

Unique Optical and Electrochemical Properties of π -Conjugated Electrically Conducting Copolymers Consisting of Electron-withdrawing Pyridine Units and Electron-donating Thiophene Units

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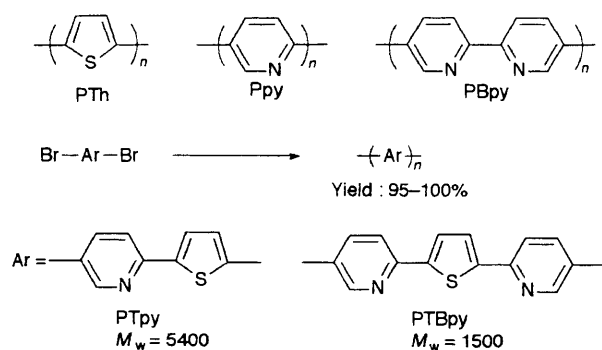
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Electrically conducting π -conjugated copolymers consisting of π -excessive thiophene-2,5-diyl and π -deficient pyridine-2,5-diyl monomer units show a unique cyclic voltammogram with an unusually large potential difference between the doping and the undoping peaks, and their electronic and fluorescence spectra support occurrence of intramolecular charge transfer showing absorption and fluorescence peaks at lower energy compared with those of the corresponding homopolymers.

The synthesis and chemical, physical and electrical properties of π -conjugated polymers are subjects of recent interest. Among various methods for synthesis of the polymers, dehalogenation polycondensation of dihalogenoaromatic monomers with nickel(0) complexes is suited to the molecular design of π -conjugated poly(arylene)s with a well defined linkage between the monomer units; the electron-donating poly(thiophene-2,5-diyl) PTh¹ and electron-accepting poly(pyridine-2,5-diyl) (Ppy)² and poly(2,2'-bipyridine-5,5'-diyl) (PBpy)³ have been synthesized by this method.

Now we report properties of new π -conjugated copolymers, PTpy and PTBpy, which include π -excessive thiophene-2,5-diyl and π -deficient pyridine-2,5-diyl units⁴ and which were



Scheme 1 Conditions: Ni(cod)₂, 2,2'-bipyridine, dimethylformamide, 60–80 °C

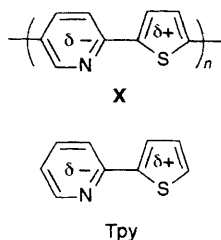
synthesized by nickel(0) complex-based polymerization (Scheme 1).[†] Analytical data for the polymers agree with the structures.[‡]

PTpy shows interesting optical and electrochemical properties. The electronic spectrum of PTpy with λ_{\max} at 490 nm [ϵ 42 000 cm⁻¹ dm³ (mol of monomer unit)⁻¹] shows a red shift compared with those of Ppy (λ_{\max} 370 nm)² and PTh (λ_{\max}

[†] The monomers were synthesized by a coupling reaction of 2-MgBr-5-Br-thiophene or 2,5-(MgBr)₂-thiophene with 2,5-dibromopyridine using Pd(dppb)₂ as a catalyst (*cf.* A. Minato, K. Suzuki, K. Tamao and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1984, 511). The polymers were obtained from the corresponding monomers by mixing with Ni(cod)₂ and 2,2'-bipyridine [monomer:Ni(cod)₂:2,2'-bipyridine = 1:1.2:1.2] followed by stirring at 60–80 °C for 20 h (*cf.* refs. 1, 2a and 3). dppb = 1,4-bis(diphenylphosphino)butane; cod = cycloocta-1,4-diene.

[‡] The polymers were characterized by microanalytical and spectroscopic data: PTpy; Found: C, 65.8; H, 3.0; Br, 1.9; N, 8.2; S, 18.6. H(C₆H₅NS)₃₃Br (*M*, 5335) requires C, 66.9; H, 3.1; Br, 1.5; N, 8.7; S, 19.8%; ¹³C NMR (HCO₂H; 500 MHz): δ : 146.3, 144.0, 143.9, 139.0, 134.0, 133.5, 130.5, 125.9, 125.8; IR (v/cm⁻¹): $\nu_{(\text{Ar})\text{C-H}}$ 3058, 3006; ν_{Ar} 1585, 1557, 1525, 1461(s); $\delta_{(\text{Ar})\text{C-H}}$ 828, 794s, 750. PTBpy; Found: C, 70.2; H, 3.5; Br, 0; N, 11.0; S, 13.1. H(C₁₄H₈N₂S)_{6.5}H (*M*, 1538) requires C, 71.1; H, 3.5; N, 11.8; S, 13.5%. ¹³C NMR (HCO₂H; 500 MHz): δ : 147.9, 144.2, 143.3, 141.4, 133.4, 133.1, 125.9; IR (v/cm⁻¹): $\nu_{(\text{Ar})\text{C-H}}$ 3052, 3010; ν_{Ar} 1588, 1539, 1460(s); $\delta_{(\text{Ar})\text{C-H}}$ 830, 805s, 749. The difference between the found and required values in the analyses may be attributed in part to the high thermal stability of the polymers. *M*_w was determined by a light scattering method.

420–480 nm).⁵ This red shift suggests that the π -excessive thiophene rings and π -deficient pyridine rings interact, causing intramolecular charge transfer to some extent (structure X). Such polarization in the corresponding monomer



compound, 2-(2'-thienyl)pyridine (Tpy), has been proposed on the basis of its chemical properties.⁶

PTpy gives rise to strong fluorescence both in formic acid and in the solid state. A dilute HCO₂H solution (3.2×10^{-7} mol of monomer unit dm⁻³) of PTpy shows fluorescence with a peak at 556 nm when pulse-irradiated by 490 nm light. The peak position is at much longer wavelength than those of Ppy (440 nm)⁷ and Tpy (362 nm),⁸ indicating that the fluorescence centre is delocalized along the polymer chain and the interaction between the thiophene ring and the pyridine ring causes a change in the fluorescence energy from that of Ppy. It is known that pyridine nuclei, in general, serve as good fluorescence centres. The copolymer PTpy adopts a rather random conformation in contrast to the rigid linear rod-like structure of Ppy,² as proved by the much smaller value of the degree of depolarization, ρ_v of PTpy (ρ_v 0.093) compared with that of Ppy (ρ_v 0.33).

PTBpy shows a π - π^* absorption peak at 440 nm in formic acid [ϵ 35 000 cm⁻¹ dm³ (mol of monomer unit)⁻¹]. A dilute HCO₂H solution (8.6×10^{-6} mol of monomer unit dm⁻³) of PTBpy shows fluorescence with a peak at 510 nm when pulse-irradiated by 440 nm light.

Fig. 1 shows cyclic voltammograms of a PTpy film on a Pt plate; the PTpy film was prepared by painting the Pt plate with an HCO₂H solution of PTpy followed by removal of HCO₂H *in vacuo*. The cyclic voltammograms reveal the following electrochemical properties of the film. (i) In the potential range between -2.4 and 0.6 V (*vs.* Ag/Ag⁺, Fig. 1a), the cyclic voltammogram shows four peaks A–D. The position of peak A corresponds to the reported oxidation potential of PTh (0.67–0.69 V *vs.* Ag/Ag⁺),⁹ and the positions of the C–D couple roughly agree with the doping and undoping potentials of Ppy (-2.58 V and -2.19 V *vs.* Ag/Ag⁺, respectively).² (ii) In the range -1.95 to 0.6 V, only the A–B couple is observed (Fig. 1b), whereas scanning in the range -2.4 to 0 V gives rise only to the C–D couple (Fig. 1c). Scanning in the range 0–0.6 V gives no peak. (iii) Both the anodic and cathodic peak currents are essentially proportional to the scanning rate. (iv) Use of various electrolytes including [Et₄N]X (X = BF₄ or ClO₄) and [Buⁿ₄N]X (X = BF₄, ClO₄ or PF₆) affords essentially the same cyclic voltammograms.

These observations indicate that the A–B couple is mainly related to the oxidation and reduction of the thiophene units [eqn. (1)], whereas the C–D couple is related to the reduction and oxidation of the pyridine units [eqn. (2)]. The doping level related to eqn. (1) is *ca.* 0.15, whereas that related to eqn. (2) is *ca.* 0.40. The positive charge and negative charged formed in the polymer chain according to eqns. (1) and (2),

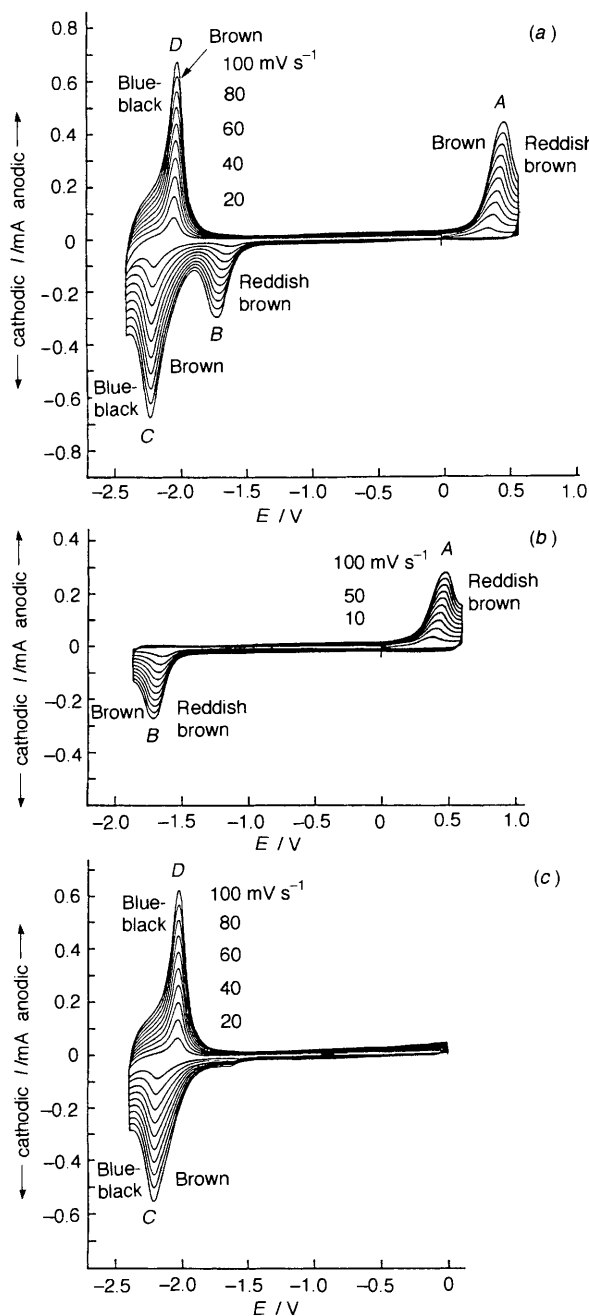
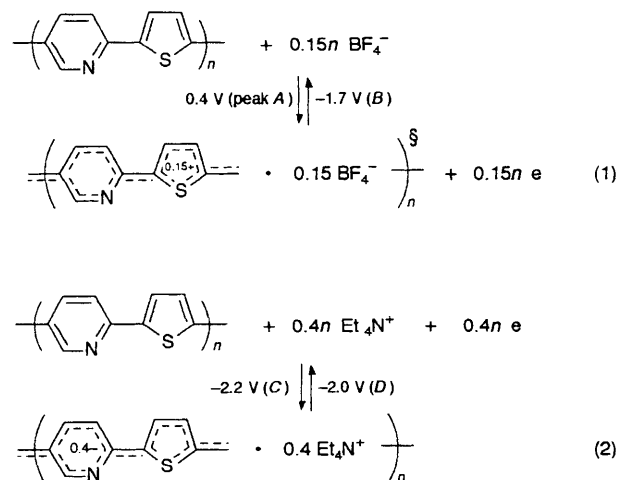


Fig. 1 Cyclic voltammograms of a PTpy film (3.8×10^{-8} mol of monomer unit) on a 1×1 cm Pt electrode in acetonitrile-0.1 mol dm⁻³ [Et₄N]BF₄. All of potentials refer Ag/Ag⁺. Potential sweep range; (a) -2.4 to 0.6 V; (b) -1.95 to 0.6 V; (c) -2.4 to 0 V.



§ This species is considered to undergo reduction at -1.7 V after certain chemical changes (EC mechanism, see text).

respectively, are delocalized along the polymer chain; however, they are considered to be mainly localized in the thiophene ring and pyridine ring, respectively.

The unusually large potential difference between the *A* and *B* peaks suggests the occurrence of a particular chemical reaction after the oxidation [eqn. (2), peak *A*] of the thiophene ring (EC mechanism). For example, a shift of a lone pair electron of the pyridine ring to the positively charged thiophene ring with shift of the anion (BF_4^-) to afford a different doping state is conceivable and the unique switching effect observed for the *A*-*B* couple may be accounted for by such an EC mechanism.

Another unique phenomenon is that the *A*-*B* couple (Fig. 1*b*) is observable only after the potential is scanned at least once beyond -2.4 V to give the *C*-*D* couple. The PTPy film was electrochemically inert and the *A* and *B* peaks were not observed when the originally prepared PTPy film was scanned only in the range -1.95 to 0.6 V (the same range as that for Fig. 1*b*); however, once the potential was scanned up to -2.4 V, the film became electrochemically active and the voltammograms shown in Fig. 1*b* were observed. The reason for this unique phenomenon is not clear, but physical and chemical changes of the film, which trigger the electrochemical reaction at the thiophene ring, probably take place after doping of the pyridine ring.

Use of PTBpy affords cyclic voltammograms similar to those of PTPy, except for some differences in the charges in the *A*-*D* peaks. When $[\text{Et}_4\text{N}]\text{BF}_4$ is used as the electrolyte, these peaks appear at 0.66 , -1.65 , -2.03 and -2.24 V, respectively, and the charges in the *A*-*B* couple and *C*-*D* couple are 0.20 and 0.58 e based on the monomer unit ($\text{C}_{14}\text{H}_8\text{N}_2\text{S}$).

Cyclic voltammogram data of a similar copolymer, which

was prepared by electrochemical oxidation of 2,5-bis(2-thienyl)pyridine and was considered to be made up from thiophene-2,5-diyl and pyridine-2,5-diyl units, have been reported.¹⁰ In this case, however, the cyclic voltammogram was recorded in the potential range from 0 to 1.1 V (vs. Ag/Ag^+) and the unique phenomena described above were not reported.

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