Stabilization of Iodine-doped Polyacetylene in Aqueous Solutions

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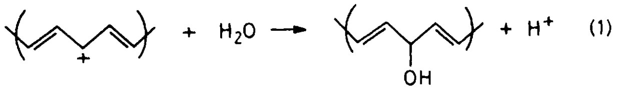
The conductivity decay which typically accompanies the storage of iodine-doped polyacetylene even in inert atmospheres can be significantly suppressed by immersion of the doped polymer in aqueous chloride containing solutions in which the chloride ion concentration is 1.0 M or greater.

The potential utility of highly conductive polymers as electrode materials has been demonstrated by polypyrrole[1] and emphasized by the fabrication of lightweight, rechargeable storage batteries based on polyacetylene,[2] $[CH]_x$, and poly-(*p*-phenylene).[3] We have begun to explore the use of conductive polymers as electrode materials in aqueous media. Although it is doubtful that n-type (reduced) organic conductors will ever have a finite lifetime in the presence of water owing to the notoriously ready protonation exhibited by carbanions, p-type (oxidized) polymers appear in general to be much less sensitive in aqueous media.[4] This is perhaps contrary to what we would expect as carbenium ions are very susceptible to nucleophilic attack by water, as illustrated in the general reaction (1) for p-type, *trans*-$[CH]_x$.



We report on the stabilization of iodine-doped, p-type $[CH]_x$ in aqueous solutions and our initial study of the reactivity of p-type $[CH]_x$ toward water and other nucleophiles.

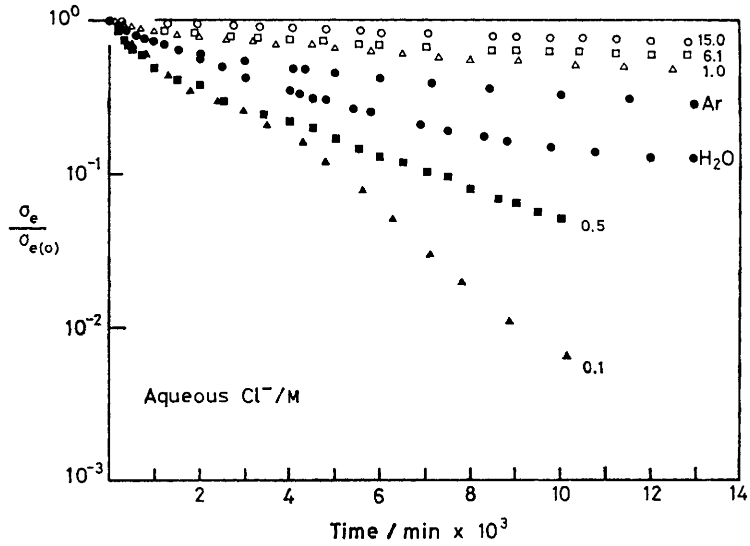


Figure 1. Plots of the normalized conductivity ($\sigma_e/\sigma_{e(o)}$) *vs.* exposure time (min) for iodine-doped polyacetylene, $[CHI_{0\cdot18-0\cdot20}]_x$, in deaerated, aqueous chloride solutions of concentrations 0.1—15.0 M compared with the behaviour under purified argon and deaerated, deionized, distilled water.

cis-Polyacetylene films were prepared at −78 °C using techniques similar to those developed by Shirakawa and coworkers.[5,6] Vapour-phase iodine doping afforded compositions of $[CHI_{0\cdot18-0\cdot20}]_x$ and four-probe conductivities of 200—300 Ω^{-1} cm^{-1}.

The conductivities of the doped films were followed as a function of exposure time under argon, in deaerated, deionized, distilled water and in aqueous solutions of analytical grade NaI, NaSCN, NaBr, and NaCl made from water of similar high quality. For the immersion exposure experiments, samples were mounted on four-probe platinum electrodes in a dry box using Electrodag 502 and the leads were individually sealed with Microstop Stopoff Lacquer. This latter step was done to ensure that the electrical conductivity of the doped $[CH]_x$ was measured without ionic contributions from the electrolyte solutions. The solutions were blanketed with argon throughout the duration of the experiment (approximately nine days).

In Figure 1 are plotted the normalized conductivities ($\sigma_e/\sigma_{e(o)}$, where $\sigma_{e(o)}$ is the initial conductivity; the subscript e is used to emphasize that it is the electronic conductivity of the film which is being measured) of the iodine-doped $[CH]_x$ film in argon, water, and aqueous solutions of various concentrations of Cl^-. The highest concentration, 15.0 M, was obtained as a saturated solution of LiCl; all other solutions were of NaCl. Several points are noteworthy. The conductivity of the doped film decays under rigorously purified argon, falling to 27% of its initial value over the nine day period. This phenomenon has been attributed to slow iodination of the $[CH]_x$ backbone.[7] It can also been seen from Figure 1 that immersion in water affords a more rapid decay of the conductivity, falling to 13% of its initial value over the nine day period. This presumably results from the consumption of carbenium ions (charge carriers) *via* the reaction shown in equation (1).

The remaining curves of Figure 1 display the stability performance of iodine-doped polyacetylene in aqueous solutions of varying concentrations of NaCl. The 0.1 M NaCl solution is more aggressive than distilled water, presumably because Cl^- is a better nucleophile than water. However, the 0.50 M NaCl solution, while still more aggressive than water, gives less conductivity decay than the 0.10 M solution. Most significant is the observation that solutions of 1.00 M or greater afford improved stability compared with water and, interestingly, argon. We have made a preliminary survey of concentrated solutions of other nucleophiles, the result of which is summarized in Table 1. It can be seen that all of these solutions are more aggressive than water itself. Furthermore, the magnitude of the conductivity decay appears to be approximately in the order of the strength of the nucleophiles ($SCN^- > I^- > Br^- > Cl^- > H_2O$) with the notable exception being the Cl^- ion as discussed previously.

Table 1. Normalized conductivity ($\sigma_e/\sigma_{e(o)}$) of iodine-doped polyacetylene, $[CHI_{0\cdot18-0\cdot20}]_x$, after 10^4 min (6.94 days) of immersion under deaerated, aqueous solutions of various nucleophiles and argon.

Nucleophile (1.0 M)	$\sigma_e/\sigma_{e(o)}$
I^-	7.0×10^{-3}
SCN^-	4.6×10^{-2}
Br^-	2.4×10^{-2}
Cl^-	5.2×10^{-1}
H_2O	1.5×10^{-1}
Ar	3.3×10^{-1}

The origin of this enhanced stability in concentrated chloride solution is not clear. We believe that a possible explanation lies in the formation of the non-reactive interhalide, I_2Cl^-, the result of the reaction of molecular iodine (decomposed I_3^- or adsorbed I_2) with chloride ions. The iodine so consumed would no longer be available for reaction with the $[CH]_x$ backbone, thus accounting for the improved stability over that found under argon. In support of this we have found that samples of iodine-doped $[CH]_x$ of composition $[CHI_{0\cdot11}]_x$ which had been immersed in deaerated 15.0 M LiCl and 6.1 M NaCl over a 17 day period, then rinsed with deaerated, deionized, distilled water and analysed for trace chloride contained the following compositions respectively, $[CHI_{0\cdot10}Cl_{0\cdot0031}]_x$ and $[CHI_{0\cdot09}Cl_{0\cdot0025}]_x$. We are as yet unsure whether the incorporated chloride results from interhalide formation or simple ion exchange (or both).

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