Regioregular poly(3-hexyl)selenophene: a low band gap organic hole transporting polymer†

Martin Heeney,*[a] Weimin Zhang,[a] David J. Crouch,[b] Michael L. Chabinyc,[c] Sergey Gordeyev,[d] Rick Hamilton,[a] Simon J. Higgins,[e] Iain McCulloch,[f] Peter J. Skabara,[d] David Sparrowe[a] and Steve Tierney[a]

Received (in Cambridge, UK) 13th August 2007, Accepted 14th September 2007
First published as an Advance Article on the web 1st October 2007
DOI: 10.1039/b712398a

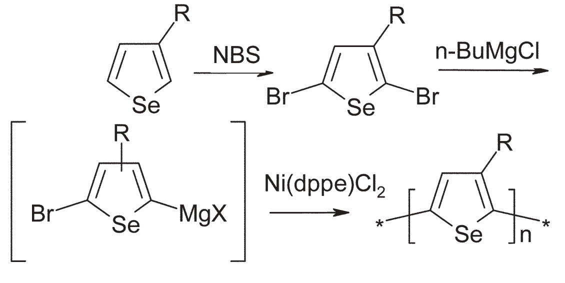
The synthesis of regioregular poly(3-hexyl)selenophene is reported, and its optical and electrical properties are compared to those of regioregular poly(3-hexyl)thiophene.

Polythiophene based materials, in particular regioregular poly(3-hexyl)thiophene (P3HT), have emerged as amongst the most promising p-type polymeric semiconductors in a variety of applications. For bulk heterojunction organic photovoltaic devices, blends of P3HT with fullerene derivatives[1–4] have shown the highest reported efficiencies to date. For these devices P3HT exhibits a desirable combination of high charge carrier mobility with relatively long wavelength absorption. The semicrystalline nature of P3HT also allows for microphase separation of the polymer from the n-type semiconductor during a thermal annealing step.[1,5] This is important in both optimising the interface between the two semiconductors to promote exciton dissociation and creating percolation pathways for charge transport. The development of polythiophene analogues that can capture more of the photon flux from the solar spectrum is one strategy to further improve photovoltaic efficiency.[6] This can be achieved by reducing the band gap of the semiconducting polymer.[7] However, an undesirable consequence with this approach can be a reduction in the open circuit voltage of the device (V_{oc}), and therefore a reduction in cell efficiency.[8] The V_{oc} in bulk heterojunction devices is derived primarily by the energy difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor.[9] Therefore strategies to reduce polymer band gap should not do so at the expense of raising the polymer HOMO level (*i.e.* the HOMO energy level should not move closer to vacuum level).

Our strategy for designing polythiophene analogues with reduced band gaps was based upon the observation that the HOMO in thiophene based oligomers and polymers has no coefficient on the sulfur heteroatom, whilst the LUMO has a significant contribution on the heteroatom.[10] We thereby reasoned that replacement of sulfur for selenium in the polymer backbone would only have a small influence on the HOMO energy level of the polymer, which would primarily result from the small difference in electronegativity between sulfur and selenium (S *vs.* Se is 2.5 *vs.* 2.4 respectively). In contrast, for the LUMO, theory predicts that the stabilising effect of the heteroatom on the LUMO can be directly related to the ionisation potential (IP) of the heteroatom,[11] such that the larger the ionisation potential of the heteroatom the smaller the stabilisation of the LUMO of the heterocycle. Since the IP of selenium is smaller than that of sulfur, we would expect the LUMO of selenophene to be lower in energy (*i.e.* further from vacuum level), and therefore poly(selenophene) to have a reduced band gap in comparison to polythiophene whilst maintaining a similar HOMO energy level, and therefore similar V_{oc} in heterojunction devices.

Poly(3-alkyl)selenophenes have been previously prepared by either electrochemical or chemical oxidation methods.[12,13] For these synthetic methods there is little control of the relative regiochemistry of the alkyl sidechains with respect to each other, and the degree of head-to-tail (HT) regioregularity (the percentage of head-to-tail alkyl couplings) is expected to be low.[14] In these cases, the polymers were reported to have similar or larger band gaps than analogous poly(3-alkyl)thiophene prepared by the same methods. This was attributed to a lack of co-planarity between selenophene rings in the backbone, which was caused by steric interactions between the larger selenium atom and neighbouring alkyl chains.[12] We reasoned the detrimental steric interactions could be reduced by the preparation of regioregular polyselenophene where the high degree of order of the alkyl sidechains could allow crystallisation of the polymer backbone.

The synthesis of regioregular poly(3-hexyl)selenophene (P3HS) is shown in Scheme 1. 3-Hexylselenophene[13] was readily dibrominated in the 2,5 positions by treatment with two equivalents of *N*-bromosuccinimide in THF to afford the product



Scheme 1 Synthetic route to poly(3-hexyl)selenophene (P3HS).

---

[a] *Merck Chemicals, Chilworth, UK.*
E-mail: martin.heeney@merckchem.co.uk; Fax: +442380763389; Tel: +44238076335
[b] *Department of Chemistry, University of Manchester, Manchester, UK M13 9PL*
[c] *Palo Alto Research Center, Palo Alto, California 94304, USA*
[d] *WestCHEM, Department of Pure & Applied Chemistry, University of Strathclyde, Glasgow, UK*
[e] *Department of Chemistry, University of Liverpool, Liverpool, UK L69 7ZD*
[f] *Department of Chemistry, Imperial College, London, UK*

† Electronic supplementary information (ESI) available: Experimental procedures, thin film X-ray, DSC and photostability data. See DOI: 10.1039/b712398a

in high yield. Polymerisation was achieved by following a similar method to the Grignard metathesis route developed for thiophene polymers.[15,16] Treatment of the monomer with 0.98 equivalents of n-butylmagnesium chloride afforded a mixture of 2-bromo-3-hexyl-5-bromomagnesio-selenophene and 2-bromomagnesio-3-hexyl-5-bromo-selenophene in a 4 : 1 ratio (as determined by GCMS analysis of a quenched sample). No bis(Grignard) product was detected. Treatment of this mixture *in situ* with a catalytic amount of Ni(dppe)Cl_2 produced the HT coupled regioregular P3HS. The crude polymer was purified by a combination of precipitation and Soxhlet extraction. The yield of the chlorobenzene soluble fraction was 70–80%. Typical weight average molecular weights (M_w) measured using GPC against polystyrene standards were in the range of 70,000 to 200,000 g mol^{-1}, depending on the catalyst and monomer concentration, with typical polydispersities around 2.

The high degree of regioregularity was confirmed by ^1H and ^{13}C spectroscopy in warm $CDCl_3$ (see ESI†). The ^{13}C NMR shows only four distinct signals in the aromatic region, attributable to the selenophene ring carbons. The ^1H NMR exhibits a clean triplet in the methylene region at 2.73 ppm, in addition to a single singlet in the aromatic region at 7.11 ppm. By analogy with P3HT,[17] the degree of regioregularity was estimated by integration of the methylene signals as greater than 97%. The fact that the selenium 77 isotope is NMR active with a spin of one half, gives an additional tool to probe the regioregularity of the polymer backbone. The ^{77}Se NMR spectrum in chloroform exhibits a single resonance at 610.61 ppm, providing additional evidence for the high degree of uniformity of the backbone.

The absorption spectra of both regioregular P3HS and P3HT in solution (chlorobenzene) and as a thin film are shown in Fig. 1. P3HS exhibits an absorption maximum at 499 nm in solution, a bathochromic shift of over 40 nm compared to P3HT. The shift is even more pronounced in the solid state, with P3HS exhibiting a maximum at 630 nm, in comparison to 550 nm for P3HT. The band gap of P3HS was estimated at 1.6 eV by the onset of the optical absorption at 760 nm, a reduction of 0.3 eV compared to P3HT. This is in contrast to regiorandom P3HS which is reported to have a larger band gap than regiorandom P3HT.[12] The observation of vibronic structure and a pronounced longer wavelength shoulder at 690 nm in the thin film is indicative of aggregation in the solid state. The photostability of thin films was also investigated in comparison to P3HT of similar M_w and regioregularity. Thus thin films of 25 nm thickness were irradiated in parallel under accelerated solar spectrum conditions in ambient air, and their absorbance spectrum recorded over time. For both polymers the intensity of λ_{max} decreases over time and slightly blue shifts, presumably as a consequence of photodegradation decreasing the conjugation length of the polymer. The ratio of the initial intensity of λ_{max} *versus* the degraded λ_{max} over time is shown in the ESI.† We find that P3HS degrades more slowly than P3HT under these conditions. Photooxidation mechanisms in P3HT are complex, but the initial step is photoexcitation of an electron from the HOMO to the LUMO to form an excited singlet state. This excited state can decay through several pathways, one of which can involve transfer of energy from the LUMO to oxygen to generate superoxide anion, which can react irreversibly with the conjugated backbone. We speculate that the lower lying LUMO of P3HS reduces the rate of this transfer, accounting for the higher photostability. P3HS was also found to exhibit good thermal stability, losing less than 5% of its weight upon heating to 350 °C, as determined with TGA under a nitrogen atmosphere.

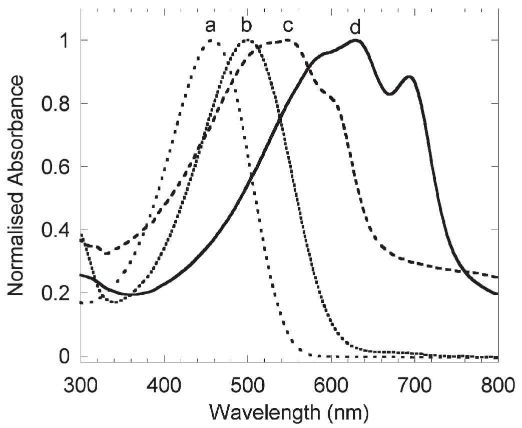


Fig. 1 UV–Vis spectra of P3HS in chlorobenzene (b) and as a thin film (d). Regioregular P3HT in chlorobenzene (a) and as a thin film (c) are shown for comparison.

The DSC thermogram of P3HS shows behaviour typical of a semi-crystalline polymer. The melt occurs at 255 °C, an increase of 15 °C compared to P3HT of similar molecular weight and polydispersity. Upon cooling a sharp, high enthalpy (16 J g^{-1}) crystallization exotherm occurs at 225 °C, indicative of a high degree of crystallinity. Grazing incidence X-ray scattering of annealed P3HS films showed sharp diffraction peaks evident of semicrystalline morphology (see ESI†). Out of plane peaks characteristic of lamellar structure were observed with a d spacing of 15.2 Å. Similar spacings have been observed in P3HT films.[4]

The ionization potential of P3HS as a thin film, determined by a UV photoelectron spectroscopic technique, was 4.8 eV, identical to the IP of P3HT measured under identical conditions.[18] The electrochemical characteristics of P3HS and P3HT films were studied by cyclic voltammetry (Fig. 2). The cyclic voltammogram revealed broad reversible oxidation and reduction peaks. The onset of the oxidation peak, E_{ox}, measured at 0 V *vs.* ferrocene, corresponds to an IP of 4.8 eV, in good agreement with the spectroscopic data. The electrochemical band gap, calculated from the onset of the reduction peak, E_{red}, at −1.8 V, was 1.9 eV, *i.e.*

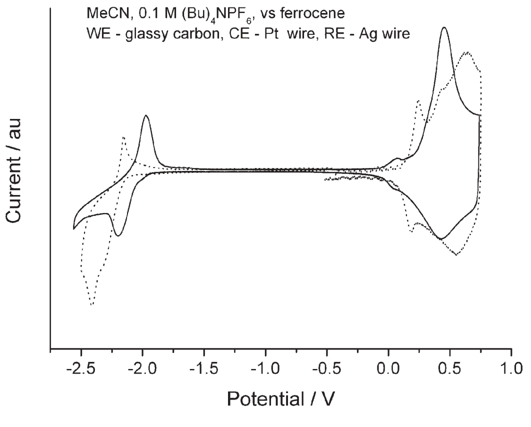


Fig. 2 Cyclic voltammetry of P3HS (solid line) and P3HT (dotted line) coated on a graphite electrode in acetonitrile containing 0.1 M Bu_4NPF_6.

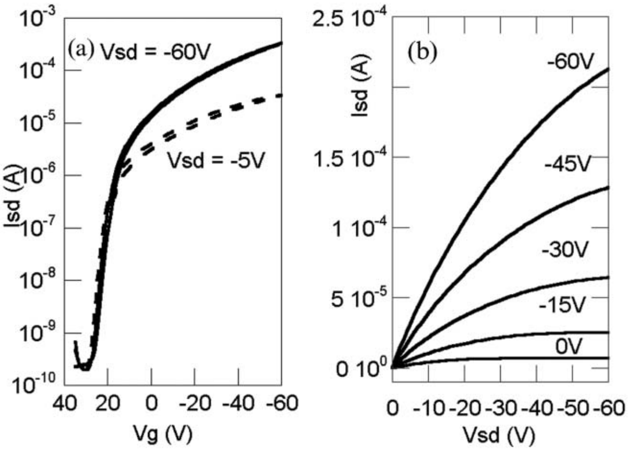


Fig. 3 Transfer and output characteristics of P3HS FET devices.

0.3 eV larger than the optical band gap. This is a common feature of conjugated polymers and may be related to structural differences in the thin film due to swelling by the solvent, or due to the exciton binding energy for conjugated polymers.[19] In comparison to P3HS, the P3HT oxidation waves are slightly shifted to more positive values (HOMO = −4.9 eV), and the LUMO is lowered significantly by 0.15 eV. The band gap of P3HT from electrochemical data was found to be 2.2 eV, in perfect agreement with the difference in optical band gaps (0.3 eV) between the two polymers. Together these results suggest the origin of the band gap reduction for P3HS is most likely due to the stabilisation of the LUMO as predicted by the frontier molecular orbital calculations.

An important aspect for efficient photovoltaic operation is that the individual components of the blend have good charge carrier properties. Thus bottom gate, bottom gold contact field effect transistors (FETs) were prepared by spin coating. The SiO_2 dielectric surface was treated with an octyltrichlorosilane solution prior to semiconductor deposition. The measurements were performed under a nitrogen atmosphere. The devices all showed classical p-type behaviour, and transfer and output characteristics are shown in Fig. 3. The devices switched on around +20 V with a current modulation of about 10^6, and exhibited low hysteresis. The saturated charge carrier mobility was typically 0.02–0.04 cm^2 (Vs)$^{-1}$ for a 10 μm channel length, with linear mobilities in the range of 0.01–0.02 cm^2 (Vs)$^{-1}$. These values were similar to those measured with P3HT devices made under similar conditions in our laboratories,[18] indicating that the inclusion of the larger, more polarisable selenium atom does not necessarily improve charge transport as had been previously observed in phenylene[20] or fluorene[21] co-polymers containing selenophene. The similarities in hole carrier mobilities for P3HS and P3HT can be rationalised by the localisation of the HOMO energy level on the carbon backbone of the polymer, rather than the heteroatoms. Since the LUMO has a significant localisation on the heteroatom we may expect to see differences in the electron mobilities for the polymers. However we were not able to observe any electron transport with these devices, possibly due to trapping at the dielectric interface[22] or to difficulties injecting electrons into the LUMO from the low workfunction gold electrodes.

In conclusion, we report the first synthesis of regioregular P3HS. The polymer exhibits attractive properties for use in both bulk heterojunction photovoltaic cells and FETs. The band gap is smaller than that of P3HT, around 1.6 eV, whilst the ionization potential is similar. In addition P3HS displays crystalline morphology which is expected to promote the nanoscale phase separation between the polymer and the n-type component that ensures effective charge separation and transport.[1,5] Detailed studies of the photovoltaic properties of P3HS/PCBM will be reported elsewhere,[23] but preliminary device data demonstrate that the cells exhibit similar V_{oc} to P3HT/PCBM cells, but with higher photocurrent due to the the enhanced spectral repsonse. Overall device efficiencies are currently similar, due to a reduced fill factor for P3HS blends.

Notes and references

1 J. Padinger, R. S. Rittberger and N. S. Sariciftci, *Adv. Funct. Mater.*, 2003, **13**, 85.
2 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864.
3 M. Reyes-Reyes, K. Kim and D. L. Carroll, *Appl. Phys. Lett.*, 2005, **87**, 083506.
4 Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha and M. Ree, *Nat. Mater.*, 2006, **5**, 197.
5 X. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, *Nano Lett.*, 2005, **5**, 579.
6 K. M. Coakley and M. D. McGehee, *Chem. Mater.*, 2004, **16**, 4533.
7 J. Roncali, *Chem. Rev.*, 1997, **97**, 173.
8 L. J. A. Koster, V. D. Mihailetchi and P. W. M. Blom, *Appl. Phys. Lett.*, 2006, **88**, 093511.
9 M. C. Scharber, D. Muhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. J. Brabec, *Adv. Mater.*, 2006, **18**, 789.
10 K. Oyaizu, T. Iwasaki, Y. Tsukahara and E. Tsuchida, *Macromolecules*, 2004, **37**, 1257.
11 H. O. Villar, P. Otto and M. Dupuis, *Synth. Met.*, 1993, **59**, 97.
12 K. Yoshino, M. Onoda, Y. Manda, K. Sawada, R.-I. Sugimoto and S. Inoue, *Jpn. J. Appl. Phys.*, 1989, **28**, L138.
13 C. Mahatsekake, J. M. Catel, C. G. Andrieu, M. Ebel and Y. Mollier, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1990, **47**, 35.
14 R. McCullough, *Adv. Mater.*, 1998, **10**, 93.
15 R. S. Loewe, S. M. Khersonsky and R. D. McCullough, *Adv. Mater.*, 1999, **11**, 250.
16 R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001, **34**, 4324.
17 T.-A. Chen, X. Wu and R. D. Rieke, *J. Am. Chem. Soc.*, 1995, **117**, 233.
18 I. McCulloch, C. Bailey, M. Giles, M. Heeney, I. Love, M. Shkunov, D. Sparrowe and S. Tierney, *Chem. Mater.*, 2005, **17**, 1381.
19 I. H. Campbell, T. H. Hagler, D. L. Smith and J. P. Ferraris, *Phys. Rev. Lett.*, 1996, **76**, 1900.
20 D. J. Crouch, P. J. Skabara, J. E. Lohr, J. J. W. McDouall, M. Heeney, I. McCulloch, D. Sparrowe, M. Shkunov, S. J. Coles, P. N. Horton and M. B. Hursthouse, *Chem. Mater.*, 2005, **17**, 6567.
21 Y. M. Kim, E. Lim, I.-N. Kang, B.-J. Jung, J. Lee, B. W. Koo, L.-M. Do and H.-K. Shim, *Macromolecules*, 2006, **39**, 4081.
22 L.-L. Chua, J. Zaumseil, J. F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus and R. H. Friend, *Nature*, 2005, **434**, 194.
23 A. M. Ballantyne, L. Chen, J. Nelson, D. D. C. Bradley, Y. Astuti, J. R. Durrant, M. Heeney, W. Duffy, I. McCulloch and W. Zhang, *Adv. Mater.*, in press.