

Organic Metals. Introduction of Indium and Thallium Tetrachloride Anions into Polyacetylene by Anodic Oxidation

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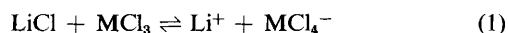
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Polyacetylene films can be oxidized electrochemically in LiCl-MCl₃-nitromethane solutions (where M = In and Tl) to give highly conducting polymers.

Anodic oxidation of polyacetylene is a convenient method by which its p-type conducting derivatives may be prepared. Typical electrochemical dopings of polyacetylene have been achieved with monovalent anions such as PF₆⁻ or ClO₄⁻ that are very stable to oxidation.^{1,2} Recently, more readily oxidizable anions such as FeCl₄⁻ and AlCl₄⁻ have been inserted into (CH)_x by anodic oxidation.³

Here we report that polyacetylene may be doped with indium and thallium tetrachloride anions by electrochemical oxidation. Electrolytes for these dopings were prepared by dissolving lithium chloride with the appropriate Lewis acid (InCl₃ or TlCl₃) in nitromethane. The MCl₄⁻ ions arise from the equilibrium shown in equation (1) which occurs in aprotic solvents. In a typical oxidation experiment a constant current of 0.1 mA/mg of (CH)_x was applied. During the electrolysis the potential of the (CH)_x anode measured vs. the Ag/AgCl reference electrode was approximately constant (ca. 0.6 V) if the doping levels did not exceed 6.5% in the case of LiCl-InCl₃ and 4.5% in the LiCl-TlCl₃ system. A rapid increase in the potential of the (CH)_x anode leading to a new plateau at ca. 0.8 V was observed when the above values of the levels of doping were exceeded.



Since both InCl₃ and TlCl₃ can oxidize polyacetylene chemically the contribution from chemical oxidation was estimated by placing in close proximity to the polyacetylene anode an

additional strip of (CH)_x not attached to the source of voltage and the changes in its mass and i.r. spectra were recorded after the electrolysis. In the case of InCl₃-LiCl-MeNO₂ chemical doping was negligible. For TlCl₃-LiCl-MeNO₂ the chemical doping never exceeded 1.5% under the conditions used. TlCl₃ is a stronger oxidising agent than InCl₃ so when it is present in the electrolyte solution even at low concentrations it can dope (CH)_x chemically to low doping levels. The current yields observed during the electrolysis were high to the 6.5% doping level for InCl-LiCl-MeNO₂ (ca. 90%) but decreased sharply at higher levels of doping. The same phenomenon was observed in TlCl₃-LiCl-MeNO₂ although the initial current yields were lower (ca. 80%) and the steep decrease began at a lower doping level (ca. 4.5%). Typical results of the electrolyses are shown in Table 1.

Table 1. Chemical composition and conductivity of polyacetylene oxidized in InCl₃-LiCl-nitromethane or TlCl₃-LiCl-nitromethane solutions.

Composition by mass uptake assuming MCl ₄ ⁻	Composition by elemental analysis	Conductivity/Ω ⁻¹ cm ⁻¹
[CH(InCl ₄) _{0.054}] _x	[CH _{1.08} (InCl _{4.06}) _{0.054}] _x	600
[CH(InCl ₄) _{0.065}] _x	—	800
[CH(InCl ₄) _{0.090}] _x	[CH _{1.14} (InCl _{3.40}) _{0.069}] _x	300
[CH(TlCl ₄) _{0.038}] _x	[CH _{1.01} (TlCl _{4.05}) _{0.039}] _x	350
[CH(TlCl ₄) _{0.045}] _x	[CH _{0.99} (TlCl _{4.05}) _{0.045}] _x	550
[CH(TlCl ₄) _{0.064}] _x	[CH _{1.05} (TlCl _{3.93}) _{0.048}] _x	450

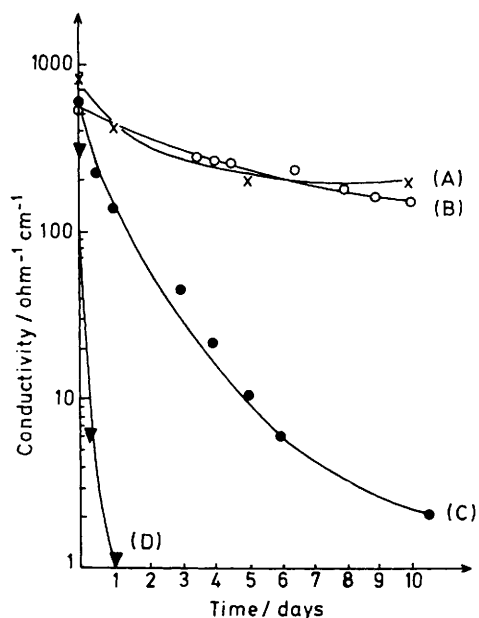
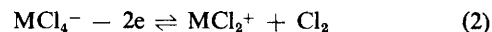


Figure 1. Conductivity vs. time of exposure to air for selected $[\text{CH}(\text{MCl}_4)_y]_x$ compounds; (A) $[\text{CH}(\text{FeCl}_4)_{0.1}]_x$, data after ref. 5; (B) $[\text{CH}(\text{InCl}_4)_{0.05}]_x$; (C) $[\text{CH}(\text{TiCl}_4)_{0.04}]_x$; (D) $[\text{CH}(\text{AlCl}_4)_{0.06}]_x$.

The data in Table 1 indicate that the conducting systems can be treated as $[\text{CH}(\text{InCl}_4)_y]_x$ and $[\text{CH}(\text{TiCl}_4)_y]_x$ at up to 6.5 and 4.5% doping levels, respectively. Above these limiting doping levels side reactions occur which lower the mobility of the charge carriers and lead to a decrease in the conductivity.

A significant increase in chlorine to metal ratios, for these doping levels, which exceed the limiting compositions is consistent with oxidative addition of chlorine to the unsaturated polyenic chain. This process can possibly occur *via* oxidation of MCl_4^- as in equation (2) and by subsequent addition of



chlorine to the double bonds in the chain. Chlorination can explain the decrease in the current yield because in this case the positive charge created on the polyacetylene is neutralised by Cl^- which is much lighter than MCl_4^- .

E.s.r. spectra of both conducting systems doped to the metallic level show characteristic Dysonian shapes with the *A/B* asymmetry ratios reaching maximums at the highest composition corresponding to the non-chlorinated samples.⁴

$[\text{CH}(\text{InCl}_4)_y]_x$ is very stable in air. The results of its stability studies, in comparison with other $[\text{CH}(\text{MCl}_4)_y]_x$ conducting systems, are shown in Figure 1.

Received, 30th June 1983; Com. 870

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