Synthesis of New Narrow Bandgap Polymers Based on 5,7-Di(2-thienyl)thieno[3,4-*b*]pyrazine and its Derivatives

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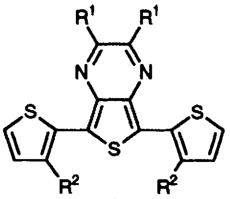
New narrow bandgap polymers with bandgaps of 1.0–1.5 eV have been synthesized from the title monomers.

The development of narrow bandgap polymers[1] ($E_g < 1.0$ eV) is of current interest in the field of materials science because of their intrinsic conductivities and good nonlinear optical properties. According to the recent theoretical investigations into producing narrow bandgap polymers, the copolymerization[2] of aromatic and *o*-quinoid heterocycles[3] will reduce a bandgap through the relaxation of bond length alternations along the polymer backbone. Another promising strategy for bandgap reduction of polymers is the copolymerization of donor and acceptor units.[1d] According to these two guidelines, we have designed a new narrow bandgap system illustrated by **2**, which consists of aromatic donor (thiophene) and *o*-quinoid acceptor (thieno[3,4-*b*]pyrazine) units. The structural feature of this system, when compared with the isoelectronic polymer of **4**,[1c] is the absence of steric repulsions between the hydrogen atom on the fused benzene ring and the adjacent thiophene ring. Therefore polymers **2** are expected to have a coplanar conformation resulting in an efficient π-electron delocalization along the main chain. We report here the synthesis and properties of the monomers **1** and their polymers **2**. The derivatives containing alkyl chains **1b–e** were synthesized in order to improve the processability of the corresponding polymers.

The monomers **1** were prepared as shown in Scheme 1. The coupling[4] of 2,5-dibromo-3,4-dinitrothiophene[5] and organotin compounds in the presence of catalytic [Pd(PPh$_3$)$_2$Cl$_2$], followed by reduction of the nitro groups, afforded oligomers **3**. Subsequently, the condensation of **3** with 1,2-diketones[6] provided **1** in 68–85% yields.† The monomers **1** have good solubilities in common organic solvents, although **1c–e** were only slightly soluble in polar solvents such as acetonitrile and acetone. The absorption maxima and the redox potentials of **1** are summarized in Table 1.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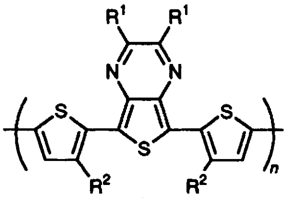
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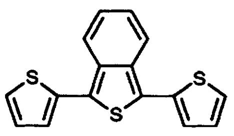
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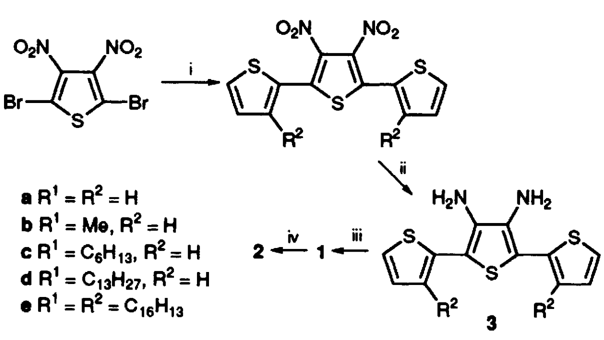

Scheme 1 *Reagents and conditions*: i, ThSnBu$^n{}_3$, [PdCl$_2$(PPh$_3$)$_2$], THF; ii, SnCl$_2$, HCl-EtOH; iii, (R^{1}CO)$_2$, MeOH or (HCO)$_2$, Na$_2$CO$_3$, H$_2$O; iv, electrochemical or chemical polymerization (Th = 2-thienyl)

The physical data suggest a higher degree of π-electron delocalization in the oligomers **1** when compared to the isoelectronic system **4** possessing a nonplanar conformation. The electronic spectra of **1** display appreciable red shifts (0.34–0.55 eV) of the lowest energy absorption band compared to **4**. In addition, the X-ray structural analysis of **1b** reveals that this molecule has an almost coplanar conformation as shown in Fig. 1. The dihedral angles between thiophene rings and the thieno[3,4-*b*]pyrazine ring are 9.5 and 11.6°, respectively. (Because of the rotational disorder, the geometrical parameters of the thiophene rings are less reliable.)‡

Another notable feature of **1** is its amphoteric redox property; the cyclic voltammograms of **1** showed both an irreversible oxidation wave and a reversible reduction wave. This fact can be attributed to the extended π-system and the electron-withdrawing property of the thieno[3,4-*b*]pyrazine moiety. There is no significant effect of the alkyl substituents on the extent of the amphoteric character. The alkyl groups decrease both oxidation and reduction potentials comparably.

Table 1 Absorption maxima and redox potentials of monomer **1**

Monomer	λ_{max}/nm(eV)[a]	E_{pa}[b]	E_{pc}[b]
1a	529(2.35)	0.97	−1.05
1b	500(2.48)	0.88	−1.36
1c	502(2.47)	0.91	−1.37
1d	500(2.48)	0.86	−1.37
1e	484(2.56)	0.79	−1.51
4[c]	427(2.90)[d]	0.80[e]	

[a] In CHCl$_3$. [b] 0.1 mol dm^{-3} Bu$^n{}_4$NClO$_4$ in PhCN, Pt electrode, scan rate 100 mV s^{-1}, V *vs.* SCE. [c] Ref. 1c. [d] In hexane. [e] In MeCN.

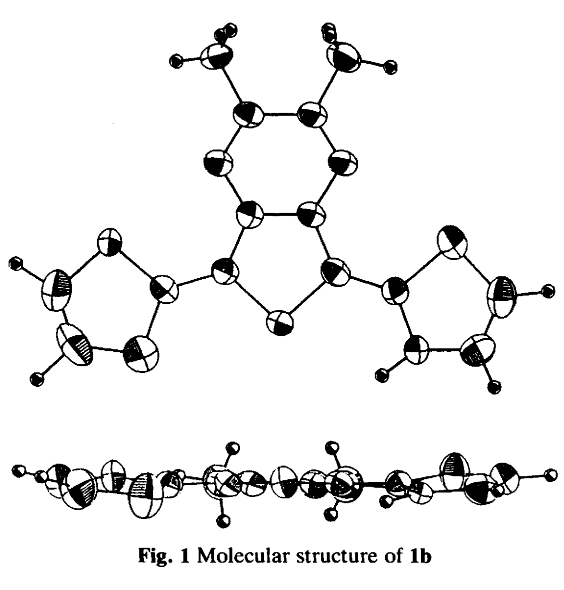

Fig. 1 Molecular structure of **1b**

Polymers **2a–d** were prepared on a Pt disk electrode and indium tin oxide (ITO) glass electrode by anodic oxidation of the corresponding monomers.§ For the most part, these polymers were insoluble in common organic solvents. In the case of **1e**, electrolysis did not give the polymer on the electrode, while chemical oxidation by $Cu(ClO_4)_2$¶ produced the polymer **2e**, which was soluble in THF and chloroform. The molecular mass M_w of **2e** measured by the GPC method is 8600 (M_n = 5800). The polymers **2a–e** in the neutral state were dark blue–black and showed high stability under normal conditions.

The cyclic voltammograms of **2** (Fig. 2) reveal that these polymers are stable to both *p*-doping and *n*-doping, in contrast to polymers consisting of benzo[*c*]thiophene units where the *n*-doping state is unstable. The small differences in threshold potentials for *p*-doping and *n*-doping (*ca.* 1.0 eV) are characteristic of narrow bandgap systems. The optical bandgaps were estimated from the absorption edges of the electronic spectra. Polymer **2a** on ITO showed a bandgap of 1.0 eV, which is 0.7 eV lower than that of the related polymer of **4**. This fact can be attributed to the coplanarity in the polymer backbone of **2a**. The contributions of the interchain charge transfer interactions to the bandgap reduction, however, cannot be estimated from the present data. The substitution of alkyl groups increased the bandgap only slightly (<0.3 eV), indicating that a good coplanar conformation should be maintained in the alkyl derivatives **2b–d**. Polymer **2e** in chloroform exhibited a bandgap of 1.5 eV.

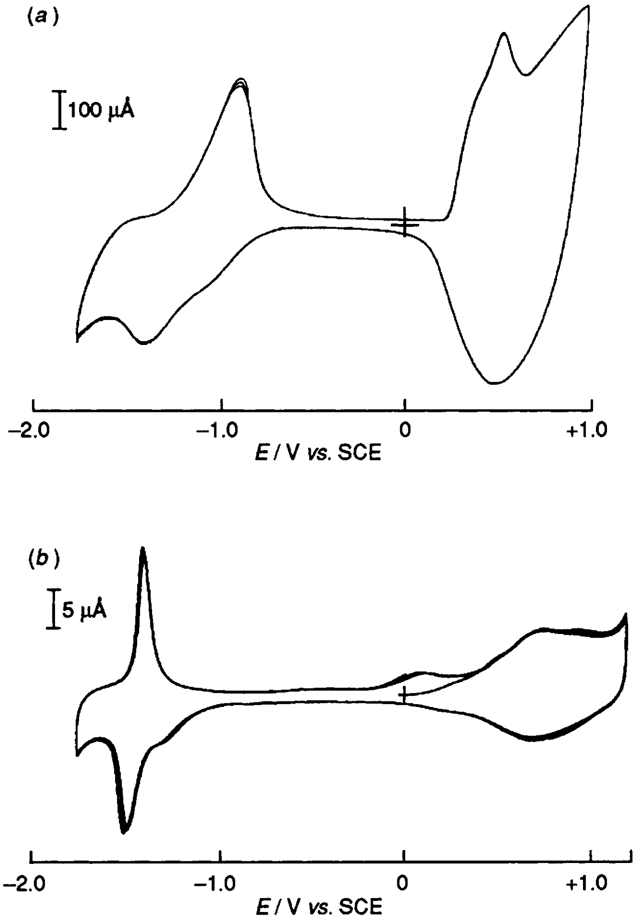

Fig. 2 Cyclic voltammograms of (*a*) **2a** and (*b*) **2e** on a Pt disk (scan rate 100 mV s^{-1}, solvent MeCN–$Bu^n_4NClO_4$)

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Footnotes

† All monomers have satisfactory elemental analyses and spectral characterization.

‡ *Crystal data* for **1b**: $C_{16}H_{12}N_2S_3$, M = 328.46, orthorhombic, space group $P2_12_12_1$, Z = 4, a = 5.6892(4), b = 8.0837(10), c = 32.8418(18) Å, V = 1510.4(2) Å^3, D_c = 1.45 g cm^{-3}. For the C and S atoms in one thiophene ring, refinement was performed with mixed atom scattering factors composed of 50% C and 50% S atoms. The final R value is 0.0529 for 1477 reflections with $|F_o| > 3\sigma|F_o|$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Polymer films were grown on an ITO electrode in the monomer solution of PhCN with 0.1 mol dm^{-3} $Bu^n_4NClO_4$ by repetitive scans and dedoped by electrochemical reduction under an argon atmosphere.

¶ To 1.25×10^{-2} mol dm^{-3} of **1e** in chloroform was added 4.75×10^{-2} mol dm^{-3} of copper(II) perchlorate in acetonitrile and stirred at room temp. for 2 h. The solution was washed with water, dedoped with hydrazine, washed with water and dried under vacuum.

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