[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

The Polymerization of *o*-*p*-Toluylbenzoic Acid

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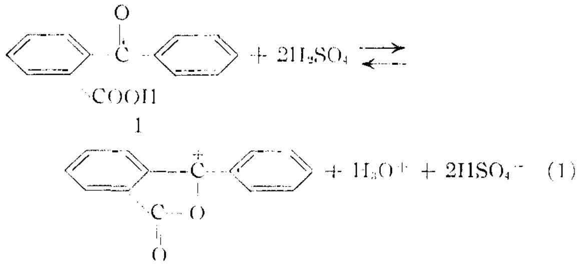
In both polyphosphoric acid and perfluorobutyric anhydride, *o*-*p*-toluylbenzoic acid reacts to give low molecular weight, red polymers. The structure XIII is proposed for the polymer, and its formation is rationalized as involving the addition of a carbonium ion VII to a quinoid form VIII.

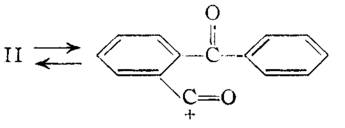
It has been shown[1] that, in sulfuric acid solution, *o*-benzoylbenzoic acid ionizes according to the equations



I

II

(1)



(2)

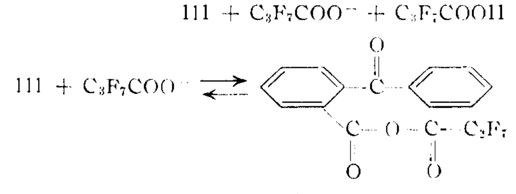
III

The presence of the ion II is demonstrated further by the fact that when *o*-benzoylbenzoic acid in sulfuric acid is treated with benzene, toluene or *t*-butylbenzene, the resultant products are 3,3-diphenylphthalide, 3-phenyl-3-*p*-tolyl phthalide or 3-phenyl-3-(*p*-*t*-butylphenyl)-phthalide (IV), respectively, all obtained in yields of better than 70%. The structure of IV follows from its preparation from *o*-(*p*-*t*-butylbenzoyl)-benzoic acid[2] and benzene, as well as from benzoylbenzoic acid and *t*-butylbenzene, from comparison of its ultraviolet spectrum with the spectrum of the known 3,3-diphenylphthalide, and from an independent synthesis by a method used for the preparation of 3,3-diphenylphthalide.

In polyphosphoric acid,[3] too, benzoylbenzoic acid ionizes to give the ions II and III. At elevated temperatures (100–140°), benzoylbenzoic acid gives anthraquinone, and *o*-(*p*-*t*-butylbenzoyl)-benzoic acid gives 2-*t*-butylanthraquinone.[2] At lower temperatures (80°), in the presence of benzene, mixtures of the phthalides and the anthraquinones are obtained, and, in the cold, benzoylbenzoic acid and benzene react to give a 90% yield of 3,3-diphenylphthalide.

Like polyphosphoric acid, perfluorobutyric anhydride is a strong dehydrating agent, which gives rise during reaction to the relatively strong acid, perfluorobutyric acid. By analogy with perfluoroacetic anhydride,[4] we would expect the following equilibria to obtain in a solution of *o*-benzoylbenzoic acid in perfluorobutyric anhydride

$$\mathrm{I} + (C_3F_7CO)_2O \rightleftharpoons \mathrm{III} + C_3F_7COO^- + C_3F_7COOH \quad (3)$$

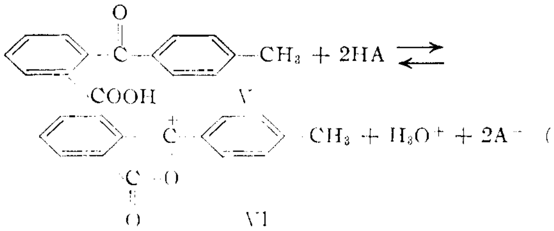


(4)

$$\mathrm{III} \rightleftharpoons \mathrm{II} \quad (5)$$

The presence of III in perfluorobutyric anhydride solutions is suggested by the ready conversion of *o*-(*p*-*t*-butylbenzoyl)-benzoic acid to 2-*t*-butylanthraquinone by this reagent. The presence of II is suggested by the fact that *o*-benzoylbenzoic acid and benzene react in perfluorobutyric anhydride to give low yields of 3,3-diphenylphthalide. However, *o*-(*p*-*t*-butylbenzoyl)-benzoic acid is recovered unchanged after refluxing with benzene and perfluorobutyric anhydride for 30 hours.

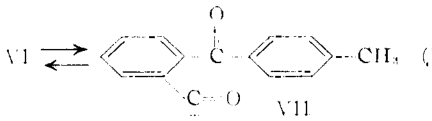
With *o*-*p*-toluylbenzoic acid a more complex ionization, involving the methyl group, becomes possible. In a strong acid, HA, the species shown in the equations below may occur



V

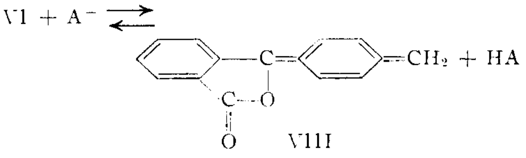
VI

(6)



(7)

VII



(8)

VIII

The reactions of *o*-*p*-toluylbenzoic acid in sulfuric acid indicate ionization to VI and VII. Thus V is cyclized readily to 2-methylanthraquinone by sulfuric acid and gives 3-phenyl-3-*p*-tolylphthalide when treated with benzene in cold sulfuric acid.

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(1) A. H. Gleason and G. Dougherty, THIS JOURNAL, **51**, 310 (1929); M. S. Newman, *ibid.*, **64**, 2324 (1942); C. W. Deane, *ibid.*, **67**, 329 (1945); M. S. Newman, H. G. Kuivila and A. B. Garrett, *ibid.*, **67**, 704 (1945).

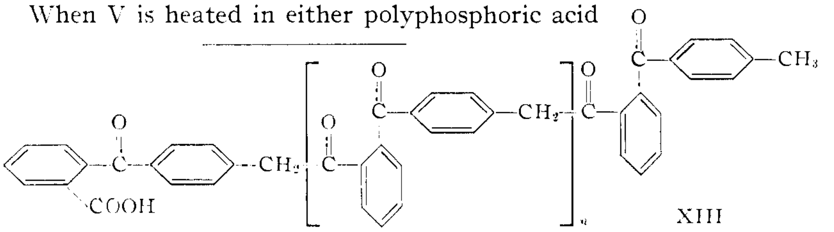
(2) A. T. Peters and F. M. Rowe, *J. Chem. Soc.*, 181 (1945).

(3) H. R. Snyder and F. X. Weber, THIS JOURNAL, **72**, 2962, 2965 (1950); J. Koo, *ibid.*, **75**, 1891 (1953).

(4) M. Stacey, E. J. Bourne, J. C. Tatlow and J. M. Tedder, *Nature*, **164**, 705 (1949); E. J. Bourne, M. Stacey, J. C. Tatlow and J. M. Tedder, *J. Chem. Soc.*, 2976 (1949); 718 (1951); E. J. Bourne, J. E. B. Randles, J. C. Tatlow and J. M. Tedder, *Nature*, **168**, 942 (1951).

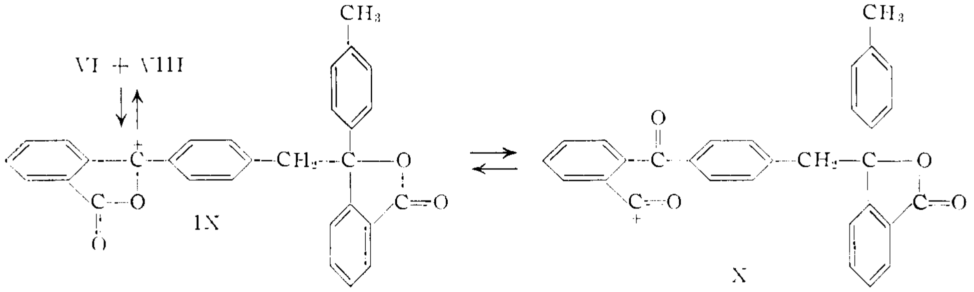
VIII probably does not exist in sulfuric acid, since bisulfate ion is too weak a base to abstract a proton from VI. In polyphosphoric acid and perfluorobutyric anhydride, both of which afford a stronger conjugate base than bisulfate ion, there is, as we shall see, indirect evidence to indicate the formation of VIII.

When V is heated in either polyphosphoric acid or perfluorobutyric anhydride, red polymeric products are obtained. Limpricht and Wiegand[5] have described similar products obtained by heating V at 260°, by heating an acetic acid solution of V with phosphorus oxychloride or by heating *o-p*-toluylbenzoyl chloride. Analyses of these amorphous, polymeric materials indicated that they were formed from V by loss of the elements of water, but definite structures were not assigned.



XIII

If solutions of V in either polyphosphoric acid or perfluorobutyric anhydride contain VI, VII and VIII, polymerization becomes possible *via* addition of VI or VII to VIII, according to equations 9 and 10.



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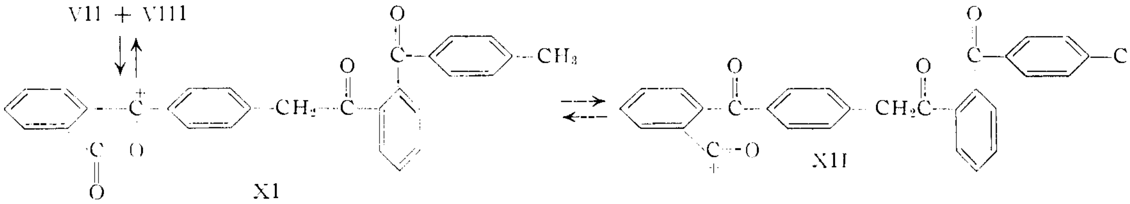
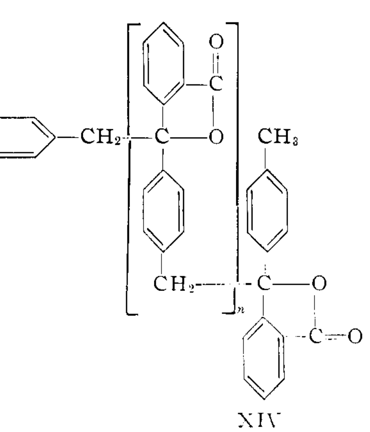


(10)

The chain could continue to grow by addition of a second molecule of VIII to IX, X, XI or XII and would be terminated by reaction of the carbonium ion with an anion or a solvolyzing molecule such as water.

For the sake of simplicity we will assume that the quinoid form VIII adds the carbonium ion preferentially in either the acylium forms VII, X and XII or the lactone forms VIII, IX and XI, and that termination is either by water or hydroxyl ions. The structures of the final polymer then will be given by XIII if the acylium forms are favored and by XIV if the lactone forms are favored. It is, of course, possible that the carbonium ion adds in both forms and that the polymer has a mixed structure.

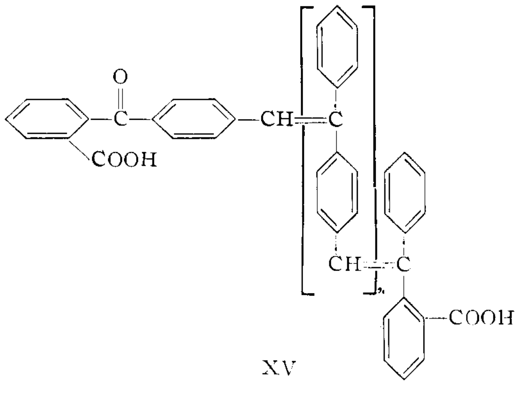


XIV

The values for the percentage C and H, and the molecular weight as a function of n would be the same for XIII, XIV and the mixed structure, however.

It can be shown readily that XIV is not a correct structural representation of the polymer. The red color of the polymer can be reconciled with XIV only by assuming a tautomeric equilibrium between XIV and XV.

If such tautomerism exists, the lactone rings of XIV should be opened readily by alkali. At the very least, an appreciable number of the lactone rings would have to be in the open form of XV to account for the observed color. A consequence of this is that the molecular weight determined by an ebullioscopic method should be far higher than the



XV

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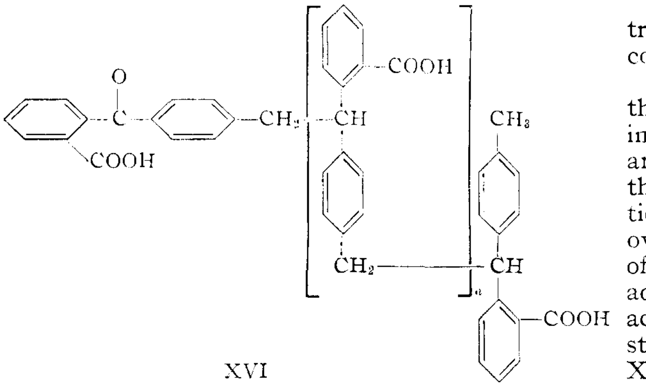
[5] H. Limpricht and O. Wiegand, *Ann.*, **311**, 178 (1900).

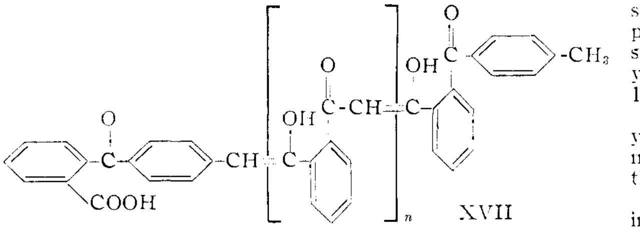
neutral equivalent. We find, however, that the neutral equivalent is identical, within experimental error, with the ebullioscopic molecular weight. On this basis, XIV may be eliminated.

This conclusion is reinforced by considering the reduction products of the polymer. Reduction of XIV would be expected to open the lactone rings to give XVI.


XVI

The neutral equivalent of XVI would be very much lower than that of XIV. We find, however, that reduction of XIV with zinc and acid results in a tan-colored product having a neutral equivalent only slightly lower than that of the starting material.

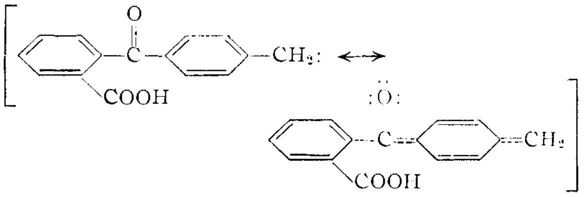
The structure XIII, on the other hand, adequately accommodates the known facts. The red color could be due to the diketone system or, more probably, to existence of the compound wholly or partly in the enolic form XVII.


XVII

It is consistent with this explanation that the color of a polymer solution is very strongly intensified by the addition of alkali, since the enolate ion would be more highly colored than the enol. Reduction is accompanied by a loss of color, since both the diketone system and the possibility of enol formation are lost.

On treatment with alkali the reaction by which the polymer is formed is reversed. Limpricht and Wiegand[5] found that they could isolate the starting *o-p*-toluylbenzoic acid after treating their products with alkali, and we find that a polymer, which initially had a neutral equivalent of 2000, had a neutral equivalent of only 704 after refluxing for four hours with potassium hydroxide in 50% ethanol–50% water. The reversal by alkali can be rationalized by assuming attack by hydroxyl ion on a carbonyl carbon followed by ejection of the carbanion XVIII.

Although we have repeated the degradative reactions reported by Limpricht and Wiegand,[5] these are of questionable structural significance, since they were carried out under alkaline conditions. Because the polymer is degraded by alkali, only transformations carried out under neutral or acidic conditions are valid for structural considerations.


XVIII

The evidence that most favors XIII is the fact that the polymers have a single carboxyl group as indicated by the identity of the neutral equivalent and the ebullioscopic molecular weight. The fact that the neutral equivalent is unchanged by reduction is further evidence for this structure. Moreover, it seems reasonable to us, from considerations of steric hindrance, that the carbonium ion should add to the quinoid form VIII preferentially in the acylium form. We conclude, therefore, that the structure of the polymer is best represented by XIII.

Experimental[6]

Experiments with Sulfuric Acid. 3,3-Diphenylphthalide.[7]—Concentrated sulfuric acid (90 cc.) was added dropwise with stirring to *o*-benzoylbenzoic acid (9.05 g., 0.04 mole) in benzene (200 cc.). The mixture was stirred 6 hours and then poured into a large volume of water. The benzene layer was separated and the aqueous layer was extracted with benzene. The benzene solutions were combined and dried, and the benzene was removed to obtain the crude product which was crystallized twice from ethanol; m.p. 118–120°, yield 8.1 g. (71%).

3-Phenyl-3-*p*-tolylphthalide.[8]—*o-p*-Toluylbenzoic acid (9.8 g., 0.04 mole) in benzene (200 cc.) was treated with concd. sulfuric acid (90 cc.) as above. This yielded 6 g. of crude product which was only partially soluble in hexane. The soluble portion was crystallized 3 times from hexane to yield 3.1 g. (26%) of 3-phenyl-3-*p*-tolylphthalide, m.p. 104–106°.

The insoluble material was crystallized from toluene and yielded 2.7 g. (28%) of recovered *o-p*-toluylbenzoic acid, m.p. 137–139°, no depression on mix-melting with an authentic sample of the acid.

Treatment of *o*-benzoylbenzoic acid (9.05 g., 0.04 mole) in toluene (200 cc.) with concd. sulfuric acid (90 cc.) as above gave 9.5 g. (75%) of 3-phenyl-3-*p*-tolylphthalide, m.p. 104–106°.

3-Phenyl-3-*p*-*t*-butylphenylphthalide.—*o*-Benzoylbenzoic acid (9.05 g., 0.04 mole) in *t*-butylbenzene (200 cc.) was treated with concd. sulfuric acid (90 cc.) to yield 9.6 g. (70%) of the phthalide, m.p. 110–112° from hexane.

Anal. Calcd. for $C_{24}H_{22}O_2$: C, 84.17; H, 6.54; mol. wt., 342.5. Found: C, 84.43, 84.50; H, 6.70, 6.88; mol. wt., 312, 328 by Rast method.

This phthalide also was prepared by a method used by Haller and Guyot,[9] to prepare 3,3-diphenylphthalide. *o-p-t*-Butylbenzoylbenzoic acid (14.1 g., 0.05 mole) was added to thionyl chloride (24 g., 0.11 mole), and the mixture was left standing at room temperature overnight. The excess thionyl chloride was removed *in vacuo*, the crude acid chloride was dissolved in benzene, and this solution was added dropwise to a cooled suspension of aluminum chloride (7 g., 0.05 mole) in dry benzene (100 cc.). The reaction mixture was kept at 40° for 3 hours and then at room temperature for 64 hours. It was then decomposed in the usual manner with ice and hydrochloric acid, and the product was extracted with benzene. The benzene solution was washed with dilute hydrochloric acid, water, 10%

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(6) Unless otherwise noted, all the analyses and molecular weight determinations reported below were performed by the Clark Microanalytical Laboratory.

(7) M. Copisarow, *J. Chem. Soc.*, **111**, 10 (1917).

(8) H. Limpricht, *Ann.*, **299**, 308 (1897).

(9) A. Haller and A. Guyot, *Bull. soc. chim.*, [3] **25**, 51 (1901).

sodium carbonate and finally water. The solution was dried, the benzene was removed, and the product was crystallized from hexane; yield 10.6 g. (62%), m.p. 109–111°.

Experiments with Polyphosphoric Acid. 2-*t*-Butylanthraquinone.—The procedure of Snyder and Weber[3] for the preparation of anthraquinone was used to convert *o*-*p*-*t*-butylbenzoylbenzoic acid to the anthraquinone, yield 42%, m.p. 105–107°.

3-Phenyl-3-*p*-*t*-butylphenylphthalide and 2-*t*-Butylanthraquinone.—A mixture of *o*-*p*-*t*-butylbenzoylbenzoic acid (50 g., 0.18 mole), polyphosphoric acid (500 g.) and benzene (1 l.) was refluxed 16 hours. The benzene layer was decanted and the benzene was removed *in vacuo*. On addition of hexane, the phthalide crystallized; yield 41 g. (67%), m.p. 109–111°. From the hexane mother liquors there was obtained 4.7 g. (10%) of the anthraquinone, m.p. 103.5–105°, no depression on mix-melting with an authentic sample of 2-*t*-butylanthraquinone.

3,3-Diphenylphthalide.—*o*-Benzoylbenzoic acid (5 g., 0.022 mole) and polyphosphoric acid (50 g.) in benzene (100 cc.) were stirred for 18 hours at room temperature. From the benzene there was isolated 4.9 g. (78%) of the phthalide, m.p. 118–120°. The polyphosphoric acid layer, when added to water, yielded 0.6 g. of recovered benzoylbenzoic acid.

When the above reaction mixture was refluxed for 25 hours, the products obtained were anthraquinone (27%) and 3,3-diphenylphthalide (30%).

***o*-*p*-Toluylbenzoic Acid Polymer.**[10]—*o*-*p*-Toluylbenzoic acid (50 g.) in polyphosphoric acid (500 g.) was heated at 70–75° for 20 hours. Treatment of the dark, viscous reaction mixture with cold water gave a red product, which was dried and then washed with ether to remove unreacted starting material; yield 32 g. This crude product was extracted continuously with acetone. The resulting acetone solution was concentrated to a volume of 300 cc., and the product was precipitated by adding hexane. The product was purified further by resolution in acetone and reprecipitated with hexane; yield 16 g., m.p. above 300°.

Anal. Found: C, 80.49, 80.53; H, 4.63, 4.71; mol. wt., 1610, 1450, ebullioscopic in chloroform[11]; neut. equiv.,[12] 2100, 1940.

These values are in good agreement with the calculated values for a polymer having n = 5–7.

The material insoluble in acetone was dissolved in chloroform and precipitated with hexane. This purification procedure was repeated two additional times, but the product was still not completely free of traces of ash.

Anal. Found: C, 76.51, 77.00, 76.58, 76.72; H, 4.56, 4.38, 5.01, 4.86.

Degradation of the Polymer by Alkali.—The above polymer of neutral equivalent 1900–2100 (2 g.) was refluxed 4 hours with potassium hydroxide (5 g.) in water (100 cc.) and ethanol (100 cc.). The solution was then added to excess hydrochloric acid in ice-water; the solid which precipitated was filtered and dried *in vacuo* first over concentrated sulfuric acid and then over potassium hydroxide; yield 2 g., neut. equiv. 704.

Experiments with Perfluorobutyric Anhydride. 2-*t*-Butylanthraquinone.—*o*-*p*-*t*-Butylbenzoylbenzoic acid (5.6 g., 0.02 mole) and perfluorobutyric anhydride (8.2 g., 0.02 mole) were refluxed 3 hours. The mixture was poured into cold water and extracted with chloroform. The chloroform extracts were washed with 5% sodium bicarbonate. The chloroform solution was dried, and the solvent was removed to yield 2.0 g. (37%) of the quinone; m.p. 103–104°; no depression on mix-melting with an authentic sample of the quinone. Acidification of the bicarbonate wash solution gave 0.5 g. of recovered starting material.

3,3-Diphenylphthalide.—Perfluorobutyric anhydride (21 g., 0.05 mole) was added to a solution of *o*-benzoylbenzoic acid (8 g., 0.035 mole) in dry benzene (100 cc.), and the mixture was refluxed 5 hours. The excess anhydride was decomposed with water, and the benzene layer was washed with sodium bicarbonate solution and water. From the benzene solution there was isolated 0.6 g. of 3,3-diphenylphthalide, m.p. 118–120°. Acidification of the bicarbonate wash liquors gave 5.8 g. of recovered *o*-benzoylbenzoic acid. When *o*-*p*-*t*-butylbenzoylbenzoic acid was treated as above, no phthalide was formed, and the acid was recovered unchanged.

***o*-*p*-Toluylbenzoic Acid Polymer.**—A mixture of *o*-*p*-toluylbenzoic acid (24 g., 0.1 mole) and perfluorobutyric anhydride (42 g., 0.1 mole) was refluxed 1 hour. The dark red reaction mixture was poured into ice-water; the solid which precipitated was dried and washed with two 300-cc. portions of dry ether to remove unreacted starting material. The crude product was then dissolved in 10% sodium hydroxide (500 cc.) and precipitated with dilute hydrochloric acid. It was filtered and dried to constant weight; yield 20 g., m.p. 160–170° dec. The product was separated into two portions by dissolving it in boiling ethanol and letting the solution cool to room temperature. That portion which separated on cooling, 3–4 g., is designated the polymer soluble in hot alcohol. It melted, with decomposition, from 214–220°, and analyses indicate that n for this polymer is 3–5.

Anal. Found: C, 79.78, 80.06; H, 4.61, 4.69; neut. equiv.,[12] 1284; mol. wt., 1460, 1330, ebullioscopic in butanone.

Removal of alcohol from the filtrate gave a product, 15 g., which is designated as the polymer soluble in cold ethanol. This product melted with decomposition from 140–150°, and analyses indicate that n = 0–1.

Anal. Found: C, 79.11, 79.39; H, 4.91, 4.86; mol. wt., 542, 580, ebullioscopic in chloroform[11]; 560, ebullioscopic in benzene.

A sample from another preparation gave the following results:

Anal. Found: C, 78.31, 78.44; H, 5.04, 4.86; neut. equiv.,[12] 570; mol. wt., 526, 537, ebullioscopic in butanone.

Reduction of the *o*-*p*-Toluylbenzoic Acid Polymer.—The reduction was carried out using Martin's[13] modification of the Clemmensen procedure. Mossy zinc (10 g.) was amalgamated with mercuric chloride (1 g.), concentrated hydrochloric acid (0.5 cc.) and water (15 cc.). The aqueous layer was decanted; water (7.5 cc.), concentrated hydrochloric acid (17.5 cc.), toluene (10 cc.), acetic acid (0.5 cc.) and the polymer soluble in cold ethanol (5 g.) were added. The mixture was refluxed 40 hours. At 6-hour intervals, fresh zinc dust (0.50 g.), concentrated hydrochloric acid (10 cc.) and toluene (25 cc.) were added. The reaction mixture was filtered and extracted with toluene. The toluene solution was dried and the toluene was removed to yield 3.7 g. of straw-colored product. This was purified further by twice dissolving it in acetone and precipitating it with hexane. Even after this treatment, the product did not prove to be free of traces of ash on combustion.

Anal. Found: C, 82.08, 82.52, 81.47, 82.00; H, 5.54, 5.99, 5.76, 5.81; ash, 0, 0.52, 0.09, 0.50; neut. equiv.,[12] 569; mol. wt., 488, 492, ebullioscopic in butanone.

This same procedure applied to the polyphosphoric acid polymer soluble in acetone gave a straw-colored product with a neutral equivalent of 1800. The neutral equivalent prior to reduction was 1900–2100.

Oxidation of the *o*-*p*-Toluylbenzoic Acid Polymer.—The polymer soluble in cold alcohol (5 g.) and potassium dichromate (25 g.) in 10% sodium hydroxide solution (300 cc.) were refluxed 4 hours. The solution was filtered, acidified and decolorized with sodium bisulfite. The crude product weighed 2.3 g. and, of this product, 100 mg. was insoluble in acetic acid. This material was converted to the acid chloride with thionyl chloride and then to the ester with methanol to yield dimethyl terephthalate, m.p. 138–139°, no depression on mix-melting with an authentic sample of dimethyl terephthalate.

The acetic acid soluble material was crystallized from acetic acid–water and gave 2.2 g. of benzophenone dicarboxylic acid, m.p. 238–241°. This was converted, as above, to the dimethyl ester, m.p. 106–108°, no depression on mix-melting with an authentic sample.

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(10) The studies on which the structural assignment for the polymer is based were carried out with the polymer obtained with perfluorobutyric anhydride.

(11) We are indebted to Dr. E. Robert Coburn of Bennington College for these molecular weight determinations.

(12) Neutral equivalents were all determined by titration in acetone–water solution with 0.05 N sodium hydroxide solution using a Beckman *p*H meter and glass electrodes to determine the end-point.

(13) E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).