

Preparation of an Electrically Conducting Polymer by the Electrolytic Polymerization of *N*-Vinylcarbazole

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The controlled-potential anodic oxidation of *N*-vinylcarbazole in dichloromethane with tetra-*n*-butylammonium perchlorate as the supporting electrolyte deposited an electrically conducting polymer on the surface of the electrode; the polymer exhibits a room temperature conductivity of $ca. 1 \times 10^{-6} \text{ S cm}^{-1}$.

It has been recognized that doping, which is a charge-transfer reaction, is important for the attainment of high electrical conductivity in polymers. This has been achieved both chemically^{1,2} and electrochemically³⁻⁵ for polymers. In recent electrochemical preparations of highly conducting linear π -conjugated polymers, *e.g.*, poly(pyrrole)⁶ or poly(thiophene),^{7,8} the electrochemical doping was carried out at the same time as the electrolytic polymerization.

We report here the preparation of an electrically conducting polymer by the electrolytic polymerization of a vinyl monomer, *N*-vinylcarbazole.

N-Vinylcarbazole (VCZ) was anodically oxidized by controlled-potential electrolysis, in dichloromethane solution ($5.0 \times 10^{-3} \text{ mol dm}^{-3}$) containing tetra-*n*-butylammonium perchlorate (0.2 mol dm^{-3}) as the supporting electrolyte, near the peak oxidation potential of VCZ as determined from its cyclic voltammogram, *i.e.*, at 0.9 V vs. Ag/Ag⁺ 0.01 mol dm⁻³ reference electrode. The electrolysis was carried out with constant stirring in a two-compartment glass cell with platinum plates ($1.0 \times 1.0 \text{ cm}^2$) as the working and counter

electrodes. As the electrolysis proceeded, the reaction solution turned green in colour, and a dark green polymer was deposited on the working electrode. A current of *ca.* 2 mA flowed, gradually decreasing to *ca.* 1 mA during the electrolysis (150 min). The resulting polymer adhering to the electrode was washed with purified dichloromethane and dried *in vacuo* (yield: *ca.* 22 mg from 24 mg of VCZ). In our studies of thermally and photochemically induced charge-transfer polymerizations of VCZ,⁹ we have found that the VCZ cation radical generated by photochemical electron transfer initiates cationic polymerization of VCZ in dichloromethane.¹⁰ In view of this and the fact that polymer deposition does not occur in the presence of 10 vol % methanol, we conclude that the anodic polymerization of VCZ proceeds by a cationic mechanism.¹¹

The polymer formed is electrochemically doped poly(*N*-vinylcarbazole), *i.e.*, the partial cation radical salt with ClO₄⁻ as counter anion, and it resembles the polymer produced by electrochemical doping of poly(*N*-vinylcarbazole) in solubility behaviour and i.r. spectra. The doped polymer, unlike

Table 1. Electrical conductivities of the polymer prepared by the electrolytic polymerization of *N*-vinylcarbazole in dichloromethane.^a

Exp. no.	Degree of doping (%) ^b	Conductivity σ (15 °C)/S cm ^{-1c}
1 ^d	65	7.6×10^{-7}
2	58	7.8×10^{-7}
3	56	1.3×10^{-6}

^a Counter anion: ClO₄⁻. ^b Determined from chlorine elemental analysis. ^c The conductivity was measured by a two-probe d.c. method with pressed pellets at a pressure of 2 kg/cm² to ensure contact between the sample and the electrode. ^d The activation energy for the conduction as measured from 15 to 80 °C = 0.17 eV.

poly(*N*-vinylcarbazole), is insoluble in benzene, tetrahydrofuran, or *N,N*-dimethylformamide. The characteristic i.r. absorption bands at 1638, 963, and 860 cm⁻¹ due to the vinyl group of VCZ were not present in the spectrum of the polymer. The doped polymer shows strong i.r. absorption bands at 1110 and 1080 cm⁻¹ due to ClO₄⁻ and a band at 790 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. This indicates that the structure of poly(*N*-vinylcarbazole), formed by the electrolytic polymerization of VCZ, is partially cross-linked at the 3- and/or 6-position of the carbazole ring by a coupling reaction of the carbazole cation radical.

As Table 1 shows, the polymer was found to exhibit room temperature conductivity in the order of 10⁻⁶ S cm⁻¹, which was lower than the value obtained for the polymer with a similar degree of doping produced by electrochemical doping of poly(*N*-vinylcarbazole).⁴

The electrolytic polymerization of vinyl and vinyl-type monomers has been studied; however, little attention has been paid to electrochemical doping of the resulting polymers. It is expected that the present study could be extended to include other vinyl and vinyl-type monomers.

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References

- 1 H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1977, 578.
- 2 D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, 1979, **71**, 1506.
- 3 P. J. Nigley, A. G. MacDiarmid, and A. J. Heeger, *J. Chem. Soc., Chem. Commun.*, 1979, 594.
- 4 H. Kanega, Y. Shirota, and H. Mikawa, *J. Chem. Soc., Chem. Commun.*, 1984, 158.
- 5 Y. Shirota, T. Kakuta, and H. Mikawa, *Makromol. Chem., Rapid Commun.*, submitted for publication.
- 6 A. F. Diaz, K. K. Kanazawa, and G. P. Gardini, *J. Chem. Soc., Chem. Commun.*, 1979, 635.
- 7 K. Kaneto, K. Yoshino, and Y. Inuishi, *Jpn. J. Appl. Phys.*, 1982, **21**, L567.
- 8 G. Tourillan and F. Garnier, *J. Electroanal. Chem.*, 1982, **135**, 173.
- 9 Y. Shirota and H. Mikawa, *J. Macromol. Sci., Rev. Macromol. Chem.*, 1977/78, **16**(2), 129.
- 10 K. Tada, Y. Shirota, and H. Mikawa, *Macromolecules*, 1973, **6**, 9; *J. Polym. Sci., Polym. Chem. Ed.*, 1973, **11**, 2961.
- 11 See also, E. B. Mano and B. A. L. Calafate, *J. Polym. Sci., Polym. Chem. Ed.*, 1983, **21**, 829.