Electrochemical syntheses and doping properties of poly(3,3′-dialkylsulfanyl-2,2′-bithiophene)s: novel materials which exhibit facile n- and p-dopability

Siu-Choon Ng,* Ping Miao and Hardy S. O. Chan

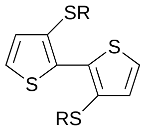
Department of Chemistry, National University of Singapore, Singapore 119260

Novel and stable electroactive polymer films which can undergo facile electrochemical p- and n-doping are successfully prepared for the first time from the electrochemical polymerization of symmetrical 3,3′-dialkylsulfanyl-2,2′-bithiophenes with long pendant chains.

In the course of our ongoing investigations into novel electrically conducting polymers, it was found that, in striking contrast to 3-alkylsulfanylthiophenes,[1–8] 3,3′-dialkylsulfanyl-2,2′-bithiophenes (DSABT) can be successfully polymerized by both chemical (using $FeCl_3$ as oxidant) and electrochemical approaches. Apart from the formation of stable films, the electrochemically derived polymers demonstrated reversible electrochemical p- and n-dopability. For most polymers, although p-doping activity has been well researched, n-type doping studies are comparatively rare due to the poor stability of the polymers at extreme negative potentials. However, from an application viewpoint, materials which are both p- and n-dopable are important, for example as light-emitting diode materials,[9] electrochemical cells[10] or in the construction of type III capacitors,[11] wherein one electrode is p-doped and the other is n-doped when the capacitor is charged. Studies on polythiophenes and polybithiophenes[12,13] have shown that p-doping generally occurs at high positive potentials whilst n-doping occurs at large negative potentials. Although introduction of pendant alkoxy groups at the 3-position of thiophene significantly reduced the oxidation potential, the n-doping process was found to be irreversible with a very small anodic current.[14] To the best of our knowledge, the electrochemical n-doping properties of alkylsulfanyl functionalized polythiophenes have not been studied.

The synthesis of monomers was accomplished starting from 3,3′-dibromo- 2,2′-bithiophene as reported previously.[15] Electrochemical polymerization of DSABTs was performed either by *via* cyclic voltammetry (CV), with the sweep potential varied from 0 to 1.1 V [*versus* a saturated calomel electrode (SCE)] at a scan rate of 20 mV s^{-1}, or by the galvanostatic method at a current density of 100 μA cm^{-2}. The monomers and electrolyte (Bu_4NBF_4 in MeCN) concentrations were 0.002 and 0.1 M, respectively. The resulting polymer films were rinsed carefully with absolute ethanol and acetone and then dried in an argon steam prior to the cyclic voltammetry studies and spectrophotometric analyses.

In contrast to 3-alkylsulfanylthiophenes, symmetrical 3,3′-dialkylsulfanyl-2,2’-bithiophenes with long pendant chains can undergo a facile oxidative polymerization *via* both the CV and galvanostatic methods, with the resulting polymers exhibiting excellent film formation behaviour. The monomer oxidation potential in $Bu^n{}_4N^+BF_4{}^-$ (0.1 M) at a scan rate of 20 mV s^{-1} was *ca.* 1.10 V. In the CV polymerization approach, a cathodic peak (*ca.* 0.75 V) was observed during the first scan, which increased in intensity with increasing number of scans. One main anodic peak at approximately 0.80 V with two shoulder peaks at 0.75 and 0.85 V were evident after the second scan. The increase in peak currents observable with the number of scans, is indicative of progressive polymer growth on the surface of the electrode. Polymer film prepared *via* galvanostatic polymerization methods exhibited a monomer oxidation potential at *ca.* 1.0 V at a current density of 100 μA cm^{-2}. The film quality was found to be dependent on the alkylsulfanyl chain lengths. Hence, monomers with lengthy alkylsulfanyl moieties (*e.g.* DSDeBT) can be electrochemically polymerized to afford excellent films with good stability on both platinum foil and ITO glass. These electrochemically generated films are completely soluble in $CHCl_3$, partially soluble in acetone, but insoluble in MeCN, MeOH and EtOH. On the other hand, electrochemical polymerization of DSABTs with short pendant chains (*e.g.* DSBuBT), results only in oligomers which are soluble in MeCN and alcohol. In this instance, even though a film can be obtained, it is not stable for long periods of time in the electrolyte solution. The p-doping mechanism for all four polymer films is highly reversibly with strong electrochromistic behaviour, being dark blue in the doped oxidised state and lilac in the neutral undoped state. The peak anodic potentials (E_{pa}) of the polymers range from 0.66 to 0.82 V and the peak cathodic potentials (E_{pc}) from 0.62 to 0.72 V. Long pendant groups resulted in a slightly increased oxidation potential of polymers, due presumably to accentuated steric effects exerted *via* the head-to-head linkages. The values of E_{pa} and E_{pc} increased slightly, whilst both the anodic and cathodic peak currents were found to scale linearly with increasing scan rate, which is characteristic of an electroactive polymer film grafted on to a electrode where the current is not diffusion controlled.[15]



DSBuBT R = C_4H_9
DSOcBT R = C_8H_{17}
DSDeBT R = $C_{10}H_{21}$
DSDoBT R = $C_{12}H_{25}$

Fig. 1 depicts the cyclic voltammograms of thin films of poly(DSOcBT), poly(DSDeBT) and poly(DSDoBT) deposited on the platinum in the potential range −2.3 to + 1.1 V at a scan rate of 100 mV s^{-1}. Both p- and n-type redox cycles exhibit characteristic wave shapes between sharp reduction peaks and the corresponding sharp oxidation peaks. The stability of p- and n-doping is related to the quality of the films. As discussed above, electrochemical polymerization of DSOcBT, DSDeBT and DSDoBT afforded high quality films. Thus, both p-doping and n-doping are stable and highly reversibly with strong electrochromism, from dark blue (p-doped) → lilac (neutral state) → dark blue (n-doped) → transparent (neutral state). On the other hand, only p-doping is observable for poly(DSBuBT), as the film is unstable in MeCN. The electrochemical oxidation potentials (E_p) of poly(DSOcBT), poly(DSDeBT) and poly(DSDoBT) are 0.75, 0.75 and 0.82 V. These three polymers have the same onset potential (E_{on}) value (0.49 V) and consequently the same ionisation potential (IP) (4.89 eV),

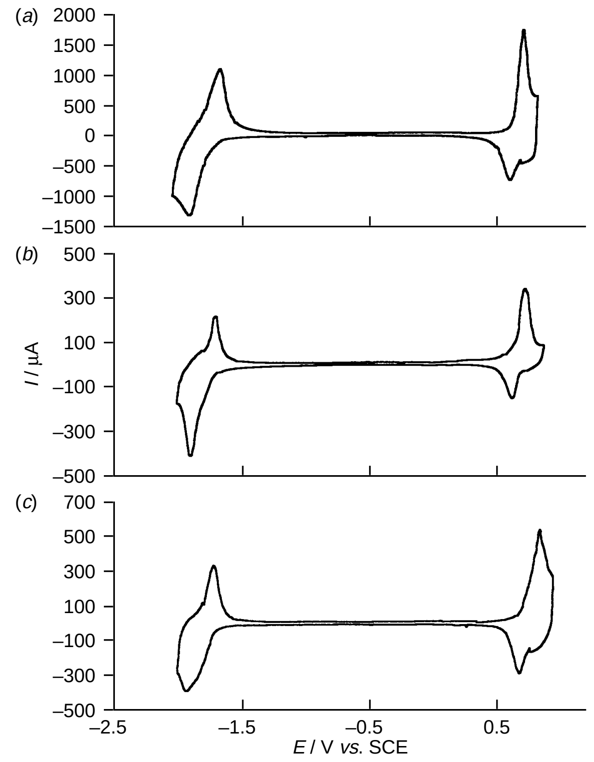


Fig. 1 CVs of (*a*) poly(DSOcBT), (*b*) poly(DSDeBT) and (*c*) poly(DSDoBT)

suggesting that the IP of DSABTs is independent of the pendant chain lengths. The peak potentials for the electrochemical reduction of the above polymers are −1.94, −1.89 and −1.98 V, with onset potentials of −1.41, −1.41 and −1.46 V, respectively. The corresponding electron affinities (EA) of these polymers are therefore 2.99, 2.99 and 2.94 eV. The observed electrochemical band gaps (the difference between the IP and the EA) are 1.90 eV for poly(DSOcBT) and poly(DSDeBT) and 1.95 eV for poly(DSDoBT). In addition, at sweep rates of 50 to 100 mV s^{-1}, both cathodic and anodic peak currents of the n-type redox cycle were found to scale linearly with respect to the sweep rate, suggesting that kinetic limitation of the electrochemical reduction of these two polymers is not significant.[16]

Fig. 2 depicts the optical absorption spectra of a typical poly(DSDeBT) film. All neutral polymer films exhibited absorption maxima at *ca.* 480, 520 and 570 nm with bandgap values between 1.77 and 1.82 eV, as derived from extrapolation of the low-energy absorption edges,[17] which agree well with the electrochemically-determined bandgap values. The high degree of conjugation in these head-to-head polymers might be ascribable to a relatively low energy barrier between their most stable configuration and the coplanar conformation.[18] Consequently, a coplanar conformation is readily attainable for poly[DSABT]s in their condensed film state. The polymer films were found to be soluble in $CHCl_3$ with solution UV absorption maxima in the range 408–450 nm depending on the length of alkylsulfanyl moiety. Thus, these pendant groups affect the conformation of polymer both in solution and the solid state.

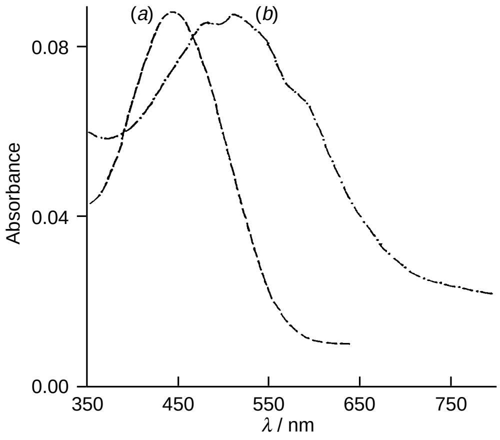


Fig. 2 UV–Visible spectra of poly(DSDeBT) in (*a*) $CHCl_3$ (λ_{max} = 441 nm) and (*b*) film state (λ_{max} at 482, 514 and 584 nm)

The authors thank the National University of Singapore for financial support through research grant RP960613. P. M. is grateful to NUS for the award of a research scholarship.

Footnote and References

* E-mail: chmngsc@leonis.nus.sg

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Received in Cambridge, UK, 8th September 1997; 7/06551E