Electrochemical Doping of Poly(*N*-vinylcarbazole) and Poly(3,6-dibromo-*N*-vinylcarbazole) and Their Electrical Conductivities

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Electrochemical doping of poly(*N*-vinylcarbazole) and poly(3,6-dibromo-*N*-vinylcarbazole) in thin films coated on a platinum electrode in acetonitrile or in dichloromethane solution by means of potentiostatic anodic oxidation in the presence of tetra-n-butylammonium perchlorate produced electrically conductive polymers with room temperature conductivities as high as 6×10^{-4} S cm^{-1}.

It has been shown that the electrical conductivity of polymers is greatly enhanced by chemical doping, as found for, *e.g.*, polyacetylene[1] or poly(*p*-phenylene).[2] It has also been shown that the doping can be carried out electrochemically, as found for polyacetylene[3] or for the electrochemical formation of conducting poly(pyrrole).[4] In the electrochemical doping of polyacetylene a strip of the polymer film was used as the anode in galvanostatic electrolysis.[3]‡

We report here the first example of the electrochemical doping of poly(*N*-vinylcarbazole) (PVCz) and poly(3,6-dibromo-*N*-vinylcarbazole) (PDBrVCz) which transforms them into conducting polymers. This was carried out for thin films coated on the electrode and for solutions by means of controlled potential electrolysis using a three-electrode system. Polymer films with thicknesses of 10—30 μm were cast from 1—3 w/v% tetrahydrofuran solution onto the surface of a platinum plate electrode with an area of $1.5 \times 1.5\,\mathrm{cm}^2$ and dried *in vacuo*. Anodic oxidation of the polymer films was carried out in acetonitrile with tetra-n-butylammonium perchlorate as supporting electrolyte ($0.1\,\mathrm{mol\,dm}^{-3}$) near the peak oxidation potentials of PVCz and PDBrVCz (1.0—1.1 V *vs.* $\mathrm{Ag/Ag}^+$, $0.01\,\mathrm{mol\,dm}^{-3}$) as determined from their cyclic voltammograms. When the potential was applied, a current of *ca.* 200—400 μA flowed, decreasing gradually with time. The films turned a bluish green in colour as the electrochemical doping proceeded. When the electrolysis was stopped after an appropriate time (10—60 min), the films that adhered to the electrode were washed with purified acetonitrile and dried *in vacuo*. Anodic oxidation of PVCz in dichloromethane solution ($1—7 \times 10^{-3}\,\mathrm{mol\,dm}^{-3}$) was also carried out in a similar manner. A current of *ca.* 300 μA flowed during the electrolysis and bluish green polymers with thicknesses of *ca.* 5—15 μm were deposited on the platinum electrode.

The electrochemically doped polymers are partial cation radical salts with $\mathrm{ClO_4}^-$ as counter anion. The electronic reflection spectra of the doped polymers show a broad, intense band with a peak at *ca.* 780 nm that is ascribable to the cation radical of the carbazole chromophore. The i.r. spectra of the doped polymers show a band at $1080\,\mathrm{cm}^{-1}$ due to $\mathrm{ClO_4}^-$. A band at $780\,\mathrm{cm}^{-1}$, which is due to the C–H out-of-plane deformation vibration of the carbazole ring substituted at the 3- and/or 6-position as observed for the undoped and electrochemically doped PDBrVCz, is absent for PVCz but appears for the doped PVCz. This suggests that the structure of electrochemically doped PVCz is partially cross-linked at

Table 1. Room temperature conductivities of electrochemically doped polymers.[a]

Polymer	Doping method[b]	Degree of doping (%)[c]	Conductivity[d] σ (S cm^{-1})
PVCz	A	23	1.2×10^{-6}
PVCz	A	30	1.7×10^{-6}
PVCz	B	51	5.9×10^{-4}
PVCz	B	—	5.3×10^{-5}
PDBrVCz	A	15	6.7×10^{-6}
PDBrVCz	A	45	5.8×10^{-4}
PDBrVCz	B	—	7.3×10^{-5}

[a] Counter anion: $\mathrm{ClO_4}^-$. [b] A: Film doping, B: solution doping. [c] Determined from both coulometry and elemental analysis for method A, and from elemental analysis for method B. [d] The conductivity was measured by a two-probe d.c. method for the films or pellets. The conduction is not ionic but electronic since the d.c. electric current shows no appreciable decay with time.

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‡ Related to this, polymer-modified electrodes have been shown to function as electrochromic transducers.[5]

either the 3- or the 6-position owing to the coupling reaction of the carbazole cation radical. The doped polymers are fairly stable in air.§

Table 1 shows the room-temperature conductivities of the electrochemically doped polymers with different degrees of doping. The conductivities of the doped polymers were found to increase with an increase in the degree of doping. The doped polymers exhibit room-temperature conductivities as high as $6 \times 10^{-4}\,\mathrm{S\,cm^{-1}}$, which are comparable to or larger than the values of PVCz partially oxidized with $SbCl_5$[6] or with tris(*p*-bromophenyl)ammonium hexachloroantimonate.[7]

The present two techniques of electrochemical doping of non-conjugated insulating polymers have proved to be useful for producing electrically conducting polymers.[8] The methods seem to have a generality and be applicable to other non-conjugated pendant polymers.

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§ When the doped polymers were allowed to stand for one month in air, no change in their appearance or i.r. spectra was observed, and the decrease in the electrical conductivities was less than one order of magnitude.

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