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CONDUCTIVE POLYMERS CONSISTING OF PARTIALLY OXIDIZED, FACE-TO-F--ETC(U)

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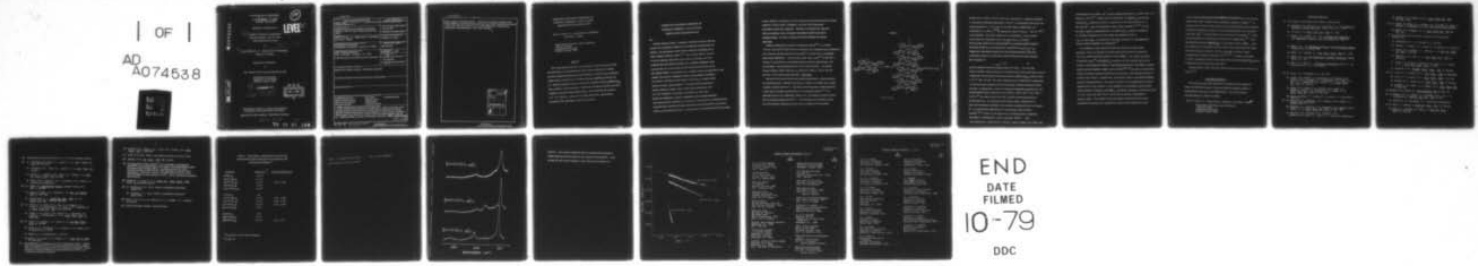
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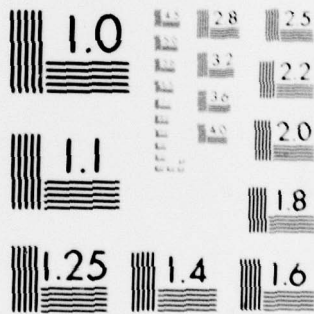
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TECHNICAL REPORT NO. 8

LEVEL II

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Conductive Polymers Consisting Of  
Partially Oxidized, Face-To-Face  
Linked Metallomacrocycles .

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Karl F./Schoch, Jr., Bhagyashree R./Kundalkar,  
and Tobin J./Marks

Prepared for Publication

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Northwestern University  
Department of Chemistry  
Evanston, Illinois 60201

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) → This communication reports on an approach to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a face-to-face orientation. Iodine doping of the face-to-face linked oligomers $[M(Pc)O]_n$ ( $M=Si, Ge, Sn$ ; $Pc = \text{phthalocyaninato}$ ) produces electrically conductive polymers $\{[M(Pc)O]_n\}_x$ $\downarrow$ $(M(Pc)O)I(x)_n$		

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with a range of  $x$  stoichiometries. Electronic and lattice structure have been studied by resonance Raman spectroscopy, which indicates the presence of  $I_3^{(-)}$  or  $I_3^{(=)}$  but no  $I_2$ , and by X-ray powder diffraction, which allows estimation of the interplanar (ring-ring) spacings.  $\nwarrow$

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CONDUCTIVE POLYMERS CONSISTING OF  
PARTIALLY OXIDIZED, FACE-TO-FACE  
LINKED METALLOMACROCYCLES

Karl F. Schoch, Jr., Bhagyashree R. Kundalkar,  
and Tobin J. Marks

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Abstract

This communication reports on an approach to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallomacrocycles together in a face-to-face orientation. Iodine doping of the face-to-face linked oligomers  $[M(\text{Pc})\text{O}]_n$  ( $M=\text{Si}, \text{Ge}, \text{Sn}$ ;  $\text{Pc} = \text{phthalocyaninato}$ ) produces electrically conductive polymers  $\{[M(\text{Pc})\text{O}]_x\}_n$  with a range of  $x$  stoichiometries. Electronic and lattice structure have been studied by resonance Raman spectroscopy, which indicates the presence of  $I_3^-$  or  $I_5^-$  but no  $I_2$ , and by X-ray powder diffraction, which allows estimation of the interplanar (ring-ring) spacings.

**CONDUCTIVE POLYMERS CONSISTING OF  
PARTIALLY OXIDIZED, FACE-TO-FACE  
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**Sir:**

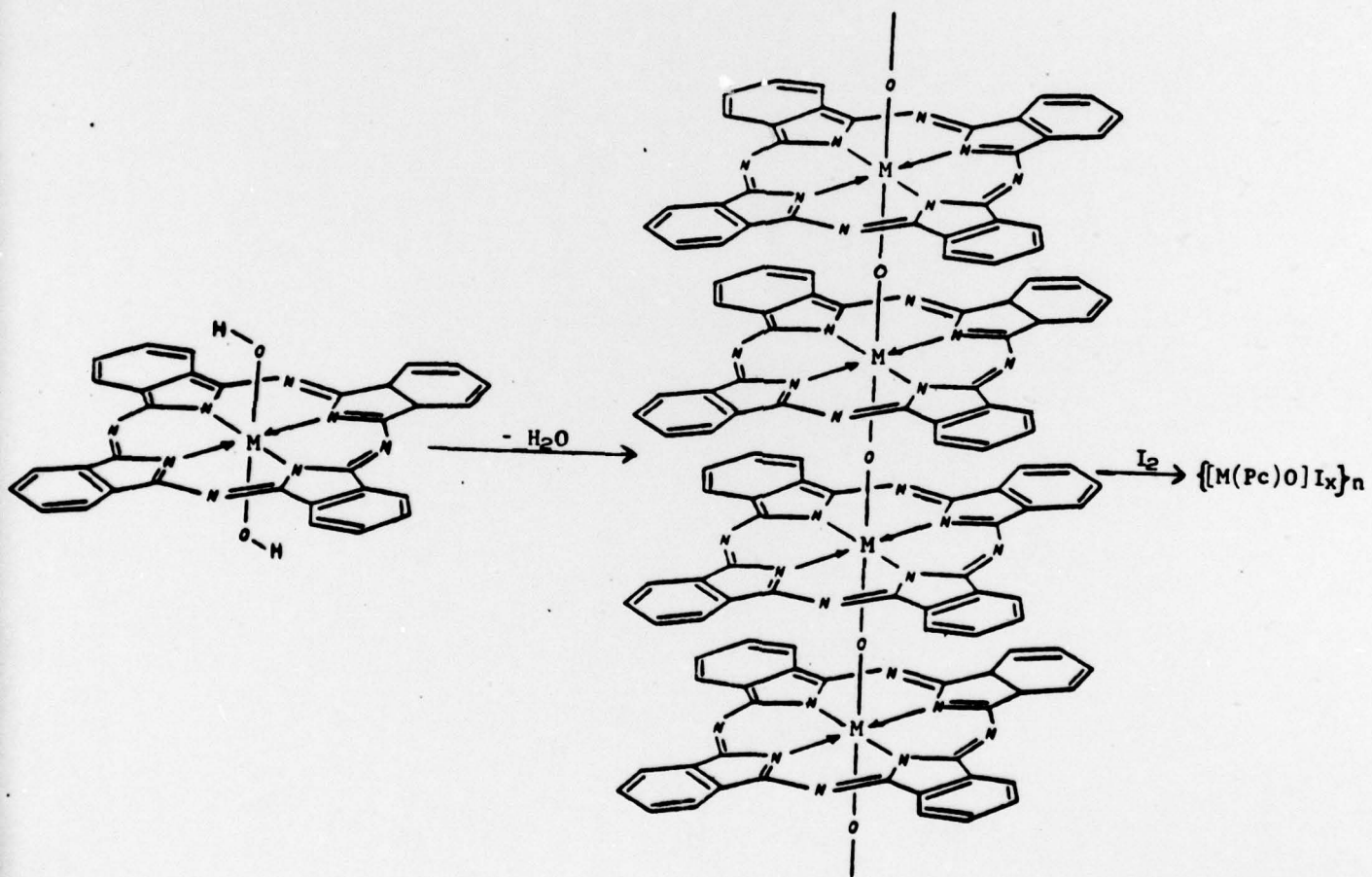
Halogen doping of planar, conjugated metallomacrocycles has been shown to be an effective strategy for the synthesis of electrically conductive, low-dimensional mixed valence materials consisting of partially oxidized molecular stacks.<sup>1-4</sup> This strategy suffers, however, as do all analogous ones based upon molecular stacking, from the weakness that solid state properties are completely dependent on the unpredictable and as yet largely uncontrollable intermolecular forces that dictate whether or not stacks form, whether stacks are integrated or segregated, the relative orientation of donors with respect to acceptors, the relative orientation of units within a stack ( $D_{nh}$  or canted stacks), and the stacking repeat distance.<sup>5</sup> It would clearly be desirable to devise methods for better control of the above parameters, both from the standpoint of providing information on how these factors are related to collective properties such as charge transport and metal-insulator transitions, as well as for learning how to manipulate these characteristics rationally through modification of stack and lattice architecture. In this communication we report on one approach to controlling molecular stacking,

partial oxidation of oligomers in which metallomacrocycles have been covalently linked in a "face-to-face" orientation, and some of the interesting properties of these new materials. Although we illustrate this approach with one particular class of halogen-doped, linked metallomacrocycle (phthalocyanine), we wish to emphasize that this strategy has obvious generality.

Using the methodology originally developed by Kenney<sup>6,7</sup> or a simpler "one-pot" procedure<sup>8</sup>, dichlorosilicon, germanium, and tin phthalocyanines ( $M(\text{Pc})\text{Cl}_2$ ) were prepared and then hydrolyzed in pyridine<sup>7</sup> to produce the corresponding dihydroxides,  $M(\text{Pc}(\text{OH})_2)$ . Polymerization under high vacuum<sup>6,9</sup> at 300-400 °C (Scheme 1) produced the corresponding phthalocyaninato polysiloxanes, polygermyloxanes, and polystannyloxanes in high yield and purity. As regards charge transport, these materials are insulators (Table I). This is not true however, of the halogen-doped polymers (vide infra).

Exposure of the powdered phthalocyaninato polysiloxane, polygermyloxane, and polystannyloxane materials to solutions of iodine or to iodine vapor results in uptake of iodine (Scheme 1). Depending upon the amount of iodine employed, a wide range of dopant stoichiometries can be achieved (Table I).<sup>10</sup> The iodinated polymers are indefinitely stable in air, and iodine can only be driven off by prolonged heating above 100 °C. That iodination has resulted in oxidation of the stacked metallomacrocycle array is evident in the resonance

Scheme 1



M = Si, Ge, Sn

Raman spectra (Figure 1) which reveal the characteristic, resonance-enhanced  $I_3^-$  symmetric stretching fundamental at  $108 \text{ cm}^{-1}$  (accompanied by the usual overtone progression) or in the case of very high iodine concentrations, the scattering by  $I_3^-$  at  $160 \text{ cm}^{-1}$ .<sup>2a,11</sup> No significant amount of free  $I_2$  ( $\nu = 207 \text{ cm}^{-1}$ )<sup>2a,11</sup> can be detected. The iodine oxidation is accompanied by a large increase in the electrical conductivity of the macromolecules, as revealed by four-probe van der Pauw measurements<sup>12</sup> on compressed pellets (Table I). The general trend in room temperature conductivity is  $\sigma_{\text{Si}} \gtrsim \sigma_{\text{Ge}} > \sigma_{\text{Sn}}$ . Temperature dependence studies show the transport behavior of the polycrystalline samples to be thermally activated (Figure 2) and least-squares fits to equation (1)

$$\sigma = \sigma_0 e^{-\Delta / k T} \quad (1)$$

give the apparent activation energies set out in Table I. The very high thermal stability of these polymers is evidenced by the observation that two-probe conductivity measurements could be performed on  $\{\text{Si}(\text{Pc})\text{O}\}_n$  samples cycled to  $573^\circ \text{K}$  with, at most, only minor decrease in room temperature conductivity. To view the charge transport data on the partially oxidized metallomacrocycle polymers in perspective, it should be noted that published parameters for compressed pellets of the "molecular metal"  $\text{Ni}(\text{Pc})\text{I}_{1.0}$   $\sigma(300^\circ) = 7 \times 10^{-1} (\Omega \text{cm})^{-1}$  and  $\Delta = 0.04 \text{ eV}$ ,<sup>3b</sup> are rather close to the most conductive polysiloxane and polygermyloxane data. It is well known that single crystal conductivities of quasi one-dimensional materials in the molecular stacking direction are typically  $10^2 - 10^3$  greater than conductivities for compressed, polycrystalline samples<sup>1,3a,13</sup> (which are averaged over all crystallographic orientations and subject to interparticle contact resistance effects). That room temperature conductivities of  $\text{Ni}(\text{Pc})\text{I}_{1.0}$  single crystals are as high in the

chain direction as ca.  $600(\Omega \text{ cm})^{-1}$  and the temperature behavior is metal-like ( $\sigma \sim T^{-1.9}$  down to ca.  $60^\circ \text{K}$ , <sup>3a-c</sup> argues that the conductivity of  $\{[\text{SiPcO}]_x\}_n$  and perhaps  $\{[\text{Ge(Pc)O}]_x\}_n$  materials will also be metal-like in the chain direction. As is the case with many low-dimensional mixed valence systems, <sup>1a, 1f, 14</sup> we find the molar magnetic susceptibilities of the  $\{[\text{M(Pc)O}]_x\}_n$  materials (measured by Faraday techniques) to be only weakly paramagnetic at  $300^\circ \text{K}$  ( $\chi_M$  is in the range of  $300\text{-}500 \times 10^{-6} \text{ emu}$  after correction for diamagnetism) and only weakly dependent on temperature. <sup>15</sup>

It is possible to make structural deductions about the halogen-doped polymers which are relevant to the discussion of the electronic properties. The X-ray powder diffraction patterns of the  $[\text{M(Pc)O}]_n$  (our results and those of Kroenke, *et al.* <sup>16</sup>) and  $\{[\text{M(Pc)O}]_x\}_n$  materials are very similar, and are also similar to the tetragonal  $\text{Ni(dpg)}_2\text{I}_{1.0}$  (dpg=diphenylglyoximate) and  $\text{NiPcI}_{1.0}$  systems which have been studied by single crystal methods. <sup>2b, 3c</sup> The latter two structures consist of partially oxidized metallomacrocycle stacks, with stacking intervals of  $3.271(1)\text{\AA}$  and  $3.244(3)\text{\AA}$ , respectively, and parallel chains of polyiodide extending along the stacking direction. The powder patterns of both halogenated and unhalogenated face-to-face polymers can be indexed in the tetragonal crystal system and by analogy to  $\text{Ni(dpg)}_2\text{I}_{1.0}$  and  $\text{NiPcI}_{1.0}$ , interplanar spacings of  $3.33(2)\text{\AA}$  (Si-O-Si),  $3.51(2)\text{\AA}$  (Ge-O-Ge) and  $3.95(2)\text{\AA}$  (Sn-O-Sn) are derived, independent of halogen content. The validity of these parameters and the structural model presented in the Scheme are supported by single crystal diffraction results

on the molecule  $[(CH_3)_3SiO]_2(CH_3)SiO[Si(PcO)]_3Si(CH_3)[OSi(CH_3)_2]_2$ , which reveals linear PcSi-O-SiPc moieties and an interplanar spacing of  $3.324(2)\text{\AA}$ .<sup>17</sup> In regard to the structures of the polygermyloxane and polystannyloxane materials, the derived interplanar spacings are in good agreement with those calculated from ionic radii,<sup>18</sup> assuming linear Ge-O-Ge and Sn-O-Sn linkages.<sup>19</sup> There is good precedent for linear Ge-O-Ge and Sn-O-Sn configurations.<sup>20</sup> Thus, the interplanar spacing in  $\{[Si(PcO)]_x\}_n$  is comparable to that in  $Ni(Pc)_x$ , while the spacings in the germanium and tin polymers become progressively larger. Since the transport properties of  $MPcI_x$  compounds are largely ligand-dominated and relatively insensitive to  $M$ ,<sup>3b,3c,21</sup> it appears reasonable to relate a significant portion of the conductivity trend in the  $\{[M(PcO)]_x\}_n$  series to differences in the plane-plane separation.

Further studies of these and other linked metallomacrocyclic systems are in progress.<sup>22</sup>

#### ACKNOWLEDGMENTS

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Karl F. Schoch, Jr., Bhagyashree R. Kundalkar, and Tobin J. Marks<sup>\*23</sup>

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- (15) Susceptibilities are expressed per mole of  $[M(\text{Pc})\text{O}]_x$  subunit. Studies have been performed to 77° K; detailed experiments at lower temperatures as a function of dopant level will be reported in the future. Small increases in the paramagnetism at temperatures below 100° K are tentatively attributed to impurities.

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TABLE I. ELECTRICAL CONDUCTIVITY DATA FOR  
POLYCRYSTALLINE SAMPLES OF HALOGEN-DOPED  
[M(Pc)O]<sub>n</sub> MATERIALS. <sup>a</sup>

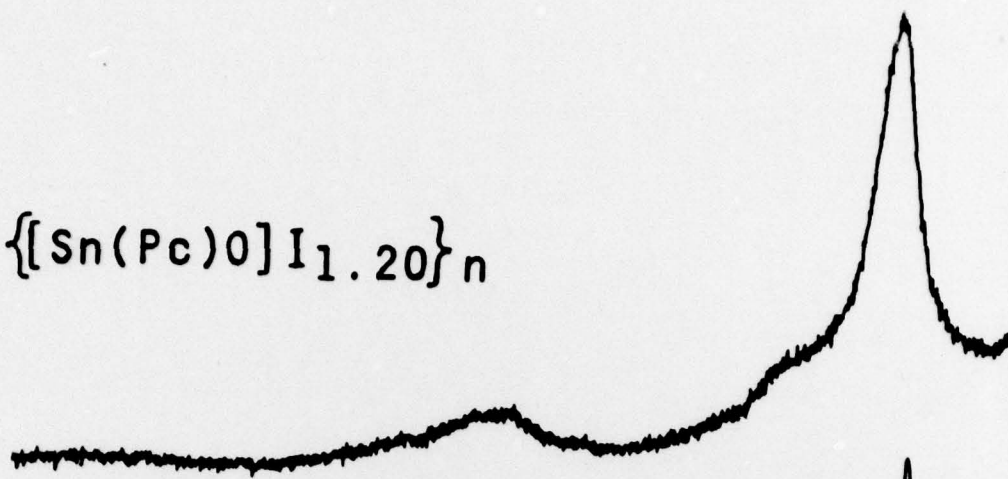
<u>Compound</u>	<u><math>\sigma</math>(ohm cm)<sup>-1</sup></u> <sup>b</sup>	<u>Activation Energy (eV)</u>
[Si(Pc)O] <sub>n</sub>	$3 \times 10^{-8}$	
{[Si(Pc)O]I <sub>0.80</sub> } <sub>n</sub>	$2 \times 10^{-2}$	
{[Si(Pc)O]I <sub>1.40</sub> } <sub>n</sub>	$2 \times 10^{-1}$	$0.04 \pm 0.001$
{[Si(Pc)O]I <sub>1.60</sub> } <sub>n</sub>	$1 \times 10^{-2}$	
{[Si(Pc)O]Br <sub>1.00</sub> } <sub>n</sub>	$6 \times 10^{-2}$	
[Ge(Pc)O] <sub>n</sub>	$< 10^{-8}$	
{[Ge(Pc)O]I <sub>1.80</sub> } <sub>n</sub>	$3 \times 10^{-2}$	$0.08 \pm 0.006$
{[Ge(Pc)O]I <sub>1.90</sub> } <sub>n</sub>	$5 \times 10^{-2}$	$0.06 \pm 0.003$
{[Ge(Pc)O]I <sub>1.94</sub> } <sub>n</sub>	$6 \times 10^{-2}$	$0.05 \pm 0.007$
{[Ge(Pc)O]I <sub>2.0</sub> } <sub>n</sub>	$1 \times 10^{-1}$	
[Sn(Pc)O] <sub>n</sub>	$< 10^{-8}$	
{[Sn(Pc)O]I <sub>1.2</sub> } <sub>n</sub>	$1 \times 10^{-6}$	
{[Sn(Pc)O]I <sub>3.5</sub> } <sub>n</sub>	$2 \times 10^{-4}$	$0.68 \pm 0.01$

<sup>a</sup> Four-probe van der Pauw techniques.

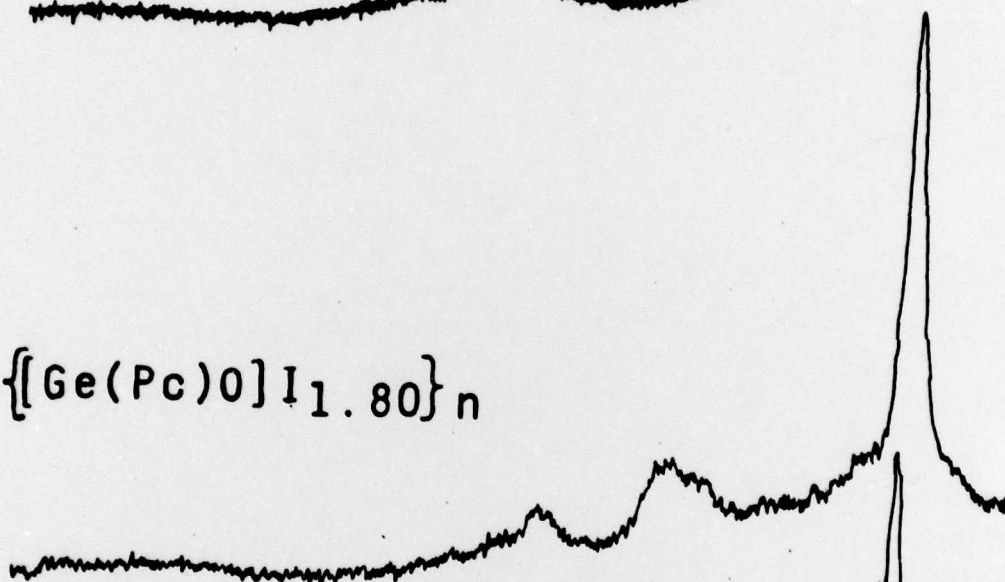
<sup>b</sup> At 300 ° K.



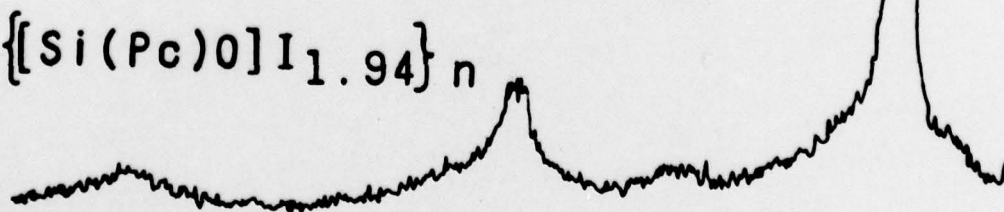
$\{[\text{Sn}(\text{Pc})\text{O}]_{1.20}\}_n$



$\{[\text{Ge}(\text{Pc})\text{O}]_{1.80}\}_n$

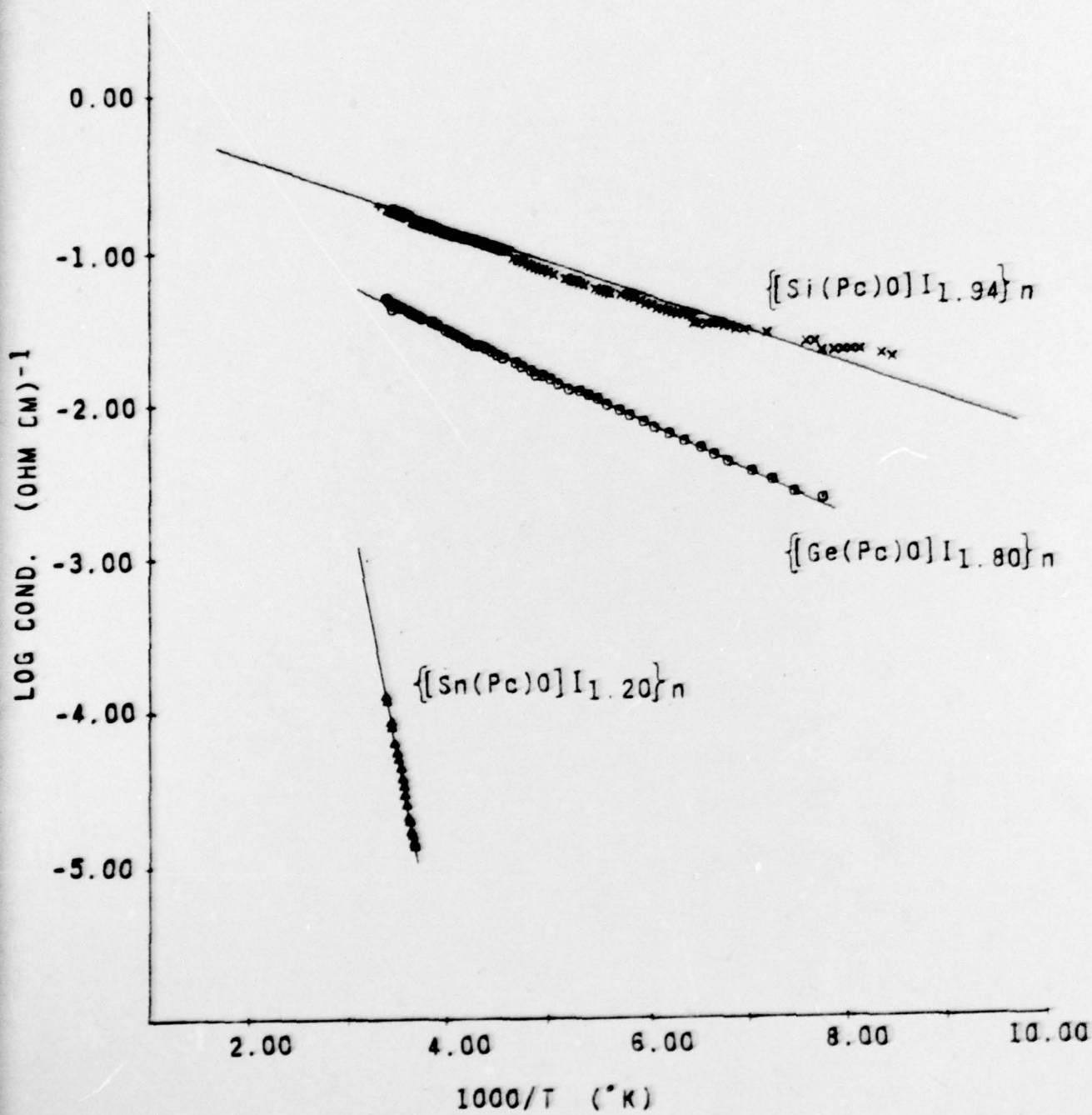


$\{[\text{Si}(\text{Pc})\text{O}]_{1.94}\}_n$



300                      200                      100  
WAVENUMBER ( $\text{cm}^{-1}$ )

**Figure 2. Four-probe conductivity data for pressed pellet samples of iodine-doped face-to-face polymers as a function of temperature. Lines through the data points represent a least-squares fit to equation (1).**



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