Novel Electrochromic Films *via* Anodic Oxidation of Poly[3-(3-bromocarbazol-9-yl)propyl]methylsiloxane

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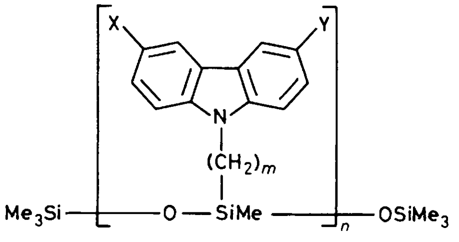
Cyclic voltammetry and quantitative *X*-ray photoelectron spectroscopy suggest a highly ordered structure for the novel electrochromic polymer film obtained *via* anodic oxidation of poly[3-(3-bromocarbazol-9-yl)propyl]methylsiloxane.

The electrochemical cross-linking of poly(*N*-vinylcarbazole) and its derivatives has received considerable attention recently with the dicarbazolyl polymers being nominated as novel electrochromic materials,[1] organic conductors,[2] and as thin film battery electrodes.[3] With a view to utilising carbazole–dicarbazolyl electrochemistry within the context of a flexible polymer backbone, we are currently investigating the siloxane polymers (**1**).[4] Recent patent disclosure[4] now prompts us to report the electrochemical oxidation of poly[3-(3-bromocarbazol-9-yl)propyl]methylsiloxane (**1a**) to give an electrochromic dicarbazolyl polymer film which reveals several novel features. The quantitative use of *X*-ray photoelectron spectroscopy (XPS), as a complement to cyclic voltammetry (CV) for film characterisation, is of particular importance.

C.v. (0 to 1.5 to 0 V, 100 mV s^{-1}) at a Au wire working electrode (Al counter and Ag quasi-reference electrodes) in a CH_2Cl_2 solution of polymer (**1a**) (3×10^{-4} M in polymer repeat unit), containing NBu_4PF_6 (0.1 M), revealed two closely overlapping anodic peaks (Figure 1a) near 1.3 V, which were accompanied by the growth of a green polymer film. The film was decolourised during the cathodic scan which contained



(**1**)

a; X = H, Y = Br, *m* = 3, *n* ≃ 35

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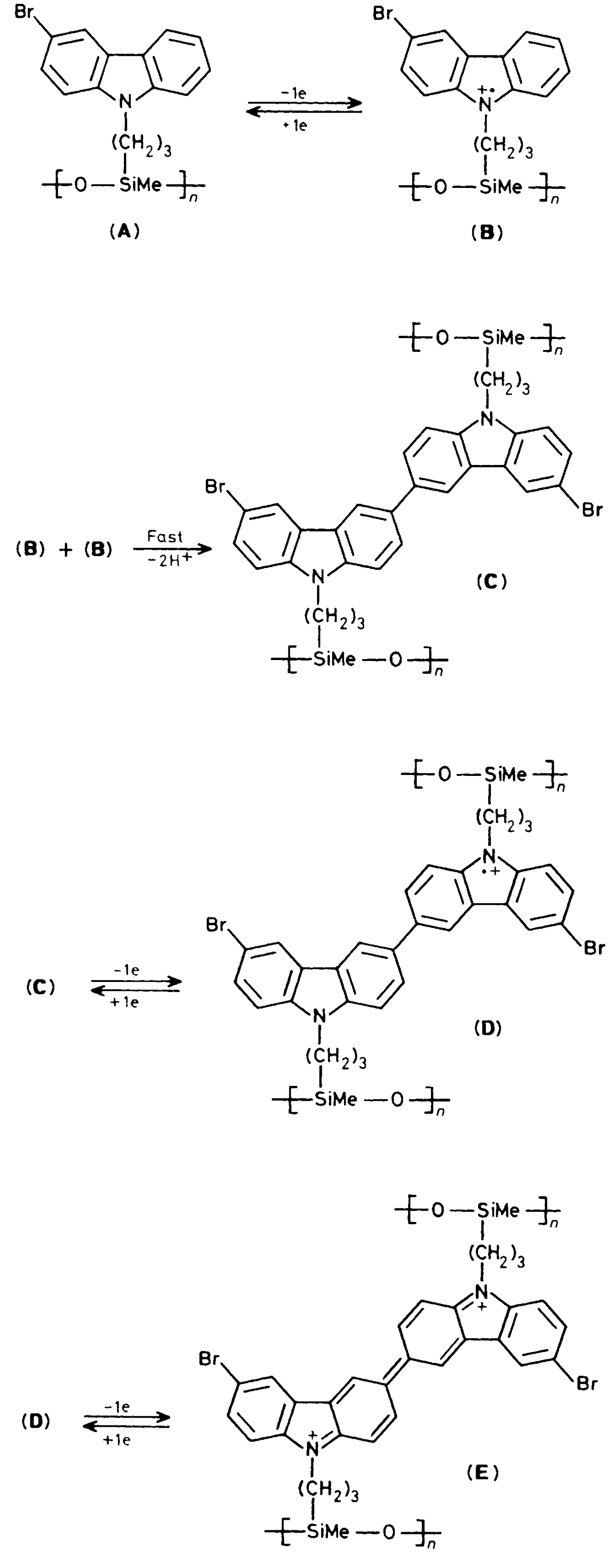
peaks at 1.1 and 0.8 V. These observations can be interpreted in terms of a reaction sequence (Scheme 1) similar to that suggested for poly(*N*-vinylcarbazole).[1] One electron oxidation of 3-bromocarbazole units (**A**) to the radical cations (**B**) is followed by fast dimerisation to give dicarbazolyls (**C**), which are then partially oxidised and subsequently reduced.



Scheme 1

The Au wire was removed from the polymer solution and the film was washed with CH_2Cl_2 prior to c.v. which, after one or two conditioning cycles, afforded stable and reproducible voltammograms (Figure 1b) with two reversible waves ($E_{\frac{1}{2}}$ 0.88 and 1.22 V) of equal intensity. The film turned green during the anodic scan and was bleached during the cathodic part of the cycle. XPS was then used to determine the stoicheiometry of the oxidised film.

The film preparation was repeated at an Au foil (0.5 × 2.0 cm) and, after one or two conditioning cycles, the foil-supported film was removed from the electrochemical cell at the end of an anodic scan, and after being held at the anodic limit until current approached background level, the dark green film was washed with CH_2Cl_2 in order to remove adsorbed electrolyte prior to XPS analysis using an improved[5] AEI/Kratos ES200A spectrometer. The foil was held at 100 °C for 20 min *in vacuo* in order to desorb residual solvent prior to irradiation. Relevant peak areas were determined more than once for several surfaces and no time dependence of their ratios was detected. Six F1s:N1s and five F1s:Br3d area ratios from three independent specimens yielded[6] a mean PF_6^-: carbazole ratio of 0.33 ± 0.02 (standard deviation), while five independent determinations of the F:P mole ratio using the P2p peak confirmed the expected mean value of 6.0 ± 1.2. These results suggest that the voltammogram of the conditioned film can be interpreted in terms of two consecutive reversible one electron oxidations, equation (1), where K_2 represents an appropriately substituted di(3-bromocarbazol-6-yl). The inability to associate integral charge with particular dicarbazolyls was supported by the presence of only one major N1s signal, at 400.4 eV binding energy relative to C1s = 285 eV, in the XPS of the oxidised films.

$$(3K_2) \underset{+1e}{\overset{-1e}{\rightleftharpoons}} (3K_2)^{+} \underset{+1e}{\overset{-1e}{\rightleftharpoons}} (3K_2)^{2+} \tag{1}$$

Electrochemistry of the unfaded film:

$$(18K_2) \underset{+6e}{\overset{-6e}{\rightleftharpoons}} (18K_2)^{6+} \underset{+6e}{\overset{-6e}{\rightleftharpoons}} (18K_2)^{12+} \tag{2}$$

First fade:

$$(18K_2)^{12+} \longrightarrow (12K_2) + (6K_2)^{12+} \tag{3}$$

Electrochemistry of the faded film:

$$(12K_2) \underset{+4e}{\overset{-4e}{\rightleftharpoons}} (12K_2)^{4+} \underset{+5e}{\overset{-5e}{\rightleftharpoons}} (12K_2)^{9+} \tag{4}$$

Second fade:

$$(12K_2)^{9+} \longrightarrow (6K_2) + (6K_2)^{9+} \tag{5}$$

Electrochemistry of the doubly faded film:

$$(6K_2) \underset{+2e}{\overset{-2e}{\rightleftharpoons}} (6K_2)^{2+} \underset{+4e}{\overset{-4e}{\rightleftharpoons}} (6K_2)^{6+} \tag{6}$$

Scheme 2

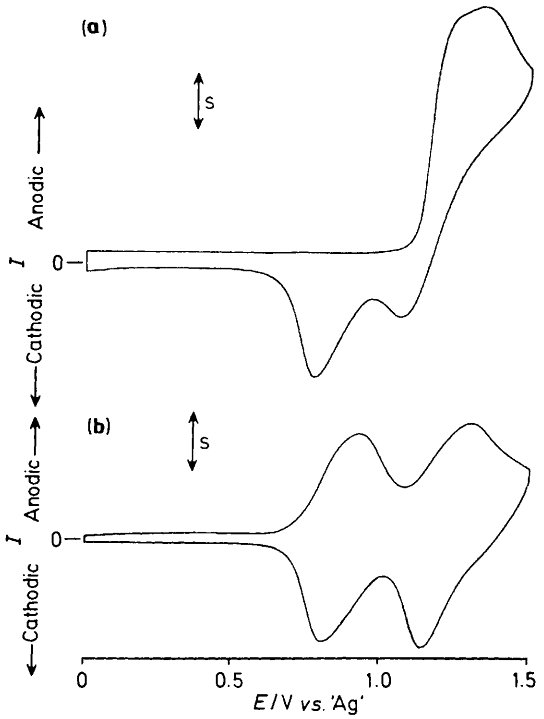


Figure 1. Cyclic voltammograms (a) taken at an Au wire in a CH_2Cl_2 solution of carbazole polymer (**1a**), and (b) of the resulting cross-linked dicarbazolyl electrochromic polymer film; scan rate = 100 mV s^{-1}; S = 100 μA cm^{-2}.

During the washing of the foil-supported film prior to analysis, its initial dark green colour faded to very pale green–golden yellow. This fading was subsequently observed when the wire supported film was treated similarly. C.v. of the faded film again showed two reversible waves, but with the intensity of the first wave (0.9 V) reduced to exactly two-thirds of its original value, and that of the second reduced only slightly. The faded film was removed from the cell at the end of an anodic sweep to give, after washing, a doubly faded material. In this case c.v. revealed the same two waves but with intensities reduced to exactly one third and two thirds of their original values. Electrochemical and fading mechanisms which account for these observations are summarised in Scheme 2, which is written to facilitate identification of charge ratios. Equations (2), (4), and (6) describe the voltammetry of unfaded, faded, and doubly faded films respectively, whereas equations (3) and (5) represent the two fading processes. It is suggested that films at the end of their second anodic wave contain significant dicarbazolyl radical cation character which is responsible for their intense green colours, and that fading results from electron transfer to give dications which are expected to be less highly coloured. This transfer requires some structural reorganisation, which might be expected to occur when the polymer environment is changed from the high ionic strength electrolyte solution to solvent alone during the washing process.

Processes outlined in Scheme 2 require PF_6^-: carbazole ratios of 0.33, 0.58, and 0.75 for the oxidised forms of the unfaded, faded, and doubly faded polymer films respectively. For foil-supported films, the first value was reproduced exactly as described above. However XPS analysis of the oxidised forms of the faded and doubly faded films was less consistent, yielding ratios in the range 0.44—0.82, based on a measurement of N1s, F1s, and Br3d peaks. Nevertheless, these values are of the right order, and exact reproduction of Au wire electrochemistry on the Au foil was difficult because of the much higher current levels. Further, the mechanism for film formation implies complete conversion of 3-bromocarbazole units into the corresponding dicarbazolyls. The excess charge evident in the anodic sweeps of the film forming and conditioning cycles was suggestive of such conversion. However precise integration was not possible and the presence of free 3-bromocarbazole moieties within the electrochromic films cannot be completely excluded. Notwithstanding these reservations, c.v. and XPS suggest a virtually complete conversion of the 3-bromocarbazoles into their dimers, and within the context of a highly ordered structure which permits considerable geometrical and electronic overlap between adjacent dicarbazyls. Such overlap accommodates formal fractional charge *via* delocalisation of integral charge over an extended stack of aromatic rings, and Figure 2 demonstrates that such a stack is theoretically possible, if hypothetical.

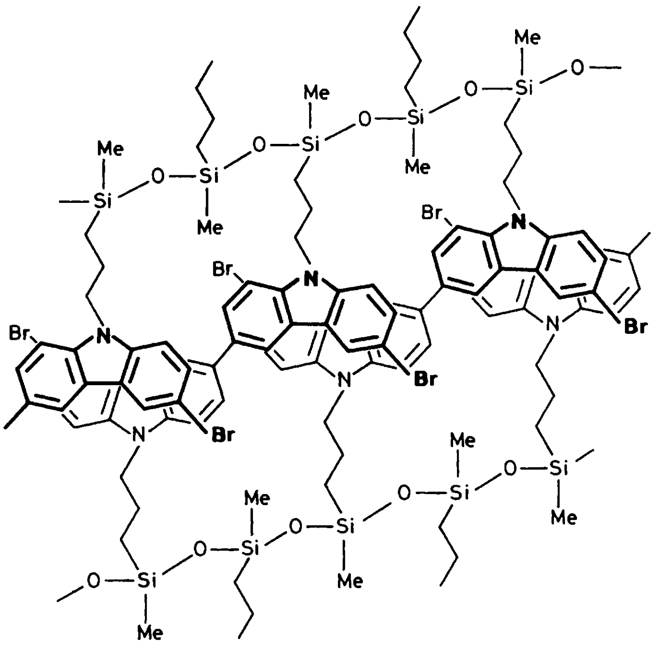


Figure 2. Putative structure for the electrochromic polymer film obtained *via* anodic oxidation of the carbazole polymer (**1a**). For clarity, C–Br bonds have been lengthened, and carbazole units lying over other carbazole units are shown in a heavier line.

We are currently studying the structural, optical and electrical properties of the electrochomic films.

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