Poly(3-bromo-*N*-vinylcarbazole): a Novel Electrochromic Material

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The cross-linked polymer produced by the potentiostatic anodic oxidation of thin films of poly(3-bromo-*N*-vinylcarbazole) on platinum electrodes is shown to display an unusually fast electrochromic response, *ca.* twenty times faster than that displayed by the related material poly(*N*-vinylcarbazole).

Poly(*N*-vinylcarbazole) (PVK) has received considerable attention recently particularly because of its potential application, when coated onto optically transparent electrodes, for electrochromic displays[1] as well as through the general current interest in useful organic metals and semi-conductors.[2] We report here the behaviour of the related material poly(3-bromo-*N*-vinylcarbazole) (PV3BrK). Like PVK[3,4] this polymer becomes cross-linked during electrochemical oxidation. Subsequently it displays dramatically faster responses to potential steps in both the reducing and oxidising directions than are found in the parent material, PVK.

PV3BrK was synthesised by free radical polymerisation of vinyl monomer using azobisisobutyronitrile as initiator. The monomer, 9-vinyl-3-bromocarbazole, was prepared using a literature method.[5] Stable polymer films with good adhesion characteristics were obtained on platinum electrodes by coating with 5 µl of a solution containing 5—7 µg of polymer in toluene–cyclohexanone (1 : 1; 5 ml) then removing the solvent *in vacuo*. The coat was then pre-swollen with acetonitrile and briefly warmed to 90 °C. Cyclic voltammograms of coated electrode were taken in acetonitrile containing $Bu^n_4NClO_4$ (0.1 mol dm^{-3}) as background electrolyte. An approximately gaussian oxidation peak (peak width at half height *ca.* 90 mV) was seen at 1.35 V (*vs.* Ag/AgCl).

By analogy with PVK[3,4] it might be expected that the chemical processes occurring in this oxidation peak can be described by Scheme 1. This was confirmed using exactly the same experiments and arguments as for PVK.[3,4] In particular current transients obtained by stepping the potential repeatedly between 0.6 and 1.40 V showed that in the initial step a charge corresponding to *ca.* 0.7 electrons per mole of carbazole moiety was passed. However on reversing the potential from 1.40 to 0.6 V only half this number of electrons were transferred. Any steps in either the oxidative or reductive directions, after the first oxidative step, passed a charge corresponding to half the initial number of electrons passed. It was also found that the timescale of the initial current transient was much longer than that of subsequent transients [Figures 1(a) and (b)]. Both these observations can be readily interpreted in terms of Scheme 1: in the initial

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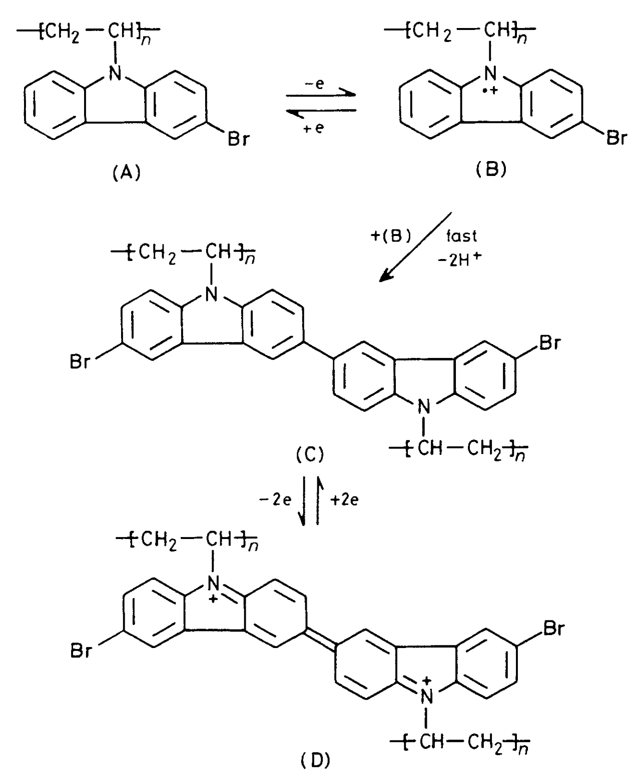

Scheme 1

oxidation (A) is converted into (D) [4 electrons per molecule of (D) formed] whereas subsequent steps only involve the interconversion of (C) and (D) (2 electrons) because of the irreversibility of the chemical step. Thus the initial transient passes twice the charge of subsequent ones. The different timescales arise because in the first transient the current response is controlled, after an initial large current due to the conversion of (A) into (B), by the rate of dimerisation of the cation radicals (B) whereas in subsequent steps the transient is governed by the rate of interconversion of (C) and (D). Since some 0.7 electrons per carbazole unit are initially removed it is clear that 35% of the pendant groups become cross-linked.

Figure 1 shows the current transients obtained from equimolar quantities of PVK and PV3BrK (2.5×10^{-8} mol of carbazole moiety coated onto a platinum foil of area 7 × 7 mm). It is clear that the latter material is oxidized significantly faster than PVK. This is true both of the initial cross-linking step and of the subsequent transients which of course are the relevant ones for practical electrochromic devices since these would have to undergo many potential cycles. The conversion of (C) into (D) must involve the uptake of charge compensating counter-ions into the coat and XPS measurements have confirmed the uptake of ClO_4^- in both the oxidation of PVK and of PV3BrK. However, whereas in PVK changing the size of the counter-ion had no effect on the rate of interconversion of (C) and (D) it was found that there were significant effects for PV3BrK and that the smaller the ion the faster the process ($BF_4^- > ClO_4^- \gg SbF_6^-$). This points to a change in the rate-determining step from electron hopping between adjacent oxidised (D) and reduced (C) dimeric units (in PVK) to counter-ion diffusion (in PV3BrK).

As can be seen from Figure 1 the timescale of the initial transient is also significantly faster in PV3BrK than in PVK. We have shown elsewhere[4] that if the tail of this transient is controlled by the rate of dimerisation of the cation radicals (B) then equation (1) should relate the current I to the second order rate constant k, where A is the area of the coated electrode, x is the film thickness, and n_0 is the initial number of carbazole moieties available for reaction within the coat. Figure 2 shows that equation (1) holds for the oxidation of PV3BrK. Data are shown for three samples of PV3BrK of differing molecular weights. It is clear that the rate of dimerisation is molecular weight dependent as is the number of electrons removed from the coat and hence the degree of cross-linking (Table 1).

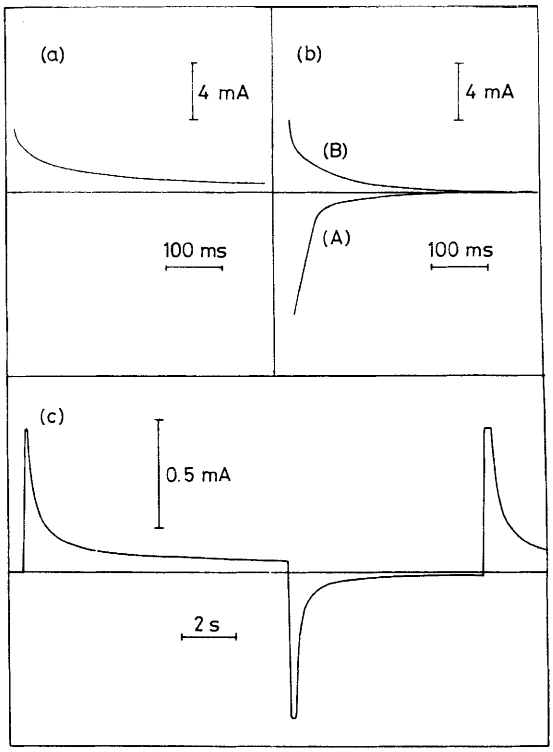

Figure 1. (a) Typical current transient obtained during the initial oxidation of PV3BrK films. (b) Typical reductive (A) and oxidative transients (B) obtained on the cross-linked film. (c) The equivalent experiments using PVK.

Table 1. Molecular weight dependence of the initial oxidative transients.

	$\bar{M}_n$	Electrons passed per carbazole unit	k^a/mol^{-1} dm^3 s^{-1}
PV3BrK	38 000	0.60	0.55
PV3BrK	60 000	0.70	0.43
PV3BrK	72 000	0.73	0.30
PVK[b]	118 000	0.85	6×10^{-3}

[a] Calculated assuming x *ca.* 10^{-7} m. [b] Ref. 4.

$$\frac{1}{\sqrt{I}} = \frac{1}{\sqrt{2FA}}\left(\frac{A}{n_0}\sqrt{\frac{x}{k}} + t\sqrt{\frac{k}{x}}\right) \qquad (1)$$

What is the origin of the improved response time of PV3BrK over PVK in both type of transients? The cause is unlikely to be electronic since the material PV3ClK showed behaviour closely similar to PVK. A clue may be in our observations that the dipole moment value (measured in solution) for PV3BrK per repeat unit was only 15% greater

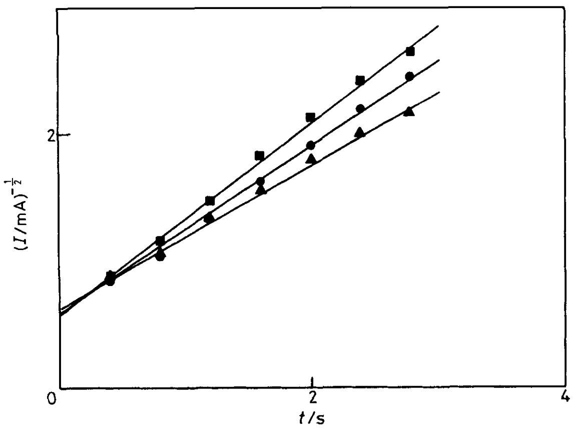

Figure 2. The analysis [using equation (1)] of initial transients obtained from three samples of PV3BrK of differing molecular weight: $\bar{M}_n$ ■ 38 000, ● 60 000, ▲ 72 000.

than the monomer dipole moments whereas PV3ClK showed a 150% increase and PVK a 350% increase. This may indicate that the bromo substituted polymer is more flexible than PVK or PV3ClK which are thought to form rod-like helices. This is consistent both with the high degree of cross-linking in PV3BrK (35%) compared to PVK (40—50%) despite 50% reduction in available sites owing to the bromine substituent and also with the improved response times.

We thank Professor H. Block for helpful discussions and the S.E.R.C. for financial support.

Received, 9th May 1985; Com. 626

References

1 A. Desbene-Monvernay, P. C. Lacaze, and J. E. Dubois, *J. Electroanal. Chem.*, 1981, **129**, 229; J. E. Dubois, A. Desbene-Monvernay, and P. C. Lacaze, *ibid.*, 1982, **132**, 177; P. C. Lacaze, J. E. Dubois, A. Desbene-Monvernay, P. L. Desbene, J. J. Basselier, and D. Richard, *ibid.*, 1983, **147**, 107; A. Desbene-Monvernay, P. C. Lacaze, J. E. Dubois, and P. L. Desbene, *ibid.*, 1983, **152**, 87.

2 H. Block, M. A. Cowd, and S. M. Walker, *Polymer*, 1977, **18**, 781; A. M. Hermann and A. Rembaum, *J. Polym. Sci., Polym. Symp.*, 1967, **17**, 107; H. H. Kanega, Y. Shirota, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 1984, 158; R. W. Murray, *Annu. Rev. Mater. Sci.*, 1984, **14**, 145.

3 F. J. Davis, H. Block, and R. G. Compton, *J. Chem. Soc., Chem. Commun.*, 1984, 890.

4 R. G. Compton, F. J. Davis, and S. C. Grant, *J. Appl. Electrochem.*, in the press.

5 J. Pielichonski and H. Kyziol, *Monatsh. Chem.*, 1974, **105**, 1306.