or 87% yield. A forerun of 10–15 ml., collected between 110 and 148°, was not identified.

B. **Under Pressure.**—Forty-nine grams (0.5 mole) of triethylborane was added to 35 g. (0.5 mole) of boric oxide in a 100-ml. Magne-Dash autoclave. The mixture was heated for 20 hours at 220° with agitation. The reaction product was distilled through a packed column at 149–151°, producing 78 g. of triethylboroxine or a 95.0% yield. The infrared spectra of the products from A and B were identical to the infrared spectrum of triethylboroxine prepared by the dehydration of ethylboronic acid.

Triethylborane from Triethylaluminum and Triethylboroxine.—To 33.6 g. (0.2 mole) of triethylboroxine was added 45.6 g. (0.4 mole) of triethylaluminum. The addition was performed dropwise with high speed stirring. The addition took one hour due to the exothermic nature of the reaction. When allowed to cool, the reaction mixture set up as a gel. The triethylborane was distilled from the reaction flask after replacing the condenser with a distilling head and receiver. The product boiled at 94–95° and weighed 56.2 g., representing a 95.6% yield. The product was determined by gas chromatography to be at least 99.3% pure. The residual aluminum oxide remaining after distillation did not fume in air and was removed easily from the flask as a free-flowing white powder.

Triethylborane from Triethylaluminum and Trimethoxyboroxine.—To 84 ml. (0.6 mole) of triethylaluminum dissolved in 100 ml. of mineral oil was added, slowly with efficient stirring, 29 ml. (0.2 mole) of trimethoxyboroxine. One hour was again required for the addition due to the large heat of reaction. The product was distilled from the reaction mass at 94–95° and weighed 49.0 g., representing an 88% yield. The infrared spectrum of the product was identical to that in the Sadtler index for triethylborane. The resulting aluminum oxide–aluminum methoxide by-product formed a white, viscous slurry in the mineral oil diluent.

Triethylborane from Ethylaluminum Sesquichloride and Trimethoxyboroxine.—To 160 g. (0.65 mole) of ethylaluminum sesquichloride dissolved in 150 ml. of mineral oil was added slowly 29 ml. (0.2 mole) of trimethoxyboroxine in exactly the same manner as described for the reaction of triethylaluminum with trimethoxyboroxine. The product was distilled from the reaction flask at 94–95° and weighed 52.0 g., representing a 91.2% yield. The infrared spectrum of the product was identical to that in the Sadtler index for triethylborane.

BATON ROUGE, LA.

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

Copper Phthalocyanine Polymers[1]

BY WILLIAM C. DRINKARD AND JOHN C. BAILAR, JR.

RECEIVED MARCH 9, 1959

Polymeric copper phthalocyanines have been produced by the reaction of pyromellitic dianhydride, copper(II) chloride, urea and catalyst at 180°. Molecular weights and equivalent weights have been determined by elemental analysis and by potentiometric titration and the shapes of the molecules have been determined. Average molecular weights as high as 4000 have been identified.

Introduction

The high thermal stability of copper phthalocyanine makes it an interesting unit for the formation of polymers. Since it is proposed that a large measure of stability is gained through the resonance energy, it would be desirable to preserve and if possible enhance the resonance feature. Several studies of polymeric phthalocyanines have been made[2–6] but only that of Marvel and Martin has led to high molecular weight substances.

The investigation reported here involves the formation of polymers by substitution of pyromellitic dianhydride for phthalic anhydride in the conventional phthalocyanine synthesis. The size of the polymer thus obtained has been investigated and the effect of reaction conditions on polymer growth has been studied. Since growth of the polymer may produce sheet-like or linear arrangements, the shape of the polymer molecules has been determined.

Experimental Results

Polymeric copper phthalocyanine has been prepared by heating a mixture of pyromellitic dianhydride, copper(II) chloride, urea and catalyst. The reaction proceeds smoothly at 180° in a manner analogous to the monomeric copper phthalocyanine synthesis.[7] The molecular weight may be varied within limits by suitable control of the reaction conditions.

It is important to note that pyromellitic dianhydride may produce sheet-like polymers, chains, or a mixture of both. The fact that elemental analysis and equivalent weights change rapidly at low molecular weights with a change in number and arrangement of the copper phthalocyanine units makes it possible to determine whether the polymers are linear, as illustrated by the trimer shown in Fig. 1, or sheet-like as illustrated in Fig. 2. No evidence for the sheet-like arrangement has been found.

Molecular Weight by Elemental Analysis.—Because the growth of a polymeric copper phthalocyanine changes the carbon to nitrogen ratio, it is possible to estimate the size of low molecular weight molecules by carbon, hydrogen and nitrogen analyses. Table I gives the relationship of structure to analysis. It may be seen that such a system works best for polymers of low molecular weight and that

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[1] This research was supported by Contract AF 33(616)-3209 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. Glen R. Buell and Lt. Robert L. Rau, project engineers. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government. The paper is based on a portion of a thesis submitted by William C. Drinkard to the Graduate College of the University of Illinois in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1956.

[2] (a) Swiss Patent 263,655 (1949); (b) U. S. Patent 2,492,732 (1949).

[3] Sprague Electric Co., Final Report under Contract No. DA-36-039-SC-87 to the U. S. Army Signal Corps, May 14–Oct. 15, 1952.

[4] E. A. Lawton and D. D. McRitchie, WADC Technical Report 57-642, November, 1957.

[5] C. S. Marvel and J. H. Rassweiler, THIS JOURNAL, **80**, 1196 (1958).

[6] C. S. Marvel and M. M. Martin, *ibid.*, in press.

[7] F. H. Moser, U. S. Patent 2,549,842, April 24, 1951.

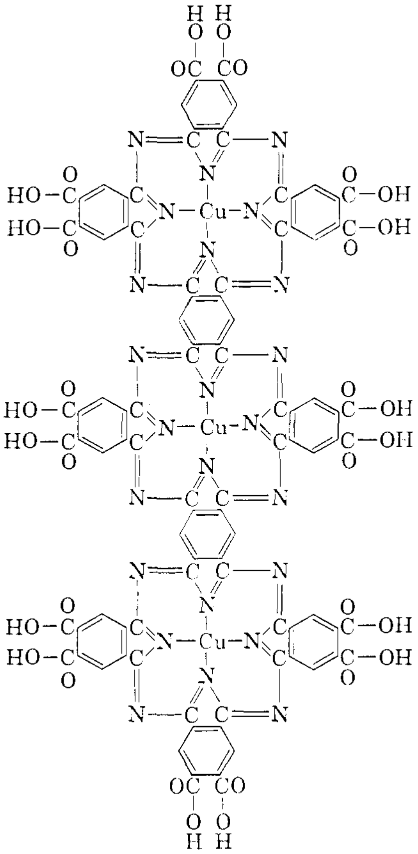

Fig. 1.

it breaks down completely as size increases. For large molecules, carbon–nitrogen analyses do not allow determination of the molecular weight. However, certain deductions can be made, since it is impossible to have linear arrangements in polymers showing more than 16.8% nitrogen.

TABLE I

RELATIONSHIP OF POLYMER SIZE AND STRUCTURE TO ANALYSES AND EQUIVALENT WEIGHT

Polymer units	Equivalent weight	Analyses, % C	H	N	Atomic ratios C/N
1	116	51.7	1.7	12.1	5/1
2	133	52.5	1.6	14.0	4.37/1
3	142	53.0	1.6	14.8	4.16/1
4 (linear)	148	53.0	1.6	15.2	4.06/1
4 (sym.)	168	53.6	1.5	16.6	3.74/1
5 (linear)	151	53.0	1.6	15.5	4.00/1
5 (unsym).	168	53.4	1.5	16.6	3.76/1
6 (linear)	153	52.2	1.5	15.6	3.96/1
6 (sym.)	190	53.8	1.4	17.7	3.54/1
6 (unsym.)	168	53.5	1.5	16.6	3.76/1
7 (linear)	155	53.4	1.5	15.8	3.94/1
8 (linear)	168	53.5	1.5	16.8	3.75/1

Equivalent Weight by End Group Titration.—If it is assumed that decarboxylation does not occur during the syntheses of the polymer, each peripheral benzene ring should have two carboxyl groups attached to it. Since the number of peripheral benzene rings varies with the size and shape of the polymeric molecule, it should be possible to determine, to some degree, the size and shape of the polymer by end-group titration. Table I shows the structure–equivalent weight relationships.

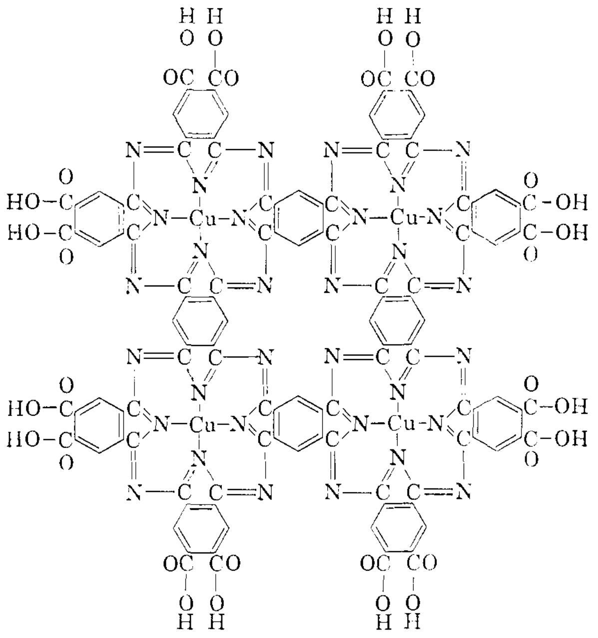

Fig. 2.

In practice it was found difficult to titrate the free carboxyl groups because of the insolubility of the polymeric complex. Additions of 0.1 *N* sodium hydroxide had to be made in small increments and twelve hours allowed for reaction after each addition. The end-point was determined from a plot of *p*H *versus* ml. of 0.1 *N* sodium hydroxide added.

X-Ray Powder Pattern.—It was found that Norelco powder patterns for the various samples of polymer showed a variation in relative peak heights between a broad diffuse peak and sharp peaks as carbon–nitrogen analysis indicated variations in molecular weight. As molecular weight increased, as determined by carbon–nitrogen ratio, the broad diffuse peak became more intense. By plotting the ratio of the diffuse peak height to that of one of the sharp peak heights against nitrogen content, it was possible to obtain a curve from which nitrogen analysis could be predicted to within ±0.5 weight per cent. It appears that the diffuse band is due to materials of large molecular weight while sharp peaks are due to low molecular weight crystalline dimers or trimers.

Molecular Weight by Freezing Point Depression.—Because copper phthalocyanine is normally processed by reprecipitation from sulfuric acid solution, it was thought that some information concerning molecular weights could be obtained from freezing point depression in that solvent. Abnormally low values of the freezing point might be expected due to salt formation by the uncoordinated nitrogen of the copper phthalocyanine. It was found, however, that solutions of the polymeric copper phthalocyanine in 100% sulfuric acid showed a rise in freezing point in the concentration range of 0.5 to 1.9 weight per cent. of solute. No explanation of this observation is known.

Color.—All the polymers investigated are olive-green in color. There is, however, a definite relationship between shade and molecular weight. Low molecular weight materials are light green while larger polymers appear almost black in the solid state.

Experimental

Equivalent Weight.—The equivalent weights were determined by potentiometric titration of 0.3 to 0.5 g. samples of the polymeric copper phthalocyanine with 0.100 *N* sodium hydroxide. A Beckman model G *p*H meter was used for the titration. Reactions were extremely slow requiring approximately a week for each titration. A somewhat easier procedure, suggested to us by Mr. John McLean, involves treatment of the polymer with an excess of standard sodium hydroxide solution, allowing the mixture to stand for a week and back-titrating.

Copper Phthalocyanine Polymers.—Various representative groups of reactions are given to indicate the effect of conditions on polymer size.

Sample Number 1.—A mixture of 20 g. of pyromellitic dianhydride (0.092 *M*), 8 g. of anhydrous copper(II) chloride (0.06 *M*), 108 g. of urea (1.8 *M*) and a catalytic amount of ammonium molybdate was heated at 160° for 30 minutes. The product was washed with 6 *N* hydrochloric acid, dissolved in 200 ml. of concentrated sulfuric acid and reprecipitated by dilution with three liters of water. The precipitate was washed by decantation with 24 liters of water in three-liter portions, filtered, and air-dried. The product was blue-green.

Anal. Found: C, 54.01; H, 1.60; N, 14.25; equiv. wt., 133.

Comparison with Table I indicates a dimer corresponding to a molecular weight of 1,500.

Sample Number 2.—The preparation was carried out as described above, using twice the weight of copper(II) chloride (0.28 *M*) and 5.0 g. of pyromellitic dianhydride (0.023 *M*). The reaction temperature was 180°. The product was dark-green.

Anal. Found: C, 53.43; H, 2.18; N, 15.95; equiv. wt., 152.

Comparison with Table I indicates a molecular weight of 4,000, corresponding to a linear molecule containing six or seven copper phthalocyanine units.

By increasing the reaction time in a similar preparation from 30 minutes to 4 hours, a dark green product was obtained.

Anal. Found: C, 52.34; H, 1.87; N, 18.69.

The ratio of carbon to nitrogen may best be interpreted as the result of amide formation by the peripheral carboxyl groups.

Sample Number 3.—A suspension of 5.0 g. of pyromellitic dianhydride (0.023 *M*), 3.35 g. of copper(II) bromide (0.015 *M*), 26 g. of urea (0.43 *M*) and 4.7 g. of $ZrOCl_2 \cdot 8H_2O$ (0.015 *M*) in 100 ml. of *o*-dichlorobenzene was refluxed for two hours. The product was filtered and reprecipitated as described previously. The product was blue-green.

Anal. Found: C, 53.44; H, 1.66; N, 16.07; equiv. wt., 155.

Comparison with Table I indicates a molecular weight of 4,000 corresponding to six or seven copper phthalocyanine units in the molecule.

End Linking of Polymer Units.—In an attempt to link polymer units through the peripheral *o*-carboxyl groups, a mixture of 2.0 g. of polymeric copper phthalocyanine (sample number 2 above), 0.1 g. of anhydrous copper(II) chloride (0.0008 *M*), 0.1 g. of ammonium molybdate and 25 g. of urea (0.43 *M*) was heated for 30 minutes at 180°. The product was reprecipitated as described above and was dark gray. No structure assignment is possible.

Anal. Found: C, 52.23; N, 20.67.

Discussion

Although it should be theoretically possible to grow the metal phthalocyanines into large graphite-like sheets, it may be seen that analyses and equivalent weight determinations indicate linear arrangements without exception. It is not possible to distinguish linear from "zig-zag" chains by the methods used. It is probable that both are present. Although the copper phthalocyanine sheet is sterically possible, it would appear that intermediates necessary for closing a symmetrical four-unit phthalocyanine system do not form. Thus, reaction takes place only at chain ends where growth occurs between a carboxylated copper phthalocyanine and three pyromellitic dianhydride molecules.

The molecular weights of the polymers reported here are deceptive as to chain length. Because of the large weight of a single unit, a molecular weight of 4,000 represents a chain of only six units. From the data reported, it may be seen that maximum size seems to be reached at six units. At reaction temperatures below 180°, shorter units may be produced. Longer heating, heating at a higher temperature or a combination of both, does not increase molecular weight. It is possible that solubility factors within the melt play a large part in fixing the maximum size of the polymer.

Ammonium molybdate and zirconyl chloride have the same effect on polymer size, whether used in catalytic or ancillary amounts.

Attempts to cross link short chains by reactions of polymer with copper(II) chloride and pyromellitic dianhydride were not successful. The analytical results show a high nitrogen content which cannot be correlated with a polymer structure. To date, attempts to produce polymers of larger size have been unsuccessful. Investigation of larger molecules will require other methods. Techniques presented here become progressively more difficult as molecular weight increases.

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