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Synthetic Metals, 1 (1979/80) 21 - 28

THE MECHANISM OF ARSENIC PENTAFLUORIDE DOPING OF POLYACETYLENE

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(Received January 29, 1979)

Summary

Doping of polyacetylene with arsenic pentafluoride is found to involve oxidation of the polymer according to the mechanism: $2(CH)_x + 3AsF_5 \rightarrow 2(CH)_x^+ + 2AsF_6^- + AsF_3$. The AsF_6^- ions intercalate between the polymer chains in a nonrandom fashion. Oxidation of the polymer is accompanied by replacement of the original interband transition in the visible by a featureless transition extending into the infrared. Treatment of the doped polyacetylene with ammonia destroys the enhanced conductivity and regenerates a visible spectrum similar to that of the undoped polymer but somewhat blue-shifted. Possible explanations are offered for these results in terms of the proposed mechanism of doping.

Introduction

Although the dramatic enhancement in electrical conductivity observed on treatment of polyacetylene [$(CH)_x$] with donors or acceptors has tended to focus attention on the physical and electrical properties of these materials [1 - 7], a fundamental understanding of the $(CH)_x$ system also requires a knowledge of the chemical interactions underlying the doping process. Recent results using transition metal salts to modify the conductivity of $(CH)_x$ have provided clear evidence for electron transfer between the polymer and the dopant [8]. Results of Raman spectroscopy on $(CH)_x$ treated with bromine [8, 11] or iodine [9 - 11] are also consistent with chemical oxidation of the polymer to give polyolefinic cations and trihalide counterions. On the other hand, the interaction of arsenic pentafluoride with $(CH)_x$ is less well understood and has therefore been the subject of some controversy. An understanding of this reaction is quite important, however, since much of the available physical data on doped polyacetylene has been obtained using AsF_5 as the dopant.

In this paper we will describe the results of a series of experiments designed to shed light on the nature of both the reduced form of AsF_5 after reaction with $(CH)_x$ and also the resultant oxidized form of the polyacetylene.

Experimental

$(CH)_x$ films were prepared at -78 °C on glass surfaces wetted with a titanium tetrabutoxide/triethylaluminum catalyst mixture according to the general procedure of Shirakawa *et al.* [12]. Depending on the duration of exposure to acetylene, films of thickness 0.1 - 100 μm could be formed. The as-prepared films were predominantly *cis* as determined by infrared spectroscopy [13]. On heating to 200 °C *in vacuo* these samples could be converted to essentially all *trans* polyacetylene. Exposure to air was found to cause gradual degradation of the undoped films.

Doping was accomplished by exposure of the pristine films to AsF_5 vapors at pressures ranging from 0.1 to 10 mm. The extent of doping was controlled primarily by the time of exposure. After doping, all samples were subjected to evacuation to $\leqslant 10^{-5}$ mm at room temperature for at least 30 min before use. Dopant concentration was determined by weight uptake. Since exposure to air was found substantially to alter the electrical properties of the doped films, manipulations were carried out under inert atmosphere where possible.

In a separate experiment a polyacetylene film was exposed to AsF_3 vapor at a pressure of 47 mm for 1 h followed by brief evacuation to 10^{-5} mm. A slight weight increase corresponding to less than one mole percent. AsF_3 absorption was observed. No significant increase in electrical conductivity was observed. Under similar conditions exposure of polyacetylene to AsF_5 leads to a weight increase corresponding to greater than 15 mole percent. AsF_5 and a conductivity greater than 10^2 ohm^{-1} cm^{-1}.

X-ray absorption, reflectance Raman and infrared spectroscopy were performed on free standing films obtained by peeling sections from the glass substrate in the preparative procedure described above. X-ray absorption studies were carried out using the high intensity X-ray source at the Stanford Synchrotron Radiation Laboratory. The very thin films used in visible and infrared transmission spectroscopy were grown directly on quartz and cesium iodide substrates, respectively.

Nature of the arsenic species after reaction with $(CH)_x$

Several mechanisms have been suggested for the reaction of AsF_5 with polyacetylene. These are summarized in eqns. (1) - (3). Results of elemental analysis [1b] and photoelectron spectroscopy [14] have been interpreted in terms of reaction (1) or (2) in which the AsF_5 unit remains intact. However, the partial charge transfer mechanism suggested by eqn. (1) is not

$$(\mathrm{CH})_x + \mathrm{AsF}_5 \rightarrow (\mathrm{CH})_x^{\delta+}(\mathrm{AsF}_5)^{\delta-} \qquad (1)$$

$$(\mathrm{CH})_x + \mathrm{AsF}_5 \rightarrow (\mathrm{CH})_x^{+} + \mathrm{AsF}_5^{\cdot-} \qquad (2)$$

$$2(\mathrm{CH})_x + 3\mathrm{AsF}_5 \rightarrow 2(\mathrm{CH})_x^{+} + 2\mathrm{AsF}_6^{-} + \mathrm{AsF}_3 \qquad (3)$$

consistent with the complete electron transfer previously demonstrated for halogen and silver salt doping [8]. Equation (2) postulates the formation of the arsenic pentafluoride radical anion, a paramagnetic species. Since e.s.r. investigation of AsF_5-treated polyacetylene shows no signals attributable to such a radical anion [15], this mechanism cannot be correct as written. Dimerization of the $\mathrm{AsF}_5^{\cdot-}$ to give the previously unreported diamagnetic species $\mathrm{As}_2\mathrm{F}_{10}^{2-}$ could account for the lack of an e.s.r. signal. Equation (3) involves the formation of the well known AsF_6^- and AsF_3 species. Moreover, this mechanism is closely analogous to that demonstrated by Bartlett *et al.* [16] in the intercalation of graphite by AsF_5.

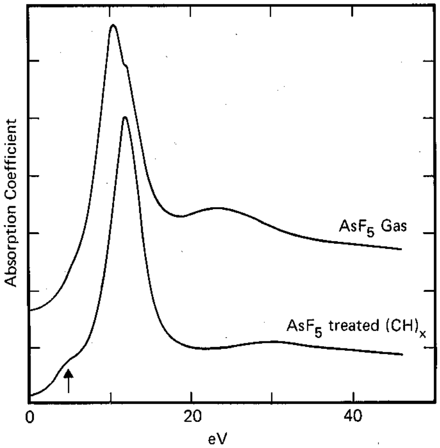

Fig. 1. Arsenic K-shell pre-absorption edge spectra of AsF_5-treated polyacetylene and of AsF_5 gas.

As was true in the case of the graphite intercalate, X-ray absorption spectroscopy has provided the data necessary to resolve this mechanistic problem. Results obtained for AsF_5-treated polyacetylene containing approximately 10 at.% of arsenic are shown in Fig. 1; also included is the spectrum of AsF_5-gas obtained at the same time. A more detailed description of these results will be published elsewhere [17]*. The 1.4 eV K-shell pre-absorption edge shift between the AsF_5 vapor and the arsenic species in the doped $(\mathrm{CH})_x$ is identical with that observed by Bartlett for AsF_6^- in graphite [16]. In addition, the shoulder located 6.7 eV below the main absorption in the doped

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*Detailed self-consistent field Hartree–Fock calculations have shown the existence of several excitonic transitions in AsF_3, AsF_5 and AsF_6^-. These suggest a more complicated line structure obscured by the effect of core hole lifetime (~ 2 eV) and instrumental resolution (~ 1.5 eV); P. Bagus and M. Morawitz, to be published.

polyacetylene corresponds to the peak identified by Bartlett as AsF_3. The ratio of the AsF_6^- and AsF_3 peaks is clearly greater than the 2:1 value expected from eqn. (3). In separate experiments, however, we have shown that AsF_3 has only a weak affinity for $(CH)_x$ and may be removed on extended evacuation. This would account for the reduced AsF_3 peak in the doped $(CH)_x$*.

The mechanism proposed in eqn. (3) is also supported by preliminary spectroscopic investigations. Using both transmission and reflection infrared techniques, absorptions attributable to AsF_6^- have been observed; no indications of other arsenic-containing species have been obtained [18].

The physical model for the interaction of AsF_5 with polyacetylene also bears some analogy to the graphite case, where intercalation of AsF_6^- ions between the graphite planes has been demonstrated [16]. X-ray and electron diffraction studies show that AsF_6^- enters the *cis*-$(CH)_x$ lattice so as to cause an increase in separation of the (100) planes. According to the structural studies of Baughman *et al.* [19] these (100) planes contain the chains of polyacetylene. On doping, the (100) peak, normally of zero intensity in *cis*-$(CH)_x$, becomes quite strong and shifts from 7.60 Å to 8.83 Å due to AsF_6^- ions occupying $(CH)_x$ chain sites in the (100) and (200) planes in a non-random fashion. A similar effect has been observed previously for bromine and iodine doped films [1a, 8, 9]. In no case has evidence for ordering of the dopant species along the $(CH)_x$ chain axis been observed. The van der Waals diameter of AsF_6^- calculated from these data is 4.98 Å, slightly higher than the value of 4.75 Å obtained in AsF_5-intercalated graphite [16].

Figure 2 shows electron micrographs of the same region of a $(CH)_x$ film before and after treatment with AsF_5. No significant change in the dimensions of individual $(CH)_x$ fibers is observed on doping, although the expansion of the $(CH)_x$ lattice was confirmed by electron diffraction on the same sample. To be consistent with the observation that the flotation density for $(CH)_x$ agrees with the expected theoretical density of 1.2 g/cm^3 [19], these results require that the individual fibers contain significant voids, allowing the unit cell to expand without causing macroscopic changes in fiber dimensions. We had previously shown that the fibers of $(CH)_x$ are not single crystal in nature, but rather are polycrystalline and only partially oriented with the preferred chain orientation parallel to the fiber axis [1a].

Nature of the polyacetylene chains after doping

By contrast with the fairly complete understanding of the fate of the dopant species, the changes occurring in the polyacetylene chains on treatment with AsF_5 are less well understood. Evidence presented above and else-

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*The failure of the sample to retain all of the AsF_3 generated on doping obviously complicates the problem of assigning a composition based on weight uptake.

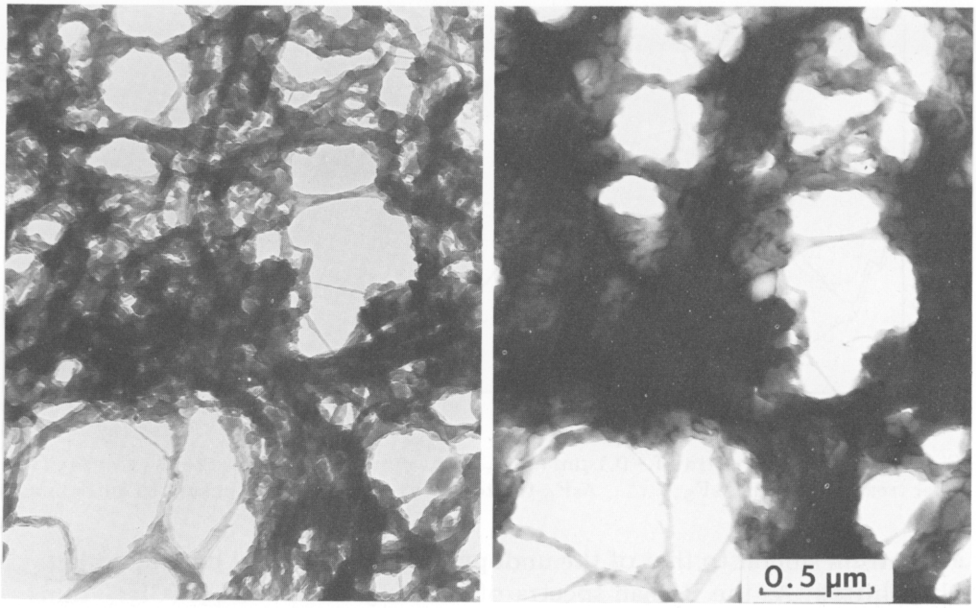


Fig. 2. Electron micrographs of $(CH)_x$ fibers before (left) and after treatment with AsF_5.

where requires that the polyacetylene chains give up electrons to the dopant. As these electrons must come from the bonding π orbitals of the $(CH)_x$, the charge transfer should lead to a change in bond strength and thus in bond stretching frequency. If comparison with shorter chain polyolefin models are valid, a tendency toward increased delocalization and decreased bond alternation might also be expected on oxidation [20]. Although these changes should be observable by Raman- or infrared spectroscopy, these techniques have not yet provided unambiguous evidence for their occurrence.

By contrast, the results of transmission spectroscopy in the visible and near infrared suggest significant change in the nature of the $(CH)_x$ chains on doping. Shown in Fig. 3 are the absorption curves for a *trans* polyacetylene film of approximately 0.1 μm thickness before, and after, doping with AsF_5. On doping, the strong interband transition of pristine $(CH)_x$ centered at ~650 nm, is replaced by a broad, featureless absorption extending out into the infrared. This pronounced red shift in the absorption spectrum is consistent with the expectation that increased electron delocalization and decreased bond alternation should accompany conversion of the neutral polyolefin to an unsaturated cation or polycation [20]. The metallic nature of the resulting absorption, however, makes such a conclusion somewhat speculative in the absence of confirming Raman data.

Also shown in Fig. 3 is the absorption spectrum of the same AsF_5-doped film on subsequent treatment with ammonia vapor. In addition to destroying the high conductivity of the doped film, this treatment generates

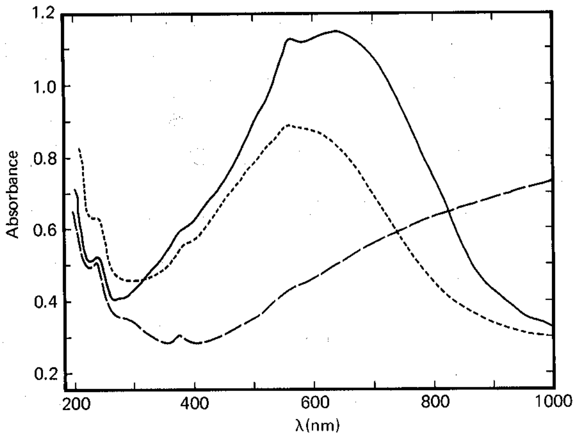
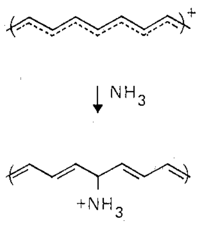


Fig. 3. Absorption spectra of ~0.1 μm $(CH)_x$ film: ——, *trans*-$(CH)_x$; -------, *trans*-$(CH)_x$ after treatment with AsF_5; ...., AsF_5-treated *trans*-$(CH)_x$ after exposure to ammonia.

a spectrum similar to that of the undoped starting material but somewhat blue shifted. As the Raman spectra of similarly treated *trans*-$(CH)_x$ films show no formation of *cis* polyacetylene in this process, the blue shift must be an indication of decreased conjugation in the treated material. At present, we are unable to distinguish between physical and chemical rationalizations of this shift. Certainly, by this point, sufficient foreign material has been added to the original polyacetylene material for physical disruption of extended conjugation to occur, *i.e.*, forced rotation about carbon–carbon single bonds which does not break the polymer chain but does diminish or interrupt conjugation. Alternatively, the chemical mechanism shown in eqn. (4) must be considered. Reaction of a certain number of cationic sites with the basic ammonia species would also serve to decrease the length of uninterrupted conjugation in the treated material. Further investigation of this effect is in process.



(4)

Conclusions

On the basis of the data presented above, it must be concluded that AsF_5 reacts with polyacetylene in much the same way as it does with graphite. This result stands in distinct contrast to the respective behaviors of these materials toward certain other oxidants. Thus, bromine has been shown to oxidize $(CH)_x$ with the concommitant formation of Br_3^-. In graphite, on the other hand, bromine intercalates as a molecular Br_2 species, albeit with an elongated bromine–bromine bond indicative of some charge transfer from graphite to bromine [21]. The bromination results are consistent, however, with the greater ease of oxidation of polyacetylene relative to graphite. As a considerably stronger oxidizing agent arsenic pentafluoride proves capable of chemically oxidizing both $(CH)_x$ and graphite.

On doping, the polyacetylene itself must give up electrons to form polyolefinic cation type species. The detailed structure of the oxidized polymer, however, is yet to be determined. We are continuing our efforts in this area [22].

Acknowledgments

We gratefully acknowledge stimulating discussions with J. F. Kwak and R. L. Greene. We thank the Office of Naval Research for partial support of this work and acknowledge the cooperation of the Stanford Synchrotron Radiation Laboratory and the United States Department of Energy.

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