Poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl). New Electron-withdrawing π-Conjugated Polymers Consisting of Recurring Five-membered Rings

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New π-conjugated polymers consisting of recurring electron-withdrawing five-membered (thiazole) rings, poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl), are prepared and are found to be electrochemically reduced (or n-doped) at *ca.* −2.0 V *vs.* Ag/Ag⁺.

Electronic, optical and electric properties of π-conjugated poly(arylene)s have been the subject of many papers.[1] Among the poly(arylene)s, those made up of recurring five-membered rings [*e.g.* poly(thiophene-2,5-diyl), PTh,[2] poly(pyrrole-2,5-diyl), PPyr[3] and their derivatives] have received much attention because of their interesting chemical and physical properties as well as their practical usefulness;[4] they are considered to take coplanar structures and form highly extended π-conjugated systems owing to their less sterically hindered structures compared with those of poly(arylene)s constituted of six-membered rings [*e.g.*, poly(*p*-phenylene), PPP].

PTh and PPyr are made up of 'electron-excessive'[5] heterocyclic units and susceptible to chemical and electrochemical oxidation (p-doping), although in the case of PTh, n-doping is also possible.[6] On the other hand, it has been recently revealed that the introduction of electron-withdrawing imine nitrogen(s) to poly(*p*-phenylene)- and poly(naphthalenediyl)-type π-conjugated polymers generally enhances the electron-accepting properties of the polymers, which makes them susceptible to n-doping (or reduction), and various poly(arylene)s consisting of recurring six-membered arylene units containing imine nitrogen(s) have been prepared.[7]

However, in spite of many examples of six-membered-ring poly(arylene)s with imine nitrogen(s), π-conjugated polymers composed of recurring five-membered heterocyclic units containing imine nitrogen(s) have received much less attention. We here report the preparation of some new π-conjugated five-membered-ring poly(arylene)s *via* an organometallic polycondensation and their redox behaviours. Dehalogenation polycondensation of $RBTzBr_2$ (BTz = 2,2′-bithiazole-5,5′-diyl), which was prepared according to the literature method,[8] in a manner similar to that previously reported[7] gave the corresponding polymers PRBTz† (Scheme 1) in 79–91% yield.

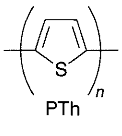
Thin films of PMeBTz, PBuBTz, and PHepBTz‡ formed on glass substrates exhibit π–π^* absorptions at 502, 450 and 433 nm, respectively. The degree of red shift (21600 cm^{-1}) from λ_{max} of methylthiazole (λ_{max} 241 nm,[9a] 41500 cm^{-1})[9] to that of PMeBTz (λ_{max} 502 nm, 19900 cm^{-1}) is comparable to those observed with thiophene (λ_{max} 231 nm,[9b] 43300 cm^{-1})–poly(thiophene-2,5-diyl) PTh (λ_{max} 420–480 nm,[1,2c,10] *ca.* 22000 cm^{-1}; red shift of *ca.* 21000 cm^{-1})[10] and 3-methylthiophene (λ_{max} 230 nm,[11] 43500 cm^{-1})–poly(3-methylthiophene-2,5-diyl) P3MeTh (λ_{max} 420 nm,[11a] 23800 cm^{-1}; red shift of 19700 cm^{-1})[11] couples. These results indicate that PMeBTz also forms an effective π-conjugation system similar to those of PTh and P3MeTh by taking an *s-trans* structure; a CPK molecular model analysis reveals the presence of only minor steric repulsions to formation of the coplanar structure.

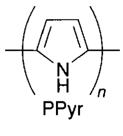
PMeBTz and PBuBTz are soluble only in acidic media such as CF_3CO_2H and CCl_2HCO_2H, and they exhibit UV–VIS absorption bands at 425 and 418 nm, respectively, in CF_3CO_2H. PHepBTz is soluble not only in the acidic media but also in $CHCl_3$, and gives absorption peaks at 420 and 405 nm in CF_3CO_2H and $CHCl_3$, respectively.

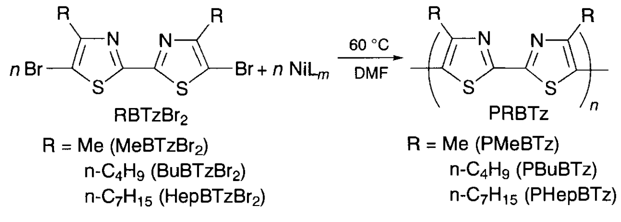
PMeBTz, PBuBTz and PHepBTz all give strong fluorescence in CF_3CO_2H with their λ_{max} values (562, 570 and 572 nm for PMeBTz, PBuBTz and PHepBTz, respectively) at the onset positions of the absorption bands of the polymers; PHepBTz exhibits fluorescence at λ_{max} = 561 nm in $CHCl_3$.

Fig. 1 shows the cyclic voltammogram (CV) of PMeBTz. Reduction (n-doping) of PMeBTz starts at *ca.* −1.5 V *vs.* Ag/Ag⁺ with a peak cathode potential E_{pc} of −2.2 V *vs.* Ag/Ag⁺. Changing the scanning direction causes n-undoping with an anodic peak potential E_{pa} of −1.9 V *vs.* Ag/Ag⁺. The n-doping and -undoping are accompanied by colour changes as shown in Scheme 2, and the CV cycle shown in Fig. 1 can be repeated five times with no observable change in the CV curve.

The redox potential, E^0, obtained as an average of E_{pc} and E_{pa} [$E^0 = \frac{1}{2}(E_{pc} + E_{pa}) = -2.05$ V *vs.* Ag/Ag⁺] appears at more positive value than those observed with PTh [E^0 (PTh) = −2.14 V[6] *vs.* Ag/Ag⁺] and P3MeTh [E^0 (P3MeTh) = −2.30 *vs.* Ag/


PTh


PPyr



Scheme 1 NiL_m = zerovalent nickel complex [a mixture of bis(cycloocta-1,5-diene)nickel(0), $Ni(cod)_2$ and 2,2′-bipyridine]; BTZ = bithiazole-5,5′-diyl

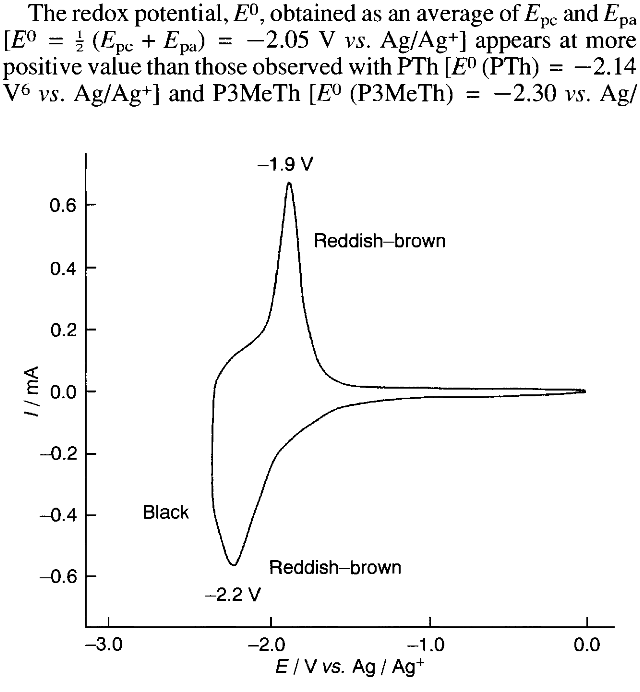
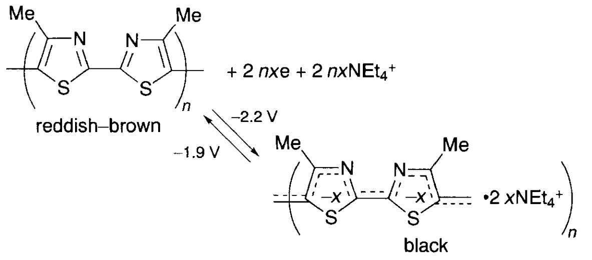


Fig. 1 CV of PMeBTz in an 0.1 mol dm^{-3} MeCN solution of $[NEt_4][BF_4]$ (at 100 mV s^{-1})



Scheme 2

Ag$^+$].§ Comparison of the E^0 data of PMeBTz and P3MeTh indicates that the introduction of the imine nitrogen to the thiophene ring also enhances the electron-withdrawing ability of the five-membered ring polymer, similarly to the case of the six-membered ring polymers, and leads to a shift of the E^0 value by *ca.* 0.25 V. The degree of the shift of the E^0 value is comparable to that (0.3–0.38 V) observed upon the introduction of the imine nitrogen to PPP and poly(naphthalenediyl) type polymers.[7,12] Owing to the enhancement of their electron-withdrawing ability, PRBTz's are not susceptible to p-doping (oxidation) up to 0.6 V *vs.* Ag/Ag$^+$, in contrast to facile p-doping of PTh at about 0.5 V *vs.* Ag/Ag$^+$. Scanning beyond 0.6 V *vs.* Ag/Ag$^+$ seems to cause degradation of PMeBTz, owing to high reactivity of the thiazole ring.[9] PBuBTz and PHepBTz are also n-doped with the E^0 value of −2.0 V *vs.* Ag/Ag$^+$ and they are also inert against the p-doping.

The present observations will contribute to design of n-type π-conjugated poly(arylene)s, which seem to be essential for the design of electronic devices such as light emitting diodes.[1c,7f] The stronger electron-withdrawing properties of thiazole as compared to thiophene have been discussed on the basis of quantum chemical calculation.[9b]

PMeBTz itself is an insulator with an electrical conductivity (σ) of 1.23 × 10^{-10} S cm^{-1}, whereas chemically n-doped PMeBTz with Na (sodium naphthalide) shows semiconductivity with a σ value of 2.5 × 10^{-4} S cm^{-1} as measured using compressed powder sample.

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Footnotes

† The polymers were characterized by microanalysis, spectroscopic (IR and NMR) data and molecular mass ($\overline{M}_w$) determined by a light scattering (LS) or GPC method. Data from microanalysis of PMeBTz, PBuBTz and PHepBTz agree with the formulae $(C_8H_6N_2S_2{\cdot}0.3H_2O)_n$, $(C_{14}H_{18}N_2S_2{\cdot}0.3H_2O)_n$ and $(C_{20}H_{30}N_2S_2)_n$, respectively. $\overline{M}_w$: 3.2 × 10^3 (PMeBTz, LS), 2.1 × 10^4 (PBuBTz, LS), and 1.1 × 10^4 (PHepBTz, GPC), respectively. ^{1}H NMR: PMeBTz (in CF_3CO_2D): δ 2.75 (br, 3H, CH_3); PBuBTz (in CF_3CO_2D): δ 0.98 (t, 3H, CH_3), 1.61 (m, 4H, CH_2), 3.01 (br, 2H, CH_2); PHepBTz (in $CDCl_3$): δ 0.84 (br, 3H, CH_3), 1.47 (m, 10H, CH_2), 2.73 (br, 2H, CH_2).

‡ The films were prepared by forming CF_3CO_2H solutions of the polymers, evaporation of CF_3CO_2H under vacuum, treatment of the film with dil. NH_3(aq), and drying under vacuum. The IR spectra of the polymers thus obtained were identical to those of the starting PRBTz's.

§ Measured with a film of chemically prepared P3MeTh[11] ($CHCl_3$ soluble part) prepared by casting on a Pt plate from $CHCl_3$ solution.

References

1 (*a*) *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, New York, 1986 vol. I and II; (*b*) W. R. Salaneck, D. T. Clark and E. J. Samuelsen, *Science and Applications of Conducting Polymers*, Adam Hilger, Bristol, 1991; (*c*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burn and A. B. Holmes, *Nature*, 1990, **347**, 539.

2 (*a*) T. Yamamoto, K. Sanechika and A. Yamamoto, *J. Polym. Sci., Polym. Lett. Ed.*, 1980, **18**, 9; (*b*) K. Sanechika, T. Yamamoto and A. Yamamoto, *Polym. Prepr. Jpn.*, 1979, **28**, 966; (*c*) T. Yamamoto, K. Sanechika and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1497; (*d*) G. Tourilon and F. Garnier, *J. Electroanal. Chem.*, 1982, **135**, 173.

3 K. K. Kanazawa, F. A. Diaz, R. H. Geiss, W. D. Gill, J. F. Kwak, J. A. Logan, J. F. Robalt and G. B. Street, *J. Chem. Soc., Chem. Commun.*, 1979, 854.

4 For example: Y. Kudo, S. Tsuchiya, T. Kojima, M. Furuyama and S. Yoshimura, *Synth. Met.*, 1991, **41/43**, 1133; M. Wakabayashi, Y. Miyazaki, T. Kanbara, K. Osakada, T. Yamamoto and A. Ishibashi, *Synth. Met.*, 1993, **55/57**, 3632.

5 G. R. Newkome and W. W. Paudler, *Contemporary Heterocyclic Chemistry*, Wiley, New York, 1982.

6 G. Zotti and G. Schiavon, *J. Electroanal. Chem.*, 1984, **163**, 385.

7 (*a*) T. Yamamoto, T. Maruyama, T. Ikeda and M. Sisido, *J. Chem. Soc., Chem. Commun.*, 1990, 1306; (*b*) T. Kanbara and T. Yamamoto, *Macromolecules*, 1993, **26**, 3464; (*c*) T. Yamamoto, T. Maruyama, Z.-H. Zhou, T. Ito, T. Fukuda, Y. Yoneda, F. Begum, T. Ikeda, S. Sasaki, H. Takezoe, A. Fukuda and K. Kubota, *J. Am. Chem. Soc.*, 1994, **116**, 4832; (*d*) N. Saito, T. Kanbara, Y. Nakamura, T. Yamamoto and K. Kubota, *Macromolecules*, 1994, **27**, 756; (*e*) N. Saito, T. Kanbara, T. Kushida, K. Kubota and T. Yamamoto, *Chem. Lett.*, 1993, 1775; (*f*) T. Yamamoto, M. Inoue and T. Kanbara, *Jpn. J. Appl. Phys.*, 1994, **33**, L250.

8 N. D. Kimpe, W. D. Cock and N. Schamp, *Synthesis*, 1987, 188; P. Karrer, P. Leiser and W. Graf, *Helv. Chim. Acta*, 1944, **27**, 624; G. Audisio, M. Catellani and S. Destri, *J. Heterocyclic Chem.*, 1990, **27**, 463. Elemental analysis and ^{1}H NMR data of the monomers agreed with the structures.

9 (*a*) A. R. Katrizky and J. M. Lagowski, *Comprehensive Heterocyclic Chemistry: the structure, reactions, synthesis and uses of heterocyclic compounds*, ed. K. T. Potts, Pergamon, Oxford, 1984, vol. 5, p. 1; (*b*) H. Hartmann and R. Radeglia, *J. Prakt. Chem.*, 1975, **317**, 657.

10 T. Yamamoto, K. Sanechika and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 1503.

11 (*a*) T. Yamamoto and K. Sanechika, *Chem. Ind. (London)*, 1982, 301; (*b*) Y. Miyazaki and T. Yamamoto, *Synth. Met.*, 1994, **64**, 69.

12 G. Schiavon, G. Zotti and G. Bontenpelli, *J. Electroanal. Chem.*, 1984, **161**, 323.