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STABILITY OF IODINE-DOPED POLYACETYLENE IN AQUEOUS ENVIRONMENTS

A. Guiseppi-Elie and G.E. Wnek

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA. 02139, U.S.A.

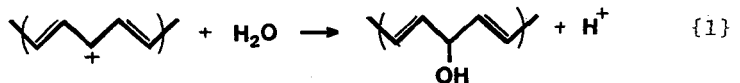
Résumé: Le polyacétylène dopé à l'iode montre une stabilité exceptionnelle dans des environnements aqueux débarrassés d'air. Il se dégrade en présence de nucléophiles aqueux avec un taux qui augmente quand l'activité du nucléophile augmente.

Abstract: Iodine-doped polyacetylene has been found to display exceptional stability in deaerated, aqueous environments and to degrade in the presence of aqueous nucleophiles with a rate which increases with increasing nucleophilicity.

I

INTRODUCTION

The potential utility of highly conductive polymers as electrode materials has been demonstrated by polypyrrole(1) and underscored 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. Water is an attractive electrolyte medium because of its ready availability, low cost, non-toxicity and because useful fuel in the form of H₂ can be obtained from its photoelectrolysis(4). Although it is doubtful that n-type (reduced) organic conductors will ever have a finite lifetime in water (due to notoriously facile protonation exhibited by carbanions), p-type (oxidized) polymers appear to be much less sensitive in aqueous media(5). In fact, polyacetylene may be rendered a p-type conductor by simple exposure to aqueous KI/I₂ solutions and by electrochemical oxidation in aqueous KI solutions² (5,6). This is contrary to our intuition concerning the susceptibility of carbenium ions to nucleophilic attack by water, as illustrated for p-type, trans-(CH)_x:



We report here our observations of exceptional stability of iodine-doped (CH)_x in aqueous environments and our preliminary study of the reactivity^x of p-type doped (CH)_x with aqueous nucleophiles. From the latter work an environment for the enhanced stabilization of (CHI_n)_x has been identified.

II

EXPERIMENTAL

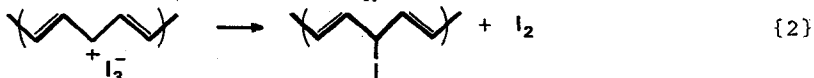
Cis-polyacetylene films were prepared at -78°C using techniques similar to those developed by Shirakawa and coworkers(7,8). Elemental analyses of the as-synthesized, pristine polymers indicated CH contents of >99%. Iodine doping was achieved by exposing the pristine polymer to a vapor stream of iodine carried in deoxygenated and dried argon. The doped polymer was subsequently subjected to dynamic vacuum (10⁻⁵ torr) for 24 hours to remove adsorbed iodine. Elemental analyses of the

resulting doped polymers produced compositions in the range $(CH_{0.18-0.20})_x$ and were in good agreement with simultaneously determined compositions via weight uptake. The resulting room temperature four-probe conductivities were in the range 200-300 $\Omega^{-1}cm^{-1}$. The conductivities of the doped films were followed as a function of exposure time under purified argon; in deaerated, deionized, distilled water; in laboratory air and in deaerated, aqueous solutions of analytical grade NaI, NaSCN, NaBr, NaCl and NaF made from water of similar high quality. For the immersion exposure experiments, samples were mounted in a dry box onto four-probe platinum electrodes using Electrodag 502 and the leads were individually sealed with Microstop Lacquer. This latter step was done to insure that the electrical conductivity of the doped $(CH)_x$ was exclusively measured without ionic contributions from the electrolyte solutions. The mounted films were quickly transferred (through air) to 250 ml three-neck flasks containing the desired deaerated, aqueous solution. The solutions were blanketed with argon throughout the duration of exposure (approximately nine days).

III

RESULTS AND DISCUSSION

Figure 1 shows the stability performance of iodine-doped polyacetylene as indicated by the variation in the normalized conductivity (σ_e/σ_{e_0}) followed as a function of exposure time in purified argon; deaerated, deionized, distilled water and laboratory air. Iodine-doped $(CH)_x$ is observed to degrade even under highly controlled, inert conditions (argon), the conductivity falling to 27% of its initial value over the approximate 9 day period. This decay in conductivity is presumed to result from slow iodination of the $(CH)_x$ backbone via:



Reaction {2} leads to an interruption of chain conjugation and annihilation of charge carriers. For this reaction the following general, chemical rate expression may be written,

$$- \frac{d(\sigma_e/\sigma_{e_0})}{dt} = K (\sigma_e/\sigma_{e_0})^n \quad \{3\}$$

where K (specific rate) is a constant and n is the reaction order with respect to the conductivity variable. Equation {3} is valid if the conductivity is proportional to the amount of chemical entity which is responsible for conduction, i.e. the charge transfer complex, charged soliton or carbenium ion. Taking \log_{10} of equation {3}

should produce a straight line of slope n. Figure 2 is such a plot of $\log_{10} \frac{d(\sigma_e/\sigma_{e_0})}{dt}$ vs $\log_{10} (\sigma_e/\sigma_{e_0})$ and is shown to not be a straight

line. This indicates that the conductivity decay does not fit the general, chemical rate expression and the assumptions inherent therein. This is at variance with the pseudo-first order kinetics observed by Pochan et al (9) for this reaction. Thus conductivity is therefore not simply proportional to the abundance of carbenium ions. This is as expected and is consistent with the fact that the conductivity is also proportional to the charge mobility as can be seen in the general conductivity expression,

$$\sigma_e = en\mu \quad \{4\}$$

where n is the number of carriers, μ the carrier mobility and e the charge on the carrier. This confirms what is often suggested and

intuitively understood about doped $(CH)_x$ - that changes in conductivity resulting from reaction of the active carbenium ions generally also result in changes in the carrier mobility. The latter results from interruption of the backbone conjugation.

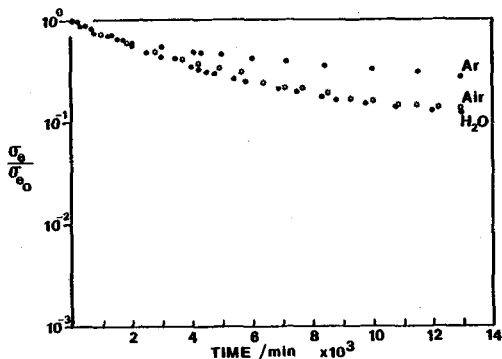


FIG. 1. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_e/σ_{e0}) VS EXPOSURE TIME (MIN.) FOR IODINE DOPED POLYACETYLENE, $(CH_{1.20})_x$, UNDER PURIFIED ARGON, DEAERATED, DEIONIZED DISTILLED WATER AND IN LABORATORY AIR.

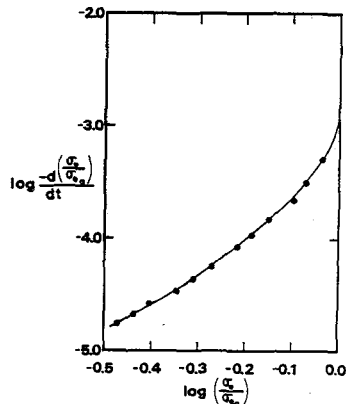


FIG. 2. PLOT OF THE GENERALIZED RATE EXPRESSION FOR THE DECAY IN CONDUCTIVITY OF IODINE DOPED POLYACETYLENE $(CH_{1.20})_x$ UNDER ARGON.

Figure 3 shows data obtained for the degradation of iodine-doped $(CH)_x$ under argon plotted as $\log \left\{ -\frac{d \log(\sigma_e/\sigma_{e0})}{dt} \right\}$ vs $\log (\sigma_e/\sigma_{e0})$. This produces a straight line of slope $n=2.9$ and intercept -3.29 with a correlation coefficient of 0.992. This suggests that the decay kinetics can be empirically represented by an expression of the form

$$-\frac{d \log(\sigma_e/\sigma_{e0})}{dt} = 5.1 \times 10^{-4} (\sigma_e/\sigma_{e0})^{2.9} \quad \{5\}$$

Such a logarithmic dependence of the conductivity on the population of carriers has also been observed by Kanicki et al(10) in their study of the iodine doping kinetics and was interpreted to support a three-dimensional variable range hopping conduction mechanism.

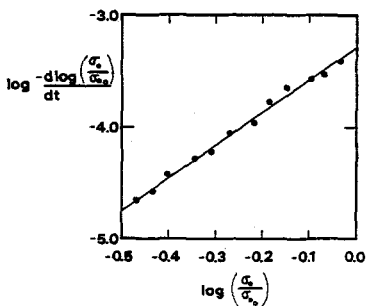


FIG. 3. PLOT OF THE MODIFIED RATE EXPRESSION FOR THE DECAY IN CONDUCTIVITY OF IODINE DOPED POLYACETYLENE $(CH_{1.20})_x$ UNDER ARGON.

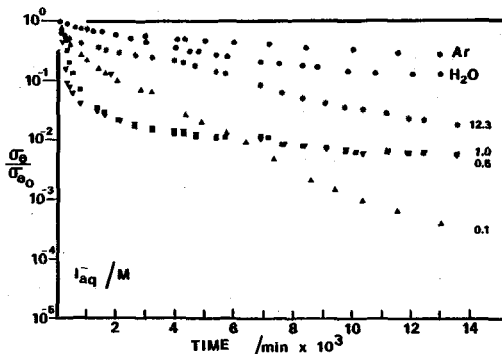


FIG. 4. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_e/σ_{e0}) VS EXPOSURE TIME (MIN) FOR IODINE-DOPED POLYACETYLENE, $(CH_{1.18-0.20})_x$, IN DEAERATED, AQUEOUS IODIDE SOLUTIONS OF CONCENTRATIONS 0.1M - 12.3M COMPARED WITH THE BEHAVIOR UNDER PURIFIED ARGON AND DEAERATED, DEIONIZED, DISTILLED WATER.

There appears in Figure 1 little difference in the performance of highly doped $(CH)_x$ in deaerated, deionized, distilled water and laboratory air. This would suggest that the influence of oxygen in accelerating degradation is secondary to that of moisture over the nine day period of observation.

Figures 4 through 8 shows the stability performance of iodine-doped $(CH)_x$ on exposure to deaerated, aqueous solutions of the nucleophiles I^- , SCN^- , Br^- , Cl^- and F^- (arranged in order of decreasing nucleophilicity). Each nucleophile was studied at concentrations of 0.1M, 0.5M, 1.0M and at saturation. In general the extent of degradation increases with increased nucleophilicity of the test anion though the effect of concentration is somewhat variable.

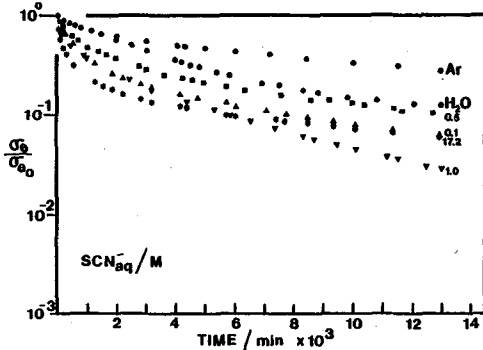


FIG. 5. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_t/σ_0) VS EXPOSURE TIME (MIN) FOR IODINE-DOPED POLYACETYLENE, $(CH)_{0.18-0.20}x$, IN DEAERATED, AQUEOUS THIOCYANATE SOLUTIONS OF CONCENTRATIONS 0.1M - 17.2M COMPARED WITH THE BEHAVIOR UNDER PURIFIED ARGON AND DEAERATED, DEIONIZED, DISTILLED WATER.

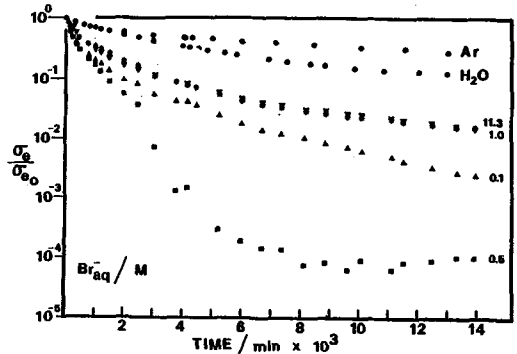


FIG. 6. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_t/σ_0) VS EXPOSURE TIME (MIN) FOR IODINE-DOPED POLYACETYLENE, $(CH)_{0.18-0.20}x$, IN DEAERATED, AQUEOUS BROMIDE SOLUTIONS OF CONCENTRATIONS 0.1M - 17.2M COMPARED WITH THE BEHAVIOR UNDER PURIFIED ARGON AND DEAERATED, DEIONIZED, DISTILLED WATER.

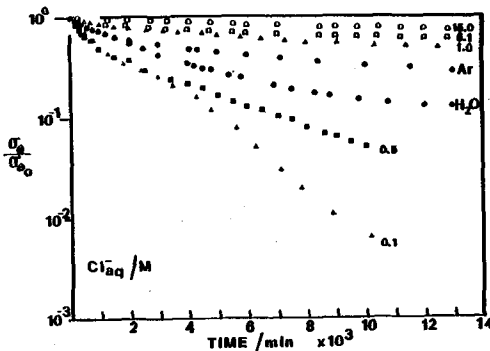


FIG. 7. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_t/σ_0) VS EXPOSURE TIME (MINS.) FOR IODINE-DOPED POLYACETYLENE, $(CH)_{0.18-0.20}x$ IN DEAERATED, AQUEOUS CHLORIDE SOLUTIONS OF CONCENTRATIONS 0.1M - 15.0M COMPARED WITH THE BEHAVIOR UNDER PURIFIED ARGON AND DEAERATED, DEIONIZED, DISTILLED WATER.

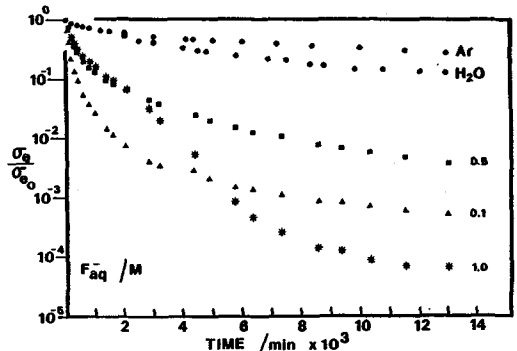


FIG. 8. PLOTS OF THE NORMALIZED CONDUCTIVITY (σ_t/σ_0) VS EXPOSURE TIME (MIN) FOR IODINE-DOPED POLYACETYLENE, $(CH)_{0.18-0.20}x$, IN DEAERATED, AQUEOUS FLUORIDE SOLUTIONS OF CONCENTRATIONS 0.1M - 17.2M COMPARED WITH THE BEHAVIOR UNDER PURIFIED ARGON AND DEAERATED, DEIONIZED, DISTILLED WATER.

The case for chloride ion is anomalous and is shown in Figure 7 to enhance stability over that observed under argon at concentrations of 1.0M and greater(11). This anomaly possibly results from the formation of the interhalide, I_2Cl_2 , which acts to decrease the concentration of free iodine and create a more stable counteranion for the charge carriers.

IV

CONCLUSIONS

The conductivity of iodine-doped polyacetylene is found to degrade even under inert conditions. The degradation kinetics is not treatable by the classical, general chemical rate expression but is found to obey a logarithmic dependence on carrier population. Highly p-doped $(CH)_x$ is found to be quite stable in aqueous environments with accelerated decay kinetics in the presence of added nucleophiles. In general the decay increases with increased nucleophilicity of the added nucleophile.

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V

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