Alternating copolymer of pyrrole and 2,1,3-benzothiadiazole

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The alternating copolymer of pyrrole and 2,1,3-benzothiadiazole is synthesized together with a set of corresponding oligomers, yielding hydrogen bonded ladder structures with push–pull character and an absorption band up to λ_{max} 700 nm.

Various routes are presently under investigation to lower the bandgap of conjugated polymers, with the ultimate aim of synthesizing zero bandgap polymers with metallic conduction properties.[1–4] Two important concepts have been developed that suggest a lowering of the bandgap when the conjugated 'backbone' consists of an alternating sequence of either aromatic and quinoid units[1] or electron-releasing and electron-withdrawing units.[2] Indeed, polymers that satisfy these requirements[3,4] have bandgaps substantially lower than those of the traditional π-conjugated polymers, like polythiophene in the undoped state. Notable are the copolymers of thiophene and benzo[1,2-*c*:4,5-*c*′]bis[1,2,5]thiadiazole and copolymers composed of [1,2,5]thiadiazolo[3,4-*g*]quinoxaline and thiophene or *N*-methylpyrrole, as studied by Yamashita *et al.*[4] We now present the synthesis and properties of the alternating copolymer of pyrrole and 2,1,3-benzothiadiazole and some corresponding oligomers, in an attempt to make use of intramolecular hydrogen bonding for planarization.[5] These compounds are likely to be examples of self-assembled ladder-like structures.[6]

Our synthetic scheme to the alternating copolymer of pyrrole and 2,1,3-benzothiadiazole is based on the Stille reaction,[7] using the *N*-Boc protecting group at pyrrole.[8,9] Well-defined alternating co-oligomers (compounds **1–3**, Fig. 1) were synthesized in order to evaluate the structure–property relationship with respect to the dependence of the π-conjugation on chain length and the presence of hydrogen bonding in these structures.

The *N*-Boc protected precursors of compounds **1** and **2** were synthesized by $Pd(PPh_3)_4$ catalysed Stille coupling of 4-bromo-2,1,3-benzothiadiazole with *N*-Boc-2-trimethylstannylpyrrole (78% yield) and of 4,7-dibromo-2,1,3-benzothiadiazole with 2 equiv. of *N*-Boc-2-trimethylstannylpyrrole (42% yield) respectively, in refluxing toluene–1 M Na_2CO_3. The *N*-Boc protected precursor of compound **3** was synthesized from the corresponding precursor of **1** by stannylation in a two step procedure consisting of α-proton abstraction with LTMP and subsequent reaction with Me_3SnCl in THF at −80 °C (57% yield). This stannyl compound (2 equiv.) was treated with 1 equiv. of 4,7-dibromobenzothiadiazole in the $Pd(PPh_3)_4$ catalysed Stille coupling in refluxing toluene–1 M Na_2CO_3 to yield the *N*-Boc protected precursor of compound **3** in 11% yield. The three *N*-Boc protected precursors were converted into the parent compounds **1**, **2** and **3** by thermal cleavage of the Boc group[9] at 200 °C in yields >95%.

The ^1H NMR spectra of compounds **1–3** feature a sharp peak at low field for the pyrrole N-*H* signal [*e.g.* δ_{N-H} ($CDCl_3$) 12.1 for compound **3**]. For compound **2**, no measurable concentration dependence and only a slight temperature dependence ($\Delta\delta/\Delta T = 1.73 \times 10^{-3}$ ppm K^{-1}) is found for the N-*H* signal. It is therefore suggested that intramolecular hydrogen bonding[10] as depicted in Fig. 1 is present, a conclusion that is supported by the X-ray crystal structure of compound **2**.† The hydrogen bond is expected to increase coplanarity of the aryl units in both the oligomers and the polymer, and hence to increase conjugation, which is beneficial for the properties of the ultimate polymer. In the absorption spectra of the consecutive oligomers, a considerable bathochromic shift is found: $\lambda_{max}(CHCl_3)$/nm = 442, 532, and 599 for **1**, **2** and **3**, respectively.‡

The synthesis of the alternating polymer is outlined in Scheme 1. Monomer **4** was prepared by the $Pd(PPh_3)_4$ catalysed Stille reaction of 1 equiv. of 4,7-dibromo-2,1,3-benzothiadiazole with 1 equiv. of *N*-Boc-2-trimethylstannylpyrrole in refluxing toluene–1 M Na_2CO_3. The monofunctionalized product was obtained in 38% yield, and subsequent stannylation with LTMP–$SnMe_3Cl$ in THF at −90 °C furnished **4** in 60% yield. Polymerization of monomer **4** was only successful in DMF at 75 °C with $Pd(PPh_3)_2Cl_2$ as the catalyst. The crude precursor polymer **5** was purified by precipitation in hexane and diethyl ether, followed by filtration over silica gel with $CHCl_3$ and subsequently THF as eluents. The THF fraction was reprecipitated in diethyl ether to give the precursor polymer **5** as a dark solid.‡ The average number of repeating units was conveniently determined by size exclusion chromatography (SEC). By comparing the chromatograms of the crude polymer reaction mixture (in which it was shown that all oligomers starting from $n = 1$ are present) with the purified polymer **5** it followed that the polymer had an average $n \cong 8$, that is 16 aromatic units linked together (M_n = 2400 g mol^{-1}). The deprotected polymer **6** was obtained as a blue transparent film

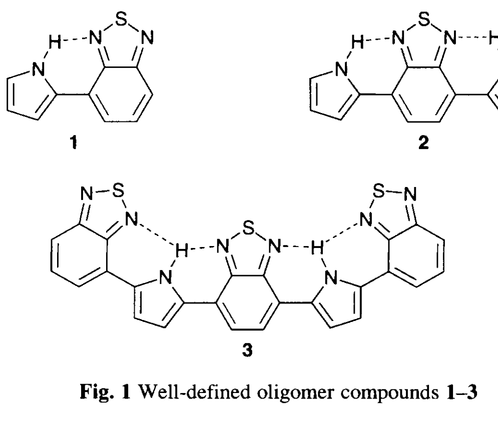
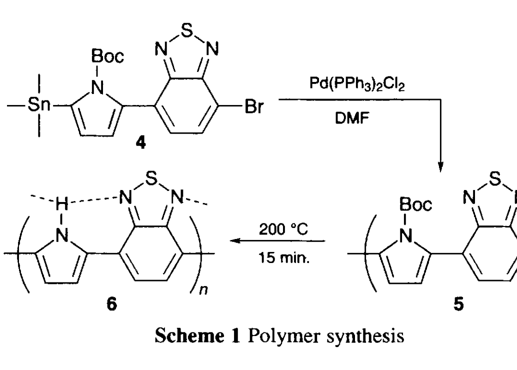


Fig. 1 Well-defined oligomer compounds **1–3**



Scheme 1 Polymer synthesis

by heating (200 °C, 15 min) a spincasted film of polymer **5** from $CHCl_3$ on glass. IR spectroscopy indicated complete elimination of the Boc groups [IR (KBr): N–H at 3347 cm^{-1}]. The absorption maximum of this polymer film was found at λ_{max} = 704 nm (1.76 eV) and the bandgap E_g was estimated at 1.2 eV (onset of absorbance at approx. 1050 nm).

Preliminary experiments have shown that films of the polymer **6** can be doped with iodine vapour, as in the UV–VIS–NIR absorption spectrum an extremely broad band emerges at about 2000 nm (0.6 eV). In the doped samples the absorption at 704 nm remains present, suggesting that oxidative doping of the film with iodine vapour cannot be brought to completion. The conductivity (determined with the four-probe method) of the doped samples is in the order of 1 S cm^{-1}.

A plot of the absorption maximum energies of compounds **1**–**3** and polymer **6** as a function of the reciprocal number of repeating units $1/n$ yields a straight line (solid line in Fig. 2), if we take a chain length of n = 8 for the polymer at 1.76 eV (diamond marker). Extrapolation to $n \longrightarrow \infty$ in Fig. 2 gives the estimated λ_{max} of the infinite chain at 800 nm (1.55 eV). A plot of the (optical) bandgap energies of the oligomers and the polymer (triangle marker) also yields a straight line (dashed line in Fig. 2), with less correlation than in the case of the absorption maxima. This is probably because the bandgaps are determined from the onset of absorbance, which is a less objective measure than the absorption maximum. Extrapolation to $n \longrightarrow \infty$ gives the estimated bandgap for the infinite chain at 1.1 eV. Despite the stronger electron donating power of pyrrole and the expected presence of hydrogen bonds in our polymer, this value falls within the range of bandgaps that Yamashita and coworkers have reported on all their thiophene based copolymers.[4] Work is now in progress to compare thiophene and pyrrole based copolymers, and to understand the delocalization in these systems in detail.

We wish to thank Dr R. A. J. Janssen and Dr E. E. Havinga for stimulating discussions and valuable comments.

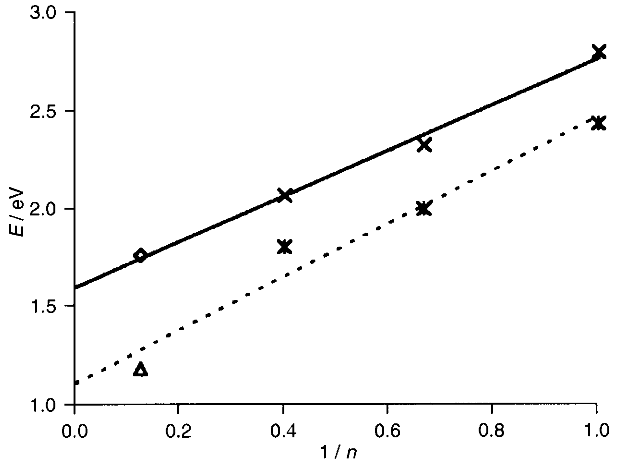


Fig. 2 Absorption maximum energies (—) and bandgap energies (---) of pyrrole-2,1,3-benzothiadiazole co-oligomers as a function of reciprocal number of repeating units

Footnotes

† Details of the X-ray crystallographic studies on compound **2** will be published elsewhere.

‡ *Selected spectroscopic data* for **1**: ^1H NMR ($CDCl_3$) δ 10.9 (br. s, 1 H), 7.78 (dd, 1 H), 7.74 (dd, 1 H), 7.55 (dd, 1 H), 7.02 (m, 1 H), 6.89 (m, 1 H) and 6.35 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.5, 151.5, 130.2, 129.2, 124.8, 121.9, 120.3, 117.7, 109.9 and 107.5; UV ($CHCl_3$): $\lambda_{max.}$/nm 442; IR (KBr) ν/cm^{-1} 3395, 1481, 1091 and 880–450; GC–MS: $M^{+\cdot}$ 266 (100%). For **2**: ^1H NMR ($CDCl_3$) δ 10.9 (br. s, 1 H), 7.84 (s, 1 H), 7.03 (m, 1 H), 6.88 (m, 1 H) and 6.37 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 152.5, 129.5, 123.2, 121.4, 120.0, 110.0 and 107.0; UV–VIS ($CHCl_3$): $\lambda_{max.}$/nm 532; IR (KBr) ν/cm^{-1} 3415, 1481, 1113 and 888–450; GC–MS: $M^{+\cdot}$ 266 (100%). For **3**: ^1H NMR ($CDCl_3$) δ 12.1 (s, 2 H), 7.94 (s, 2 H), 7.89 (dd, 2 H), 7.83 (dd, 2 H), 7.66 (dd, 2 H) and 7.1 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 130.1, 123.5, 122.3, 118.2, 110.0 and 109.6 (owing to the poor solubility of this compound in $CDCl_3$, only the signals corresponding to carbon nuclei bearing a proton could be detected); UV–VIS ($CHCl_3$) $\lambda_{max.}$/nm 599; IR (KBr) ν/cm^{-1} 3308 (br.), 1475, 1120 and 875–450; ES/MS: M + 1 = 534 (100%). For **5**: ^1H NMR ($CDCl_3$) δ 7.8 (s), 6.6 (s), 0.8. Minor peaks corresponding to 2,1,3-benzothiadiazole and *N-tert*-Boc-pyrrole endgroups are present too; ^{13}C NMR ($CDCl_3$) δ 154.2, 149.1, 132.4, 128.1, 127.5, 114.2, 83.4 and 27.0; UV–VIS ($CHCl_3$): $\lambda_{max.}$/nm 434 (side peak due to partial deprotection also present); IR (KBr) ν/cm^{-1} 2976, 1749, 1306, 1136 and 872–731.

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Received, 26th June 1996; Com. 6/04479D