

Polyimides from Diisocyanates, Dianhydrides, and Their Dialkyl Esters

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Synopsis

High molecular weight polyimide polymers have been prepared by the reaction of diisocyanates and a mixture of dianhydrides and their dialkyl esters in aprotic solvents. No catalyst is necessary, but high polymer formation is affected by the anhydride/ester ratio and temperature. Dianhydrides such as PMDA, BTDA, TMA, and their esters have been used successfully. Mixtures of these materials have also been used. Tough, flexible films can be obtained from these polymers.

INTRODUCTION

In an earlier paper¹ we described the preparation of polyimides from diisocyanates and mixtures of tetracarboxylic acids and their dianhydrides. It was shown that temperature affected the course of the reaction. Below 10°C, high polymer was not formed and a voluminous precipitate separated from the reaction mixture. Subsequent heating of the reaction to higher temperatures also failed to produce high molecular weight polymer. It was suggested that the rate of reaction of isocyanate with free carboxyl groups is substantially faster than the reaction with anhydrides at low temperature. Since the free acid is tetrafunctional, most of the isocyanate reacts with the carboxyl groups, leaving a major portion of the anhydride unreacted. It seemed reasonable to assume that if the tetraacid were replaced by its dialkyl ester, the reaction would be less sensitive to temperature and easier to control because of the reduced functionality of the diester. It has been reported² that a highly viscous polymer solution was obtained by reacting 4,4'-diisocyanatodiphenylmethane (MDI) with dimethyl dihydrogen pyromellitate in dimethylformamide (DMF). This solution was cast on a plate and converted to a tough film. We have run this reaction both with and without a tertiary amine catalyst in N-methylpyrrolidone (NMP) and DMF using both the dimethyl and dibutyl ester of pyromellitic dianhydride. Our attempts have been unsuccessful in preparing high molecular weight polymer by this procedure.

These findings prompted a trial of mixtures of dianhydrides and dialkyl esters in a manner of previous successes with mixtures of tetraacid and dianhydride.¹

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) was obtained from du Pont de Nemours; 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), from the Gulf Oil Corp. These materials were purified by recrystallization from acetone and acetic anhydride. 4,4'-Diisocyanatodiphenylmethane was obtained from the Upjohn Chemical Co. and used as received. N-Methylpyrrolidone was obtained from GAF Corp. and used as received and after purification by distilling in the presence of a small quantity of PMDA. Benzyl dimethylamine (BDMA) was obtained from Fisher Scientific. Trimellitic anhydride (TMA) was obtained from Amoco Chemical Co.

Properties

Inherent viscosity measurements were made on 0.5% solutions of the polymers in NMP at 25°C using a Cannon-Fenske viscometer (Size 75). Gardner-Holdt viscosity was also measured. IR spectra were obtained on a Beckman IR-12 instrument.

Films were prepared by casting the polymer solution on a suitable substrate using a coating bar with an adjustable gap to control the wet film thickness. The films were cured to 150°–200°C, removed from the substrate, and clamped on metal frames for further curing to 300°C.

Preparation of Dialkyl Esters

Dimethyl Pyromellitate (DME-PMA). PMDA, 300 g, was dissolved in 800 g methyl alcohol (MCB-acetone free containing 0.016% H₂O). The solution was refluxed for 2 hr. On cooling, 65 g of a white solid melting at 235°–240°C was obtained by filtration. By alkali titration, the equivalent weight was 139 compared to a calculated value of 141. The wide melting point is expected as two isomers would result from this reaction.

Di-*n*-butyl Pyromellitate (DBE-PMA). PMDA, 200 g, was dissolved in 350 g *n*-butyl alcohol and heated to 80°C for 1/2 hr. Then 180 g of the excess *n*-butyl alcohol was distilled in vacuo. An equal volume of toluene was added to the residue and cooled to ambient. About 125 g of product separated and was filtered and dried. The product melted at 159°–160°C and had an equivalent weight of 181 (calcd. 183).

Dimethyl Ester of Benzophenonetetracarboxylic Acid (DME-BTDA). BTDA, 200 g, was dissolved in 500 g methanol and the solution heated to 80°C for 1/2 hr. When cooled to ambient, no precipitate formed. Most of the methanol was then distilled off. Water was added and a liquid organic layer was separated. This was dried in vacuo at 110°C. Yield was 145 g of a viscous liquid. The equivalent weight was 198 (calcd. 193).

Dibutyl Ester of Benzophenonetetracarboxylic Acid (DBE-BTDA). BTDA, 100 g, was dissolved in 77 g butyl alcohol and heated to 100°–115°C for 1 1/2 hr. The excess alcohol was distilled off. The product was a viscous liquid with an equivalent weight of 229 (calcd. 223).

Methyl Ester of Trimellitic Anhydride (ME-TMA). A mixture of 192 g trimellitic anhydride and 250 ml dry methanol was refluxed with stirring for 3 hr. Most of the solid dissolved in the first few minutes, and then a granular white precipitate slowly formed. Most of the excess methanol was distilled off, and the residual thick slurry was spread in a thin layer and dried by passing nitrogen over it at room temperature for 24 hr. The product was a white powder weighing 226 g (calcd. 224), mp 180°–208°C. The neutral equivalent was found to be 116 (calcd. 112). This product is a mixture of 1-methyl trimellitate (mp 177, 203.5–205.5) and 2-methyl trimellitate (mp 208).

Polymer Preparation

The diisocyanates were condensed at both ambient and elevated temperatures with a mixture of the dianhydride and the dialkyl ester either with or without a tertiary amine catalyst (0.1% benzyldimethylamine, BDMA).

A general procedure for preparing the polymers is as follows: To a heated mixture (50°–60°C) of the dianhydride and the diester dissolved in NMP to provide a final solids content of 18%–19% is added a stoichiometric amount of the diisocyanate. The reaction mixture is stirred at the desired temperature until maximum viscosity is reached and CO₂ evolution subsides. The reaction mixture is cooled to room temperature and can be diluted with additional solvent to adjust the viscosity of the solution. Inherent viscosities range from 0.3 to 1.3 dl/g.

RESULTS AND DISCUSSION

Reaction of Dimethyl Ester of PMA, PMDA, and Diisocyanate

Table I shows a series of reactions in which the ratio of PMDA to the dimethyl ester was varied. The reactions showed similarity to the PMDA-PMA reactions in that the optimum ratio lies in the range of 4–60% PMDA. Above this percentage gelation occurs, and below, high molecular weight polymer does not result.

Table II shows the effect of temperature on a 50-PMDA/50 DME-PMA/diisocyanate reaction. Unlike the case of the PMDA/PMA reaction, the course does not appear to be altered by the temperature up to 75°C where premature

TABLE I
Effect of Ratio of PMDA to DME-PMA^a on Viscosity^b

PMDA, mol-%	DME-PMA, mol-%	Gardner viscosity	Inherent viscosity, dl/g
70	30	Gelled	—
60	40	Z-1	0.80
50	50	X-Y	0.60
30	70	G-H	0.31
0	100	<A	—

^a Dimethyl ester of PMA.

^b Reaction temperature 50°–60°C.

TABLE II
Effect of Temperature on PMDA/DME-PMA/MDI Reaction

Temperature of addition of MDI, °C	Temperature of reaction, °C	Time of reaction	Gardner viscosity
5-10	50-60	1½ hr	W-X
25	25	5 hr	X
50-60	50-60	1½ hr	X-Y
75	75	20 min	Gelled

TABLE III
Effect of Reaction Ratio and Temperature on PMDA/DBE-PMA/Diisocyanate Reaction

PMDA, mol-%	DBE-PMA, ^a mol-%	Temperature of reaction, °C	Gardner viscosity
60	40	50-60	ppt
50	50	50-60	ppt
40	60	50-60	ppt
35	65	50-60	X
30	70	50-60	Q-R
0	100	50-60	<A
46	56	30-35	V
50	50	30-36	X
60	40	31-38	Z-8

^a Dibutyl ester of PMA.

TABLE IV
Reaction of BTDA/DME-BTDA/MDI

BTDA, mol-%	DME-BTDA, mol-%	Temperature, °C	Catalyst	Gardner viscosity
50	50	80	Yes	Precipitate
50	50	80	No	I
55	45	80	Yes	S
55	45	80	No	T
60	40	80	Yes	J
60	40	80	No	E
60	40	120	Yes	Precipitate
60	40	120	No	Precipitate

gelation occurs. In the PMDA/PMA reaction, a solution mixed at 5°-10°C could not be subsequently bodied at higher temperatures.

Reaction of the Dibutyl Ester of PMA and PMDA with Diisocyanate

Based on the finding with the dimethyl ester reaction that 50°-60°C was a satisfactory temperature range, a series of reactions were run at this temperature with the dibutyl ester. As can be noted in Table III, however, normally operative ratios resulted quickly in the formation of voluminous precipitate. Higher percentages of the ester gave clear solutions but not of satisfactory viscosity.

TABLE V
Mixed Anhydride-Ester Reactions

Anhydride	Ester	Ratio	Temp., °C	Catalyst	Gardner viscosity
PMDA	Methyl-TMA	50/50	30	yes	W
PMDA	Methyl-TMA	50/50	30	no	G
PMDA	Methyl-TMA	60/40	30	yes	Z4
PMDA	Methyl-TMA	60/40	50	yes	Gel on cooling
PMDA	Methyl-TMA	70/30	50	yes	Cloudy gel
PMDA	Methyl-TMA	70/30	75	no	gel
PMDA	Dibutyl-BTDA	60/40	80	no	Z7
PMDA	Dibutyl-BTDA	70/30	80	no	Cloudy gel
BTDA	Methyl-TMA	50/50	80	yes	X
BTDA	Methyl-TMA	50/50	80	no	Z
BTDA	Methyl-TMA	55/45	80	no	Z2
BTDA	Methyl-TMA	60/40	30	yes	Z3
BTDA	Methyl-TMA	60/40	30	no	X
BTDA	Methyl-TMA	60/40	60	yes	Z5
BTDA	Methyl-TMA	60/40	60	no	Z2
BTDA	Methyl-TMA	60/40	80	yes	Cloudy gel
BTDA	Methyl-TMA	60/40	80	no	Cloudy gel
BTDA	Methyl-TMA	60/40	90	yes	Z6
BTDA	Methyl-TMA	60/40	90	no	V

TABLE VI
Properties of Reconstituted Solutions

Formulation	Initial viscosity—solids	Reconstituted viscosity—solids	Film properties
PMDA ₆₀ /DBE-PMA ₄₀	Z-8 at 18%	W at 20%	Flexible
PMDA ₆₀ /DME-PMA ₄₀	X at 18%	W at 20%	Flexible

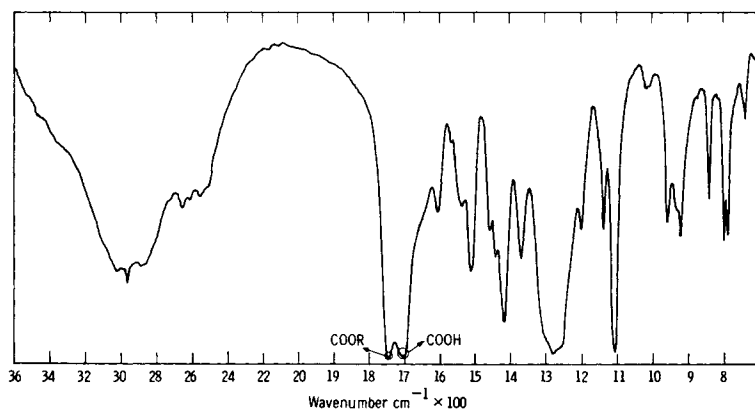


Fig. 1. Precipitate isolated by evaporation of filtrate (mp 251°C) (PMDA + DME-PMA + MDI).

On the assumption that the butyl group was sterically hindering reaction of the free carboxyls and therefore the isocyanate was preferentially reacting with the anhydride causing precipitation of low molecular weight imide, further reactions were carried out at lower temperature.

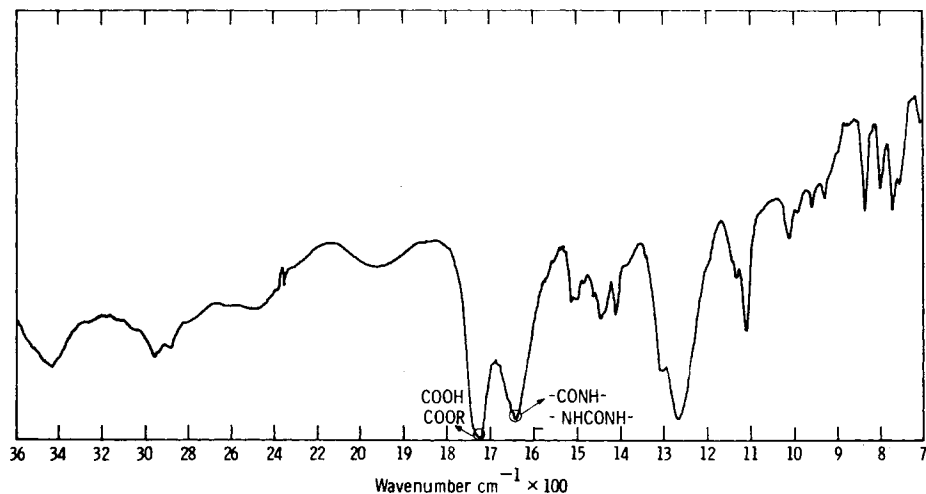


Fig. 2. Precipitate for H₂O wash of product shown in Fig. 1. (mp 45°C) (PMDA + DME-PMA + MDI).

As shown in Table III, reaction at temperatures of 30°–40°C provided solutions of good viscosity. The 60 PMDA/40 DBE-PMA solution had an inherent viscosity of 1.48.

Experiments with Dimethyl Ester of BTDA

Efforts have been unsuccessful in making high molecular weight polymer employing the dimethyl ester of BTDA. BTDA, by itself, has been demonstrated to be much slower in reaction with diisocyanates than PMDA. The usual variables of temperature and anhydride/ester ratio produced only precipitates or small increases in viscosity. This may be complicated by the fact that the dimethyl ester of BTDA is not of high purity. The data for these reactions is shown in Table IV.

If the dibutyl ester of BTDA (DBE) is substituted for the DME, highly viscous solutions are obtained. At present, only two reactions were run using the DBE of BTDA, and these were at 50/50 and 55/45 anhydride/ester ratios. These reactions were run at 80°C with no catalyst, and the Gardner viscosities of the final solutions were Z and Z4, respectively.

Mixed Anhydride-Ester Reactions

A number of mixed anhydride/ester reactions were run at various temperatures with and without catalyst that covered a broad ratio of these ingredients. It was thought that the greater reactivity of the PMDA would impart a "catalytic" effect to the BTDA and TMA systems to produce high molecular weight polymer intermediate. The results of these experiments are shown in Table V. Depending on reaction conditions for a given anhydride/ester combination, high molecular weight polymer can be obtained. We have not critically examined the effect of temperature, catalyst, ratio, etc., on the production of high polymer, but certainly a catalyst is not necessary. It should be noted that the incorporation of PMDA and/or the methyl ester of TMA do yield higher molecular weight resins compared to the straight BTDA/BTDA ester system.

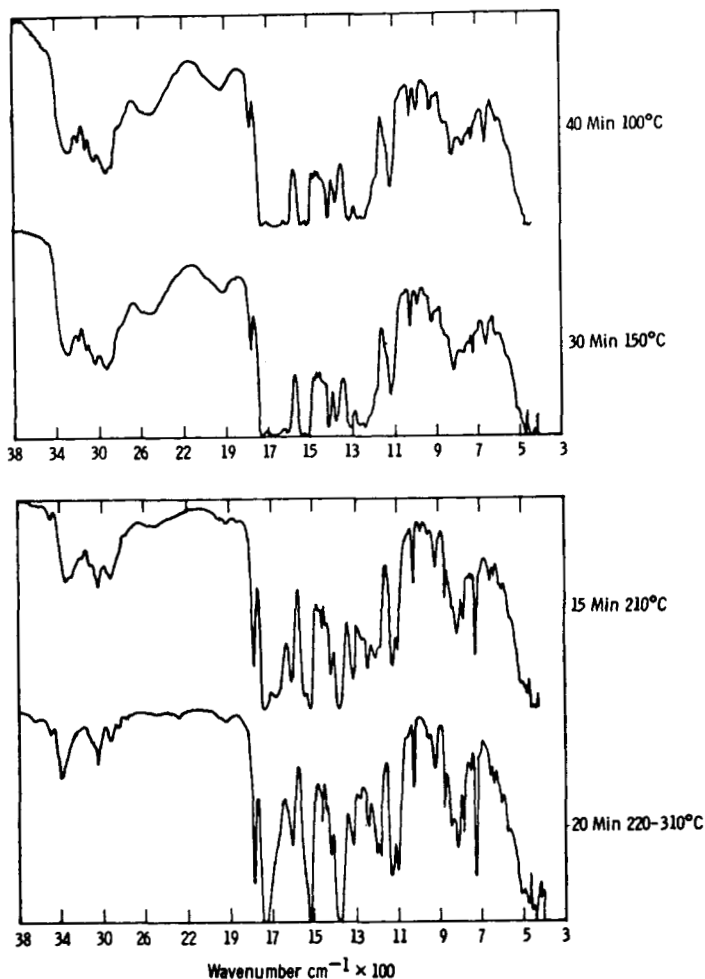


Fig. 3. Infrared spectra of polymer from the reaction PMDA + DME-PMA + MDI at various stages of cure.

Film-Forming Properties

In spite of the fact that solutions of high inherent viscosity were produced from both the dimethyl and the di-*n*-butyl esters of pyromellitic acid in admixture with the dianhydride, flexible films could not be produced directly. If the polymer solution is poured into a nonsolvent (e.g., methyl alcohol), the polymer precipitates. It is then washed with additional nonsolvent and dried under vacuum at 80°C. When this isolated polymer is redissolved in an appropriate solvent (e.g., NMP), a flexible film can be obtained by curing at 150°–200°C. Table VI summarizes the properties of such reconstituted solutions. It should be noted that these solutions have lower viscosity at higher solids.

Apparently, precipitation and re-solution remove some contaminants which interfere with film formation in the virgin materials. Evaporation of the filtrate from the polymer isolation did provide a small amount of solid material (about 1 g corresponding to approximately 17% based on solid polymer). Washing this solid with water and subsequent evaporation provided another solid fraction (1% based on solid polymer). Figures 1 and 2 are the infrared spectra of these

fractions. The presence of acid (1700 cm^{-1}) and ester groups (1740 cm^{-1}) in the filtrate and ester amide or urea groups (1640 cm^{-1}) in the water wash would indicate that the contaminants are unreacted materials or low molecular weight products.

That the film is indeed polyimide is shown in the infrared spectra of Figure 3. This shows changes during various degrees of cure. These changes are analogous to those of the conventional PMDA/diamide reaction and the PMDA/PMA/diisocyanate reaction, and indeed the infrared spectra of the cured film is virtually identical with that of a polyimide derived from PMDA + MDA.¹ In an earlier paper¹ the rate of cure of a film derived from the anhydride/acid reaction was followed spectrophotometrically at various temperatures. This was similarly done for a film derived from the anhydride/ester reaction in the present paper. By comparing these spectra, the relative rates of cure could be ascertained. It appeared that the cure rate for the ester-derived film was slower as evidence by the slower rate of disappearance of the carbonyl band at 1600 cm^{-1} .

The reactions of the dianhydride/diester combinations reported in this paper as well as the dianhydride/tetraacid mixtures¹ are further described in the patent literature.^{3,4}

CONCLUSIONS

We have shown that high molecular weight polyimide polymers can be produced by the reaction of diisocyanates with dianhydrides and their dialkyl esters. This reaction works well with PMDA, BTDA, TMA, and their esters as well as mixtures of these materials. The polyimide polymers produced are identical to those derived from dianhydrides and diamines. A catalyst is not necessary, but high molecular weight polymer does depend on the anhydride/ester ratio and temperature. Tough flexible films can be obtained from precipitated and redissolved polymer solutions.

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Received January 27, 1977

Revised April 26, 1977