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PRELIMINARY NOTE

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Fluorinated Polyacetylene

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SUMMARY

The fluorination of polyacetylene,  $(CH)_x$ , with fluorine gas can be controlled by first doping the  $(CH)_x$  with  $AsF_5$ . A final product with the approximate formula  $(CF)$  is obtained. This method of moderating the fluorination may have general applicability in conjugated systems.

The doping of polyacetylene,  $(CH)_x$ , and the intercalation of graphite with inorganic fluorides have been shown to be analogous in numerous respects, particularly with respect to enhancement of metallic properties[1]. It has been shown that fluorine can be intercalated into graphite with resultant increase in conductivity until a certain concentration is reached beyond which the conductivity decreases drastically[2]. This has prompted us to conduct analogous experiments with polyacetylene.

The polyacetylene was obtained in the form of large films (thickness - 0.05mm) from BASF. Infrared measurements [3] showed it to have a cis/trans ratio of about 1.5. Direct exposure of polyacetylene to fluorine at room temperature causes deflagration and charring of the polyacetylene. The reaction can be controlled to some extent by keeping the polyacetylene at liquid nitrogen temperature and reducing the

fluorine pressure to a few torr. Under these milder conditions the conductivity increases eight orders of magnitude to about  $30 \text{ S-cm}^{-1}$ . However, the conductivity decreases thereafter to very low values even if the fluorine is removed. The conductivities were measured with a standard four-point probe.

We have now found that by first doping the polyacetylene with  $\text{AsF}_5$ , followed by exposure to fluorine up to about two hundred torr, the reaction proceeds smoothly without charring. Infrared spectra taken from an in-situ fluorination in an IR cell of a piece of  $(\text{CH})_x$  previously doped with  $\text{AsF}_5$  show appreciable amounts of HF, some  $\text{AsF}_5$ , and small amounts of  $\text{CF}_4$  being liberated. At higher fluorine pressures large amounts of  $\text{CF}_4$  are formed. Most experiments were conducted on a Sartorius Magnetic Suspension Balance which allows continuous weight measurements in a corrosive (e.g.  $\text{AsF}_5$  or  $\text{F}_2$ ) atmosphere. The polyacetylene was first exposed to  $\text{AsF}_5$  until a desired level of doping was attained, followed by pumping to constant weight. Exposure of the  $\text{AsF}_5$ -doped  $(\text{CH})_x$  to fluorine causes an initial weight decrease indicating that the doped  $\text{AsF}_5$  as well as perhaps some  $\text{CF}_4$  is released as the  $(\text{CH})_x$  is fluorinated. More than 90% of the weight increase (e.g. about 30 mg for a 22 mg  $(\text{CH})_x$  sample) takes place within two to three hours of initial exposure to  $\text{F}_2$ . The approximate stoichiometry of the product, assuming it contains no hydrogen and  $\text{AsF}_5$ , is  $\text{CF}_{1+\delta}$  where  $\delta$  is small (Found: 59.7, 59.4% F; calculated for CF, 61.3%). Further weight increase takes place extremely slowly at a rate of about 0.1mg per hour. The results of several experiments are given in the Table.

Weight $(\text{CH})_x$ (mg)	Amt. Doping $\text{AsF}_5$ (%)	Total Weight Increase (mg)*	$(\text{CH})/\text{F}$
23.5	2.3	35.3	0.97
21.2	2.5	34.0	0.95
22.2	1.6	33.2	0.98
18.2	2.0	30.0	0.88
14.8	11.4	22.5	0.96

\*corrected for weight loss of hydrogen as HF

The final product is a white film resembling Teflon tape. It is, however, quite brittle and can be easily ground into powder. It contains only traces of arsenic showing that the arsenic pentafluoride has been largely released. Infrared spectra obtained on KBr pellets show a very strong absorption band at  $1211\text{cm}^{-1}$  due to C-F vibrations, some weak absorptions at  $839$  and  $1884\text{cm}^{-1}$  but none in the  $2900$  to  $3100\text{cm}^{-1}$  region showing the absence of C-H vibration. Raman spectra yielded no useful information because of a high fluorescence background. X-ray powder diffraction patterns ( $\text{CuK}\alpha$ ) of both fluorinated  $(\text{CH})_x$  and polyparaphenylene(PPP) show broad peaks centered at  $2\theta = 12^\circ$  in contrast to that of  $14^\circ$  observed for graphite fluoride.

The above results indicate that initially the  $(\text{CH})_x$  is doped to an intermediate conductive state, possibly  $(\text{CH})^+\text{F}^-$  or  $\text{CH}(\text{H}^+\text{F}^-)_y$  [4], but eventually covalent C-F bonds are formed leading to an insulating material. In this respect, this material closely resembles graphite intercalation with fluorine. This method of moderating the fluorination by first abstracting charge from the conjugated system may possibly be generally applicable to conjugated systems. Similar results have been obtained with the fluorination of PPP and the conjugated ladder polymers - BBL and BBB[5]. These results will be published elsewhere[6].

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