A New Method for the Chemical Modification of Polymers

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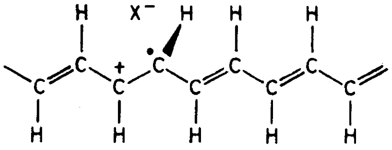
Summary Polyacetylene has been modified chemically by ion implantation.

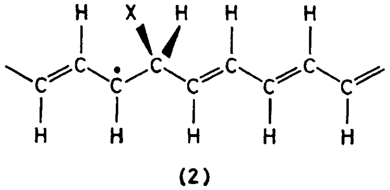
Ion implantation has become an established technique for modifing metals, alloys, and semiconductors,[1,2] but has not been applied successfully to covalent molecules. We have extended the use of ion implantation to polymers and demonstrated for the first time the unique potential of this technique to modify organic polymers chemically and physically.

In this report we summarize our results for the halogen cations (F^+, Cl^+, Br^+, and I^+) implanted into free-standing films of the conjugated polyacetylene polymer[3] $(CH)_x$. The typical experimental conditions for implanting halogens involve an ion beam energy of 10—40 keV, a total ion dosage between 1×10^{15} and 3×10^{17} ions/cm^2, and a beam current of *ca.* 1 μA. In the region of highest ion concentration (*ca.* 10—20 Å thick) the implanted ions resulting from these experimental conditions ranged from 0·1 to 10 atom %. The ion beam was rastered across the sample at a rate sufficient to keep local heating effects to a minimum while also ensuring a uniform ion depth concentration gradient across each sample. Implanted $(CH)_x$ films have been characterized by *X*-ray photoelectron spectroscopy (XPS), e.s.r., ^{19}F n.m.r., i.r., and u.v.-vis. spectroscopies as well as He^+ backscattering and scanning electron microscopy (*ca.* 100 Å resolution).

Pristine or chemically doped $(CH)_x$ films decompose in air in a matter of days, but the process of ion implantation appears to 'stabilize' the films. Most implanted films have retained the silvery metallic appearance of pure $(CH)_x$ and exhibit relatively high reflectivities through the visible region after long exposures to air. Some $(CH)_x$ films, under certain conditions, have permanent red (25 keV, 3×10^{16} F^+/cm^2), brown (25 keV, 1×10^{17} F^+/cm^2), or blue (25 keV, $3{\cdot}1 \times 10^{17}$ F^+/cm^2) metallic hues. These colour changes are obtained reproducibly and studies are under way to ascertain whether the colours are due to a bulk type interference pattern or local, chemically induced colour centres.



(1)



(2)

We believe that implanting $(CH)_x$ with the halogens results in one of the two ion-substrate interactions (**1**) and (**2**) (where X is the halogen atom used in the beam). A variety of spectroscopic techniques were employed to determine which of the two proposed structures occurs after implantation; most of the data were obtained for the F^+-implanted $(CH)_x$.

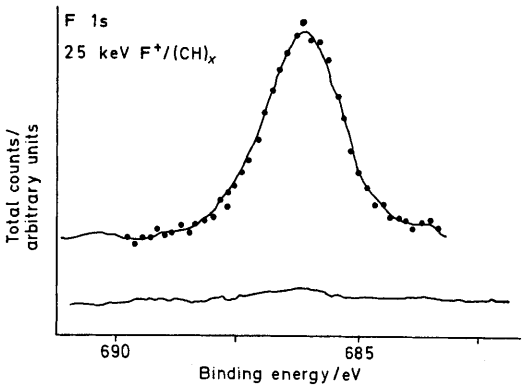


FIGURE. XPS spectra of the F 1s region of F+-implanted $(CH)_x$; $3{\cdot}1 \times 10^{17}$ F+/cm^2 (top) and $1{\cdot}8 \times 10^{16}$ F+/cm^2 (bottom).

The transmission and attenuated total reflectance i.r. spectra (4000—400 cm^{-1}) are identical to the spectrum of pure $(CH)_x$ and no new bands or relative intensity changes in existing bands were found. Careful analysis by both X- and Q-band e.s.r. spectroscopy of a film doped with $3{\cdot}1 \times 10^{17}$ F$^+$/cm^2 at 25 keV gave an identical *g*-value (2·0019—2·0025), linewidth (5—6 G), and lineshape as that observed for pure $(CH)_x$.[4] The signal from the implanted sample exhibited a Curie–Weiss temperature dependence as does pure $(CH)_x$. XPS was helpful particularly for detecting and examining implanted ions, *e.g.* the Figure shows the F 1s spectrum of F$^+$-implanted $(CH)_x$ for two different F$^+$ fluences ($3{\cdot}1 \times 10^{17}$ F$^+$/cm^2 and $1{\cdot}8 \times 10^{16}$ F$^+$/cm^2). The narrow (full width at half maximum of 1·7 eV), symmetric F 1s peak indicates the presence of a *single* type of fluorine interaction with the sample. The narrow single peaks indicate single chemical species found also for Cl$^+$(Cl 2p)-, Br$^+$ (Br 3d)-, and I$^+$ (I 3d$_{5/2}$)-implanted samples. The C 1s line in implanted $(CH)_x$ retains the peak shape and position recorded for pure $(CH)_x$ with no new C 1s peaks being found. The lower kinetic energy photoelectrons are preferentially attenuated, indicating that the ions are in a layer below the surface of the polymer film. Also, the core levels signals of the implanted ions increase with increasing ion fluence, indicating that ion diffusion does not take place after implantation. These findings are substantiated by high-energy helium ion backscattering spectra which demonstrate that the implanted species remain in a narrow quasi-surface layer. In the F$^+$-implanted samples, the Auger parameter, defined here as the quantity (B.E. F 1s − B.E. F *KLL*; Al-K_α source), is found to be 90·6 eV compared with 89·5 eV for poly(tetrafluoroethylene). A ^{19}F n.m.r. signal has been obtained at 4·5 K for F$^+$-implanted $(CH)_x$ in which the total fluence of 4×10^{18} F$^+$/cm^2 was distributed homogeneously to a depth of approximately 1800 Å. The signal is similar in intensity, position, and bandwidth to the signal recorded under the same conditions for a Teflon sample containing *ca.* 10^{18} fluorine atoms. However, ^{19}F–^{19}F coupling was not observed in the implanted sample with the present signal/noise levels, although this coupling was observed for Teflon.

Our results demonstrate that ions implanted into polyacetylene can modify the material by chemically adding to the polymer backbone, altering the optical reflectivity, and stabilizing the modified polymer. By selecting the appropriate ion beam, beam energy and total fluence, the extent or type of modification can be controlled.

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