A Novel Conducting Polyacetylene Derivative

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Summary Doping of predominantly *cis* polyacetylene with FSO_2OOSO_2F in SO_2F_2 solutions at low temperatures yields materials that possess apparently metallic electrical conductivities with, for example, $\sigma_{RT} = 700\ \Omega^{-1}\ cm^{-1}$, increasing to a maximum of $800\ \Omega^{-1} cm^{-1}$ at 150 K before declining to $640\ \Omega^{-1}\ cm^{-1}$ at 4·2 K.

Shirakawa *et al.*,[1] have found that the electrical conductivity of polyacetylene (PA) can be increased over seven orders of magnitude by doping with iodine. This remarkable effect is also seen with oxidizing, Lewis acid dopants (*e.g.* AsF_5),[2] and with sodium.[3] The PA–I_2 conductor may be viewed as a partially oxidized PA chain with I_3^- and possibly I_5^- counter anions.[3–5] We sought to achieve high conductivities by increased charge transfer from PA using the powerful oxidizing dopant, bis(fluorosulphuryl) peroxide, FSO_2OOSO_2F. This compound has been used for the oxidation of chalcogens to polyatomic cations, *e.g.* $Se_4^{2+}(SO_3F^-)_2$[6] and recently for the preparation of conducting BN and graphite salts.[7]

Films of *ca.* 85% *cis* (15% *trans*) polyacetylene were prepared by polymerization of C_2H_2 catalysed by $(C_5H_5)_3(C_5H_4)Ti_2$,[8] as previously described.[4] Platinum wire electrodes were wrapped on to the films with contacts assisted by use of Electrodag +502.† The assembly was enclosed in an evacuable glass cell; conductivities were measured by standard DC four point probe techniques. The FSO_2OOSO_2F was obtained by electrolysis of HSO_3F–KF[9] and other sources. Addition of a small aliquot (*ca.* 2 mmol) of FSO_2OOSO_2F vapour to PA caused a rapid increase in conductivity (σ_{RT}) from $<10^{-7}$ to *ca.* $10^{-1}\ \Omega^{-1} cm^{-1}$. Incremental additions over several hours gave a material (I) with $\sigma_{RT} = 240\ \Omega^{-1} cm^{-1}$; however, this conductivity dropped to *ca.* $140\ \Omega^{-1} cm^{-1}$ upon further treatment with the dopant. Resultant films were brittle, tarnished, and swollen in thickness by *ca.* 30%. I.r. spectra of (I) displayed an intense carbonyl absorption at $1730\ cm^{-1}$. To minimize degradation we then conducted the doping at low temperatures in an inert solvent.

A PA film ($\rho = 0{\cdot}91\ g\ cm^{-3}$), mounted as before, was covered with liquid SO_2F_2 at −111 °C (with no change in conductivity). Aliquots of FSO_2OOSO_2F vapour were added to the SO_2F_2 at temperatures from −111 to −56 °C over 2–5 days, until no further increase in conductivity occurred. The solution was decanted and the film washed with SO_2F_2 at −80 °C. Evacuation and drying at room temp. gave a greyish film (II) with $\sigma_{RT} = 470\ \Omega^{-1}\ cm^{-1}$. Doping another sample of polymer ($\rho = 0{\cdot}94\ g\ cm^{-3}$) with FSO_2OOSO_2F at −111 to −56 °C over 10 days gave a film (III) having a golden lustrous appearance with $\sigma_{RT} = 700\ \Omega^{-1}\ cm^{-1}$. Conductivities of (II) and (III) were found to increase upon lowering the temperature, with maxima in σ_T occurring at 190 K and 150 K, respectively (Figure). This 'metal-like' behaviour (at least down to 150 K) of PA–FSO_2OOSO_2F prepared at low temperatures contrasts with that previously reported for PA–AsF_5 which shows a monotonic decrease in conductivity with temperature.[2] Remarkably, the conductivity of (III) at 4·2 K is *ca.* 90% of that at 300 K.

Materials (II) and (III) were examined by vibrational spectroscopy (inert atmosphere as samples are moisture sensitive). Raman spectra display line broadening but no change in the *cis/trans* ratio with doping. The i.r. bands observed at 1240 and $1460\ cm^{-1}$ are assigned to the symmetric and anti-symmetric S=O vibrations, respectively, of an $R^1R^2SO_2$ molecule. Band positions and contours are similar to those observed for FSO_2OOSO_2F vapour[10] and the $FSO_2O\cdot$ radical.[11] They are notably different from ν_{SO} frequencies of 1080 and $1228\ cm^{-1}$ for ionic fluorosulphates.[12,14] It thus seems that the doped polymer

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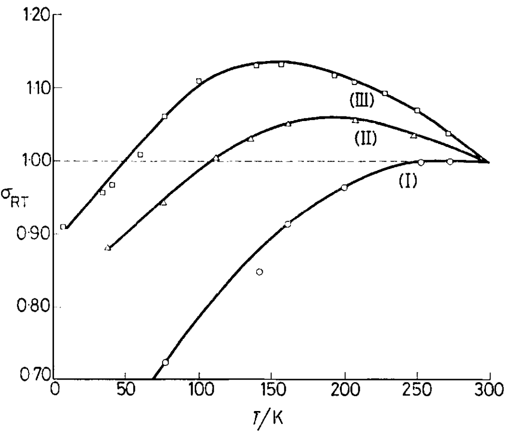

FIGURE. Conductivity ratio–temperature dependence of PA–FSO_2OOSO_2F. (I) PA + FSO_2OOSO_2F vapour, tarnished film; (II) PA + FSO_2OOSO_2F in SO_2F_2, 2·5 days, dull grey film, *ca.* 45% w/w dopant; (III) PA + FSO_2OOSO_2F in SO_2F_2, 10 days, shiny gold film *ca.* 21% w/w dopant.

cannot simply be described as a partially oxidized, cationic polyene having discrete SO_3F^- counter ions. The S=O stretching frequencies in $R^1R^2SO_2$ molecules may be related to the electronegativity of the R^1 and R^2 groups.[12] A plot of ν_{sym}(SO) *vs.* $\nu_{antisym}$(SO) frequencies [13,14] for SO_2Cl_2,[13] $MeSO_2F$,[13] $MeSO_3F$,[14]‡ PA–FSO_2OOSO_2F, $ClOSO_2F$,[15] FSO_2OOSO_2F,[10] and $FOSO_2F$[14] is approximately linear. The position of PA–FSO_2OOSO_2F in this plot suggests that the fluorosulphate may be bonded covalently on to the polymer chain. Spectroscopic characterization studies of PA–FSO_2OOSO_2F are in progress.

It is remarkable that as powerful an oxidizing agent as FSO_2OOSO_2F can be used to oxidize polyacetylene non-degradatively and yield highly conducting materials. The very small temperature coefficient of these doped polyacetylenes suggests that their inherent conductivity is metallic,[3] and that the small activation energy for conduction observed arises from interfibril contact resistance. It may be expected that doping of partially chain-aligned polyacetylenes will give higher conductivities.

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‡ ν_{sym} = 1235 cm^{-1}, $\nu_{antisym}$ = 1465 cm^{-1}.

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