# The Formation of Polyimides
# from Anhydrides and Isocyanates

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## Synopsis

The addition of water to the reaction of isocyanates with carboxylic acid anhydrides
has been observed to increase markedly the rate of formation of the corresponding imide.
This effect has been observed with both monofunctional and difunctional reagents as
well as in different solvents. Evidence is presented which suggests that water hydro-
lyzes the isocyanate either to the corresponding urea or amine.

The neat, uncatalyzed reaction of alkyl and aryl isocyanates with car-
boxylic acid anhydrides has been reported[1,2] to give the corresponding imide
and carbon dioxide. Acetic anhydride and ethyl isocyanate require 180°C.
An example from more recent literature[3,4] claims that N-phenylphthalimide
can be obtained in 85% yield when the neat reagents are heated at 180°;
however, lower yields of N-phenylphthalimide (63% and 27%, respec-
tively) were observed when pyridine or a trace of perchloric acid was used:



$$+ CO_2 \quad (1)$$
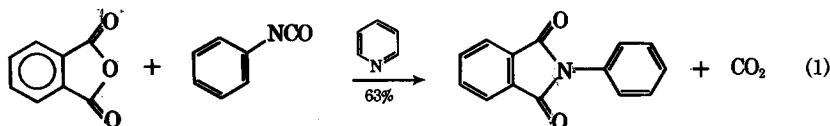
Also, two papers and two patents have appeared,[5–7] the former disclosing
that this reaction can be used to synthesize polymeric imides, and suggesting
that the mechanism involves a seven-membered ring (I):
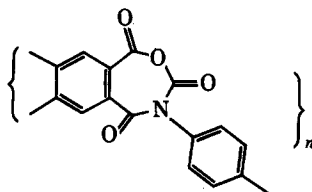


I

We now report that water permits the rapid formation of imides from an-
hydrides and isocyanates at much lower temperatures;[6,8]* these observations
allow an alternative explanation for imide formation.

* Reference 6 describes the addition of catalytic quantities of water but does not discuss
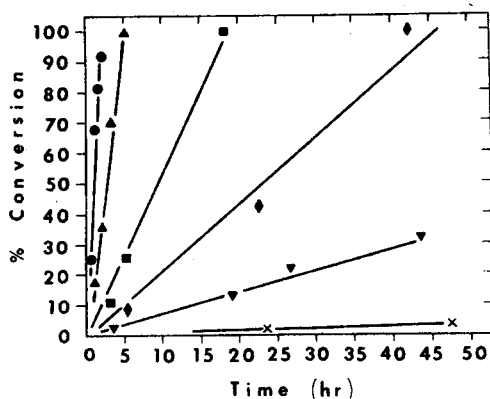the chemistry.
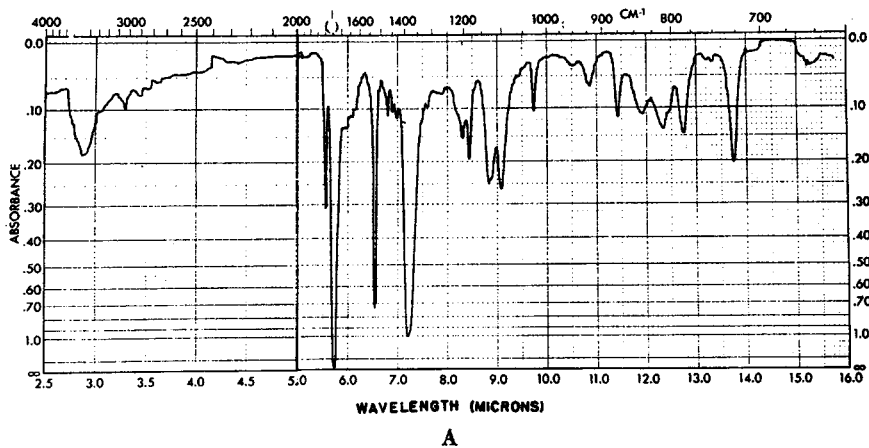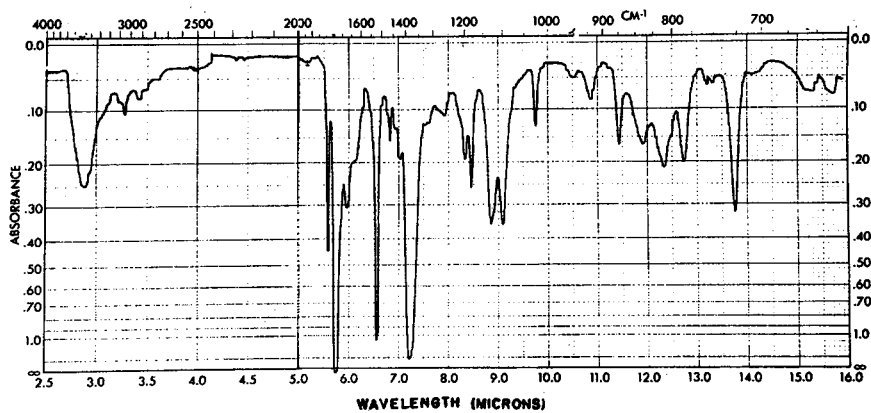
Fig. 1. Effect of added water on the phenyl isocyanate–phthalic anhydride reaction: (●) equivalent water; (▲) 0.020 eq.; (■) 0.010 eq.; (◆) 0.0050 eq.; (▼) 0.002 eq.; (✕) no added water.
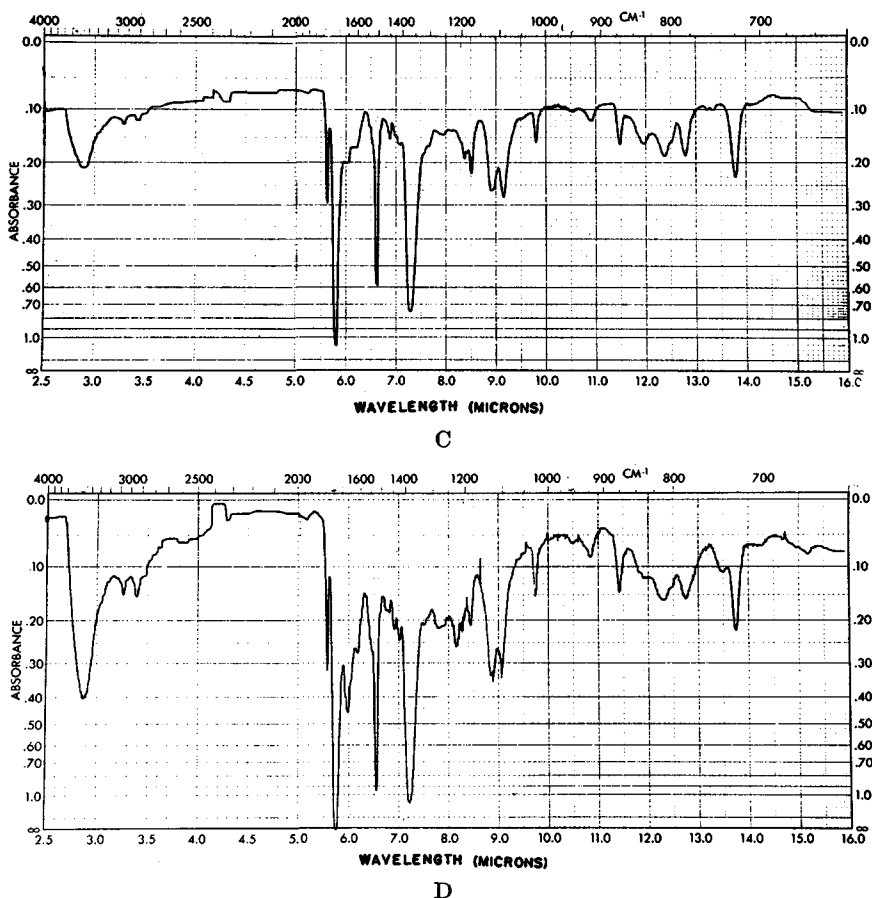


A



B

Fig. 2 (*continued*)

Fig. 2. Polyimide: A, from MDI—PMDA in dry, distilled DMF; B, from MDA–PMDA in DMF; C, from MDI–PMDA in DMF as received; D, from MDI–PMDA in dry, distilled MDF containing 0.25 equiv. water.

In a study of solvent effects upon the reaction of phenyl isocyanate with phthalic anhydride,[8] we found that in refluxing pyridine only traces of gas evolved and very little N-phenylphthalimide was obtained. On repeating this reaction there was isolated only 7% imide from a pyridine solution initially 1.0$M$ in phenyl isocyanate and phthalic anhydride after refluxing for 24 hr. It then became of interest to determine whether or not such a reaction is catalyzed by impurities such as active hydrogen-containing compounds.

Carefully purified starting materials (freshly distilled phenyl isocyanate, freshly sublimed phthalic anhydride and pyridine distilled from KOH pellets onto freshly roasted molecular sieves) showed 13% conversion to imide by infrared, the maximum obtained after 143 hr at reflux. Furthermore, no dimer or trimer[9] was found. Thus, when moisture is excluded, phenyl isocyanate and phthalic anhydride react very slowly, if at all.

Conversely, however, when a trace of water (0.056 equivalent) is added to the reaction in pyridine, the rate of formation of imide as determined by infrared absorption at 1378 cm$^{-1}$ (7.25 $\mu$) is doubled (see Fig. 1). Greater amounts of water further increase the rate until 1 molar equivalent is reached; a slower rate is observed with 2 molar equivalents. With 1 equivalent of water present, the reaction is complete within 2 hr, and 97% N-phenylphthalimide can be isolated. No other products save water and carbon dioxide are indicated. The small amount of reaction observed in the dried pyridine is probably due to traces of water.

The attempt to conduct a completely anhydrous reaction was not extended to highly polar solvents such as dimethyl sulfoxide (DMSO), dimethylformamide (DMF), etc., since these materials are known to contain small amounts of water, amines, and similar active hydrogen-bearing materials, which are extremely difficult to eliminate.[9,10] However, results similar to those in pyridine are obtained when water is added to dimethylformamide used as received. Qualitatively, the effect of water is to increase the rate of imide formation (see experimental section).

The continued increase in rate with increasing amounts of water is not suggestive of catalytic activity, but indicates that a different reaction is occurring. Gas evolution, disappearance of isocyanate, and isolation of diphenylurea in 96% yield from a mixture of reagents treated with water indicate that hydrolysis of the isocyanate is the first step. Moreover, the reaction of diphenylurea and phthalic anhydride proceeds at a similar rate and gives the same yield of imide. Ureas are known to react with anhydrides[12-17]; the reaction is rapid and clean:



$$+ CO_2 + H_2O \quad (2)$$
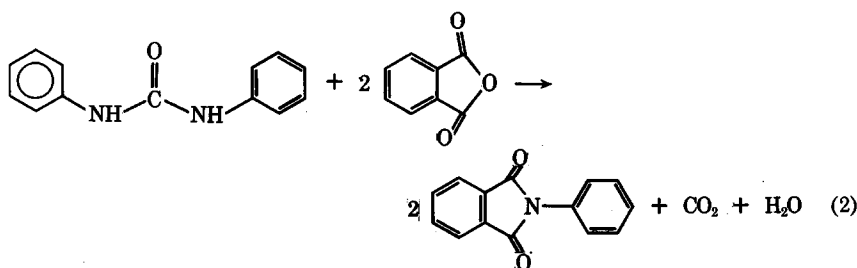
Depending upon the structure of the isocyanate, water may hydrolyze it to the corresponding amine.[18] Although the mechanism of the urea–anhydride reaction is not clear, amines add to anhydrides giving amide acids, which by dehydration are converted to imides. In either case, the effect is to provide a low-energy pathway to the product.

On the other hand, Meyers has described[5] a direct reaction of isocyanate and anhydride to form cyclic intermediate I, which subsequently decomposes to imide. Thus, 4,4'-diisocyanatodiphenylmethane (MDI) and pyromellitic dianhydride (PMDA) are reacted in DMF to give a soluble fraction and the insoluble polyimide. The infrared of the polyimide is shown in Figure 2a. We have also isolated this soluble fraction from a repetition of

Meyers' experiment, and it is nearly identical, in infrared (Fig. 2b) and NMR spectra, to the product obtained from 4,4'-diaminodiphenylmethane (MDA) and PMDA under the same reaction conditions (Fig. 2c). Note that adding water to the MDI–PMDA reaction increases the intensity of the 6.0 $\mu$ band (Fig. 2d). The three carbonyl bands reported by Meyers result from a mixture of imide and amide acid in the short-chain soluble polymer. From the relative intensity of the acidic proton in the NMR of the MDI–PMDA reaction without added water ($\delta$ (DMSO-$d_6$) 10.58), we would judge the amide acid/imide ratio to be approximately 1/3. The presence of a polyurea, from the reaction of MDI with traces of moisture, could not be established or disproved. Some urea linkages in the soluble product mixture could account for the carbon dioxide observed by Meyers.

Solvents other than DMF may be used to make polyimides from MDI and PMDA. In DMSO and DMAc, for example, polymer of good molecular weight can be obtained. Inherent viscosities (0.5% in sulfuric acid) of 0.6–0.9 dl/g can be obtained.

In conclusion, the effect of water on the isocyanate–anhydride reaction is to allow imide formation at temperatures substantially below that required for the neat, uncatalyzed reaction. The intermediate formation of a urea has been demonstrated in one case, and of an amide acid in a second. Enhanced rates of imide formation have also been observed in pyridine and DMF.

## EXPERIMENTAL

The reagents used are commercially available. Phenyl isocyanate was redistilled. Phthalic anhydride was sublimed prior to use. Pyridine dried over freshly roasted molecular sieves for at least 24 hr was distilled.

### N-Phenylphthalimide

**Pyridine.** A solution of phenyl isocyanate (4.35 ml. 0.040 mole) and phthalic anhydride (6.0 g, 0.04 mole) in pyridine (40 ml; 0.09% water by Karl Fisher) was refluxed under exclusion of moisture. The absorption intensity at 7.25 $\mu$ ( 1379 cm$^{-1}$) of various samples was recorded.

**Effect of Water.** Distilled water was added to solutions prepared as described above (Table I). The absorptions of phthalic anhydride at 5.4 $\mu$ (1852 cm$^{-1}$) and 5.6 $\mu$ (1787 cm$^{-1}$) were followed.

TABLE I
Addition of Water to Phenyl Isocyanate-Phthalic Anhydride Reaction

| Expt. no. | Amount of water added |
|-----------|-----------------------|
| 1 | 0 mg |
| 2 | 20 mg (0.0002 equiv.) |
| 3 | 45 mg (0.005 equiv.) |
| 4 | 90 mg (0.010 equiv.) |
| 5 | 180 mg (0.020 equiv.) |
| 6 | 360 mg (0.040 equiv.) |

| Expt. no. | Water added | Absorbance | |
|---|---|---|---|
| | | $5.82 \mu$ | $7.25 \mu$ |
| 1 | 0        equiv. | 0.60 | 0.50 |
| 2 | 0.0024 equiv. | 0.96 | 0.77 |
| 3 | 0.0080 equiv. | 1.6 | 2.0 |

After cooling expt. 6, colorless plates of N-phenylphthalimide, mp 201–205°C, (7.0 g) separated and were filtered. The filtrate was evaporated under vacuum treated with CHCl$_3$, from which an additional 1.55 g of imide (total yield 8.55 g, 96%) was isolated.

**Effect of Ethanol.** Absolute ethanol was added to reaction mixtures as above. The analysis and work-up were similar, except that the CHCl$_3$ solution was washed with NaHCO$_3$ solution to remove ethyl hydrogen o-phthalate, and ethyl carbanilate was determined by comparison of the infrared spectrum of the CHCl$_3$ solution with spectra of known mixtures of N-phenylphthalimide and ethyl carbanilate.

**Dimethylformamide.** To phthalic anhydride (6.0 g, 0.04 mole) in dimethylformamide (40 ml, used as received) in three separate experiments were added 0, 21.5, and 72 mg water (Table II). Phenyl isocyanate (4.35 ml, 0.04 mole) was added to each and the solutions were heated to 50°C for 3.5 hr. Samples were quenched in CHCl$_3$, and infrared spectral intensities of $N$-phenylphthalimide at 5.82 $\mu$ (1720 cm$^{-1}$) and at 7.23 $\mu$ (1380 cm$^{-1}$) recorded.

## Poly(dimethylmethanepyromellitimide)

Pyromellitic dianhydride (10.0 g, 0.046 mole), 4,4'-diisocyanato diphenylmethane (11.4 g, 0.046 mole), and 143 g (152 ml) of dimethylacetamide were combined at room temperature 23°C) to form a clear solution with stirring. Stirring was continued for approximately 24 hr at the ambient temperature (23–24°C), which yielded a gel. Adding the gel to rapidly stirring acetone in a Waring blendor caused the precipitation of the polyimide as a yellow powder. It was collected, washed with fresh acetone, and dried under vacuum to provide an almost quantitative yield of polyimide; $\eta_{inh}$ (0.5% concd H$_2$SO$_4$) = 1.82 dl/g.

## Pyromellitic Dianhydride (PMDA) with MDI in DMF

To 4,4'-diisocyanato diphenylmethane (MDI, 25.0 g, 0.10 mole) dissolved in 30 ml DMF contained in a previously flamed and CO$_2$-flushed 1-liter three-necked flask equipped with a mechanical stirrer, thermometer, reflux condenser, and gas inlet tube was added PMDA (21.8 g, 0.10 mole) in 370 ml of dry, distilled DMF, producing a greenish-yellow solution. The solution was heated to 40°C for 2.5 hr, then increased to 130°C over 2 hr and held at 130° for 2 hr. Gas evolution was observed at 64°C (225 min) and precipitate formation at 77°C (230 min).

The reaction mixture was allowed to stand at 25° for 16 hr, and the precipitate was filtered, washed with acetone (ca. 1–2 hr), and dried at 80° (0.5 mm), yielding 29.7 g of yellow polyimide.

The filtrate from the reaction mixture was stirred 2 hr in 1.5 liter distilled $H_2O$. The gelatinous precipitate was filtered with difficulty, washed twice with methanol, and dried at 100°C (0.5 mm), yielding 5.5 g solid (see Fig. 2a).

### PMDA with MDA in DMF

Diphenylmethanediamine (MDA, 19.8 g, 0.10 mole, Upjohn Co.), PMDA (21.8 g, 0.10 mole, Princeton Chem. Co.), and DMF (400 ml, no purification, Fisher Scientific Co.) were added to a 1-liter three-necked flask equipped with mechanical stirrer, thermometer, reflux condenser, and gas inlet tube. After heating the yellow-orange mixture to 40°C for 2.5 hr, the temperature was slowly increased to 103°C. It was then necessary to remove water to attain 130°C. Within 20 min, a fine yellow precipitate formed, and heating was continued for 2 hr. The reaction mixture was cooled for 16 hr, and the yellow precipitate was filtered, washed with acetone (1–2 hr) and dried at 80°C (~0.5 mm), yielding 24.6 g polyimide. The yellow filtrate of the reaction mixture was stirred 2 hr in 1.5 liter $H_2O$, causing precipitation of a yellow solid. The solid (8.9 g) was obtained by filtering, washing with methanol, and drying at 60°C (0.5 mm) (see Fig. 2b).

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