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Synthesis of Poly(terephthalic Anhydride) by Hydrolysis of Terephthaloyl Chloride/Triethylamine Intermediate Adduct. Characterization of Intermediate Adduct

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ABSTRACT

Terephthaloyl chloride and triethylamine in a 1:2 ratio react in acetone to form a solid adduct. On the basis of IR spectra, chemical properties, and by analogy to 1:1 adducts between acid chlorides and tertiary amines, the structure of the 1:2-adduct is postulated to be that of a quaternary salt-type involving both acid chloride groups. A 1:1-adduct of terephthaloyl chloride involving only one of the acid chloride groups could not be prepared. The title polymer was prepared in 97% yield by hydrolysis of the adduct with a stoichiometric quantity of water. Similar results were obtained by substituting tri-n-propylamine for triethylamine. Infrared spectra and an x-ray powder diffraction pattern of the polymers are discussed. The latter shows the polymer to be noncrystalline. The polymer was not hydrolyzed by hydrochloric acid but slowly dissolved in concentrated sodium hydroxide solutions as would be expected from carboxylic acid end groups. Resistance to hydrolysis is tentatively attributed to hydrophobicity.

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INTRODUCTION

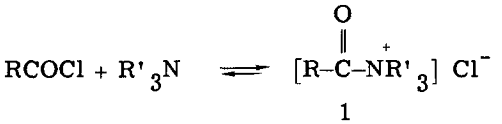
Carothers and Hill [1] prepared polyanhydrides by reacting dicarboxylic acids with acetic anhydride or acetyl chloride (Eqs. 1 and 2):

$$HO_2C\text{–}R\text{–}CO_2H + 2Ac_2O \longrightarrow AcOCORCOOAc \qquad (1)$$

$$AcOCORCOOAc \longrightarrow nAc_2O + \left(OCORCO\right)_n \qquad (2)$$

Although strong fibers can be melt-drawn from high molecular weight polyanhydrides, these filaments are readily hydrolyzed in contact with atmospheric moisture when the R group is aliphatic [2, 3]. Polyanhydrides with aromatic groups [4, 5] of the type $\left(OCOAr\text{–}R\text{–}ArCO\right)$, for example, however, are more stable to hydrolysis [6]. It has been speculated that the hydrolytic stability of such polymers is attributable to the hydrophobic nature of the polymer [4, 6], steric hindrance [4], or partly to a high degree of crystallinity, since amorphous modifications hydrolyze more rapidly [3, 4]. Bucher and Slade [7] as early as 1909 reported obtaining poly(terephthalic anhydride) from the reaction of terephthalic acid and acetic anhydride. They obtained similar results with isophthalic acid. However, they did not investigate these products. The preparation of low-molecular-weight poly(terephthalic anhydride) by partial hydrolysis of terephthaloyl chloride with stoichiometric amounts of water ($n \geq 2$) and in the presence of pyridine ($n \geq 5$) has been reported in a patent [8]. Yoda and Miyake [9] prepared mixed polyanhydrides of terephthalic acid and various aliphatic acids by reacting terephthaloyl chloride with aliphatic dicarboxylic acid in the presence of pyridine in ether or by heating a mixture of the two acids with acetic anhydride.

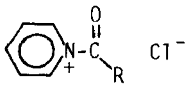
In connection with the formation of amides by the reaction of primary or secondary amines with acid chlorides, many textbooks erroneously assert that no reaction occurs between tertiary amines and acid chlorides. As early as 1886 Dennstedt and Zimmermann reported [10] a reaction between acetyl chloride and pyridine. In 1892 Minunni reported [11] the isolation of a solid from the reaction of benzoyl chloride and pyridine and benzoic acid but formed benzoic anhydride in 78% yield when treated with a limited quantity of water. The early structures of adducts of acid chlorides with tertiary amines were depicted with chlorine and the acyl group bound to a pentavalent nitrogen. A great deal of activity and discussion concerning the nature of the reactions took place at the time [12]. Later Adkins and Thompson [13] isolated stable 1:1-adducts from the reactions of various acid chlorides with pyridine or triethylamine; however, they did not postulate a structure for the adducts. Tertiary amines are commonly used for the catalysis of acylation reactions with acid chlorides. An equilibrium (Eq. 3) between the acid chloride and tertiary amine and a quaternary saltlike intermediate (1) has been postulated [14].



$$\mathrm{RCOCl} + \mathrm{R'_3N} \rightleftharpoons [\mathrm{R}-\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{C}}-\overset{+}{\mathrm{N}}\mathrm{R'_3}]\ \mathrm{Cl^-} \qquad (3)$$

1

Shriner et al. [15] have designated a quaternary salt (2) as the structure of the adduct from pyridine and acid chlorides.



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In connection with another problem, interactions of tertiary amines and acid chlorides were investigated. The reaction between terephthaloyl chloride and triethylamine was an extension of these studies. In the present paper we report the isolation and study of an adduct obtained from terephthaloyl chloride and triethylamine and the formation of poly(terephthalic anhydride) on hydrolysis of the adduct.

RESULTS AND DISCUSSION

Isolation and Characterization of 1:2-Adduct from Terephthaloyl Chloride and Triethylamine

Two equivalents of triethylamine quantitatively reacted with one equivalent of terephthaloyl chloride to form a solid adduct (hereafter referred to as the 1:2-adduct). In the IR spectrum (Fig. 1B) of the adduct the peak corresponding to C(O)–Cl at 850 cm^{-1} in terephthaloyl chloride was absent in the spectrum of the 1:2-adduct and new peaks between 2500-2700 cm^{-1} appeared, suggesting complexation of the amine with the acid chloride groups. Stavrova and Chikhacheva [16] have noted a hypsochromic shift of the carbonyl group stretching frequency in the salt they obtained from terephthaloyl chloride and diethylamine at about 1800 cm^{-1}, as compared with the absorption of terephthaloyl chloride at 1775 cm^{-1}, and the appearance of new absorption bands at 2480-2720 cm^{-1} (amide bond) and 700-900 cm^{-1} (C–Cl absorption) with analogous spectra for other salts. Such changes have been attributed [17] to the formation of quaternary ammonium salts.

The 1:2-adduct was easily hydrolyzed by aqueous sodium hydroxide even though it was practically insoluble in most common organic solvents; this behavior suggested an ionic structure for the adduct (3)

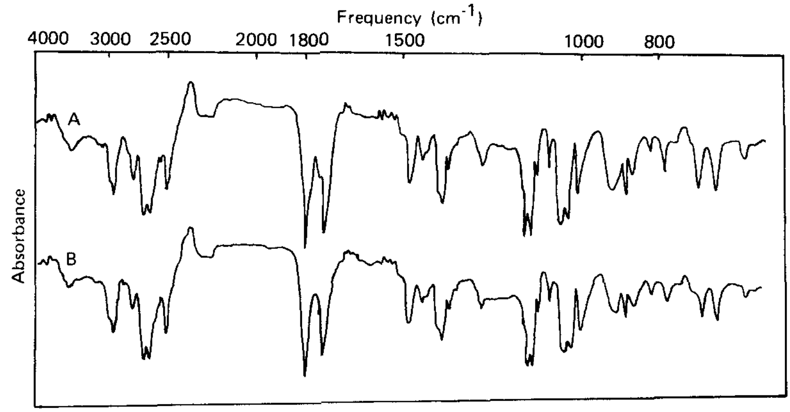
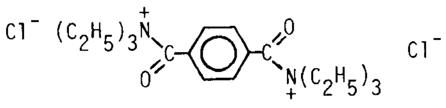


FIG. 1. Infrared spectra of the adduct obtained from triethylamine and terephthaloyl chloride in a molar ratio of (A) 1:1 and (B) 1:2 (potassium bromide disk).

analogous to that proposed [15] for the 1:1-adducts from acid chlorides and tertiary amines.



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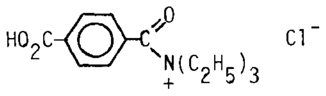
In order to compare the reactivity of the two acyl chloride groups in the starting material and also to explore the possibility of isolating a mono (1:1) adduct (4), the reaction was attempted with equimolar amounts of terephthaloyl chloride and triethylamine.



4

However, the attempted reaction of equimolar amounts of the two reactants produced only the 1:2-adduct and unreacted terephthaloyl chloride. The similarity of the IR spectra (Figs. 1A and B) of the adducts further corroborated the fact that the reaction involved both acid chloride groups even when an insufficient amount of amine was used.

Preparation and Characterization of Poly(terephthalic Anhydride)

The polymer was obtained by reaction of the terephthaloyl chloride-triethylamine adduct with a stoichiometric quantity of water. The polymer slowly dissolved in dilute sodium hydroxide but was insoluble in 10 N hydrochloric acid. In the sodium fusion analysis of the insoluble product, both nitrogen and chlorine were undetectable; however, the presence of chlorine was detectable by the more sensitive Beilstein copper test. It is most probable that the trace of chlorine results from the entrapping of a small trace amount of a chlorine-containing impurity since it was not possible to purify the polymer because of its insolubility. On the basis of these experiments, large values of "n" are probable for the polyanhydride.

In the IR spectrum of the insoluble product (Fig. 2A), the carbonyl group is split into a doublet at 1790 cm^{-1} which is characteristic of p-substituted diesters [18]. An x-ray powder diffraction pattern of the poly(terephthalic anhydride) sample was obtained (Table 1). The peaks corresponding to the product were broad and of low intensity, suggesting a noncrystalline product. The absence of sharp peaks indicated the absence of any detectable quantity of triethylammonium chloride which may have been trapped in the polymer during its formation.

Since the acylated quaternary terminal group would be too reactive to be present, it is assumed that both endgroups are carboxyl. On this basis the structure of poly(terephthalic anhydride) as obtained in the present study is postulated to be (5).

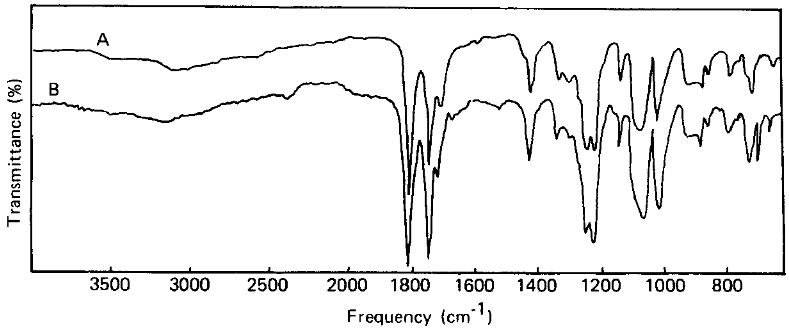
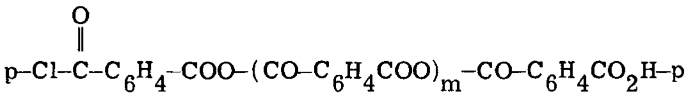


FIG. 2. Infrared spectra of poly(terephthalic anhydride) obtained from (A) triethylamine and (B) tri-n-propylamine (potassium bromide disk).

TABLE 1. X-Ray Diffraction Pattern for Poly(terephthalic Anhydride) from Hydrolysis of Terephthaloyl Chloride/Triethylamine Adduct

d[a]	2θ[b]	I/I_o[c]
5.34	16.6	35
5.27	16.8	40
3.15	28.3	100

[a] Spacings between parallel planes.
[b] Angle of diffraction.
[c] Ratio of intensity of diffraction to intensity of strongest line in percent.



$$p\text{-}Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}COO\text{-}(CO\text{-}C_6H_4COO)_m\text{-}CO\text{-}C_6H_4CO_2H\text{-}p$$

5

Since poly(terephthalic anhydride) is not sterically hindered and is not crystalline, as evidenced by the x-ray powder diffraction studies, the stability of the polymer to hydrolysis may be primarily attributed to hydrophobicity as has been previously suggested [4, 6, 19].

EXPERIMENTAL

Purification of Terephthaloyl Chloride

A commercial sample of terephthaloyl chloride was dissolved in a hot (1:1) mixture of petroleum ethers (30-60 and 55-110°C). A hot filtration removed the terephthalic acid present as an impurity. When the solution was cooled to room temperature, terephthaloyl chloride separated from solution as a crystalline solid. The supernatant liquid was decanted, and the crystals were dried in a vacuum desiccator over phosphorus pentoxide, mp 83°C (Ref. 20, 83-84°C).

Preparation of 1:2-Adduct from Terephthaloyl Chloride and Triethylamine

To a solution of terephthaloyl chloride (2.04 g, 0.0100 mol) dissolved in 20 mL of dry acetone, 2.04 g (0.0200 mol) of freshly distilled triethylamine was added with constant stirring under a nitrogen atmosphere. The reaction was exothermic, and a solid product pale yellow in color immediately precipitated from the solution. Spectral measurements and other experiments were conducted with this product.

Attempted Isolation of 1:1-Adduct from Terephthaloyl Chloride and Triethylamine

To a solution of terephthaloyl chloride (2.04 g, 0.0100 mol) dissolved in 20 mL of dry acetone, 1.02 g (0.0100 mol) of freshly distilled triethylamine was added with constant stirring under a nitrogen atmosphere. After stirring the solution for 1 h, it was filtered under a nitrogen atmosphere through a preweighed sintered crucible. The weight of the insoluble product after drying in a vacuum desiccator was 2.02 g. The filtrate on evaporation yielded 0.95 g of unreacted terephthaloyl chloride (48% of the starting material).

Preparation of Poly(terephthalic Anhydride)

The polymer was prepared from the 1:2-adduct by adding 0.18 g (0.0100 mol) of water dissolved in 5 mL of acetone to the acetone solution containing the solid 1:2-adduct and stirring the solution overnight (12 h). The insoluble polymer was collected by filtration and dried in a vacuum desiccator (yield 3.76 g, 97%).

The polymer was also obtained by using tri-n-propylamine as the base using the same procedure reported above. The IR spectrum (Fig. 2B) was similar to that obtained with triethylamine. The yield of polymer was 90-95%.

Hydrolysis of poly(terephthalic anhydride) was attempted. Little if any hydrolysis took place after refluxing 1.0 g for 6 h with 25 mL of 10 N hydrochloric acid. The starting material (0.95 g, 95%) was recovered by filtration. The compound slowly dissolved in concentrated sodium hydroxide solution (15-20%) as would be expected from a structure having terminal carboxyl groups.

Preparation of low molecular weight poly(terephthalic anhydride) ($n \geq 5$) reported in a patent [8] was attempted by direct hydrolysis of terephthaloyl chloride in order to obtain a sample for comparative purposes. The cited procedure was followed but only terephthalic acid was obtained as the major product.

Infrared and X-Ray Diffraction Spectra

Infrared spectra were obtained with Perkin-Elmer Model 337 and Model 525 grating infrared spectrophotometers. Samples were examined as potassium bromide pressed disks. In the case of the intermediate 1:2-adduct, both the powdered salt and KBr were dried in an oven at 100°C overnight before making the disk.

The x-ray powder diffraction pattern was run using a Picker X-ray

Diffractometer (CuK$_\alpha$, Ni *filtered*, 30 kV, 20 mA). The solid sample was dried in a vacuum desiccator for 2 h prior to the experiments. It was ground to a fine powder and dried again for 1 h in the desiccator. The dry sample was then pressed into a holder and a diffraction pattern was obtained.

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