

Poly(2,3-dihexylthieno[3,4-*b*]pyrazine). A New Processable Low Band-gap Polyheterocycle

Martin Pomerantz,* Benjamin Chaloner-Gill, Larry O. Harding, John J. Tseng and Wendy J. Pomerantz

Center for Advanced Polymer Chemistry, Department of Chemistry, Box 19065, The University of Texas at Arlington, Arlington, Texas, 76019, USA

A new soluble, low band-gap polymer, poly(2,3-dihexylthieno[3,4-*b*]pyrazine) **2b**, which is dark blue–black in the neutral state and which becomes transparent light yellow when doped has been prepared; it has a doped film conductivity of $3.6 \times 10^{-2} \text{ S cm}^{-1}$ and a band-gap (film) of *ca.* 0.95 eV making it one of the lowest band-gap polymers prepared to date.

Highly conjugated organic polymers that can be made electronically conducting have been of interest to scientists for a number of years. These systems are generally highly coloured in the neutral, non-conducting state and upon doping, typically oxidatively, new electronic states are formed resulting in shifts in the optical absorptions to longer wavelength. This means that oxidatively doped conducting polymers are generally even more highly coloured and opaque than their neutral counterparts. There has been considerable effort recently to find low band-gap ‘transparent’ conducting polymers, that is, systems which absorb less visible light in the doped conducting state than in the neutral non-conducting state. This was initiated by the report in 1984 by Wudl *et al.*¹ that poly(isothianaphthene) **1a** {poly(benzo[*c*]thiophene)} was a low band-gap dark blue–black polymer, which became greenish-yellow and ‘transparent’ upon doping.² The band-gap of the film was shown to be about 1.0–1.1 eV.^{1–3} Unfortunately **1a** is not particularly soluble,⁴ does not melt below its decomposition temperature and so cannot easily be processed.

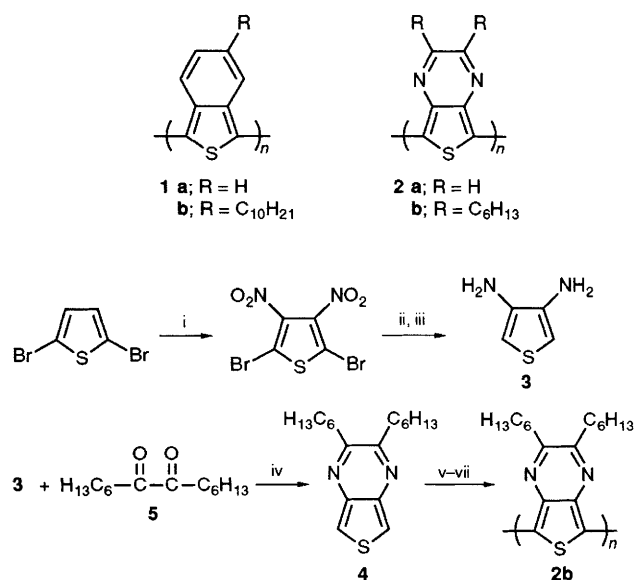
The current interest in low band-gap polymers coupled with the paucity of reports of processable systems, prompts us to report our results on a new processable low band-gap polymer, poly(2,3-dihexylthieno[3,4-*b*]pyrazine) **2b**. We chose this system since, first, recent theoretical calculations suggested a lower band-gap for the parent poly(thieno[3,4-*b*]pyrazine) **2a** (0.70 eV) than for the parent **1a** (0.80 eV)⁵ and second, the alkyl groups would render the material soluble in typical organic solvents and therefore processable.⁶

Interestingly, the theoretical calculations (see ref. 5 and references cited therein) for poly(isothianaphthene) **1a** sug-

gested that the planar quinoid form was more stable than the aromatic form [by *ca.* 2.4 kcal per unit chain length (1 cal = 4.184 J)] and that the backbone of the aromatic form was twisted. The band-gaps for the quinoid form and the twisted aromatic form were calculated to be 0.80 and 1.64 eV, respectively.⁵ On the other hand, for the parent poly(thieno[3,4-*b*]pyrazine) **2a** the planar quinoid form was 4.2 kcal per unit chain length more stable than the aromatic form which in this case was also planar. The band-gaps for the quinoid and aromatic forms were calculated to be 0.70 and 0.12 eV, respectively.

The monomer, 2,3-dihexylthieno[3,4-*b*]pyrazine **4**, was prepared as shown in Scheme 1. It involved preparation of 3,4-diaminothiophene **3** by a multiple, one-pot reduction of 2,5-dibromo-3,4-dinitrothiophene,^{7a} which was then condensed with tetradecane-7,8-dione **5**,⁸ following the procedure described in the literature.^{7b} Spectroscopic data and elemental analysis were in full accord with the structure.

Polymerization of monomer **4** was carried out in CHCl_3 solution using FeCl_3 in the presence of dry air (Scheme 1).^{9,10} After washing and dedoping with hydrazine hydrate, the resulting black powder was dissolved in chloroform and dialysed (M_w cutoff 3500) against chloroform. After precipitation from methanol, poly(2,3-dihexylthieno[3,4-*b*]pyrazine) **2b** was obtained as a dark blue–black powder which was soluble in a number of organic solvents such as CHCl_3 . The elemental analysis as well as the spectral properties of **2b** agreed with the structure. Thus, the strong bands present in the IR spectrum of the monomer **4** at 3072 and 3054 cm^{-1} were absent in the polymer **2b** indicating that the aromatic C–H bonds had reacted. In addition, the ^1H NMR spectral peak at δ 7.80 in the monomer **4** was absent in the polymer **2b** and the remaining peaks due to the hexyl groups were rather broad. The ^{13}C NMR spectrum of **2b** showed the hexyl carbons broadened somewhat compared to the monomer and the aromatic peaks were extremely broad. Even after prolonged treatment with hydrazine or ammonia in an effort to completely dedope the polymer, an EPR signal was observed indicating that the material was paramagnetic. This para-



Scheme 1 Reagents and conditions: i, fuming HNO_3 , fuming H_2SO_4 , 20–30 °C; ii, Sn , HCl , 30 °C then 0 °C; iii, 4 mol dm^{-3} NaOH –diethyl ether; iv, diethyl ether– MeOH , reflux, followed by TLC; v, FeCl_3 , CHCl_3 , dry air, 50 °C, 3 days; vi, N_2H_4 – H_2O ; vii, dialysis in CHCl_3 (M_w cutoff 3500) and precipitation with MeOH

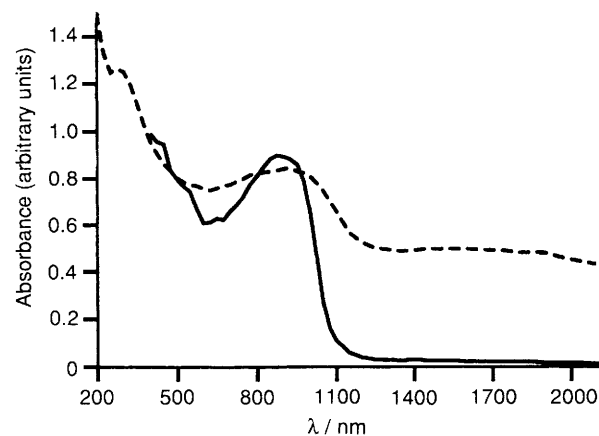


Fig. 1 UV-VIS-NIR spectra of **2b** in chloroform solution (—) and as a film (---)

magnetism would explain the broad peaks in the NMR spectrum.

Thermogravimetric analysis under N₂ showed the onset of decomposition at about 230 °C with approximately 50% weight loss at 600 °C while under O₂ the onset of decomposition was about 190 °C with approximately 90% weight loss at 600 °C. Differential scanning calorimetry (DSC) between -80 and 200 °C showed no observable phase transitions.

The UV-VIS-NIR spectrum showed λ_{max} (CHCl₃ solution) at 875 nm with the band-gap (band edge) at 1.14 eV (Fig. 1). A film of this polymer **2b** showed the expected bathochromic shift (see e.g. ref. 6), λ_{max} = 287 and 915 nm, with the band-gap (band edge) of the latter between 0.86–1.02 eV (Fig. 1). The uncertainty is due to the observation that the baseline did not return to zero above 1300 nm (to 2100 nm) presumably owing to scattering of the film. The band-gap of the film of 0.95 ± 0.1 eV agrees quite well with the value calculated for the planar quinoid form (0.70 eV)⁵ and is lower than that for poly(isothianaphthene) **1a** [or poly(5-decylisothianaphthene) **1b** which we have also recently prepared]¹¹ as predicted.⁵ This means that this polymer is one of the lowest band-gap conjugated polymers prepared to date.

Doping of a dark blue-black chloroform solution with nitrosonium tetrafluoroborate (22% per monomer unit) afforded a light-yellow solution of the doped polymer with a UV-VIS-NIR absorption at about 1600 nm. Upon further doping with additional NOBF₄ the absorption shifted to somewhat shorter wavelength and then, with considerably more dopant, a new peak with a maximum >2100 nm began to appear, perhaps signaling over oxidation. The absorption of the undoped polymer at 875 nm initially diminished and moved to somewhat shorter wavelength and on continued doping disappeared.

The material that had been doped with NOBF₄ in solution could be cast into films (ca. 2–7 μm thick). Four-probe

conductivity measurements of these films provided conductivities, σ , of up to $3.6 \times 10^{-2} \text{ S cm}^{-1}$.

In summary, we have prepared a new low band-gap polymer, poly(2,3-dihexylthieno[3,4-*b*]pyrazine) **2b**, which is dark blue-black in the neutral state and becomes transparent light yellow when doped. It has a band-gap of ca. 0.95 eV (film), making it one of the lowest band-gap polymers prepared to date, and the doped film has a conductivity of $3.6 \times 10^{-2} \text{ S cm}^{-1}$.

Financial support through grants from the Defense Advanced Research Projects Agency monitored by the Office of Naval Research and the Robert A. Welch Foundation is gratefully acknowledged. We also thank Professor Ronald L. Elsenbaumer for technical help.

Received, 27th July 1992; Com. 2/04010G

References

- 1 F. Wudl, M. Kobayashi and A. J. Heeger, *J. Org. Chem.*, 1984, **49**, 3382.
- 2 M. Kobayashi, N. Colaneri, M. Boysel, F. Wudl and A. J. Heeger, *J. Chem. Phys.*, 1985, **82**, 5717.
- 3 Y. Ikenoue, F. Wudl and A. J. Heeger, *Synth. Met.*, 1991, **40**, 1.
- 4 P. Chandrasekhar, A. M. Masulaitis and R. W. Gumbs, *Synth. Met.*, 1990, **36**, 303.
- 5 K. Nayak and D. S. Marynick, *Macromolecules*, 1990, **23**, 2237.
- 6 J. R. Reynolds and M. Pomerantz, in *Electroresponsive Molecular and Polymeric Systems*, ed. T. A. Skotheim, Marcel Dekker, New York, 1991, vol. 2, ch. 4, pp. 187–256.
- 7 (a) F. Outurquin and C. Paulmier, *Bull. Soc. Chim. Fr.*, **II**, 1983, 153; (b) *II*, 1983, 159.
- 8 N. S. Srinivasan and D. G. Lee, *J. Org. Chem.*, 1979, **44**, 1574.
- 9 M. Pomerantz, J. J. Tseng, H. Zhu, S. J. Sproull, J. R. Reynolds, R. Uitz, H. J. Arnott and M. I. Haider, *Synth. Met.*, 1991, **41**, 825.
- 10 K.-Y. Jen and R. Elsenbaumer, *Synth. Met.*, 1986, **16**, 379.
- 11 J. J. Tseng and M. Pomerantz, unpublished observations. The band-gap of the film is ca. 1.0–1.3 eV.