

Polyimidazopyrrolones and Related Polymers. II. Polyimidazopyrrolones from Aromatic Dianhydrides and 3,3'-Dichloro-5,5'-Diaminobenzidine

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Synopsis

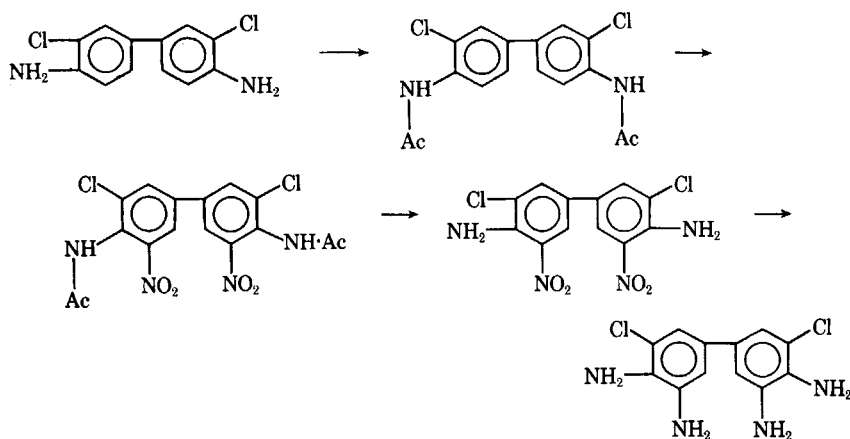
The preparation of 3,3'-dichloro-5,5'-diaminobenzidine and its polymeric reaction products with pyromellitic dianhydride and 3,4,3',4'-benzophenonetetracarboxylic dianhydride are described. The soluble amine-acid-amide form of the polymer is stable at higher concentrations than the corresponding polymers from 3,3'-diaminobenzidine or 3,3',4,4'-tetraaminodiphenyl ether. Infrared spectra indicate that polybenzimidazopyrrolone structure is formed after cure. The preparation and properties of films and glass-reinforced laminates prepared from the polymers are described.

INTRODUCTION

The preparation of polyimidazopyrrolones (pyrrones) from aromatic tetraamines (bisortho-diamines) and aromatic dianhydrides has been reported earlier by several authors.²⁻⁵ Because of the tendency of the tetraamine to behave as a tetrafunctional monomer, gelation occurs during solution polymerization unless the solution is kept quite dilute (10% and lower) and care is taken to prevent local excess of dianhydride.³ In an earlier paper,¹ we described the use of acetyl groups to block one of the amine groups in each of the amino pairs as a means of preventing gelation. This modification prevented gelation, but thermal removal of the acetyl groups and formation of the pyrrone structure did not occur satisfactorily. Another method of reducing gelation is to add a deactivating group adjacent to one amino group of each ortho pair. The deactivation may be either steric or electronic. We have synthesized a tetraamine of this type, 3,3'-dichloro-5,5'-diaminobenzidine (DCDAB), and have prepared novel pyrrone polymers from it with pyromellitic dianhydride (PMDA) and with 3,4,3',4'-benzophenonetetracarboxylic dianhydride (BTDA).

DISCUSSION

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



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

The sequence of reactions by which DCDAB and PMDA form the pyrrone structure is shown below. The amine-acid-amide (AAA) polymer forms exothermally in a variety of polar solvents such as dimethylacetamide (DMAC), dimethylformamide (DMF), N-methylpyrrolidone (NMP), and dimethyl sulfoxide (DMSO) and is reasonably stable. In the

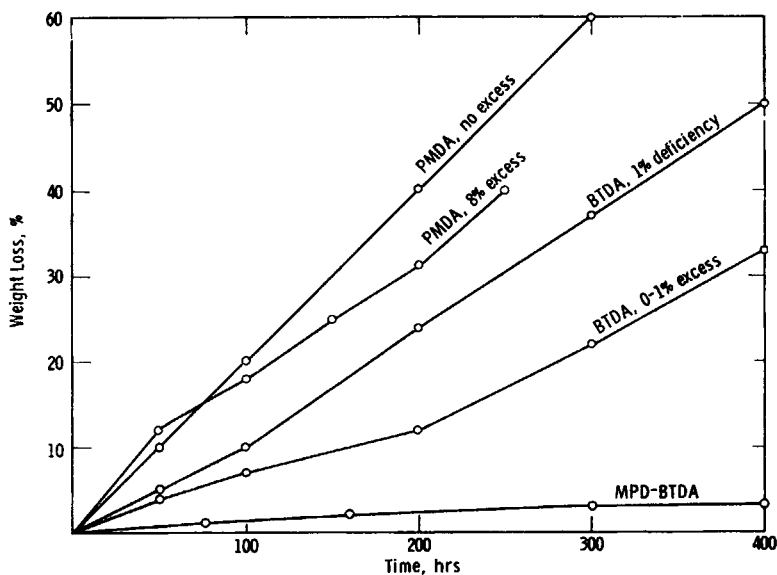
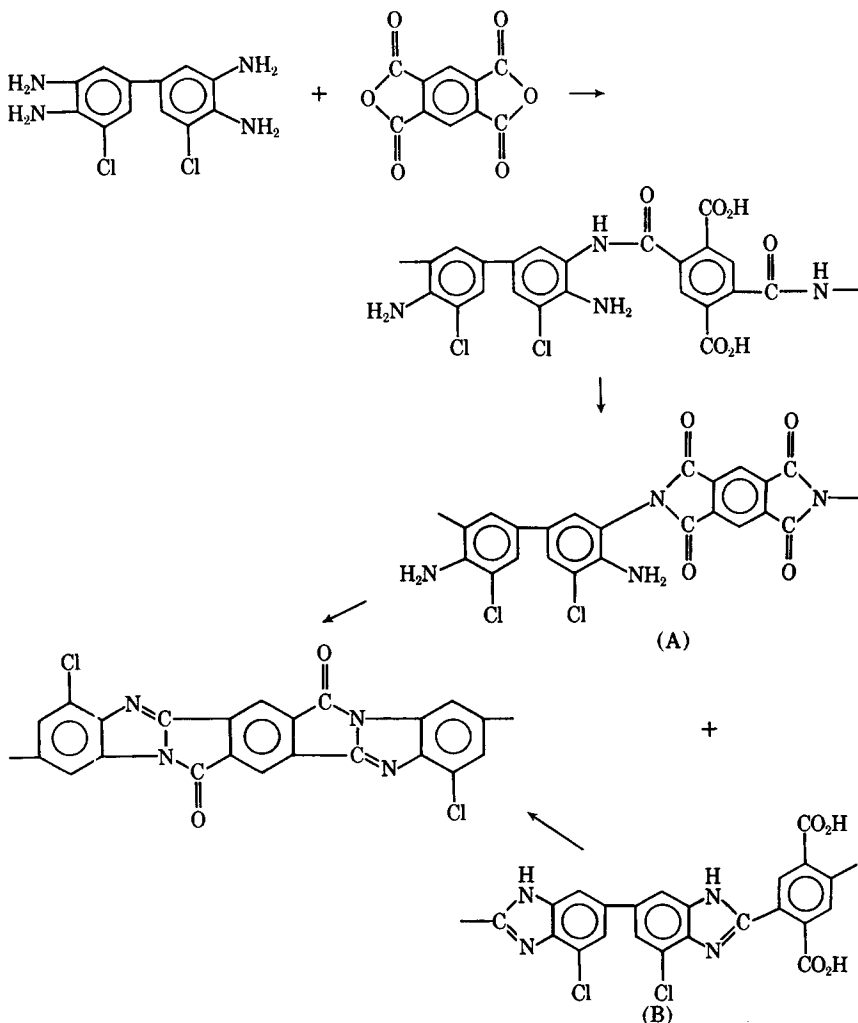


Fig. 1. Weight loss of DCDAB pyrrones at 325°C in air.

second step, solvent is removed and condensation to amine-imide (A) or benzimidazole-acid (B) occurs on heating at 200°C. The final pyrnone structure is formed by heating the polymer at 300–400°C:



In general, polymers prepared from DCDAB and dianhydrides showed the expected gelation and cure tendencies. Their solutions were more stable than those from unhindered tetraamines, but less stable than those from diacetylated tetraamines. Final conversion to pyrrones required no more severe conditions than the preparation of pyrrones from unhindered tetraamines.

When solid PMDA was added to a DMAC solution of DCDAB, gel formed around the PMDA particles. Addition of PMDA as a solution in DMAC gave no gel, even with up to 9% excess PMDA, although gelation could be induced by adding more PMDA after aging the solution for a few

days. Solutions containing a slight excess of PMDA increased very slightly in viscosity on aging and did not gel in 54 days.

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

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

Weight loss data on films of these polymers are shown in Figure 1 in comparison with a polyimide prepared from BTDA and *m*-phenylenediamine (MPD) aged concurrently in the same oven. Apparently, BTDA gives better stability than PMDA in this system, but both polymers are inferior to a good polyimide. Polymers containing an excess of tetraamine were less thermally stable than those in which the dianhydride was present in at least an equivalent amount.

Laminates were prepared from DCDAB-BTDA polymer containing about 2% excess BTDA. Glass cloth (181-A1100, E-glass) was hand dipped, precured, and pressed at 325°C and 500 psi. Properties of the laminates are given in Table I. The strength and modulus values compare favorably with those of polyimide laminates,⁶ but are inferior to the best pyrrones made by the ester method.⁷ The quantity of material available was insufficient for a complete aging study, but, for a screening test, weight loss measurements at 325°C were made on pieces of laminates. Although the data are not strictly comparable, these results (Table I) suggest that, in thermal stability, DCDAB-BTDA polymers rank between polyimides⁶ and pyrrones made by the ester method.⁷

TABLE I
Properties of DCDAB-BTDA Laminates

Laminate number	E69-85-2	E69-87-2
Precure temperature, °C	125	150
Resin in prepreg, %	38	42
Resin in laminate, %	30	36
Flexural strength, K psi ^a		
25°C	57.2	50.0
316°C (600°F)	42.9	49.4
Flexural modulus, M psi ^a		
25°C	2.8	2.7
316°C (600°F)	2.5	2.7
Weight loss at 325°C, % of resin		
24 hr	8.0	6.5
110 hr	37.4	27.2

^a Average of three specimens.

EXPERIMENTAL

BTDA and PMDA were purified by recrystallization from acetone. DMAC was dried by storing over molecular sieves. Melting points were derived from minimum points on DTA curves.

Preparation of DCDAB

3,3'-Dichlorobenzidine was acetylated with acetic anhydride to give a quantitative yield of the diacetyl derivative, mp 305–311°C. Recrystallization from DMAC–acetic acid gave a product of mp 311°C. (Cain and May⁸ report 304°C)

Dry Ice was added with stirring to 5 pints of fuming nitric acid until the temperature reached 5°C. Over a period of 15 min, 362 g diacetyldichlorobenzidine was added, together with enough Dry Ice to maintain a temperature of 5–10°C. The dark solution was stirred for 15 min at 5–10°C and then poured into an ice–water mixture. The yellow precipitate was filtered off, washed thoroughly with water, and dried at 140°C. Three such batches were combined to give 1233 g crude product. Recrystallization from 12 liters DMAC gave 437 g (32% yield) N,N'-diacetyl-3,3'-dichloro-5,5'-dinitrobenzidine. This compound does not have a melting point, but decomposes vigorously (DTA exotherm) at about 390°C.

ANAL. Calcd for $C_{16}H_{12}Cl_2N_4O_6$: C, 44.98%; H, 2.83%; N, 13.12%; Cl, 16.60%. Found: C, 45.10%, 45.26%; H, 2.84%, 2.77%; N, 13.15%, 13.29%; Cl, 16.63%, 16.53%.

Two liters concentrated sulfuric acid was stirred while 254 g of the above product was added. The mixture was warmed to 60°C and poured into ice–water. The precipitate was filtered off, washed with sodium bicarbonate solution and water, and dried to give 201 g 3,3'-dichloro-5,5'-dinitrobenzidine, mp 315°C.

ANAL. Calcd for $C_{12}H_8Cl_2N_4O_4$: C, 42.00%; H, 2.35%; Cl, 20.67%; N, 16.33%. Found: C, 42.16%, 42.35%; H, 2.69%, 2.82%; Cl, 20.44%, 20.66%; N, 16.18%, 16.21%.

A slurry of 125 g 3,3'-dichloro-5,5'-dinitrobenzidine, 2 pints 95% ethanol, 12 g 5% palladium-on-charcoal, and 110 ml 85% hydrazine hydrate was stirred. The mixture gradually warmed spontaneously to reflux temperature and maintained reflux for about 15 min. Heating was then used to maintain reflux for another 27 min. The catalyst was removed by filtration, and 500 ml deionized water containing a pinch of sodium hydrosulfite was added. A white precipitate formed as the solution was cooled and concentrated under nitrogen. After filtration and drying, 35.3 g (34%) DCDAB was obtained, mp 175°C. Further concentration of the mother liquor gave about 17 g of material with an endotherm at 152°C. Recrystallization from ethanol–water raised the mp to 178°C.

ANAL. Calcd for $C_{12}H_{12}Cl_2N_4$: C, 50.90%; H, 4.27%; Cl, 25.04%; N, 19.79%. Found: C, 51.79%, 51.59%; H, 4.39%, 4.35%; Cl, 24.34%, 24.47%; N, 19.44%, 19.55%.

Polymers from DCDAB

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

TABLE II
Preparation of DCDAB-PMDA

Resin number	DCDAB, g	DMAC, g	PMDA, g	DMAC, g	Solids, %	Remarks
D36-104-1	2.83	15	2.18	none	25.0	gel particles
D36-104-2	2.83	5	2.18	15	20.0	very thin liquid
D36-106-1	5.66	10	4.72 (9% excess)	19	26.3	gel particles
D36-106-2	5.66	10	4.66 (8% excess)	22	24.4	2.75 stokes
D36-127-1	5.6632	12	4.3626	18	25.0	5.5 stokes

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

DCDAB-BTDA polymers were prepared as follows:

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

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

The weight losses of samples D36-120-1, 2, 3, and 4, D36-125-1, and D36-127-1 in air at 325°C are given in Table III and Figure 1. Samples D36-120-1, 2, 3, and 4, placed together because of close similarity, showed the lowest rate of weight loss, especially for the first 200 hr. After 200 hr, the rate of loss became nearly constant at about 0.1% hr, which is almost the same as that of D36-125-1 through its aging period. The DCDAB-BTDA polymers, both D36-125-1 and the D36-120-1, 2, 3, 4 group, show a lower weight loss than the DCDAB-PMDA polymers D36-127-1 and D36-106-3.

TABLE III
Weight Loss of DCDAB-BTDA and DCDAB-PMDA Polymers at 325°C

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

A check on the weight loss data was made by concurrently running samples of a polyimide prepared from MPD and BTDA. Samples of this material lost 3-4% and then remained at a nearly constant weight at 325°C.

The infrared spectrum of a fully cured DCDAB-BTDA polymer is presented in Figure 2. The bands at 1770 and 1740 cm^{-1} are typical of pyrrone structure.

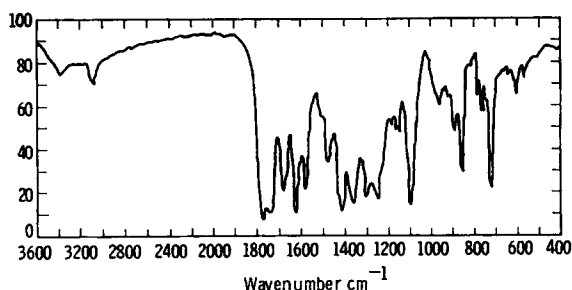


Fig. 2. DCDAB-BTDA film, cured 60 min at 350°C.

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