added to a warm solution of 0.250 g. of D-glutamic acid[25] in 30 cc. of 50% ethanol. After evaporation to dryness, the salt was dissolved in 80 cc. of diluted alcohol (100 cc. of alcohol + 10 cc. of water) and left overnight at 22°. After three crystallizations from diluted alcohol, the glutamate had a constant m.p. of 136–138°. The salt was dissolved in warm water and a little ethanol, the solution was made alkaline with *N* sodium hydroxide and extracted with ether. After evaporation of the ether, the base was converted into the triacetyl derivative which was recrystallized from acetone and melted sharply at 103.5–104°, $[\alpha]^{24}\mathrm{D}$ $-12.8°$. The natural triacetyl derivative[26] has $[\alpha]^{25}\mathrm{D}$ $-11.7°$ and m.p. 101–102°.

REHOVOTH, ISRAEL

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[25] Glutamic acid was first used by Grob for the resolution of dihydrosphingosine; C. A. Grob and E. F. Jenny, *Helv. Chim. Acta*, **35**, 2106 (1952).

[26] H. E. Carter, W. P. Norris, F. J. Glick, G. E. Phillips and R. Harris, *J. Biol. Chem.*, **170**, 269 (1947).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

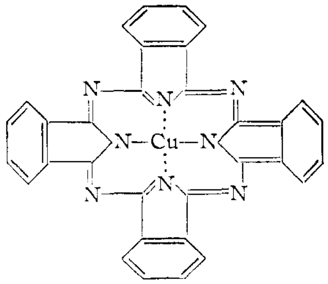
Polymeric Phthalocyanines[1]

BY C. S. MARVEL AND JOHN H. RASSWEILER

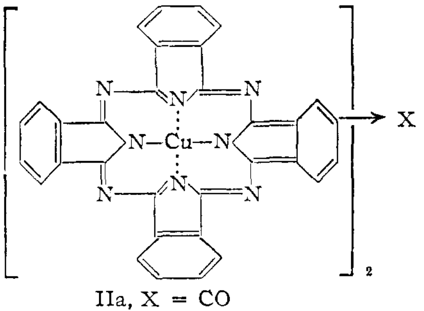
RECEIVED SEPTEMBER 23, 1957

Low molecular weight soluble polymeric phthalocyanines have been prepared from mixtures of pyromellitic acid and phthalic anhydride and of 3,3',4,4'-tetracarboxydiphenyl ether and phthalic anhydride. The polymers are dark blue-green to black powders with fair heat stability and which show visible absorption bands and infrared absorption bands characteristic of phthalocyanines.

Copper phthalocyanine (I) has been found to have great thermal stability since it can be sublimed under nitrogen at 560° without decomposition.[2] The work described in this communication was undertaken to see whether this unit might be incorporated into a polymeric structure to produce an equally thermostable polymer.



I



IIa, X = CO
b, X = SO_2

Dyes containing two phthalocyanine residues (IIa and b) have been prepared by use of a ratio of six parts phthalonitrile to one part of 3,3',4,4'-tetracyanobenzophenone and of the same ratios of phthalonitrile and 4-cyanodiphenylsulfone-3,3',4'-tricarboxylic acid.[3] This proves that mixed units can be introduced into a phthalocyanine structure and hence by use of properly substituted aromatic molecules it should be possible to arrive at polymeric phthalocyanines. In fact, workers at the Sprague Electric Co.[4] have prepared some polymeric phthalocyanines from 3,3',4,4'-tetracyanobiphenyl, and Bailar and Drinkard[5] have prepared polymers from pyromellitic acid and urea under phthalocyanine-forming conditions. However, in both of these cases the polymeric products are quite insoluble and the characterizations of the polymers were difficult.

We have used the principle of introducing mixed aromatic systems into the phthalocyanine-forming reaction to produce linear polymers which are soluble and more readily studied. Two systems have been used with some success. These are pyromellitic acid, phthalic anhydride and urea, and 3,3',4,4'-tetracarboxydiphenyl ether, phthalic anhydride and urea. It was hoped that the first would give a polymer with the recurring unit shown in formula III or the second would yield copolymers with the recurring unit shown in formula IV. It is, of course, realized that the individual units in the phthalocyanine structure may not be so symmetrically arranged as this idealized case but the over-all structure might be that of a linear polymer if the tetrasubstituted and disubstituted aromatic units could be introduced into the molecule in equal molar quantities.

The 3,3',4,4'-tetracarboxydiphenyl ether was prepared from 3,4-dimethylphenol and 4-bromo-1,2-dimethylbenzene by making first the aryl ether and then oxidizing with potassium permanganate.

When a ratio of three moles of phthalic anhydride to one mole of either of the above tetrasubstituted aryl acids was heated under phthalocyanine-form-

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[1] The work discussed herein was initiated as part of the synthetic rubber research project sponsored by the National Science Foundation and completed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman, project engineer.

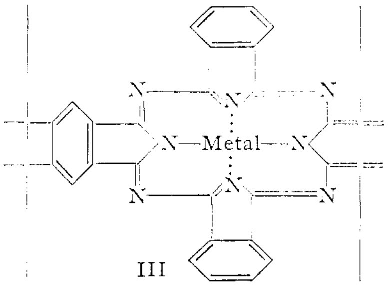
[2] R. P. Linstead, *J. Chem. Soc.*, 1027 (1934).

[3] A. Bucher, U. S. Patent 2,492,732 (December 27, 1949).

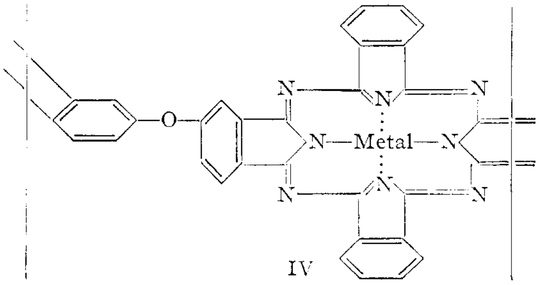
[4] Sprague Electric Co. Final Report under contract No. D.A.-36-039-SC-87 to the United States Signal Corps, May 14 through October 15, 1952; ASTIA AD No. 6116.

[5] W. C. Drinkard, Ph.D. Thesis under Professor J. C. Bailar, University of Illinois, 1956.

ing conditions, reaction occurred. The colored substance produced was partially a simple metal phthalocyanine and partly the desired polymer. Fortunately the less symmetrical polymeric material was somewhat soluble in dimethylformamide and could thus be extracted from the metallic phthalocyanine. The polymers could be reprecipitated from dimethylformamide by the addition of chloroform.



III



IV

The polymers were powders ranging in color from blue-green to greenish black. The deeper colors were observed in the case of the products with greatest viscosity in solution.

Considerable difficulty was experienced in getting satisfactory analyses on these polymeric materials, particularly those made in the presence of molybdenum catalysts. Usually fair values for nitrogen were obtained and the analyses for the metal component when only one was present were reasonably good. The best evidence that the products were really polymeric phthalocyanines was obtained by their absorption in the visible spectrum in the 6000–7000 Å. range,[6] by their absorption in the 12–14 μ range in the infrared[7] and by the fact that their solutions in dimethylformamide were more viscous than the solvent itself.

It is impossible to assign definite molecular structures or molecular weight ranges to these polymers at the present time. They are quite stable to heat, but are decomposed slowly in the air at temperatures above 350°. They burn with difficulty and this is partly the cause of erratic carbon analyses, but part of the difficulty is the lack of uniformity of polymers. Further research will be needed to clarify these points.

Experimental

3,3′,4,4′-Tetramethyldiphenyl Ether.[7]—One hundred grams (0.85 mole) of 3,4-dimethylphenol and 40 g. (0.704 mole) of potassium hydroxide were heated to 150° for 15 minutes, then cooled to 90° at which point 92.5 g. (0.496 mole) of 4-bromo-*o*-xylene was added in one batch; 0.5 g. of copper powder was added and the mixture was brought to reflux at 148°. After 15 minutes, liquid was distilled from the reaction flask through a 12-inch Vigreux column. The temperature in the flask rose from 148 to 247°. The reaction mixture was cooled and treated with 25 g. of sodium hydroxide dissolved in 750 ml. of water. The product was extracted with chloroform. The chloroform solution was washed with water and saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The chloroform was removed on the steam-bath and the product distilled; 5.6 g. of forerun, b.p. 103–107°, was discarded. The product, b.p. 196–202° (12 mm.), was collected in 75.9% yield (85.5 g.). Three recrystallizations from methanol gave white crystals, m.p. 58–59.2°.

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.90; H, 7.97. Found: C, 84.88; H, 8.26.

3,3′,4,4′-Tetracarboxydiphenyl Ether.—Crude 3,3′,4,4′-tetramethyldiphenyl ether (17.95 g., 0.0795 mole) was dissolved in 400 ml. of pyridine and 200 ml. of water. The solution was heated until reflux and then 50 g. (0.316 mole) of solid potassium permanganate was added as rapidly as was necessary to maintain the refluxing temperature. After the addition was complete, the suspension was refluxed for one hour, filtered hot through a Celite filter bed, washed with pyridine and water, and the light yellow filtrate evaporated to 50 ml. under vacuum. The residue was dissolved in a solution of 35 g. of sodium hydroxide in 500 ml. of water. The basic solution was oxidized and filtered exactly as before, using 65 g. of potassium permanganate. The excess permanganate was destroyed with ethanol. The filtrate from this oxidation was cooled to 5° and acidified to *p*H 1. The acid solution was allowed to stand overnight and the white precipitate was collected by filtration and washed with a small portion of cold water; 6.9 g. (25.1%) of product was isolated and recrystallized by dissolving in hot acetone and precipitating with Skellysolve C. The product, m.p. 229–231.5° dec., was a white powder.

Anal. Calcd. for $C_{16}H_{10}O_9$: C, 55.50; H, 2.79. Found: C, 55.57; H, 2.70.

Pyromellitic Acid–Phthalic Anhydride Phthalocyanine Polymers. Using Both Copper Salts and Molybdate.—Three and eighty-one hundredths grams (0.015 mole) of pyromellitic acid (or 3.27 g. if pyromellitic anhydride was used), 6.66 g. (0.045 mole) of phthalic anhydride, 40 g. of urea and 0.4 g. (0.0032 mole) of ammonium molybdate were mixed in an oil-bath at 120° and the temperature then was raised to 170°. When the reaction mixture turned black, 3.6 g. (0.036 mole) of cuprous chloride and 1 g. (0.008 mole) of ammonium molybdate mixed with 5 g. of urea were added. The reaction mixture was shaken and heated to 200° for three hours; 1.8 g. (0.018 mole) of cuprous chloride, 0.1 g. (0.0008 mole) of ammonium molybdate and 10 g. of urea were then added. The heating was continued for three hours at 200°.

The blue-green-black solid was washed from the flask with 300 ml. of boiling water and collected by filtration. The mixture was slurried successively with 400 ml. of 18% hydrochloric acid, 600 ml. of water, 500 ml. of 6% ammonium hydroxide, 200 ml. of water, 200 ml. of 18% hydrochloric acid and 600 ml. of boiling water. The dark powder was dried at 110° and treated in a beaker with 200 ml. of dimethylformamide. The suspension was allowed to stand for four hours, heated to 60° and filtered warm. The blue-purple insoluble copper phthalocyanine was washed with 50 ml. of chloroform. The green-black dimethylformamide solution was treated with three volumes of chloroform and allowed to stand overnight.

The precipitated polymer was collected and washed with 200 ml. of chloroform and dried. The powder was placed in a sublimation apparatus at 190° (11 mm.) for 10 hours to remove a small amount of white impurity which melted below 250°. The dark powder was then slurried twice in 400-ml. portions of water and dried at 110°. The powder was used directly for analysis. The yield of one run (no. 1) was 2.9 g. and of the second run (no. 2) was 2.11 g. The description of the products is given in Table I.

Using Copper Salts without Molybdate.—A mixture of 3.81 g. (0.15 mole) of pyromellitic acid, 6.66 g. (0.45 mole)

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(6) P. A. Barret, E. F. Bradbrook and R. P. Linstead, *J. Chem. Soc.*, 1820 (1939); M. A. Dahlen, *Ind. Eng. Chem.*, **31**, 839 (1939); J. S. Anderson and R. P. Linstead, *J. Chem. Soc.*, 1151 (1938); R. P. Linstead and F. T. Weiss, *ibid.*, 2975 (1950); P. A. Barret, R. P. Linstead, F. G. Rundall and G. Tuey, *ibid.*, 1079 (1940); A. Stern and F. Pruchner, *Z. physik. Chem.*, **178**, 435 (1937); J. H. Helberger, *Ann.*, **536**, 173 (1938).

(7) A. A. Ebert and H. B. Gottlieb, This Journal, **74**, 2806 (1952).

TABLE I

PROPERTIES OF POLYMERIC PHTHALOCYANINES

Polymer No.	Nitrogen, %		Ash, %	Copper, %		Visible[d] absorption, Å.	Viscosity in dimethylformamide, g./100 ml.
	Calcd.[a]	Found[b]		Calcd.[a]	Found		
1	20.41	18.5	11.61		3.8	6980 6500 6100	0.56 (0.006)
2	20.41	19.13	27.08		3.84	6670 6410 6030	1.84 (0.003)
3	20.41	22.25	15.87	11.56	14.77	6680 6390 6010	0.65 (0.014)
4	20.41	19.35	16.51	11.56	15.21	6670 6390 6020	0.83 (0.009)
5	20.41	17.52	18.76	11.56	13.66	6670 6400 6020	0.38 (0.007)
6	20.41	15.09	31.92 (Mo)			6920 6850 6580	0.19 (0.003)
7	15.43[c]	15.02	21.46		4.32	6700 6500 6030	0.507 (0.007)
8	15.43	17.81	8.41	8.75[c]	9.2	6690 6420 6040	1.58 (0.10)

[a] Calculated for the recurring unit III, assuming five recurring units and terminal carboxyl groups. [b] We are indebted to Mr. Jozsef Nemeth for the Dumas nitrogen determinations. [c] Calculated for the recurring unit IV, assuming three recurring units and terminal carboxyl groups. [d] The visible absorption bands were determined for us by Mrs. M. S. Chao with a Cary recording spectrometer, model 14M.

of phthalic anhydride and 40 g. of urea was heated to 180° and the clear melt was then treated with 6 g. (0.6 mole) of cuprous chloride in 10 g. of urea. The temperature was then raised to 200–210° for three hours. An additional 3 g. (0.3 mole) of cuprous chloride and 10 g. of urea were added and the heating continued at 200–210° for 7 hours. The product was then isolated as before except 400 ml. of dimethylformamide was used to dissolve the polymeric material. The color of these products ranged from blue-green to dark green, and very little copper phthalocyanine was isolated. Polymers no. 3 (3.3 g.), no. 4 (3.7 g.) and no. 5 (1.2 g.) were thus obtained.

Using Only Molybdate.—The same amount of reagent as above was used except in place of cuprous chloride 18.51 g. (0.015 mole) of ammonium molybdate was added at first and 2 g. of this reagent and 10 g. of urea were added after two hours of heating. This mixture was heated only four hours. The product was a black powder readily soluble in 100 ml. of dimethylformamide; polymer no. 6, 0.8 g., was thus obtained.

3,3′,4,4′-Tetracarboxydiphenyl Ether–Phthalic Anhydride Polyphthalocyanines. Using Copper and Molybdenum.—A mixture of 3.46 g. (0.01 mole) of 3,3′,4,4′-tetracarboxydiphenyl ether, 4.44 g. (0.03 mole) of phthalic anhydride, 25 g. of urea and 0.4 g. of ammonium molybdate was heated at 120° and then this temperature was raised gradually to 170°. Then 1 g. of ammonium molybdate, 3.6 g. of cuprous chloride and 5 g. of urea were added and the temperature was raised to 202° for six hours, then 1.8 g. of cuprous chloride in 10 g. of urea was added and the heating continued for three hours. The product (no. 7, 5.7 g.) was isolated as in previous cases. It was a soluble greenish-black powder.

Using Copper Alone.—A mixture of 3.46 g. of 3,3′,4,4′-tetracarboxydiphenyl ether, 4.44 g. of phthalic anhydride, 25 g. of urea and 6 g. of cuprous chloride was heated as before to 170° for four hours and then 3 g. of cuprous chloride and 10 g. of urea were added and heating was continued for 8 hours. Purification was carried out as before. Only 200 ml. of dimethylformamide was required to dissolve the dark green powder. Polymer no. 8, 3 g., was thus obtained.

Analyses.—Combustion analyses were carried out in oxygen at 900°, but gave unsatisfactory results and the carbon and hydrogen values were meaningless. We have since learned[8] that phthalocyanines must be burned at at least 1000° to obtain good values. Dumas nitrogen analyses gave satisfactory results. Copper was determined by weighing the ash left on heating the samples at 350° in an electric oven for three hours and then at 550° for two hours and determining the weight of the copper oxide residue. Copper was also determined iodometrically by fusing the polymers with excess sodium bisulfate at dull red heat for one to two hours, cooling the residue, dissolving in water and titrating with potassium iodide and sodium thiosulfate.

Inherent Viscosities.—Samples weighing exactly 0.0150 g. were dissolved in a volumetric flask in 100 ml. of dimethylformamide, the undissolved material was separated, and weighed again to determine the amount of product in solution. The viscosities were determined in an Ostwald viscometer at 25°. The time of flow for this solution was compared to that of the solvent.

Properties of the Polymeric Phthalocyanines.—As noted above, the polymeric materials were powders which varied in color depending on the metal or metals present and the method of preparation. They were of varying degrees of solubility in dimethylformamide and usually those with higher viscosities (molecular weight?) were more soluble. The properties and analyses are collected in Table I.

Infrared.—Ebert and Gottlieb[7] reported that copper phthalocyanine in a Nujol mull gave fairly sharp bands at 8.8, 9.1, 9.2, 11.5, 12.8 and 13.3 μ, whereas the metal-free dye had in addition a band at 10 μ. We checked bands at 8.8, 9.1, 11.1, 12.7 and 13.4 in our preparation of copper phthalocyanine. Polymer no. 1, which was a mixed metal salt of the product from pyromellitic acid and phthalic anhydride in a Nujol mull, gave bands at 8.9, 10.6, 11.1, 12.9, 13.3 and 13.9 μ. Polymer no. 8, which was the copper salt of the product prepared from 3,3′,4,4′-tetracarboxydiphenyl ether and phthalic anhydride, gave bands at 8.5, 9.4, 10.4, 12.8 and 13.6 μ.

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(8) Private communication from Dr. G. F. Palfrey, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware.