and BTDA. - A slurry was made of 0.5454 g. (1.828 mmoles) of DADAB and 4.54 g. of DMAC (dried over 4A Molecular Sieve), in which it is only slightly soluble at room temperature. BTDA (recrystallized from acetone) was added in portions, with stirring, until 0.5888 g. (1.828 mmoles) had been added. A clear yellow solution of 20% solids was obtained. Inherent viscosity in DMAC (0.5% solution, 25°C) was 0.28 dl/g. A thin film cast from the 20% solution by baking for 2 hrs. at 165°C was clear yellow, very brittle and cracked. An additional 30 min. at 300°C gave a red-brown color and some small blisters. Eighteen hrs. at 300° gave a nearly black crumbly product.

DADAB and PMDA. - D92-123-5. A mixture of 29.835 g. (0.1 mole) of DADAB and 207 ml. of dry DMAC was stirred under dry nitrogen while 21.813 g. (0.1 mole) of PMDA was added in about 10 min. A somewhat exothermic reaction occurred, giving a very cloudy orange solution

(D92-124-1) weighing 239.8 g. (21.54% solids). Apparently, both DADAB itself and the resulting polymer are only partly soluble in DMAC. It was found necessary to dilute a sample of D92-124-1 with DMAC to 1% or less in order to get a clear solution. The inherent viscosity (0.5%, 26°C) in DMAC was found to be 0.32 dl/g. Dilution of D92-124-1 with an equal volume of DMF or DMSO (about 11% solids) gave a clear solution, but dilution with NMP did not give a clear solution even at 7% solids. A film cast from D92-124-1 was very fragile and crumbled easily.

D92-126-1. Since D92-124-1 was soluble in DMSO, the same polymer was prepared in DMSO (dried over 5 A Molecular Sieve, using the same quantities of reactants and procedure as in D92-123-5. A clear viscous solution was obtained. Increments of PMDA solution (0.5 ml. of solution containing 0.1 g. PMDA/ml.) in DMSO were added to the resulting solution. Three such increments were added. The first gave a slight increase in viscosity. The second gave no change. The third gave a slight decrease. The product was a clear amber solution (D92-126-2) weighing 275 g. (18.84% solids). Inherent viscosity (0.5%, 28°C) in DMSO was 0.56 dl/g. A film cast from it was brittle. On standing overnight at room temperature, D92-126-2 became cloudy. A few days later it was an opaque, grease-like material that would not pour. Warming to 100°C did not liquefy it.

A sample of the product in DMSO was diluted to 4% solids with DMSO. It remained cloudy. Dilution to 4.5% solids with either DMF or DMAC gave cloudy solutions which became clear within an hour. On the basis of the mixed solvent tests a DMF-DMAC mixture was chosen for the next preparation of DADAB-PMDA.

D92-138-1. All apparatus was dried overnight at 250°C and allowed to cool in dry nitrogen. A mixture of 29.835 g. (0.1 mole) of DADAB, 100 ml. of DMF and 100 ml. of DMAC (both dried over 5A Molecular Sieve) was stirred while 20.000 g. (0.0917 mole) of PMDA was added. A very cloudy mixture of moderate viscosity was obtained. The intention was to add the remainder of the required PMDA slowly in solution until maximum viscosity was reached. However, when the solution did not become clear after three days of stirring, additional experiments with solvent mixtures were carried out (described below), which suggested that more DMAC was needed. Accordingly, 200 ml. of DMAC was added (about 11% solids). After two days of stirring the mixture was still very cloudy.

D92-138-5. A mixture of 14.9175 g. (0.05 mole) of DADAB and 10.906 g. (0.05 mole) of PMDA was ground under dry nitrogen to a fine powder and thoroughly blended. Two gram samples of the powder were mixed with 8.00 g. quantities of various solvent mixtures. Observations on the resulting mixtures are summarized in Table VI. Apparently DMAC is the best solvent after all, but there was some confusing time-dependent behavior, and none of the systems gave a stable 20% solution.

Several preparations of the type described were filtered. The precipitates were washed several times with the solvent used in the preparation and several times with tetrahydrofuran, and were dried under vacuum at 45°C. The amount of polymer left in solution was calculated from TGA data on the filtrate (% residue after heating to 400°C at 10°C/min.), by difference, or by precipitation with acetone and weighing. Results are summarized in Table VII.

Table VI - Preparation of DADAB-PMDA in Solvent Mixtures

Solvent Composition, %			Appearance of 20% Solution of DADAB-PMDA	
DMF	DMAC	DMSO	2 hours	18 hours
75	25	0	Very cloudy	A
50	50	0	Cloudy	A
25	75	0	Clear	D
0	25	75	Very cloudy	A
0	50	50	Very cloudy	C
0	75	25	Clear	C
25	0	75	Very cloudy	A
50	0	50	Very cloudy	C
75	0	25	Very cloudy	B
0	100	0	Clear	D
0	0	100	Initially clear; cloudy in 1 hr.	A
12.5	75	12.5	Moderately cloudy	C
37.5	62.5	0	Cloudy	C

A - Opaque, no flow.

B - Opaque, partial flow.

C - Opaque, fairly easy flow.

D - Clear orange liquid and small particles, which appear crystalline.

Table VII - Partial Precipitation of DADAB-PMDA Solutions

Run No.	Solvent	% Solids	Aging, Hrs.	Polymer Solids				
				Total,[a]	Insoluble[b]		Soluble[c]	
				g.	g.	%	g.	%
D92-141-3	DMAC	3	265	0.75	trace	0	0.75	100
D92-141-4	DMAC	6	265	1.50	<0.1	<7.0	>1.4	>93
D92-141-5	DMAC	12	265	3.00	0.23	7.7	2.77	92.3
D92-141-6	DMAC	24	265	6.00	0.69	11.5	5.31	88.5
D92-141-7	DMAC	30	267	7.70	0.73	9.5	6.97	90.5
D92-139-11	DMAC	25	220	2.00	0.30	15.0	1.70	85.0
D92-123-5	DMAC	21.5	1370	--	6.65	15.5 14.3	36.4[d] 39.8[e]	84.5 85.7
D92-141-8	DMF + 3 DMAC	11	480	51.6	2.55	4.9	49.0	95.1
D92-126-1	DMSO	18.8	1320	--	8.00	20.1	31.7[d]	89.9

a Total weight of PMDA + DADAB used. Corresponds to weight of amic acid form of polymer. In two cases an unknown portion of the original solution was used, so this value was not known.

b Precipitate washed with THF, dried at 45°C under vacuum. Polymer in amic acid form.

c By difference, except as noted below.

d Calculated for amic acid form from TGA data (to 400°C at 10°/min.), assuming TGA residue to be imide.

e Precipitated with acetone, washed with acetone, dried at 45°C under vacuum.

Batches D92-141-3 to 7 were prepared at the same time, from the same batch of dry-mixed reactants. A clear solution was obtained in each case. The 24 and 30% solutions precipitated about two hours after preparation. Fifteen hours after preparation, the other three clear solutions were seeded with a trace of solid from the first two. Precipitation occurred slowly over a period of several hours. The amount of precipitate was substantial for the 12% solution, small for the 6% solution, and a trace for the 3% solution. The amount of precipitate in the 6% solution was not measured, but estimated visually to be considerably less than half that of the 12% solution.

A 51.3 g. sample of the clear solution obtained by filtration of the product from D92-123-5 was added, with stirring, to 500 ml. of acetone. The mixture was allowed to stand for 2 hrs., and filtered. The precipitated polymer was washed with acetone and dried for 24 hrs. at 45°C under vacuum to give 11.5 g. of pale yellow powder.

Analyses of various DADAB-PMDA precipitates were made, with the results shown in Table VIII.

The soluble and insoluble fractions from D92-123-5 were studied further. Samples of each were heated for 2 hrs. at 150°C, 300°C, 350°C, and 400°C (not successively). The 150° and 300° bakes were in ovens in air. The 350° and 400° samples were heated in nitrogen in a TGA apparatus from 25° to temperature at 10°C/min. and then held at temperature for 2 hrs. Observed weight losses were:

	% Weight Loss	
	350°C	400°C
Soluble fraction	32	37
Insoluble fraction	23	31

Table VIII - Analysis of DADAB-PMDA Polymer Precipitates

Run No.	Analysis of precipitate (%). Average of two determinations.				
	C	H	N	O	S
D92-141-5	59.66	4.57	9.17	26.48	--
D92-141-6	57.92	4.81	9.82	27.77	--
D92-139-11	56.92	4.28	9.88	--	--
D92-141-8	57.88	4.78	9.68	27.41	--
D92-123-5 (soluble fraction)	58.12	4.87	11.31	25.81	--
D92-123-5 (insoluble fraction)	59.10	4.74	9.85	26.21	--
D92-126-1	54.56	4.65	8.44	24.70	7.56
Calc.[a] for					
DADAB-PMDA·1.5 DMSO	55.0	4.62	8.84	24.0	7.58
DADAB-PMDA·DMAC·H_2O	58.0	5.03	11.27	25.75	--
DADAB-PMDA	60.5	3.91	10.85	24.8	--

a Amide acid form of polymer

Another sample was heated in nitrogen at 10°C/min. to 750°C, with a weight loss of 51%. The nine samples obtained were pressed in KBr discs, and infrared spectra were run.

Another sample of the soluble fraction was sealed in a vacuum apparatus and heated. Volatile products were allowed to distil into a trap cooled in liquid nitrogen. Weight loss was measured periodically, and the volatiles were analyzed qualitatively by infrared. The results were as follows:

Time, hrs. (a)	Temp., °C (a)	Wt. loss, % (b)	Volatile Products
2.2	105	7.8	H_2O, DMAC
2.0	150	5.0	" "
2.0	300-309	8.8	H_2O, CO_2, aliphatic acetate
2.0	350-353	5.6	acetic acid, acetic anhydride, H_2O

(a) Successive heating of same sample.

(b) Based on original sample weight.

DATAB Preparation and Polymer

The acetylation of m-phenylene diamine with acetic anhydride went easily in good yield to give 1,3-diacetamidobenzene (DAMPD) m.p. 187-190°.

Several nitration procedures were tried using different combinations of acetic acid, acetic anhydride and fuming nitric acid. For example, 100 g. of DAMPD was slurried with 200 ml. of acetic anhydride and cooled to -10°C in an ice-salt bath. A solution containing 60 ml. fuming nitric acid and 60 ml. acetic anhydride was added slowly. When the

mixture became too pasty to stir a mixture of acetic acid and acetic anhydride was added. After about an hour the mixture was poured into 4 l. of ice and water. Yield of dried solid was 105 g. After recrystallization from glacial acetic acid, 85 g. of light yellow solid was obtained. The melting point (DTA endotherm) of 248°C indicated that the material was probably 4-nitro-1,3-diacetamidobenzene (m.p. 246°C, Beilstein 13, 57) rather than the dinitro compound (m.p. 228°, Beilstein 13, 59). In addition, upon hydrogenation of the product, the amount of hydrogen absorbed corresponded roughly to only one nitro group.

A nitrating solution was prepared by adding 155 ml. of 71% HNO_3 to 900 ml. of acetic anhydride, with cooling (temp. below 25°C). The solution was stirred and kept below 25°C while 144 g. (0.75 mole) of DAMPD was added slowly. As a precipitate separated 1200 ml. of acetic acid was added to facilitate stirring. The precipitate was collected on the filter, washed with acetic acid and dried in a vacuum oven at 110°. Yield was 126 g. of product with a melting point of 247-248°C.

A solution of 500 g. of fuming HNO_3 (90% HNO_3) and 20 g. of urea nitrate was cooled to -5°C. One hundred g. of DAMPD was added at such a rate that the temperature did not rise above 5°. After an additional 20 minutes the dark red solution was poured into 3 l. of ice and water. The light yellow precipitate was collected on the filter and dried in a vacuum oven. Yield was 93 g., m.p. 225-235°C. A 5 g. sample was recrystallized from acetic acid to give 3.3 g. of a product of m.p. 247-248° and a 2nd crop of 0.4 g., m.p. 225-235°C.

Apparently the major part of the material is still the mononitro compound.

Ten g. of 1,3-diamino-4,6-dinitrobenzene (purchased from Burdick & Jackson) was placed in a flask with 50 ml. of acetic anhydride. The mixture was warmed with stirring to 90°C with no apparent reaction and without dissolving the solid. At this point 3 drops of sulfuric acid was added. The temperature rose rapidly to 110°C and the material dissolved. The temperature was further raised to 134°C for 15 minutes. On cooling, a precipitate separated, which was collected on the filter and dried. A yield of 9.8 g. of yellow solid, m.p. 197°, was obtained. The filtrate was treated with distilled water and the solid that separated was dried and filtered. This procedure gave a yield of 3 g. of yellow material, m.p. 145°C.

The less soluble product, m.p. 197°C, is believed to be the expected product 1,3-diacetamido-4,6-dinitrobenzene. The IR spectrum was inconclusive, but the relative intensity of NMR peaks in deuterated DMSO solution agrees perfectly with the expected structure. The elemental analysis also agrees well.

Anal. Calc. for $C_{10}H_{10}N_4O_6$: C, 42.56; H, 3.57; N, 19.86.
Found: C, 43.00, 42.90; H, 3.59, 3.63; N, 19.89, 19.92.

The more soluble product, m.p. 145°C, is apparently N,N,N'-triacetyl-1,3-diamino-4,6-dinitrobenzene. The relative intensity of 3 NMR proton peaks (1-1-1) and the elemental analysis are consistent with this structure.

Anal. Calc. for $C_{12}H_{12}N_4O_7$: C, 44.45; H, 3.73; N, 17.28.
Found: C, 43.91, 43.77; H, 3.63, 3.60; N, 17.69, 17.58.

A slurry composed of 10 g. of 1,3-diacetamido-4,6-dinitrobenzene, 0.2 g. 5% Pd-on-C, 50 ml. of DMAC, and 150 ml. of methanol was shaken in the Parr hydrogenation apparatus under an initial pressure of 57 psi.

After 33 min. with moderate heating the outside temperature was 65°C and the pressure had dropped to 40 psi. After cooling, the slurry was filtered. Most of the product was collected as a precipitate with the catalyst. After drying at 60°C under vacuum the mixture of catalyst and product weighed 6.4 g. From the filtrate an additional 0.8 g. of material was collected. The DTA gave a complex pattern. There was a slight endotherm at 185°C, a larger endotherm at 260°C, followed by an exotherm at 277°C. The material was still solid at this point. Melting was finally shown by an endotherm at 467°C. Hydrogenation in DMAC, using a greater relative amount took a much longer time and the product was still insoluble. Since excessive heating is ruled out by the danger of benzimidazole formation, purification is a real problem.

A polymer was prepared from 25 g. of DMAC, 4.44 g. (0.02 mole?) of the mixture of catalyst and DATAB and 6.44 g. (0.02 mole) of BTDA. A moderately viscous solution was obtained. It was diluted with 12 g. of DMAC and filtered to remove hydrogenation catalyst. Samples baked out in aluminum dishes gave very poor films.

Trimethylsilylation Reactions

Attempted Trimethylsilylation of 3,3'-Dinitrobenzidine (DNB). - A mixture of 2.74 g. (.01 mole) of DNB, 2.4 ml. of hexamethyldisilazane, one ml. of trimethylchlorosilane and 50 ml. of pyridine (dried over KOH) was allowed to stand for 3 hrs. at room temperature and was then boiled for 2 hrs. Evaporation to dryness in a stream of nitrogen gave a dark red solid, which was extracted successively with 75 ml. of boiling benzene and 75 ml. of boiling acetone. The residue was dissolved in 50 ml. of DMAC. A small sample of the solution was diluted with water to give a precipitate which was filtered off and dried to give 0.1 g. of orange solid. The remainder of the DMAC solution was evaporated to dryness in a stream of nitrogen. The residue was dried at 130°C in vacuum to give 1.79 g. of red powder (D92-76-6). The benzene extract was evaporated to dryness to give 0.30 g. of red powder (D92-75-6). The acetone extract similarly gave 0.38 g. of red powder (D92-75-7). All of the products gave essentially identical IR spectra. D92-75-7 gave a sharp endotherm at 277°C, corresponding to that for DNB.

Trimethylsilylation of DAB. - A mixture of 2.14 g. of DAB, 50 ml. of pyridine, 2.4 ml. of hexamethyldisilazane, and 1 ml. of trimethylchlorosilane was stirred for a few minutes, allowed to stand at room temperature for 48 hrs., and filtered. The filtrate was evaporated to dryness in a stream of nitrogen. The residue was dried at 75°C under vacuum to give 2.1 g. of brown solid, m.p. 167-170, apparently impure DAB.

A mixture of 2.14 g. of DAB and 50 ml. of pyridine was stirred while 2.6 ml. of trimethylchlorosilane was added slowly. The mixture became warm and a heavy yellow precipitate formed. After standing 48 hrs. at room temperature the product was filtered, and the filtrate evaporated to dryness to give only a trace of tarry product. Apparently the reaction product was not soluble in pyridine.

A mixture of 10.7 g. (.05 mole) of DAB and 250 ml. of pyridine (dried over KOH) was stirred while 13 ml. (0.10 mole) of trimethylchlorosilane was added slowly. The mixture became warm and a heavy yellow precipitate formed. After 72 hrs. at room temperature the solid product was filtered off and dried at 75°C under vacuum to give 13.1 g. (calc. 17.9 g.) of gray powder (D92-87-9). Evaporation of the filtrate gave 0.40 g. of a black powder, which was discarded. A DTA curve of D92-87-9 showed a small endotherm at 190°C, moderate ones at 267 and 309°, and a very deep and jagged one at about 348°C. Partial melting occurred at 267°, and complete melting with effervescence at 327°C.

The preceding procedure was repeated, using a 2.14 g. (.01 mole) of DAB, 50 ml. of pyridine, and 5.7 ml. (.044 mole) of trimethylchlorosilane. The dried precipitate was a tan powder (D92-87-10) weighing 3.08 g. (calc. 5.02 g.). Evaporation of the filtrate gave .09 g. of black powder. The DTA curve for D92-87-10 shows a single endotherm at 335°C. Melting occurred at 329-335°C, with decomposition. In an effort to obtain an analytical sample of higher purity, one gram of D92-87-10 was sublimed. After 2 hrs. at 150-180°C/0.1 mm a trace of yellow solid was obtained, DTA endotherm 74°C, probably $(CH_3)_3SiCl$ · pyridine.

Sublimation of the residue at 280°C/0.1 mm gave 0.76 g. of a gray powder (D92-92-2).

A solution of 10.7 g. (0.05 mole) of DAB in 107 ml. of pyridine (dried over KOH) was stirred while 28 ml. (0.22 mole) of trimethylchlorosilane was added slowly. The reaction mixture was blanketed with nitrogen throughout the run. A slightly exothermic reaction occurred, with formation of a heavy yellow precipitate. After the addition was complete, the mixture was refluxed for 9 hrs. and let stand at room temperature for about 85 hrs. The product was filtered, and the solids washed twice with pyridine and dried at 100°C under vacuum for 24 hrs. to give 12.3 g. of gray powder (D92-94-3).

DTA curves were determined for D92-94-3 and for related products obtained from the reaction of DAB with trimethylchlorosilane. The simplest curve was given by D92-87-10 (DAB + 4 Me_3SiCl, 25°), with a single strong endotherm at 335°C (m.p. 329-335°C, decomp.). A trace of an endotherm was also present at 265°C. Strangely, the product obtained by subliming D92-87-10 gave a very complex curve, with definite, reproducible endotherms at 175°C, 210°C, and 264°C; a very sharp exotherm at 85°C; a broader exotherm at 305°C; and endothermic decomposition above 305°C. There was no change in appearance below 260°C. Rapid darkening, shrinking, and partial melting occurred at 260-265°C, with complete melting at about 315°C.

D92-87-9 (DAB + 2 Me_3SiCl, 25°) gave a complex curve, with endotherms at 190°C, 267°C (darkening, shrinking, partial melting) and 309°C. Exotherms occurred at about 290°C and 325°C, with vigorous endothermic

decomposition above 325°C. Complete melting occurred at about 327°C. D92-94-3 (DAB + 4 Me_3SiCl, reflux) showed a strong endotherm at 262°C (m.p. 262-4°C), weak endotherms at 180°C (probably DAB) and 212°C, and the usual exo-endothermic behavior at 300-350°C, with vigorous decomposition.

The DTA curves are somewhat confusing, but an endotherm at about 265°C was common to all of them. Sample D92-94-3, which was prepared under the most severe conditions, showed no other strong endotherms below its decomposition temperature. It also melted rather sharply at 262-4°C, and seemed most likely to be a relatively pure silylated derivative. A sample was submitted for elemental analysis. The results indicate that it is slightly impure DAB·HCl.

Anal. Calc. for $C_{12}H_{15}N_4Cl$: C, 57.5; H, 6.03; N, 22.4; Cl, 14.14.
Found: C, 57.28, 57.13; H, 6.07, 5.95; N, 21.52, 21.70; Cl, 15.02, 15.06; Si, 0.29, 0.30.

Since the amount of D92-94-3 obtained represents a 98% yield, it is apparent that essentially no trimethylsilylation occurred. The other endotherms observed in some samples may be due to polyhydrochlorides or pyridine complexes.

Attempted Trimethylsilylation of 3,3'-dinitro-4,4'oxydianiline (DNODA). - A mixture of 5.8 g. (.020 mole) of DNODA (obtained from Dr. Bell, NASA) and 50 ml. of pyridine (dried over KOH) was stirred while 5.2 ml. (.040 mole) of trimethylchlorosilane was added. The mixture became warm and formed a clear dark red solution. On standing for 72 hrs. at room temperature the solution deposited large dark red crystals, which were filtered off and dried at 75°C under vacuum. The dried product was an

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Trimethylchlorosilane (2.6 ml.) was added to 10 ml. of pyridine. A white precipitate formed immediately. The mixture was allowed to stand overnight and was filtered. The solid product was dried at room temperature in a stream of nitrogen to give 0.3 g. of white powder (D92-90-7), m.p. 146-147°C.

DTA curves of D92-89-5, D92-89-6, and D92-90-7 were compared. Although the melting point (upper endotherm) of D92-89-5 is 8° lower than that of the authentic specimen D92-90-7, the difference may be due to a difference in purity. Both specimens show a sharp endotherm at 73°C, which is not accompanied by any visual change. The melting point and endotherm at 152°C shown by D92-89-6, agree well with the values observed for the product before sublimation and for the authentic specimen of $C_{17}H_{16}N_5O_5Cl$, D92-91-7.

Because of the tendency of pyridine to form complexes, it was decided to try other bases as HCl acceptors. A mixture of 5.8 g. (0.02 mole) of DNODA, 50 ml. of triethylamine, and 5.2 ml. (0.041 mole) of trimethylchlorosilane were refluxed with stirring for 4 hrs. The solid material did not dissolve, but gradually changed from dark red to tan. After standing overnight at room temperature the product was filtered. The solid product was washed with triethylamine and dried at 100°C under vacuum to give 7.9 g. of pink powder (D92-91-1). The filtrate was evaporated to dryness to give 1.1 g. of residue (D92-91-2). A sample of D92-91-1 was separated into five fractions by solvent extraction with benzene and butanone. Two of the fractions were identified as triethylamine hydrochloride by melting point (258°C), water solubility,

precipitation with silver nitrate, and production of triethylamine odor when made basic.

Two others were found to have the same analysis and DTA behavior and were combined. A one gram sample of this product was recrystallized from benzene to give 0.80 g. of fine dark red crystals (D92-102-2). A series of DTA curves for D92-102-2 were determined. When the sample was allowed to cool and then reheated twice in the DTA apparatus, a double peak at 123-128°C decreased in intensity and merged into a single broad peak. At the same time a peak at 174° moved up to 176°C. Another sample of D92-102-2 was dried for an additional 18 hrs. at 110°C. After this treatment, the peak at about 125°C disappeared entirely and the upper peak rose to 179°C, which is the melting point of DNODA. Apparently this fraction was a mixture of unreacted DNODA with a volatile silicon compound. Two likely possibilities are diethylaminotrimethylsilane, b.p. 126.3°C, and hexamethyldisilazane, b.p. 126.2°C. These compounds could have been formed from diethylamine and ammonia, respectively, either of which might have been present as an impurity in the triethylamine.

A 0.67 g. sample of the remaining fraction from D92-91-1 was recrystallized from benzene and dried for 5 hrs. at 100°C under vacuum to give 0.40 g. of dark red crystals (D92-104-2). The DTA curve of this material shows a sharp endotherm at 130°C, with partial melting, followed by a broad, shallow endotherm at about 160°C, with complete melting. The IR spectrum was almost identical to that of DNODA, and the NMR spectrum showed no CH_3-Si protons.

An attempt was made to separate the crude product, D92-91-1, into fractions by chromatography. A 1.0 g. sample of D92-91-1 was warmed with 50 ml. of butanone (dried over $CaSO_4$), and the solution filtered to remove triethylamine hydrochloride. The filtrate was passed slowly through a 1 x 25 cm. column of adsorption alumina (dried at 300°C), followed by more butanone until the product was completely eluted. A rather diffuse orange band formed in the column and moved slowly downward as elution continued. When the filtrate began coming through colored, fractions were collected. Each fraction was evaporated to dryness in a stream of nitrogen. The residues were weighed and a DTA curve run for each. The results are summarized below.

Fraction No.	Wt. Soln., g.	Wt. Solids, g.	Conc., %	DTA Endotherm, °C
D92-105-3	9.8	0.05	0.5	173 (broad)
" " 4	10.3	0.15	1.5	178 (sharp)
" " 5	18.8	0.19	1.0	180 (sharp)
" " 6	28.1	0.16	0.6	158 (broad)
" " 7	26.2	0.05	0.2	182 (sharp)
" " 8	25.5	0.06	0.2	152 (broad)
" " 9	26.7	0.02	0.08	179 (sharp)
" " 10	29.6	0.01	0.03	181 (fair)
" " 11	33.6	0.01	0.03	177 (sharp)

A single maximum in the concentration column indicates the presence of only one component, although the presence of small amounts of a second component is suggested by the DTA results on fractions D92-105-6 and D92-105-8. Apparently DNODA is the only compound present in substantial quantity.

Reaction of 4,4'-Oxydianiline (ODA) with Trimethylchlorosilane. - A solution of 32 ml. (0.25 mole) of trimethylchlorosilane in 125 ml. of benzene was stirred while a solution of 20.0 g. (0.10 mole) of ODA (recryst. from acetone) in 120 ml. of pyridine (dried by acetropic distillation with benzene) was added rapidly. A precipitate formed rapidly. The mixture was refluxed for 8 hrs., let stand at room temperature for 16 hrs., evaporated to 150 ml. in a stream of nitrogen and filtered. Evaporation of the filtrate to dryness gave 7.27 of recovered ODA, m.p. 189°C. The precipitate was washed with hot benzene and dried at 100°C under vacuum to give 15.06 g. of a gray powder (D92-108-9). The benzene washings yielded only 0.05 g. of material. The DTA curve of D92-108-9 showed the following endotherms:

187°C	very small
195	very small
234	deep, sharp
262	smaller, broader

Analysis of D92-108-9. Calc. for ODA · pyridine · 2HCl ($C_{17}H_{19}ON_3Cl_2$): C, 57.96; H, 5.44; N, 11.93; Cl, 20.12. Found: C, 58.72, 58.52; H, 5.51, 5.42; N, 11.47, 11.62; Cl, 17.59, 17.82; Si, 0.25, 0.20. Apparently this product is primarily a somewhat impure complex of ODA, pyridine and HCl.

A solution of 20.0 g. (0.10 mole) of ODA (recryst. from acetone) in 100 ml. of DMF and 100 ml. of benzene was dried by distilling off 30 ml. of benzene. The residual solution was stirred while 32 ml. (0.25 mole) of trimethylchlorosilane was added. A yellow solution was obtained, which rapidly formed a precipitate. The mixture was refluxed

for 1.5 hrs., let stand for 16 hrs. at room temperature, and filtered. The solid was washed with warm benzene and dried at 100°C under vacuum to give 29.94 g. of yellow, granular material (D92-108-8). A DTA curve showed a deep, jagged endotherm at about 334°C and a broad, shallow one at 374°C.

Analysis of D92-108-8. Calc. for ODA • DMF • 2HCl ($C_{15}H_{21}O_2N_3Cl_2$): C, 52.03; H, 6.12; N, 12.14; Cl, 20.49. Found: C, 53.70, 53.57; H, 6.11, 6.14; N, 12.75, 12.84; Cl, 19.92, 20.14; Si, 0.36, 0.40. Again, no trimethylsilylated product was isolated.

Tosyl Derivatives

ODA (20 g.) was dissolved in 100 g. of pyridine, and 38 g. of p-toluenesulfonyl chloride was added. The temperature rose to approximately 90°C. After 20 minutes the solution was poured into ice-water. An oily precipitate separated, which was washed with water and then dissolved in a boiling mixture of 200 g. of water and 1 l. of methanol. The solution was treated with charcoal and filtered. After drying, 40 g. (79% yield) of product, m.p. 151°C, was obtained. Ray & Soffer[14] reported a m.p. of 179-180°C.

Anal. Calc. for $C_{26}H_{24}N_2O_5S_2$: C, 61.39, H, 4.76; N, 5.51; S, 12.64. Found: C, 61.34, 61.50; H, 4.86, 4.82; N, 5.23, 5.27; S, 12.61, 12.54. In spite of the discrepancy in melting points there seems to be little doubt that this compound is N,N'-di-p-tosylaminophenyl ether.

Nitration of the ditosyl derivative above was carried out in a solution of acetic anhydride and nitric acid. Thus 60 g. of nitric acid was added to 400 ml. of cold acetic anhydride. To this solution 71 g.

of the ditosyl derivative was added over a 5 minute period. The temperature of the solution rose from about 0° to 31°C. A yellow precipitate separated, which was filtered, washed with acetic acid and dried in a vacuum desiccator to give 72 g. of product m.p. 185°C (DTA).

Polymers from DNODA and PMDA

A solution of 2.74 g. of DNODA in 20 g. of dry DMAC was stirred while 2.18 g. of PMDA was added. There was no exotherm or viscosity change, and the PMDA did not dissolve. The mixture was heated to 140-165°C and held there for 7 hrs. A red-black solution of low viscosity was obtained. However, when a sample was baked out at 150°C a continuous film was obtained. A second run was then made.

A mixture of 29.024 g. (0.1 mole) of DNODA, 21.813 g. (0.1 mole) of PMDA, 200 ml. of dry DMAC, and 50 ml. of toluene was refluxed with stirring, using a Dean-Stark trap to remove any water that was produced. At a pot temperature of 150°C, a second phase slowly collected in the trap. After six hours of refluxing, 2.9 ml. of aqueous layer collected. Since this layer probably contains some DMAC, the amount of water produced is not known, but 2.9 g. of water corresponds to 80% of the quantity calculated for complete imide formation. This may be considered an upper limit. The residual product was a dark brown solution containing a little granular solid. It was mixed with 2 g. of 5% Pd- on C catalyst and hydrogenated at 45-55 psi and 35-65°C. Total hydrogen absorption was 45 psi (calc. 47 psi). The resulting solution was filtered and passed through a 2 x 20 cm. column of adsorption alumina to give a nearly black solution (D92-128-2) of moderately low viscosity. A film

cast from it by baking for 2 hrs. at 150°, 1 hr. at 250°, and 1 hr. at 300°C was clear red-brown, continuous, and moderately flexible, although it could not be stripped intact from the substrate. After standing at room temperature for three days, D92-131-2 became a very soft gel, which gradually became more firm.

Reaction of DAB and BTDA in DMAC

A mixture of 10.714 g. (.05000 mole) of DAB (Burdick and Jackson) and 16.110 g. (.05000 mole) of BTDA (recrystallized from acetone) was ground in a mortar and pestle to give a fine powder, which was added in small portions to 241 ml. of DMAC (dried over 4A Molecular sieve) with rapid stirring in a Waring blendor. All operations except the initial weighing were done in a glove box under dry nitrogen. When 19.74 g. of the powder had been added (7.6% solution), gelation occurred. An additional 140 ml. of DMAC was added, giving a 4.9% solution, but the gel did not liquefy on stirring. The remaining 7.083 g. of powder was added to 142 ml. of stirred DMAC in the blendor to give a clear brown 5% solution of low viscosity. A film cast from it (1 hr. at 160°C + 1 hr. at 250°C) was continuous, but rather brittle. The 4.9% gel, on standing at room temperature under nitrogen for 3 days, liquified to a low viscosity solution containing a few small gel particles. A film cast from this solution was similar to film from the 5% solution.

Preparation of DAB-BTDA in the Presence of Acids and Bases

Table IX summarizes the results of a series of runs using an added tertiary amine. The addition of a base such as triethyl amine (TEA) enables more concentrated pyrrone solutions to be made, though they are unstable and gel within a few days. For example, a resin solution containing 16% solids, with 2 moles of TEA per mole of DAB, did not gel until after about 8 days. Without the added TEA a solution this

Table IX

Preparation of DAB-BTDA Resin with Tertiary Amines

Batch Number	Mole Ratio, Base* to DAB-BTDA	% Solids	Initial Viscosity	Approximate Time to Gelation
D36-36-1	0.2	10.3	Very thin	Still thin after 20 days
D36-36-2	1.0	10.3	Very thin	Still thin after 20 days
D36-38-1	1.0	13.7	580 ctsks.	100 hours
D36-38-2	1.0	15.6	4630 ctsks.	20 hours
D36-39-1	2.0 (flask)	15.2	165 ctsks. + gel	70 hours
D36-40-1	2.0	16.0	700 ctsks.	200 hours
D36-44-1	2.0	15.0	--	
D36-48-1	2.0*	15.0	500 ctsks.	20 hours

*N,N-dimethylaniline used in Batch D36-48-1. In all others triethylamine (TEA) was used.

concentrated could not be prepared. A similar solution at 15% solids, with 2 moles N,N-dimethylaniline per mole of DAB, gelled on standing overnight. Apparently the weaker base (pK_b 8.94, compared to TEA 3.36) does not exert as strong an effect as does TEA. (D36-48-1 vs. D36-40-1). At a TEA to DAB mole ratio of one, gelation occurs more promptly than when two moles are used (D36-38-2 vs. D36-40-1). As would be expected the polymers prepared with lower solids content are more stable. The 10% solutions were still quite thin 20 days after preparation.

Table X summarizes the important details of DAB-BTDA resin preparation in the presence of acids. These solutions were very unstable, gelling within a few hours. In particular, the resin prepared with the strongest acid (dichloroacetic, pK_a 1.29) gelled during preparation.

All of the resins in Tables IX and X, with the exception of D36-39-1, were prepared by the blendor procedure. In these runs, 90% of the dianhydride was added in solution to the stirred DAB solution in about 10-30 min. The remaining 10% of BTDA was added as a 10% solution in DMAC over a 30-50 min. period. D36-39-1 was prepared in a round-bottom flask with conventional stirring, a procedure which apparently is not adequate.

Several batches of polymer were prepared using varying proportions of TEA and acetic acid. The proportions are given in Table XI. All the resins were prepared in a Waring blendor by slow addition of BTDA solution to stirred DAB solution except D36-33-1 which was prepared in a flask with ordinary stirring. A film sample prepared from D36-32-1 could be creased without breaking in a thin section after baking at 150°C. Further baking at higher temperatures caused it to become more brittle.

Table X

Preparation of DAB-BTDA Resin with Organic Acids

Batch Number	Acid	pK_a	Mole Ratio, Acid to DAB-BTDA	% Solids	Initial Viscosity, Cstks.	Approx. Time for Gelation, hrs.
D35-92-2	Acetic	4.75	10.0	10.0	low	48
D36-43-1	Acrylic	4.26	2.0	14.1	624	< 20
D36-43-2	Acrylic	4.26	4.0	14.5	3600	< 20
D36-48-2	Dichloro-acetic	1.29	2.0	15.0	Gelled	--
D36-49-1	Lactic	3.87	2.0	15.0	880	< 20
D36-49-3	Lactic	3.87	3.0	12.1	581	< 20
D36-49-4	Lactic	3.87	3.0	12.1	2700	< 20

Table XI

Preparation of DAB-BTDA Resin with TEA and Acetic Acid

Batch No.	Moles BTDA	DAB	TEA	Acetic Acid	g DMAC	% Solids[a]	Viscosity[b], Ctsks.
D36-32-1	0.05	0.05	0.11	0.16	190	11.3	165
D36-32-2	0.05	0.05	0.054	0.08	185	12.0	200
D36-33-1[d]	0.05	0.05	0.054	0.13	160	13.4	mushy gel
D36-33-2	0.05	0.05	0.054	0.08	160	13.4	400
D36-33-3	0.05	0.05	0.054	0.08	170[c]	9.2	gel
D36-33-4	0.06	0.06	0.059	0.067	160	15.7	2800 gel particles

a. TEA and Acetic acid are considered solvents.

b. Measured with Gardner-Holdt tubes and converted.

c. Also contains 80 g acetone.

d. Prepared in a flask with stirring; others prepared in a Waring Blender.

The other batches were attempts to make more concentrated solutions. Batch D36-33-2 at 13.4% solids was the most successful. Batch D36-33-4 at 15.7% solids contained gel particles and consequently films cast from this resin were spotty.

D36-40-1 (Table IX) was coated on glass cloth and cured up to 180°C. This treated cloth was pressed at 500 psi and 350°C (D36-70-2). The sheets pulled apart readily. D36-44-1 (Table IX) was coated on glass cloth but cured to only 125°C (60 min.). This material, when pressed at 500 psi and 350°C gave a laminate (E68-79-1) which was somewhat thick (0.139") for the number of plies (12). Apparently, flow in the press was not very good. The flexural strength, 47,200 psi at RT and 31,600 at 600°F, is not impressive.

D36-49-3 (Table X), which was made with added lactic acid, was coated, cured and pressed identically to give laminate number E68-85-1, which had insufficient flow in the press and very low flexural strength.

Preparation of Imide-Pyrrone Copolymer

A solution composed of 10.8 g. (0.1 mole) of MPD and 21.4 g. (0.1 mole) of DAB in 100 g. of DMAC was placed in a one l flask equipped with stirrer and thermometer. A second solution composed of 57.4 g. (0.178 mole) BTDA and 186 g. DMAC was warmed and added to the first solution via a dropping funnel at a fairly rapid rate. Some gel particles formed. A third solution prepared from 7 g. (0.022 mole) BTDA and 100 g. DMAC was added slowly to the resin solution. The product gelled before all of the BTDA solution had been added.

The preceding run was repeated except that a Waring blender was used and addition of the BTDA solutions were much slower. The first BTDA solution was added over a 30 min. period. All but 5 g. of the second BTDA solution was added over a period of 90 min. The solution became so thick that good stirring could not take place. The addition of 50 g. of DMAC did not help appreciably and the remainder of the BTDA was not added. This solution had a viscosity of about 435 centistokes. It gelled on standing overnight. A third run was then made at a lower concentration.

E68-61-1. To a solution composed of 10.8 g. MPD, 21.4 g. DAB and 300 g. DMAC in a 2 l. flask was added a warmed solution of 57.4 g. BTDA in 300 g. DMAC. Addition time was 30 min. After another 30 min. a second solution composed of 7 g. BTDA in 270 g. DMAC was added over a period of about 45 min. The viscosity of this 10.9% solution was below the lowest viscosity Gardner standard. A fairly good film was obtained.

Reaction of Tetramines with Esters

A number of DAB-BTDA solutions were prepared by heating BTDA with about a stoichiometric amount of an alcohol dissolved in either DMAC or NMP to 100-110°C, cooling to 35-40° and then adding to a DAB solution. Table IV gives details of each preparation.

Four of the resins were prepared using ethylene glycol as the alcohol. In D35-122-3, only 80% of the stoichiometric amount of ethylene glycol was used. This sample gelled upon addition to the DAB solution. The other differences between D35-122-2, D35-122-3, D35-124-1, and D35-124-2 were in solvent and concentration.

The remaining 3 solutions, D35-125-1, D35-125-2, and D35-125-3 all contained stoichiometric amounts of Cellosolve based on the amount of BTDA present. The molar ratios of BTDA to DAB were 1.0, 1.1, and 1.2 respectively. The highest viscosity was found for a ratio of 1.1.

All of these solutions formed brittle films. Thin films gave only a few free fragments. Some thicker sections separated from the aluminum dish and possessed moderate strength and flexibility. In other samples the dish and film curled up together.

The weight losses of 5 of these samples at 325°C in circulating air are given in Table V. Some difficulty was encountered in getting the oven to equilibrium, so that the temperature is not exact but approximately ± 5°C. The samples were cured for approximately 16 hours, at gradually increasing temperatures, to a maximum of 321°C. The largest part (14 hours) was at over 300°.

BTDA was refluxed with an excess of methanol until it dissolved. After most of the methanol was removed under nitrogen an equivalent amount of DAB was stirred into the viscous material. Since it did not dissolve completely, DMAC was added until a dark solution was obtained. With Cellosolve as the alcohol, additional solvent was not needed.

Glass cloth was coated with resin solutions prepared from methyl-BTDA and DAB in DMAC solutions. Precure of these resins has apparently been at too high a temperature, because little flow occurred on pressing and the resulting laminates were of very low strength.

One laminate, F68-116-1, was prepared from the BTDA-DAB Cellosolve resin solution. The precure was at 85°C for 1 hour. The prepreg had a resin content of 38% resin. On pressing, flow was noted at 130°C.

Final pressing temperature was 325°C. At room temperature the laminate had a flexural strength of 58,000 psi and a modulus of 2.92×10^6 psi. At 315°C flexural strength averaged 37,000 psi with a modulus of 2.22×10^6 psi.

CONCLUSIONS

1. The presence of an ortho acetamido group does not greatly reduce the reactivity of an aromatic primary amine group toward an anhydride. Consequently, difunctional compounds, such as 2,4 -diamino-acetanilide and 4,4'-diacetamido-3,3'-oxydianiline, react readily with dianhydrides in polar aprotic solvents to give solutions of linear acetamido 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 acetamido acid amide polymers are stable in solution and show no tendency to crosslink or gel.

3. The acetamido acid amide polymers are converted cleanly to acetamido 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 acetic acid is eliminated, with, however, only slight conversion to a pyrrone structure. Pyrrone formation is far less complete than for polymers derived from tetramines and dianhydrides.

4. Extremely brittle films were cast from the acetamido 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. 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.

7. 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.

8. The reaction of a tetramine and 3,3', 4,4'-benzophenonetetracarboxylic 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.

9. 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.

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