Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Kuznesof, P. M. , Nohr, R. S. , Wynne, K. J. and Kenney, M. E.(1981) 'Conducting Polymers: Partially Oxidized Bridge-Stacked Metallophthalocyanines', Journal of Macromolecular Science, Part A, 16: 1, 299 — 312
To link to this Article: DOI: 10.1080/00222338108082053
URL: http://dx.doi.org/10.1080/00222338108082053

J. MACROMOL. SCI.-CHEM., A16(1), pp. 299-312 (1981)

Conducting Polymers: Partially Oxidized Bridge-Stacked Metallophthalocyanines

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ABSTRACT

The synthesis and characterization of a novel class of polymeric phthalocyanines (Pc), $(PcMX)_n$ (M=Al,Ga,Cr; X=F and M=Si,Ge,Sn; X=O) of exceptional thermal stability are summarized. These materials possess a linear MX backbone surrounded by a sheath of cofacial M-centered Pc rings.

$(PcAlF)_n$ and $(PcGaF)_n$ are sublimable (10^{-3}mmHg,540°C and 430°C, respectively) allowing for thin film formation. Iodine-doping leading to compositions $(PcMXI_y)_n$ with y ranging from 0.06 to 5.5 is reported. Thermogravimetric analysis has proven useful for iodine analyses and has revealed that the order of thermal stability with regard to loss of iodine is $(PcCrFI_y)_n < (PcGaFI_y)_n \sim (PcAlFI_y)_n < (PcSiOI_y)_n$. Raman spectra point to I_3^- and I_5^- as the principle polyiodide species, though their relative proportions vary depending on M and doping level. Increases in the electrical conductivity by as much as 10^9 with maximum conductivities in the range of 0.01-1 $ohm^{-1}cm^{-1}$ result from iodine doping. Conduction appears to be thermally activated (77-300K) with an apparent activation energy of 0.04eV. It is likely that electron transport is primarily ligand based and is metal-like in character.

INTRODUCTION

Development of new semiconducting and conducting organic and organometallic polymers continues to be sparked by the multitude of potential applications in solid state electro-optical systems (1). These advanced technology materials may assume prime roles in devices such as sensors, detectors, and electrophotographic units where low density, combined with thermal, photo and chemical stability will be demanded. The use of chemically modified electrode surfaces for studies of electrochemical electron transfer, electrocatalysis, and photoassisted electrode reactions is also undergoing intensive exploration (2). Investigation of these processes employing coatings of electroactive polymeric materials can be expected to be highly rewarding. Currently, widespread application of these new substances is limited by the necessity for specialized film deposition procedures and the lack of materials which demonstrate ease of fabrication and processibility. Evidence of progress in these areas is beginning to appear (3).

Phthalocyanines (4), because of their thermal, photo, and hydrolytic stabilities, intense colors, and ready availability have received their share of attention in the quest for new electroactive materials (5-14). The purpose of this account is to summarize recent studies on a novel class of bridge-stacked phthalocyanine polymers (Figure 1) which have been made highly conducting ($\sigma_{RT} \sim 1$ ohm^{-1}cm^{-1}) by halogen (I_2, Br_2)) doping (5-7,10,11). These systems meet criteria established for the preparation of new conductive materials in that (a) the metal-macrocycle units are stacked cofacially and (b) these stacks can be partially oxidized so that each unit is formally in a non-integral oxidation state. Furthermore, the bridged polymers are unique in that they are exceptionally robust both chemically and thermally. This stands in contrast to simple metallomacrocyles for which there is no guarantee of stacking

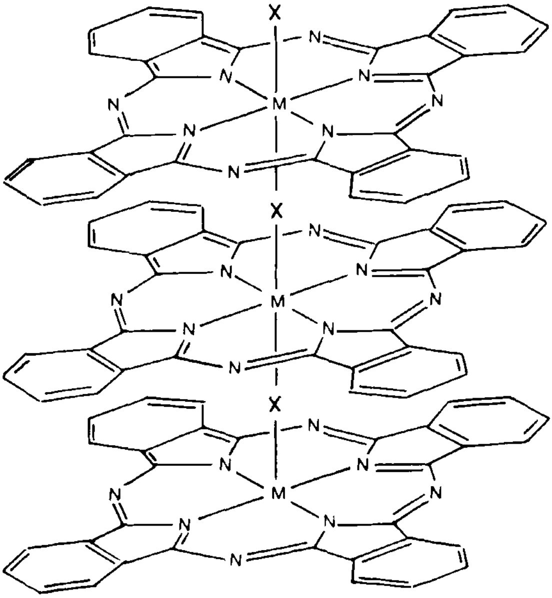

FIGURE 1. Proposed Structure for $(PcMX)_n$ (M=Al,Ga,Cr;X=F and M=Si,Ge,Sn;X=O).

ab initio in linear arrays or of remaining stacked upon treatment with typical oxidizing or reducing agents.

SYNTHESIS and CHARACTERIZATION

The phthalocyanine polymers $(PcMX)_n$ (M=Si,Ge,Sn, X=O; M=Al,Ga, X=F) were originally prepared by Kenney and co-workers (15-18). The oxo-bridged group IVA phthalocyanines (18) are easily obtained in high yield and purity by vacuum polymerization (300 - 400°C) of the dihydroxo precursor:

$$nPcM(OH)_2 \xrightarrow{-nH_2O} (PcMO)_n \quad M=Si,Ge,Sn.$$

$(PcSiO)_n$ is an exceptionally stable material: it is unaffected by aqueous HF at 100°C, aqueous 2M NaOH at reflux and H_2SO_4 at room temperature (18). The fluorobridged aluminum and gallium phthalocyanines are prepared (15,16) first by converting PcAlCl and PcGaCl to their hydroxo derivatives followed by repeated evaporation to dryness with concentrated (48%) aqueous hydrofluoric acid:

$$PcMCl \xrightarrow[\text{reflux}]{NH_3(aq),\ py} PcMOH.xH_2O$$

$$nPcMOH{\cdot}xH_2O \xrightarrow{48\%\ HF} (PcMF)_n \quad M=Al,Ga.$$

Heating these substances several hours at 300°C in vacuo results in good yields of satisfactory purity. High purity $(PcMF)_n$ is obtainable by vacuum sublimation (540°C, M=Al; 430°C, M=Ga). $(PcCrF)_n$ is available commercially (Eastman) or may by synthesized from $Cr(CO)_6$ and phthalonitrile (19) followed by hydrofluoric acid treatment of the resulting PcCrOH (7).

The extremely high thermal stabilities of the $(PcMX)_n$ compounds are apparent from thermogravimetric analysis (TGA) investigations (5-7). The onset of initial weight loss (i.e. 5% loss in weight) was recorded at *ca.* 430°, 450°, 490°, and 540°C for $(PcSiO)_n$, $(PcCrF)_n$, $(PcGaF)_n$, and $(PcAlF)_n$, respectively. A second weight loss between 600-700°C occurs for all of these compounds after a 35-40% decrease in initial sample weight.

A variety of physical evidence points to the structure shown in Figure 1 for the oxo- and fluorometallophthalocyanines. Certain relatively broad bands in the infrared spectra have been attributed to M-X stretching along the $(MX)_n$ polymer backbone (16-18). Interplanar spacings which were derived from x-ray powder diffraction data are compared in Table 1. The expected increase in ring-ring distance upon descending a family is evident and there is excellent agreement with the distances calculated from ionic radii (11,16) assuming linear M-X-linkages.

From electron microscopy studies (15, 16) on sublimed crystals of $(PcAlF)_n$ and $(PcGaF)_n$, micrographs were obtained which exhibited lattice image lines. These lines, spaced by *ca.* 1300 to 1500 pm - which corresponds to the van der Waals

TABLE 1.

Ring-Ring (M-X-M) Spacing (pm) for $(PcMX)_n$

	$(PcSiO)_n$	$(PcGeO)_n$	$(PcSnO)_n$	$(PcAlF)_n$	$(PcGaF)_n$	$(PcCrF)_n$
obs:	332(2)[a]	350(2)[a]	383(3)[a]	366[b]	386[b]	387[c]
obs[d]:	333(2)	351(2)	395(2)			
calc[e]:	332[d]	358[d]	390[d]	364[b]	381[b]	380

(a) Ref. 18. (b) Ref. 16. (c) Ref. 7. (d) Ref. 11.

(e) Calculated using the pertinent ionic radii: R. D. Shannon, Acta. Crystallogr., A, 32, 751(1976).

width of the phthalocyanine ring (16) - are oriented parallel to the long axis of the needle-like crystals. This suggests that linear chains of $(PcAlF)_n$ and $(PcGaF)_n$ are packed parallel to the long crystal axis and indicates that the $(PcAlF)_n$ structure may be regarded as pseudo-one dimensional.

Halogen doping (partial oxidation) of low dimensional materials has proved to be an effective strategy for transforming a normally insulating (or poorly semiconducting) substance ($\sigma_{RT} < 10^{-6} ohm^{-1}cm^{-1}$) to a conductive material ($\sigma_{RT} > 10^{-2} ohm^{-1}cm^{-1}$). Uptake of iodine by $(PcMX)_n$ to yield $(PcMXI_y)_n$ has been accomplished (5-7,10,11) either by exposure of the powdered material to iodine vapor or by stirring slurries of the phthalocyanine in iodine-saturated solutions of heptane, carbon tetrachloride, ethanol, or chlorobenzene. Depending on reaction conditions and $(PcMX)_n$ purity, a wide range of dopant concentrations can be obtained. Thus, I/M ratios of 0.061 for one sample of $(PcCrF)_n$ (7) to 5.5 for a sample of $(PcSnO)_n$ (11) have been reported. Conductivity data for maximum halogen/M compositions are summarized in Table 2. For the Al, Ga and Cr derivatives, maximum iodine uptake is achieved within 24 hours if the reaction is carried out using the slurry technique (5-7) whereas the solid/vapor route requires one to three weeks (5,6).

Physical methods including TGA, IR, Raman, mass spectrometry, and magnetic susceptibility measurements have been applied to the characterization of these materials. TGA has been shown to be particularly useful for determining the iodine content of doped oxo- and fluorphthalocyanines (5-7). The thermograms in Figure 2 for pure $(PcAlF)_n$ (curve D) and at several iodine doping levels are typical. Thus, thermogram A exhibits two weight losses between room temperature and the onset of the plateau at 240°C which signals complete loss of iodine. The

TABLE 2.

Composition and Conductivity Data for Halogen-Doped $(PcMX)_n$[a]

Compound	(ohm^{-1}cm^{-1})[b]	E_a(eV)
$(PcAlFI_{3.4})_n$[c]	0.59(0.51)	0.03
$(PcGaFI_{2.1})_n$[c]	0.15(0.11)	0.04
$(PcCrFI_{3.2})_n$[d]	0.62	____[f]
$(PcSiOI_{4.60})_n$[e]	(0.1)[i]	0.04[g]
$(PcSiOBr_{1.00})_n$[e]	(0.06)	____[f]
$(PcGeOI_{2.0})_n$[e]	(0.1)	0.05[h]
$(PcSnOI_{5.5})_n$[e]	(2x10^{-4})	0.68

(a) Data are present only for maximally doped samples. (b) Room temperature linear four point probe and van der Pauw, ( ), conductivities, pressed discs. (c) References 5,6. (d) Reference 7. (e) Reference 11. (f) Temperature dependence of conductivity not reported. (g) for I/Si ratio of 1.40. (h) for I/Ge ratio of 1.94. (i) A conductivity of 0.2 ohm^{-1}cm^{-1} is reported for $(PcSiOI_{1.4})_n$.

44% weight loss to this point translates to I/Al = 3.4. Above 240°C the thermogram is identical to that for pure $(PcAlF)_n$. The iodine-doped gallium derivatives exhibit weight loss processes in the same temperature regimes as the aluminum species. Thermograms for $(PcCrFI_y)_n$ (7) also reveal evidence for two weight loss processes at 130 and 170°C prior to removal of all iodine. The weight loss-temperature profiles for two moderately doped samples of $(PcSiO)_n$ (I/Si = 1.3 and and 1.4) show a low temperature (*ca.* 80°) loss of iodine, but the second stage loss is not completed until *ca.* 340°C (6,20). In terms of thermal stability with regard to loss of iodine, the order is $(PcCrFI_y)_n < (PcGaFI_y)_n \sim (PcAlFI_y)_n$

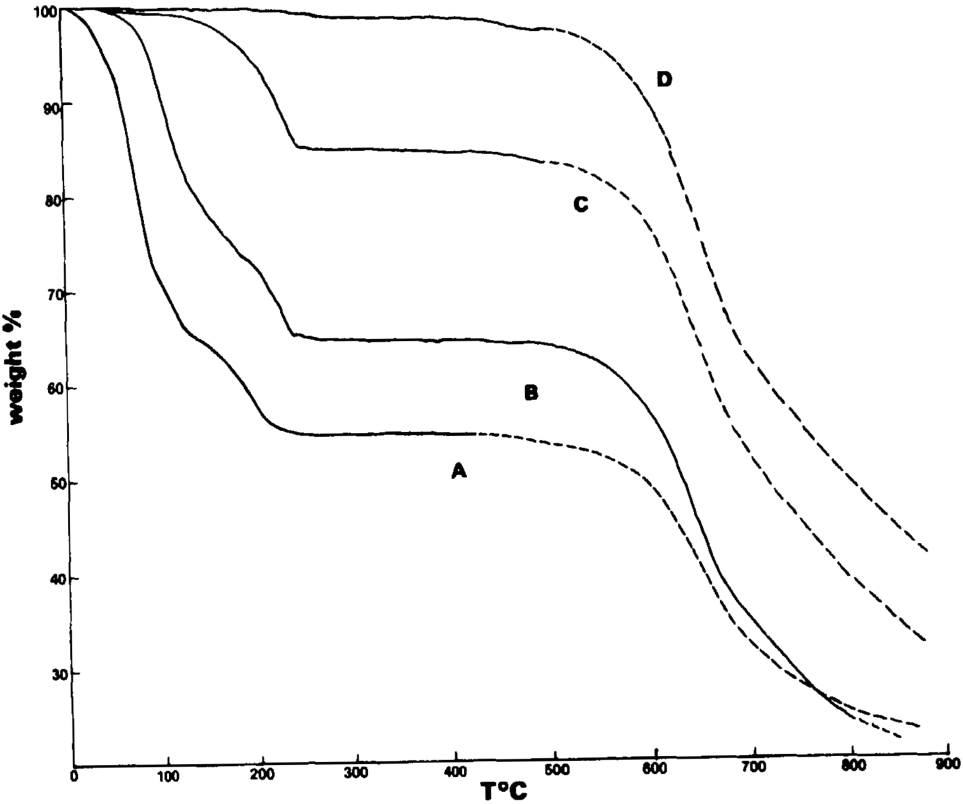

FIGURE 2. Thermograms for (A) $(PcAlFI_{3.4})_n$, (B) $(PcAlFI_{2.4})_n$, (C) $(PcAlFI_{0.75})_n$ and (D) $(PcAlF)_n$. Heating rate 5°/min (——) and 10°/min (---), N_2 flow rate 50 ml/min.

< $(PcSiOI_y)_n$. It is worth noting that all doped samples of the Al, Ga, and Cr fluorophthalocyanines including those brought to constant weight under dynamic vacuum, evolved iodine when stored at ambient temperature and pressure, as evidenced by the discoloration of the polyethylene caps of the storage vials (6). This stands in contrast to the report that the iodine-doped Si, Ge, and Sn oxophthalocyanines are

indefinitely stable in air, and that iodine can only be driven off by prolonged heating above 100°C (11).

Raman spectroscopy has proved indispensable for characterizing the polyiodide species formed upon oxidation of a wide variety of low dimensional materials (9,14,20,21). Raman data for the doped oxo-bridged group IVA phthalocyanines (11) show I_3^- to be the principle polyiodide species; at moderate to high dopant levels, scattering due to I_5^- can be observed. On the other hand, for all $(PcCrFI_y)_n$ compositions scattering attributable to I_5^- dominates the spectrum although a band due to I_3^- is clearly evident (7). The spectra for highly doped $(PcAlF)_n$ and $(PcGaF)_n$ exhibit intense scattering for both I_3^- and I_5^- with the former dominant (6). The presence of two polyiodide species shown by Raman spectroscopy correlates with TGA data such as shown in Figure 2 for $(PcAlFI_y)_n$. Curve B shows the TGA of $(PcAlFI_{2.4})_n$. Two weight loss processes at 90 and 200°C are apparent. After heating this sample to 90°C under dynamic vacuum $(PcAlFI_{0.75})$ was obtained. In contrast to the parent composition, little weight loss is observed below 150°C for this composition (Figure 2, Curve C) and the Raman spectrum shows a less prominent I_5^- peak relative to I_3^-. Thus, the combination of TGA and Raman data indicate that the first weight loss process for the heavily doped materials can be primarily associated with I_5^- decomposition; the second stage is prinicpally due to loss of I_3^-. One particular composition, $(PcGaFI_{0.62})_n$, exhibited a thermogram with a single broad weight loss beginning at *ca.* 60°C. The Raman spectrum for this sample showed the I_5^- peak to be dominant, consistent with the recorded thermogram. To summarize, all work reported to date on iodine-doped oxo- and fluorophthalocyanines (5-12) shows I_3^- and I_5^- to be the primary polyiodide species present, presumably occupying channels between the $(PcMX)_n$ chains. No evidence for I_2 (detectable by Raman spectroscopy) has been noted and, although Mössbauer spectra have not been reported for $(PcMXI_y)_n$, there does not seem to be any precedence for significant concentrations of I^- in any iodine doped conducting phthalocyanine material.

For iodine-doped $(PcAlF)_n$ and $(PcGaF)_n$, variable temperature (ambient to 300°C) mass spectral data were collected (6) which confirmed iodine as the predominant volatile species during thermolysis. Profiles of I_2^+ ion intensity vs temperature also showed I_2 was lost in two stages, in agreement with the Raman and TGA data cited above.

ELECTRICAL CONDUCTIVITY

$(PcMX)_n$ compounds are typical insulators, but partial oxidation results in increases in conductivity by as much as 9 orders of magnitude compared to the undoped material (5-7, 10,11). The conductivity rises rapidly as the I/M ratio approaches 0.2 with relatively slight increases thereafter up to the maximum doping level. Room temperative conductivities (compressed discs) for these compositions are collected in Table 2 and, with the exception of the tin phthalocyanine, fall between 0.01 and 1 $ohm^{-1}cm^{-1}$.

Trends within a family are apparent if conductivities for a given I/M ratio are compared. Thus, $\sigma(Al) > \sigma(Ga)$; $\sigma(Si) > \sigma(Ge) > \sigma(Sn)$. These trends correlate with the inter-phthalocyanine ring spacings given in Table 1 (smaller spacing, higher conductivity) and support the idea that the conductive pathway is primarily ligand based via a conduction band generated by inter-ring pi-orbital overlap. These systems, then, along with related highly conductive stacked metallomacrocyclic systems (22), stand in contrast to Krogmann salts and related compounds which are low dimensional conductors in which charge transport occurs mainly along a transition metal backbone.

The variation of conductivity with temperature (77-300K) has been examined (6,11) for various $(PcMXI_y)_n$ compositions, $(M \neq Cr)$. The four-probe studies indicated that conduction is thermally activated, and the linearity of log σ vs 1/T plots allowed for evaluation of the apparent activation energies listed in Table 2. The remarkably low activation energies and high conductivities are comparable to those observed for compressed discs of $PcNiI_{1.0}$, single crystals of which were found to behave as a "molecular metal" (8). Furthermore, Faraday-type magnetic susceptibility data collected for the iodine-doped Si, Ge, and Sn compounds (11) appear consistent with magnetic behavior typical of many low-dimensional mixed valence systems - weak paramagnetism at 300K and only weakly temperature dependent.

SUMMARY

Bridge-stacked $(PcMX)_n$ compounds constitute a new class of low-dimensional materials which can be made highly conducting by halogen doping. That this conductivity is probably metal-like along the chain direction can be inferred from the physical studies which have been performed and from studies of related systems for which metallic conduction has actually been observed. Although iodine-doped $(PcAlF)_n$ and $(PcGaF)_n$ appear to have lower thermal stability with regard to loss of iodine compared to iodine-doped $(PcSiO)_n$, the volatility of the former materials, due to polymer chain linkage *via* coordinate covalent bonds, allows for formation of thin films. Because of this processing advantage $(PcMF)_n$ in films may find application in solid state devices or as electro-optic materials.

ACKNOWLEDGEMENT

We thank the Office of Naval Research for partial support of this work.

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