Polymer Bulletin 2, 841–846 (1980)

Polymer Bulletin

Polymer Phthalocyanines and Their Precursors
2*. The Structure of Polyphthalocyanines

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SUMMARY

The structural uniformity of polyphthalocyanines 3 depends strongly on the starting compounds. With 1,2,4,5-tetracyanobenzene (1) and metallic copper or octacyanphthalocyanine 2 and copper salts structural uniform 3 are received. Polymers, obtained in a reaction of 1 and copper salts, contain structure elements of 3 and polyisoindolenines 4.

INTRODUCTION

1,2,4,5-tetracyanobenzene (1) is taken as bifunctional monomer for the synthesis of metal containing polymer phthalocyanines 3 (ref. 2,3). In connection with the excellent catalytic electrocatalytic and electric properties of 3 (ref. 2-6) information concerning structural uniformity and purity is highly important to get a correlation between structure and activity. But until now this problem was not solved. The aim of this paper is therefore to present first results about the structural uniformity of 3. The synthesis of 3 may lead to three different reaction products: 3, polyisoindolenines 4 (polynitriles), polytriazines 5 (ref. 6-14).

RESULTS AND DISCUSSION

1 was heated with copper powder or plates and different copper salts in mass or high boiling solvents. Moreover the octacyanphthalocyanine 2 was converted with copper salts to polymers. IR and UV/VIS spectroscopic data are in agreement with the following results:

a) Polyphthalocyanines 3 are received in a reaction of 1 with metallic copper or 2 with copper salts. These dark blue coloured polymers contain only phthalocyanine rings with nitrile end groups.

b) Dark brown or black coloured copolymers of 3 and 4 are obtained in the reaction of 1 with copper salts.

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*Part 1 see ref. 1

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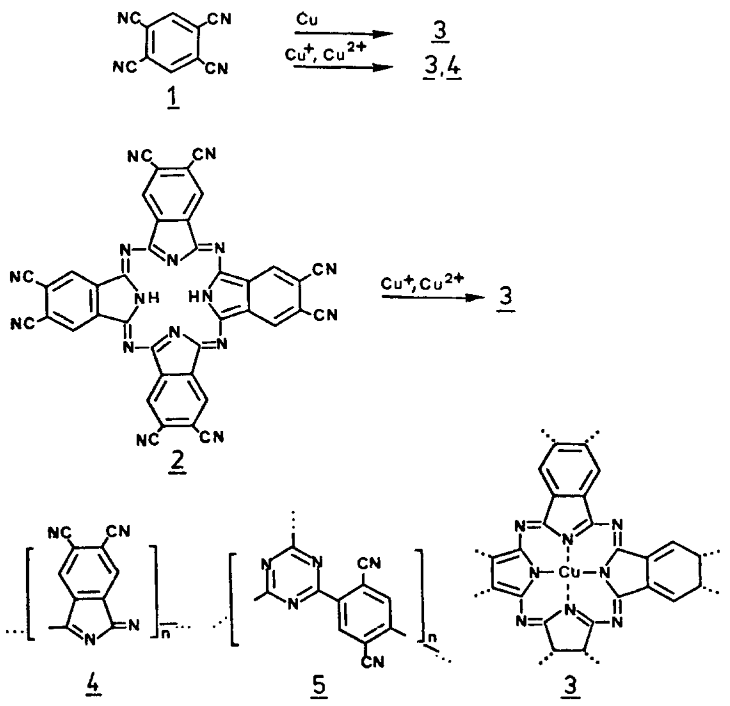

In the latter case the copper salts as Lewis acids initiate the cationic polymerisation of the nitrile group (ref. 2,14) leading to structural elements 4. Starting from 2 the rigid and stable structure of the first phthalocyanine ring may promote the formation of 3 also with copper salts present. In every case no structural elements 5, which are an intermediate of nitrile polymerisation with Lewis acids (ref. 2,14), could be observed.

Corresponding to the literature the reaction of 1 to 3 was carried out almost only (ref. 2,15) with metal salts. Therefore nearly all synthesized polyphthalocyanines are of low uniformity and purity.

IR-spectra (Fig. 1):

As reported (ref. 2,3) the polymers from 1 and copper salts show absorptions with low intensity at 2225 cm^{-1} (nitrile group), 1730 cm^{-1} (carboxylic acid groups) and a region of broad absorptions without fine structure between 1700 and 1000 cm^{-1}. The last mentioned region is characteristic for polynitriles from benzonitrile (ref. 14) and succinonitrile (ref. 16) or oligo-

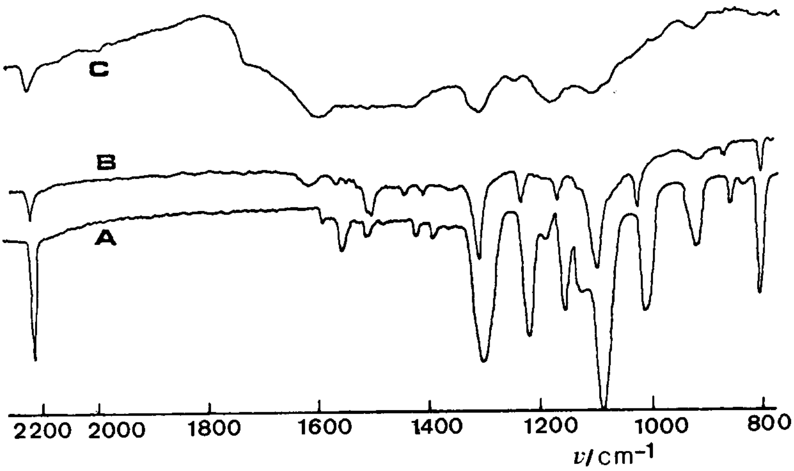

Fig. 1 IR-spectra (in KBr) of copper octacyanphthalocyanine 2 (ref. 1) (A), copper polyphthalocyanine 3 from 1 and copper (B), copolymer 3, 4 from 1 and copper salt (C).

isoindolenines from 1,2-dicyanobenzene (ref. 9,10). They indicate structure elements 4 in the copolymers. The polymers starting from 1 and metallic copper or 2 and copper salts give good resolved spectra. These are in agreement with the spectrum of the monomer 2. The absence of absorptions at 1730 cm^{-1} and a small band at 2225 cm^{-1} indicate that 3 contains only nitrile and no carboxylic acid end groups.

UV/VIS-spectra (Fig. 2):

The UV-VIS were taken in conc. sulfuric acid. The polymers 3 derived from 1 and metallic copper or from 2 and copper salts exhibit characteristic absorptions analogous to those of the monomer 2: Q-band at 735 nm with a new shoulder at 760 nm typical for all polymers; B-band at 230 nm. In contrary the polymers from 1 and copper salts show a very intensive absorption beginning at 500 nm and increasing with shorter wave length. This is typical for polynitriles (ref. 9,10,16,17) indicating structure element 4 in the polymers. An absorption of lower intensity at 735 nm indicates also the presence of structure element 3.

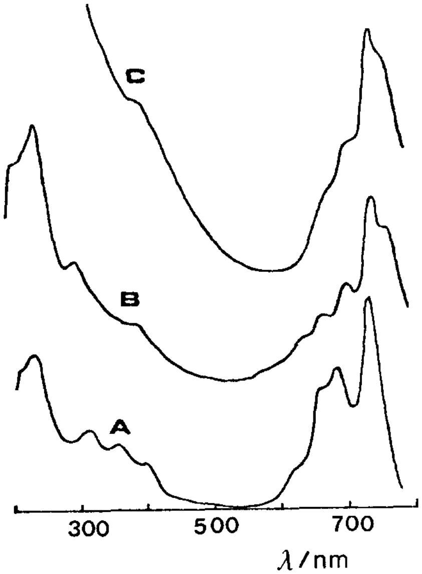

Fig. 2

UV/VIS-spectra (in conc. sulfuric acid) of copper octacyanphthalocyanine 2 (ref. 1) (A), copper polyphthalocyanine 3 from 1 and copper (B), copolymer 3, 4 from 1 and copper salts (C).

The influence of different metal salts and their valence states on uniformity and molecular weight of polyphthalocyanines extended by the correlation of structure and activity will be considered in succeeding papers.

EXPERIMENTAL

Reaction of 1 with copper powder: 1.78 g (10 mmol) of 1 (sublimed) and 0.32 g (5 mmol) copper for analysis) were heated in a closed bomb vessel at 350°C for 24 hours. The dark blue polymer was treated with aceton in a soxhlet apparatus and dried. No octacyanphthalocyanine 2 was extracted with aceton. Yield of 3 1,95 g (93 %):

Calculated:				
$(C_{20}H_4\ N_8Cu)_n$	C 57.2	H 0.96	Cu 15.1	N 26.7
$(C_{20}H_4\ N_8Cu\cdot 2H_2O)_n$	C 52.7	H 1.77	Cu 13.9	N 24.6
Found:	C 52.3	H 1.42	Cu 13.1	N 23.9

Reaction of 1 with a copper plate: A polished copper plate (1 cm^2 was heated in a closed bomb vessel with 2 mg of 1 at 400°C for 24 hours. The small amount of 1 evaporizes and reacts at the surface of the metal plate forming a homogeneous layer of blue coloured polymer.

3 was detected by dipping the plate in conc. sulfuric acid and recording a UV/VIS-spectrum of the dissolved polymer. IR spectrum of the detached coatings are taken in KBr.

Reaction of 1 and copper salts: 10 mmol 1 was heated with 5 mmol copper salt (copper-II-acetate,copper-I-chloride, copper-II-acetylacetonate) in mass for 6 hours at 300^{o}C or in high boiling solvents (quinoline, ethylene glycol) under reflux for 24 hours. The dark brown or black coloured polymers were treated with acetone and DMF in a soxhlet apparatus. Yields of copolymer 3, 4 1.6 - 2.05 g.

Found (Polymer from 1 and copper acetylacetonate):

C 58.3 H 1.8 Cu 8.8 N 27.3

Reaction of 2 with copper salts: 0.75 g (1 mmol) 2 (as dihydrate, ref. 1) and 2 mmol copper salts were converted like above described. Yield of DMF unsoluble dark blue coloured polymer 3 0.46 - 0.78 g (53 - 89 %).

Found (3 from 1 and CuCl):

C 53.1 H 1.53 Cu 12.9 N 23.7

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support from Diamond Shamrock Electroresearch S.A. (Dr. J. Gauger), Genf.

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Received June 21, 198o
Accepted June 3o, 198o