

Short Communication

Poly(11-vinylfluoranthene): A Novel Conducting Material

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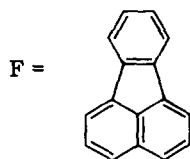
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Abstract

The oxidation of a poly(11-vinylfluoranthene) (PVF)-coated electrode in 0.1 M tetrabutylammonium perchlorate/acetonitrile solution has been studied at low temperature using *in situ* electrochemical ESR. This revealed similarity with the behaviour observed from the oxidation of fluoranthene, F, under similar conditions, and suggested that the PVF oxidised under such conditions may contain conducting material analogous to the Wegner salts $[F_2]^{+}X^{-}$.

Introduction

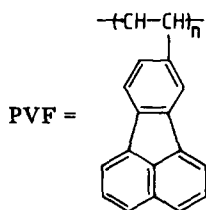
At low temperatures, below -30°C , the anodic oxidation of simple arenes, such as fluoranthene, F, in the presence of suitable anions (perchloro-



rate, tetrafluoroborate or hexafluorophosphate) has been shown to lead to the deposition of crystals at the electrode surface [1, 2]. These are highly conducting and have unique electrical and magnetic properties [3]. The structure of these so-called 'Wegner crystals' involves stacks of the radical cation salt of the arene dimer $[Ar_2]^{+}X^{-}$ [3]. The electron spin resonance (ESR) spectra of the dimer radical cations has revealed some interesting characteristics. The fluoranthene dimer radical cation was found to be anisotropic, with an extremely small linewidth, as low as 20 mG [3]. The temperature dependence of the ESR signal amplitude revealed two distinct regions. At temperatures greater than 170 K the ESR spectrum was tempera-

ture independent, whereas below this temperature it was found to be thermally activated [3]. The transition in the behaviour of the ESR signal was linked to a phase change in the crystal structure. Crystallographic data revealed a change at 200 K from a fixed orientated structure (high temperature) to one which was rotated from the fixed structure (low temperature) [2]. The Wegner crystals were only conducting in the fixed orientated structure.

The properties observed for the radical cation dimers of fluoranthene lead us to consider the anodic oxidation of poly(11-vinylfluoranthene) (PVF)-coated electrodes under similar conditions and, in particular, to see if the ESR of an oxidised polymer coat containing fluoranthene displays characteristics similar to molecular fluoranthene.



Experimental and results

The PVF used in the experiments described below was prepared by the free-radical polymerisation of 11-vinylfluoranthene monomer, using AIBN as initiator. The PVF prepared by this method was shown to have a molecular weight of approximately 30 000 [4]. The polymer was coated onto platinum electrodes (dimensions 4.0×4.0 mm) by the application of $5 \mu\text{l}$ of a solution of the polymer (0.5 mg cm^{-3}) in dichloromethane. The solution was left to evaporate and smooth, even films resulted. Assuming the deposited polymer density to be identical to that of the bulk polymer, this procedure was estimated to produce coats of thickness of about 10^{-5} cm.

The anodic oxidation of PVF-coated electrodes was carried out in 0.1 M tetrabutylammonium perchlorate (TBAP)/acetonitrile solution, in a vessel immersed in a solid CO_2 /acetone bath at -40°C . The resulting cyclic voltammogram can be seen in Fig. 1. The process is electrochemically irreversible, and it is possible to distinguish two anodic peaks: one at a potential of 0.980 V, versus the saturated calomel electrode (SCE), and another at an approximate potential of 0.750 V versus SCE. This behaviour shows similarity with that seen in the anodic oxidation of the fluoranthene monomer under analogous conditions [2].

ESR spectra were recorded of PVF-coated electrodes which had been oxidised in this manner using a Bruker ER200D spectrometer, equipped with a variable temperature unit. Two different spectra were observed, depending upon the potential used to oxidise the coat. Oxidation at potentials < 0.750 V versus SCE, gave a broad, single-line ESR spectrum of linewidth 7.1 G. At

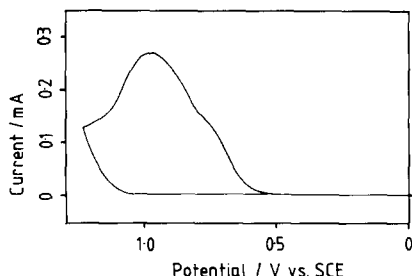


Fig. 1. Cyclic voltammogram of the anodic oxidation of a PVF-coated electrode in 0.1 M TBAP/acetonitrile at -40°C ; scan rate 50 mV s^{-1} .

more anodic potentials the recorded spectrum revealed two contributions, and a narrow single-line spectrum of linewidth 1.2 G was superimposed on the broad spectrum. The relative proportion of the narrow signal increased with oxidation potential.

To probe the nature of the two spectra observed from the PVF coats, a variable temperature study was undertaken. Spectra were recorded of a PVF-coated electrode, oxidised at 1.00 V (versus SCE) in 0.1 M TBAP/acetonitrile at -40°C ; the spectra contained contributions from both the broad and narrow lines. As shown in Fig. 2, significant changes in the spectra occur as the temperature is decreased. The change differs for the broad and narrow lines. The former (1.7 G) line increases in amplitude as the temperature is decreased. This behaviour is consistent with Curie's law [5] in that

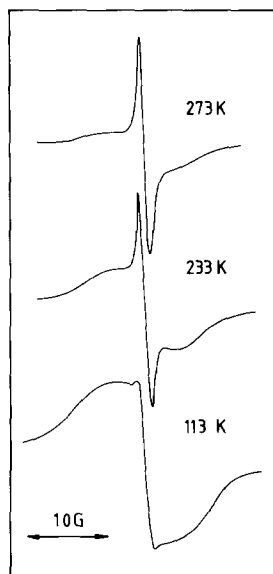


Fig. 2. ESR spectra observed from a PVF-coated electrode, formed by oxidation at a potential of 1.00 V (vs. SCE) in 0.1 M TBAP/acetonitrile at -40°C , as a function of temperature.

the signal amplitude is inversely proportional to the temperature. In contrast, the narrow (1.2 G) line exhibits considerably different behaviour — the variation of the amplitude of the ESR signal with temperature is shown in Fig. 3. Over the temperature range studied, there was no observable change in the linewidth of this spectrum. The behaviour can be described as temperature independent up to 193 K, but below this a thermally activated signal is observed.

The temperature dependence of the ESR spectra may be used to infer the nature of the species giving rise to the signals. We attribute the broad-line spectrum to the radical cation of fluoranthene pendant groups in the polymer, resulting from a one-electron oxidation. The linewidth is comparable with previous observations of radical species formed at such groups in polymer-coated electrodes [6, 7], and the Curie-type behaviour suggests an absence of rapid spin exchange between radical species within the PVF coat. The narrow 1.2 G line we attribute to the production of 'Wegner'-type species within the PVF, i.e. where two fluoranthene pendant groups or more are linked as radical cation dimers and form extended stacks over some distance within the polymer. The formation of such species, similar to that formed by the fluoranthene molecule, could explain the linewidth of 1.2 G, which is considerably smaller than many reported previously for pendant radical species in a polymer coat [6, 7]. The linewidth could be a facet of the rapid spin exchange that can take place in stacks of radical cation dimers [1 - 3]. Rapid spin exchange would also explain the non-Curie-type behaviour observed from this signal.

Consistent with this is the temperature dependence of the ESR signal and, in particular, the transition from the non-Curie behaviour to a thermally activated signal at a temperature of 195 K. Such behaviour shows similarity with that observed for the 'Wegner' species produced from the fluoranthene molecule, where a transition in ESR behaviour is observed at 175 K [3],

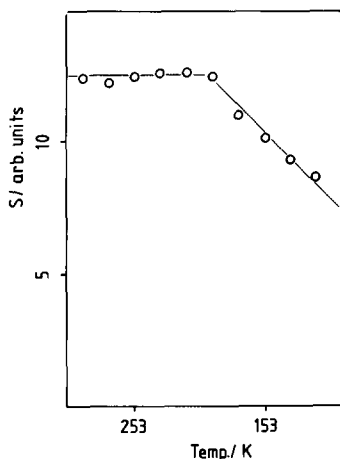


Fig. 3. The temperature variation of the ESR signal amplitude (S) of the 1.2-G linewidth spectrum (see text).

linked to a phase transition at 200 K. At temperatures greater than 200 K the crystal symmetry restricts the orientation of the radical cation dimers in the stack, giving efficient spin exchange, which is lost with the symmetry at temperatures below 200 K.

The large similarity in the observed ESR behaviour of oxidised PVF-coated electrodes and the radical cation dimers produced from the fluoranthene monomer suggest that analogous physical processes may be occurring in the two situations. In any case, the ESR measurements clearly show the existence of two types of environment of radical species within the coat. Further information will be gleaned from conductivity studies.

Acknowledgements

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References

- 1 V. Enkelmann, G. Wegner and C. Kronkhe, *Mol. Cryst. Liq. Cryst.*, **86** (1982) 103.
- 2 C. Kronkhe, V. Enkelmann and G. Wegner, *Angew. Chem.*, **92** (1980) 941.
- 3 H. Eichele, M. Schwoerer, C. Kronkhe and G. Wegner, *Chem. Phys. Lett.*, **77** (1981) 311.
- 4 R. G. Compton, R. J. Northing, G. W. J. Fleet, J. C. Son and B. P. Bashyal, *J. Physiol. Meas. Clin. Phys.*, **9** (1989) 133.
- 5 J. E. Wertz and J. R. Bolton, *Electron Spin Resonance*, McGraw-Hill, New York, 1986, p. 171.
- 6 W. J. Albery, C. C. Jones and R. G. Compton, *J. Am. Chem. Soc.*, **106** (1984) 469.
- 7 W. J. Albery and C. C. Jones, *Faraday Discuss. Chem. Soc.*, **78** (1984) 193.