

# Studies on Heat-Resistant Thermosetting Phthalocyanine Polymers

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## Synopsis

New thermosetting poly(copper phthalocyanine) imide polymers with good toughness, superior thermal stability, chemical inertness, and fire resistance characteristics have been prepared. The studies of polymerization of two bisphthalonitriles were made using metal powder or metallic salt. Infrared, differential scanning calorimetry and thermogravimetric studies were used in determining the optimum conditions for polymerization and in characterizing the polymers produced. These polymers are noteworthy for their high char yield (73–76%) at 800°C in nitrogen atmosphere. These phthalocyanine, imide-thermosetting polymers are expected to be useful in preparing heat-resistant molded articles or laminates.

## INTRODUCTION

The high thermal stability, chemical inertness, water resistance, and fire resisting properties of the phthalocyanine type of compounds make this a desirable structure to use in the synthesis of polymers with superior properties. Many attempts have been made to synthesize thermosetting phthalocyanine polymers including an earlier attempt which was based on the reaction between 3,3',4,4'-tetracyanodiphenyl ether and copper bronze.<sup>1</sup> This material was not well characterized and seems to be a polymer of low molecular weight with less thermal stability than the parent phthalocyanine molecule. The large size of the phthalocyanine molecule is believed to cause steric hindrance to the formation of polymers with a high degree of polymerization. For that reason, a series of amide- and ether-linked bisphthalonitrile derivatives with increased lengths of the connecting groups between the two phthalonitrile units was synthesized.<sup>2-5</sup> These derivatives were cured either by heat or by using metallic powder or metallic salt. Amide-linked bisphthalonitriles were found to cure at about 220°C in approximately 48 h and ether-linked bisphthalonitriles cured at 280°C in 7 days. The use of powdered metal or metallic salt was observed to catalyze the polymerization reaction at a lower temperature. For example, the curing temperature of the ether-linked bisphthalonitrile derivative can be decreased from 280°C to 220–250°C and the time of reaction from 7 days to 24 h in the presence of stannous chloride. Powdered metal was preferred over metallic salt as the latter was found to effect foaming and to produce materials of lower structural strength. However, these polymers have not shown the thermal

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stability anticipated from the phthalocyanine structure. Many side reactions are suspected to have taken place during the curing process and the extent of phthalocyanine formed was shown to be incomplete.<sup>6</sup> Further, hydroquinone, catechol, resorcinol, benzoic acid, etc., were examined and hydroquinone was proposed to be superior in reducing the time of reaction and the temperature. But this curing reagent increased thermal stability only to a slight extent. To prepare phthalocyanine polymers based on imide linkage, two monomers were prepared based on the reactions between 4-aminophthalonitrile; 3,3',4,4'-benzophenonetetracarboxylic dianhydride and 1,2,4,5-benzenetetracarboxylic dianhydride.<sup>7</sup> Present work deals with the study of the synthesis of the thermosetting polymers using these monomers and their characterizations.

## EXPERIMENTAL

**Materials and Methods.** 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BPTDA), and 1,2,4,5-benzenetetracarboxylic dianhydride (BTDA), from the Aldrich Chemical Company were purified by recrystallization from dry acetic anhydride. 4-Aminophthalonitrile (APN) was obtained from Eastman Kodak Co., and purified by recrystallizing twice from water. Monomer I was prepared by the reaction of APN + BPTDA and monomer II was prepared by the reaction of APN + BTDA as described earlier.<sup>7</sup> All other reagents were of analytical grade.

Infrared (IR) spectra were recorded using the Nicolet MX-1 FT-IR Spectrometer. Thermogravimetric Studies were conducted using a DuPont Model 990 Thermal Analyzer with a 951 Thermogravimetric Module. A DuPont DSC plug-in module was used for the differential scanning calorimetric analyses. A heating rate of 10°C/min was used both in air and in nitrogen atmospheres with flow rates of 100 mL/min.

## POLYMERIZATION

**Copper Phthalocyanine Polymer I.** A combination of 2.0 g of monomer I and 0.173 g of cuprous chloride was finely ground and mixed well in a small, vibrating ball mill. This mixture was placed in a reaction tube provided with a thermocouple and an inlet and outlet for nitrogen purging. The reaction mixture was heated at 280°C for 1.5 h in a current of nitrogen gas. A tough, glistening, bluish-black material was obtained. The reaction can also be conducted in air atmosphere.

**Copper Phthalocyanine Polymer II.** A combination of 2.0 g of monomer II and 0.211 g of cuprous chloride was finely ground and mixed well. This mixture was placed in a tube as described above and heated at 420°C for 15 min in a nitrogen atmosphere. A tough glistening, bluish-black material was obtained.

## RESULTS AND DISCUSSION

The dynamic thermogravimetric analyses on the purified phthalocyanine and metal phthalocyanines showed that metal phthalocyanines are more stable in an anaerobic atmosphere. The metal phthalocyanines that resist attack by

concentrated sulfuric acid contain metals whose metallic radii are close to 1.35 Å. Copper, cobalt, and nickel have atomic radii of about the same magnitude, and phthalocyanine compounds of these metals showed considerable resistance to the hydrolytic action of concentrated sulfuric acid. Powdered metals, metallic salts, and organic compounds such as hydroquinone, catechol, resorcinol, benzoin, etc., have been proposed in curing the bisphthalonitrile derivatives in obtaining phthalocyanine polymers. Powders of metals whose atomic radii are close to 1.35 Å, or their salts, are the most desirable reactants in obtaining thermally and hydrolytically stable phthalocyanine polymers from these nitrile derivatives. Polymerization of monomer I and monomer II were studied using copper powder, cuprous chloride, cupric chloride, copper sulphate, copper acetate, etc.

### IR Spectral Studies

A theoretical amount of the powdered metal or metallic salt was mixed well with the bisphthalonitrile monomer and heated at the desired temperature either in an air or a nitrogen atmosphere. At the end of every 15 min, 1 mg of the reaction mixture was removed and mixed well with 350 mg of KBr to prepare a pellet, and the IR spectra were recorded. The time required for the disappearance of the cyanide group absorption around  $2235\text{ cm}^{-1}$  (and no other change in the IR spectral bands) was taken as the optimum time required for the completion of the reaction. The metallic salts were found to be in the following order of effectiveness:  $\text{CuCl} > \text{CuCl}_2 > \text{CuSO}_4 > \text{Cu}(\text{CH}_3\text{COO})_2 > \text{SnCl}_2$ . Dark, bluish-black, tough, and thermally stable phthalocyanine-imide polymers were obtained when monomer I and monomer II were heated in the presence of cuprous chloride (Fig. 1).

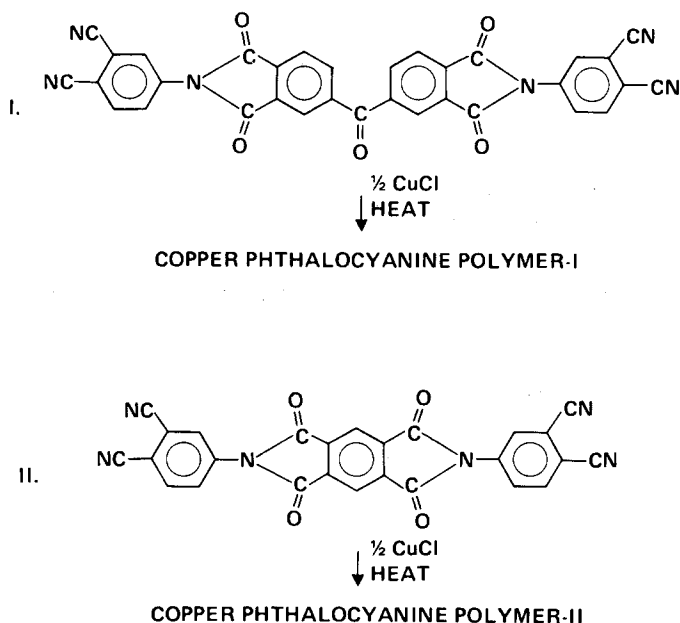


Fig. 1. Polymerization of the monomers.

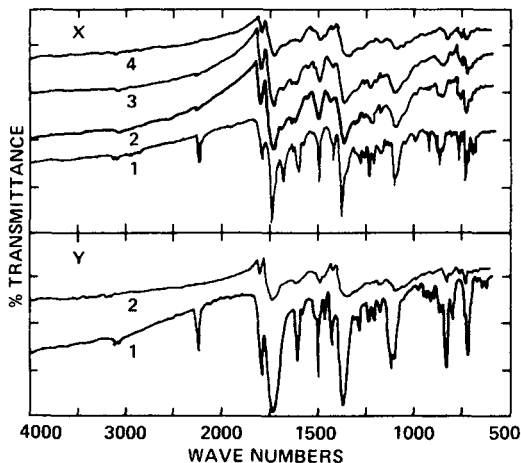


Fig. 2. (X) IR spectra of the reaction mixture (monomer I + CuCl): before heating (1) and after heating at 280°C for (2) 0.5 h, (3) 1.0 h, and (4) 1.5 h. (Y) IR spectra of the reaction mixture (monomer II + CuCl): before heating (1) and after heating at 420°C for (2) 15 min.

Similar reaction products can also be obtained when the monomers are heated in the presence of cupric chloride, cobaltous chloride, or nickel chloride. The polymerization reaction was found to be very slow when using metal sulfate, oxalate, or acetate. The preferred metal salts are the halides of copper, cobalt, and nickel. The thermal stability of the phthalocyanine polymers may be changed to a slight extent depending upon the type of metal used.

The IR spectra of the polymerization reactions with the two monomers and cuprous chloride are given in Figure 2(X,Y). Optimum temperatures for the polymerizations of monomer I + CuCl and monomer II + CuCl were found to be 280°C and 420°C, respectively. IR spectral studies indicated that 1.5 h of heating in the case of polymer I and 15 min of heating in the case of polymer II were found to be sufficient to complete the polymerization reactions. The important IR absorptions with their probable assignments are given in Table I. The sharp bands at 1782, 1732, 1377, 1086, and 720  $\text{cm}^{-1}$  caused by the imide structure of monomer I appeared as broad bands at 1779, 1722, 1355, 1089, and 723  $\text{cm}^{-1}$  in the spectrum of copper phthalocyanine polymer I. Similar absorptions at 1783, 1732, 1371, 1115, and 721  $\text{cm}^{-1}$  of monomer II appeared as broad bands at 1779, 1722, 1338, 1085, and 725  $\text{cm}^{-1}$  in the spectrum of copper phthalocyanine

TABLE I  
The IR Spectral Data for the Polymers<sup>a</sup>

Polymer	Phthalocyanine skeleton vibration	Imide structure	Aromatic	C=O
I. Copper phthalocyanine polymer I	1158; 1050; 965; 870; 745	1779, 1722; 1355; 1089; 723	3079	1668
II. Copper phthalocyanine polymer II	1164; 1052; 966; 886; 746	1779; 1722; 1338; 1085; 725	3069	

<sup>a</sup> In wave numbers ( $\text{cm}^{-1}$ ).

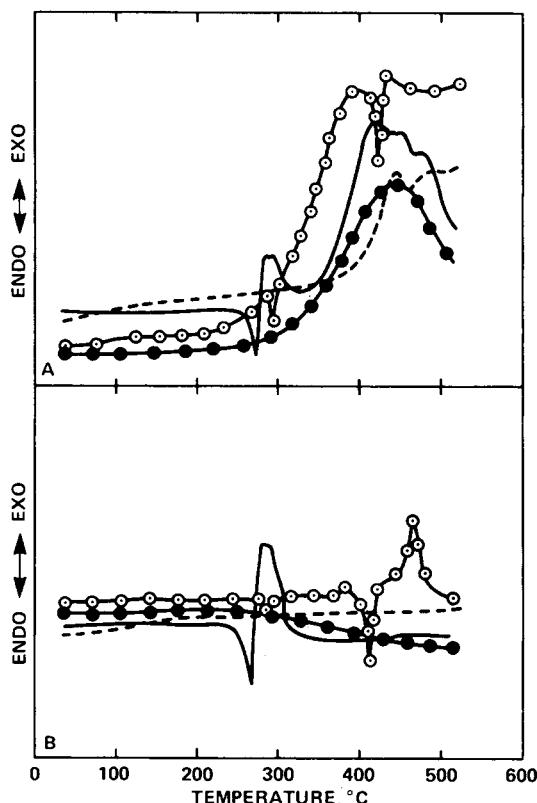


Fig. 3. DSC analytical curves (A = in air, B = in nitrogen) for monomer I + CuCl (—) before polymerization and (---) after polymerization and for monomer II + CuCl. (O) before polymerization and (⊙) after polymerization.

polymer II. The spectra of the polymers also showed absorptions at 1158–1164, 1050–1052, 965–966, 870–886, and 745–746  $\text{cm}^{-1}$  assignable to the phthalocyanine skeleton. The spectra of the polymers are characterized by a loss of fine structures and by a lowering of the intensities of the bands in comparison with the parent compound.

### Differential Scanning Calorimetric (DSC) Analyses

The DSC analytical curves for the mixtures of the monomers with cuprous chloride and after the polymerization reactions are given in Figure 3(A,B). The DSC curves for the monomer I + CuCl reaction mixture in air and in nitrogen atmospheres showed endotherms at 265°C caused by melting, followed by exotherms at 280°C because of the polymerization reaction. In addition, the DSC curve in air showed a broad exotherm at 420–470°C. These data indicate that any temperature above the melting point to 280°C would serve for the polymerization reaction. Polymerization can occur either in air or in a nitrogen atmosphere, but the nitrogen atmosphere is preferred. When the monomer II + CuCl mixture was heated, it turned pale green at about 275–280°C; the color deepened with increasing temperature, and finally an almost black material was obtained at about the melting point of the monomer. The DSC curves in

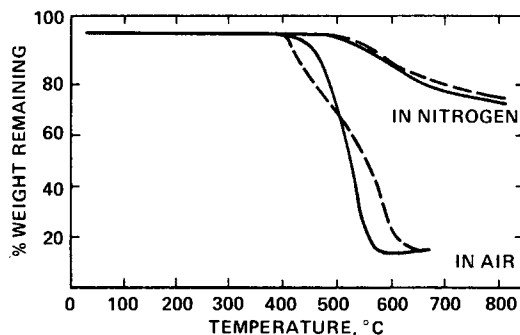


Fig. 4. The dynamic, thermogravimetric analytical curves for copper phthalocyanine polymer I (—) and copper phthalocyanine polymer II (○).

nitrogen for the monomer II + CuCl mixture showed a small endotherm at 280°C, a small exotherm at 370°C, a sharp endotherm at 406°C, and an exotherm at 445°C. The exotherms at 370°C and 445°C, and the endotherm at 280°C may be due to the various reactions involved during the polymerization process whereas the endotherm at 406°C is due mainly to the melting of the mixture. The DSC curve for monomer II + CuCl in air also showed a similar pattern. This curve also showed a broad exotherm at 220–440°C, which may be assigned to the various reactions involved during the polymerization process. DSC curves in air and in a nitrogen atmosphere are different, indicating either that there may be different types of reactions or that the polymerization may be catalyzed in the presence of an oxidizing atmosphere. The DSC curves of the cured copper phthalocyanine polymer I and copper phthalocyanine polymer II showed neither exotherms nor endotherms up to 500°C in a nitrogen atmosphere, whereas, in an air atmosphere, broad exotherms were observed around 445°C and 430°C for the polymer I and polymer II, respectively, which may be assigned to the decomposition of the polymer.

### Dynamic Thermogravimetric Analytical Studies

The thermogravimetric analytical curves for the polymers prepared from monomer I + CuCl and monomer II + CuCl are given in Figure 4 and the relevant analytical data are presented in Table II. These polymers showed greater thermal stability both in air and in nitrogen atmospheres than did the parent copper phthalocyanine compound, and are noteworthy for their high char yield in a nitrogen atmosphere. Polymer I showed a char yield of 73% and polymer II showed a higher char yield of 76%, higher than any of the thermosetting phthalocyanine polymers heretofore synthesized. The nature of the polymers may be either a ladder-type or a sheetlike structure. The materials produced are tough, fire-resistant, and chemically inert. These polymers may have promising applications in preparing heat-resistant molded articles or laminates. Phthalocyanine is a macrocyclic, planar, tetradentate bivalent ligand, with a stronger binding energy than the chloride ion. The copper ion has a greater preference for the phthalocyanine ligand than for the chloride ion. Part of the chloride ions may react with the peripheral benzene of the phthalocyanine molecule, thereby evolving hydrogen chloride gas, and the remaining part may be

TABLE II  
The Dynamic Thermogravimetric Analytical Data for the Polymers

Polymer	Air		Nitrogen		Char yield at 800°C (%)
	PDT (°C)	PDT max (°C)	PDT (°C)	PDT max (°C)	
I. Copper phthalocyanine polymer I	470	575	510	585	73
II. Copper phthalocyanine polymer II	420	570	530	580	76

expelled as chlorine gas. If the chloride enters the benzene group, it is expected to improve the fire resistance of the phthalocyanine polymer.

### CONCLUSIONS

Two novel, thermally stable, tough, and chemically inert dark bluish-black thermosetting, phthalocyanine polymers were synthesized and characterized. Metal halides were found to be efficient in the polymerization of monomer types I and II. IR spectral and DSC studies indicated that the optimum conditions for the polymerization of monomer I with CuCl was heating at 280°C for 1.5 h and for monomer II with CuCl was heating at 420°C for 15 min.

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