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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A series of experiments are reported which demonstrate that donors or acceptors can dope polyacetylene to n-type or p-type respectively, and that the two kinds of dopants can compensate one another. The formation of a rectifying p-n junction is demonstrated. The results suggest the possibility of utilizing doped polyacetylene in a variety of potential semiconductor device applications.

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by

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Polyacetylene, $(CH)_x$: n-Type and p-Type Doping and Compensation

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Abstract

A series of experiments are reported which demonstrate that donors or acceptors can dope polyacetylene to n-type or p-type respectively, and that the two kinds of dopants can compensate one another. The formation of a rectifying p-n junction is demonstrated. These results suggest the possibility of utilizing doped polyacetylene in a variety of potential semiconductor device applications.

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We have recently reported that when flexible, crystalline films of the covalent polymer, polyacetylene, $(\text{CH})_x$, are doped, their conductivity can be systematically and controllably varied over a range of more than eleven orders of magnitude.¹⁻³ The most highly conducting films exhibited a conductivity at room temperature of order $10^3 \text{ ohm}^{-1} \text{-cm}^{-1}$, by far the highest observed for any covalent organic polymer. The electronic properties are similar to those of a simple classical semiconductor with thermally activated conductivity at low dopant levels and a transition to metallic properties at high levels.² The dopant can be either an acceptor such as bromine, iodine or AsF_6 ;^{1, 2} or the dopant can be a donor such as lithium, sodium and potassium.^{3, 4} We report in this paper on a series of experiments which demonstrate that both donors and acceptors can dope polyacetylene to n-type or p-type material respectively, and that the two kinds of dopants can compensate one another. The demonstration of successful n-type and p-type doping together with compensation indicates the possibility of utilizing doped polyacetylene in a variety of potential semiconductor device applications.

The $(\text{CH})_x$ polymer films were prepared using refinements of the techniques developed by Shirakawa et al.⁵ The doping techniques were developed recently in our laboratories. Details on the preparation and doping are published elsewhere.^{1, 3, 4}

When pure polyacetylene is doped with an acceptor, the electrical conductivity increases sharply over many orders of magnitude at low

concentration, then saturates at higher dopant levels, above approximately 1%.²⁻⁴ The maximum conductivity we have reported to date at room temperature was $560 \Omega^{-1} \text{ cm}^{-1}$ for $\text{cis}[\text{CH}(\text{AsF}_6)_{0.14}]_x$.^{2,3} Donor doping leads to qualitatively similar results. The highest conductivity obtained thus far through donor doping was $200 \Omega^{-1} \text{ cm}^{-1}$.⁴ The typical behavior for the electrical conductivity as a function of dopant concentration is shown in Figure 1. The general features appear to be the same for the various donor and acceptor dopants, but with detailed differences in the saturation values and the critical concentration for the metal-insulator transition.

Earlier studies^{2,3} suggested that compensation could be achieved. The sensitivity of $(\text{CH})_x$ to impurities implies that the residual conductivity in "pure" $(\text{CH})_x$ is probably due to residual impurities or defects at very low levels. Exposure of pure $(\text{CH})_x$ to vapor of the donor, NH_3 , causes the conductivity of trans- $(\text{CH})_x$ to fall more than four orders of magnitude without detectable weight increase. The exposure to NH_3 thus results in compensation of the residual impurities and/or defects.

Compensation of n-type material by subsequent acceptor doping has been successfully demonstrated using Na (donor) and iodine or AsF_6 (acceptors). Figures 2 and 3 show the compensation of Na-doped polyacetylene by iodine and AsF_6 , respectively. The Na-doped films were prepared by treating the polymers with a solution of sodium naphthalide,³ $\text{Na}^+(\text{C}_{10}\text{H}_8)$, in THF whereupon electron transfer from the naphthalide

radical anion to the $(\text{CH})_x$ occurred. In each case the pure cis-polyacetylene was first doped with sodium until the conductivity was in the saturation range. Subsequent exposure to iodine or AsF_5 vapor resulted in the compensation curves plotted in Figs. 2 and 3. The compensation proceeds more slowly than the original doping; the electrical conductivity of the n-type sample gradually decreases and reaches a minimum. Continued doping with iodine or AsF_5 results in conversion to p-type material with an associated increase in conductivity.

Due to the relatively high concentration of ionic impurities in the sample, the conductivity of the fully compensated sample (at minimum) remained higher than that of the original polymer prior to doping. Nevertheless Figures 2 and 3 show compensation over approximately four orders of magnitude starting from the highest doping levels where the samples are metallic. Even more precise compensation can be expected using intermediate to low initial doping.

Starting with an initial composition $(\text{CHNa}_{0.27})_x$, the compensation point with iodine occurred at $(\text{CHNa}_{0.27}\text{I}_{0.28})_x$; all compositions being determined by measurement of weight increase. Thus the compensation point corresponds approximately to a stoichiometric sodium to iodine ratio consistent (within the limits of error) to the presence of equal concentrations of Na^+ and I^- in the compensated polymer. Continued doping leads to p-type material, where the iodine is known to be present as I_3^- from Raman studies.^{6,7}

From these observations, the overall shape of the compensation curves, and the fact that the doping can be removed chemically,⁴ we believe the doping results from charge transfer, and the compensation is best viewed as of direct chemical origin. Charge transfer occurs from polymer to acceptor (A) with the polymer chain acting as a polycation in the presence of an A^- species (in the case of iodine, the compensation and Raman experiments suggest I^- in the presence of excess Na^+ going over to I_3^- in the p-type material). For a donor (D), the polymer chains act as a polyanion in the presence of the D^+ species. The charge transfer need not be complete. The resulting electron (or hole) on the polymer chain is weakly bound to the D^+ (or A^-) ions by the Coulomb potential, forming donor (or acceptor) states in the gap. At low levels, thermal activation out of the bound states results in carriers for transport along the polymer chain. Above approximately 1 mole% doping, the bound states are screened, and the carriers are free to move along the polymer chains resulting in metallic behavior.² Compensation at least in the case of iodine evidently occurs through formation of (D^+A^-) leaving the polymer chain essentially neutral and without electronic carriers.

The assignment of donor doped material as n-type and acceptor doped material as p-type follows from the chemical properties of the donor and acceptor dopants. Moreover, the assignments are consistent with the results obtained from studies of graphite intercalated with alkali

metals and iodine or AsF_6 respectively.⁸ Finally thermoelectric power measurements on acceptor doped $(\text{CH})_x$ yield a positive Seebeck coefficient consistent with p-type material. Moreover, the value of $+15 \mu\text{V/K}$ found at room temperature for $(\text{CH})_x$ heavily doped with AsF_6 is consistent with metallic behavior. Initial experiments directed toward fabrication of p-n junctions are encouraging as shown in Fig. 4. The junction was made by mechanically pressing together n-type (Na-doped) and p-type (AsF_6 -doped) strips of polymer film. Although some hysteresis is evident, a typical diode characteristic is seen in the I-V curve. Junctions have also been made using a single polymer strip doped n-type on one-half and p-type on the other half. Note that in all cases the forward bias direction was consistent with the p-type and n-type character of the acceptor and donor doped material.

In summary, polyacetylene exhibits many attractive features for potential device applications. From optical studies,⁹ we conclude that the intrinsic band gap is at approximately 1.6 eV; i. e. reasonably well matched to the solar spectrum. In addition to the ability to dope to n-type or p-type and to compensate, the chemical and mechanical properties are attractive. The material can be synthesized in the form of strong, flexible, free-standing films or as films on glass or metal substrates.

Considering possible polyacetylene derivatives, replacement of some or all of the hydrogen atoms in $(\text{CH})_x$ with organic or inorganic

groups, copolymerization of acetylene with other acetylenes or olefins and the use of different dopants, this large new class of organic polymer semiconductors offer the possibility of unique chemical tuning of electrical properties.

Acknowledgement: This work was supported by the Office of Naval Research.

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Figure Captions:

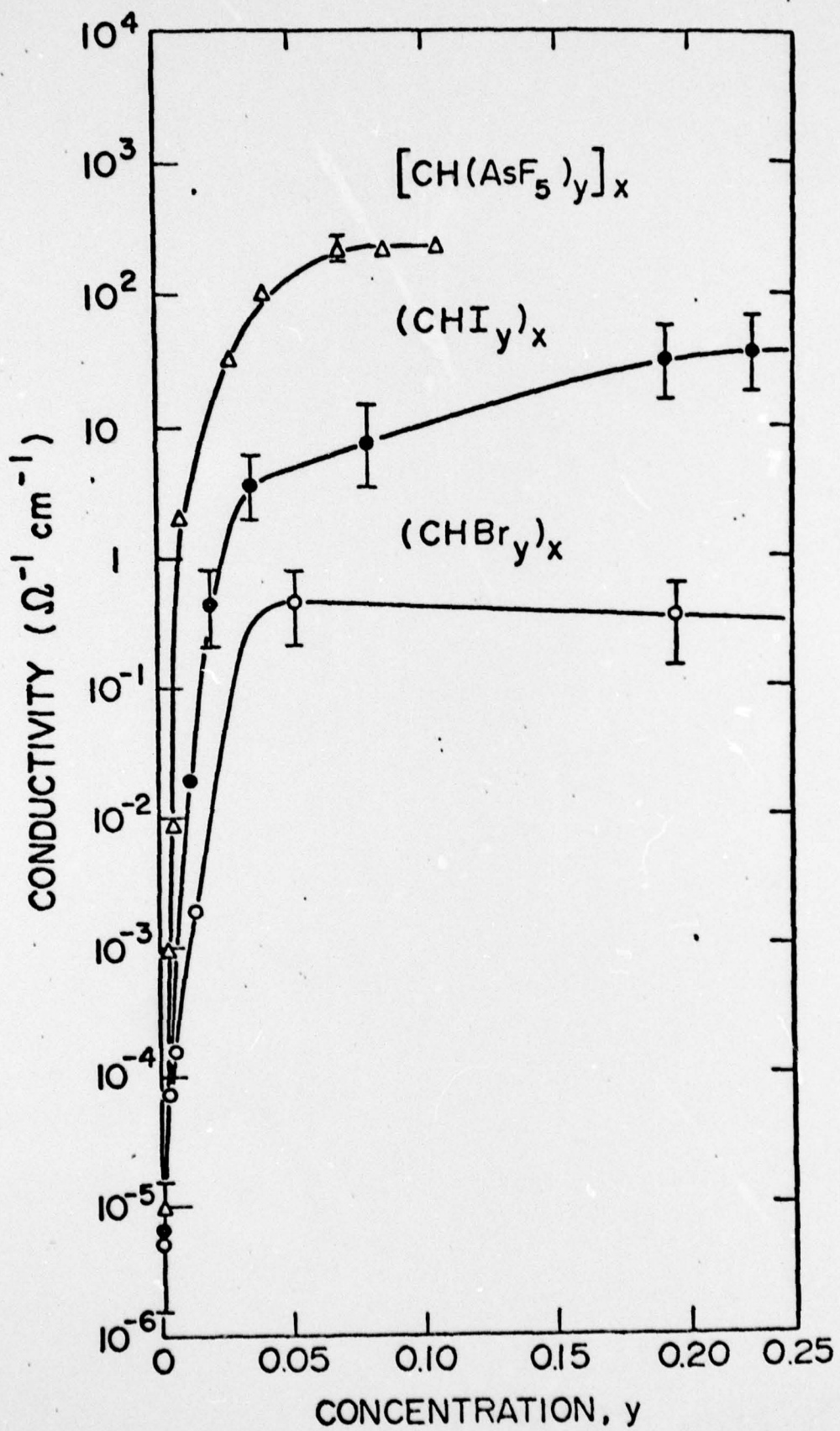
Figure 1: Electrical Conductivity (room temperature) as a function of dopant concentration:

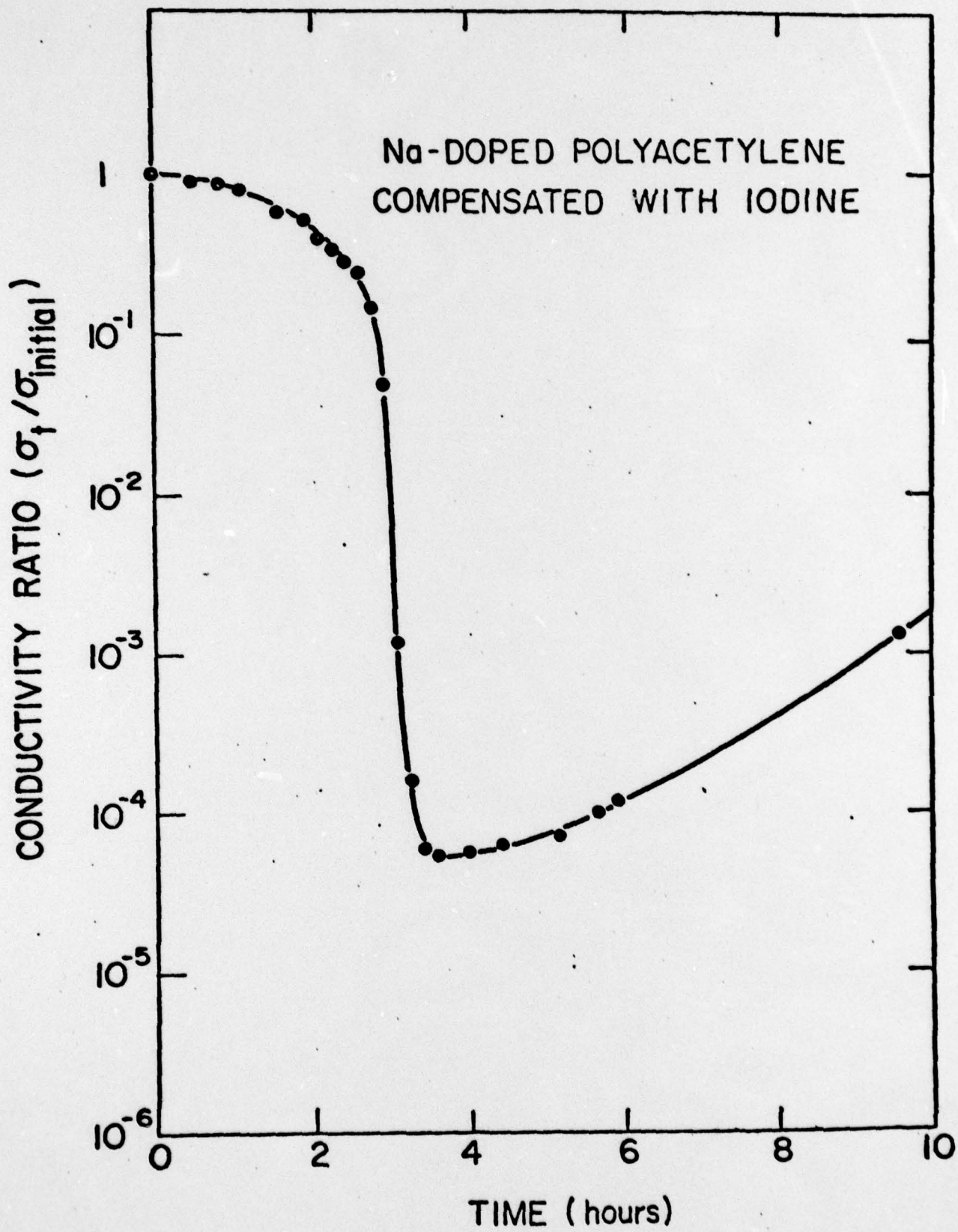
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Figure 2: Compensation curve for Na-doped polyacetylene; conductivity ratio ($\sigma(t)/\sigma_{\text{initial}}$) vs. time. The sample was initially doped n-type and subsequently exposed to iodine vapor.

Figure 3: Compensation curve for Na-doped polyacetylene; conductivity ratio ($\sigma(t)/\sigma_{\text{initial}}$) vs. time. The sample was initially doped n-type and subsequently exposed to AsF₅ vapor.

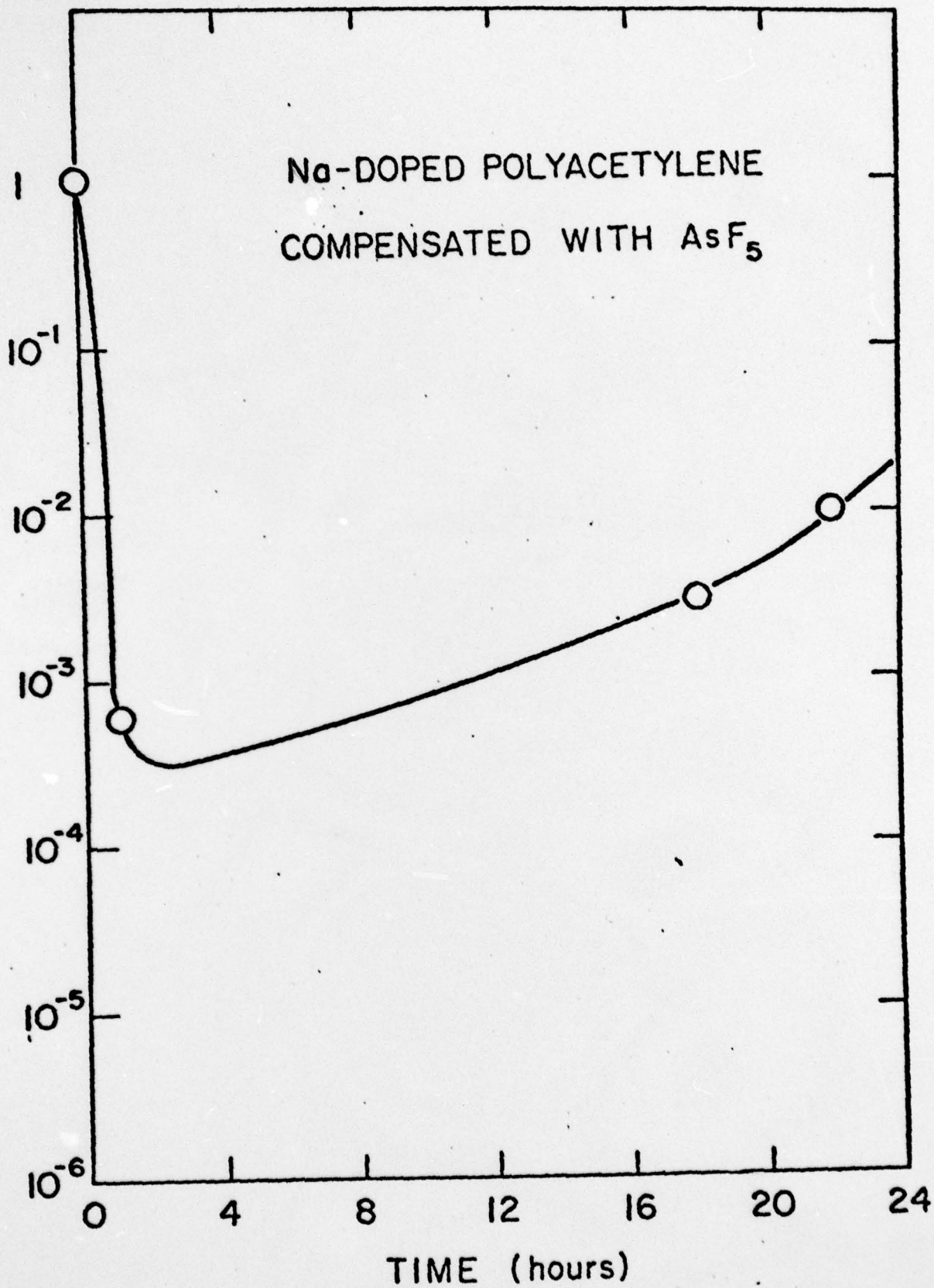
Figure 4: I-V curve for a doped polyacetylene p-n junction.

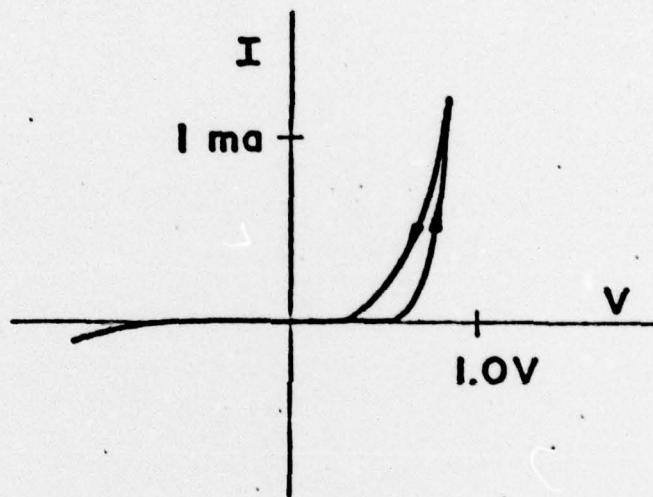




Na-DOPED POLYACETYLENE
COMPENSATED WITH AsF_5

CONDUCTIVITY RATIO ($\sigma_t / \sigma_{initial}$)





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