

Unsaturated polymers containing boron and thiophene units in the backbone

Robert J.-P. Corriu,^{*a} Thomas Deforth,^a William E. Douglas,^{*a†} Gilles Guerrero^a and Walter S. Siebert^{*b}

^a CNRS UMR 5637, Université Montpellier II, 34095 Montpellier cedex 5, France

^b Anorganisch-Chemisches Institut der Universität, 69120 Heidelberg, Germany

2,5-Dialkynylthiophenes (RC≡C)₂C₄H₂S (R = Ph, Me₃Si or Bu^t) treated successively with HBCl₂ and Et₃SiH in CH₂Cl₂ undergo hydroboration polymerization to give intensely coloured polymers of general structure $-\text{[CH=CR-BCl-CR=CH-C}_4\text{H}_2\text{S]}_n-$ for which the ¹¹B NMR resonances occur *ca.* 50 ppm upfield of those for analogous monomers.

Polythiophenes are important conjugated electroactive polymers. They possess interesting optical and electrical properties, and have many potential applications, for example in energy storage, electrochromic devices and electrochemical sensors.¹ Several of these effects depend on the nature and extent of doping of the polythiophene, usually with electron acceptors. We report here the synthesis by hydroboration polymerization of unsaturated polymers containing both thiophene and boron units. It was expected that such polymers possessing both electron-donor (sulfur) and electron-acceptor (boron) sites would show interesting properties, the boron with a vacant 2p orbital being available to act as an *in situ* electron-acceptor dopant.

Hydroboration polymerization has been previously described for polyaddition between thexylborane–dimethyl sulfide complex and either dienes² (affording saturated organoboron polymers) or diynes³ (giving unconjugated unsaturated organoboron polymers). The hydroboration polymerization of dienes has also been performed with monobromoborane–dimethyl sulfide complex to give functional organoboron polymers.⁴ However, for all these polymers the boron 2p orbitals are occupied because of the presence of the dimethyl sulfide donor ligand. We describe here the preparation of analogous polymers containing thiophene and alkene units in which the boron 2p orbital remains vacant.

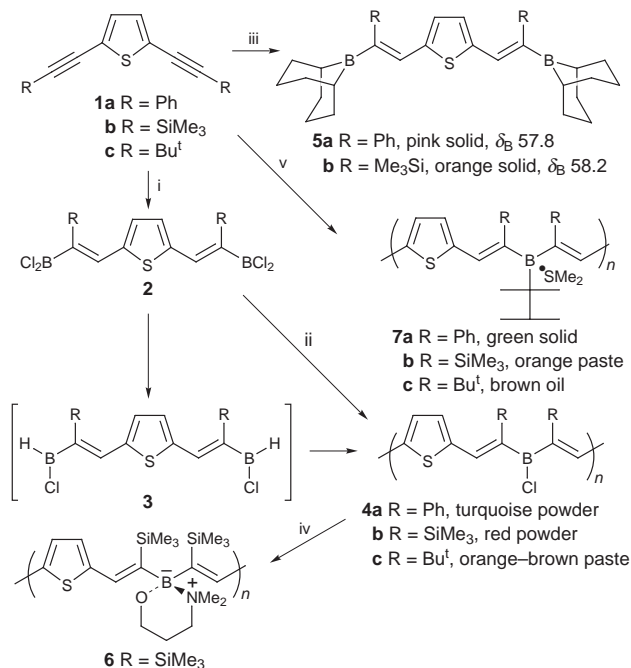
The starting diynes **1a**,⁵ **1b**⁶ [$\nu(\text{C}\equiv\text{C})$ 2146 cm⁻¹ (CCl₄)] and **1c** [$\nu(\text{C}\equiv\text{C})$ 2220 cm⁻¹ (CCl₄)], which were synthesized from 2,5-dibromothiophene and the corresponding alkynylzinc reagent RC≡CZnCl, undergo hydroboration with HBCl₂ (formed *in situ* from BCl₃ and Et₃SiH⁷) at -80 °C to give the bis(dichloroborane) derivatives **2** in 60–70% yield (Scheme 1). Subsequent reduction of **2** with Et₃SiH in the presence of additional diyne **1** gives the corresponding polymers **4**, most probably by hydroboration polymerization of intermediate bis(monochloroborane) derivatives **3** (Scheme 1).[†] The polymers are highly sensitive to oxygen and water and so far it has not been possible to obtain either satisfactory UV–VIS spectra or consistent molecular weight data by size exclusion chromatography (SEC) because of the very dilute nature of the solutions required in both cases. However, the SEC chromatograms show a component of molecular weight in excess of 100 000, which is possibly an overestimate since it was determined using polystyrene calibrants. The polymer colour is strongly dependent on the substituent R groups, being turquoise in the case of phenyl substituents (**4a**), red for trimethylsilyl groups (**4b**), and green for the homologue containing both phenyl and trimethylsilyl substituents.

The ¹¹B NMR resonance for the polymers in CDCl₃ solution occurs at δ_{B} 6–7 (e.g. **4a**: δ_{B} 6.5), about 50 ppm upfield of the resonance for **2** (δ_{B} 53) or chlorodivinyllborane (δ_{B} 56).⁸ These remarkable properties suggest the existence of electronic

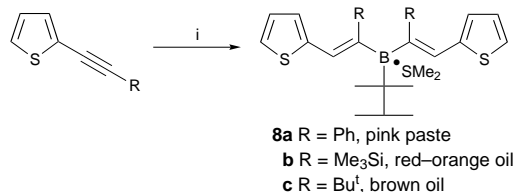
interactions between the boron and thiophene groups along the polymer chain. Further support for this interpretation is provided by the contrasting properties of model monomers **5a** and **5b** prepared by hydroboration of **1a** and **1b**, respectively, with 9-borabicyclo[3.3.1]nonane (9-BBN) in THF solution (Scheme 1). The model monomers are pale-coloured solids exhibiting ¹¹B NMR resonances around δ_{B} 58 as expected.⁸ The formation of all three structural isomers for each model monomer **5** is to be expected since the reaction of 9-BBN with alkynes is known to be of low regioselectivity.⁹

The polymers **4** can be stabilized by transformation of the boron chloro functional group. Thus, treatment of **4b** with 3-dimethylaminopropan-1-ol in toluene under reflux afforded **6** as a red paste in 80% yield. SEC indicates that **6** is an oligomer of about 8 units and therefore polymer degradation has occurred during the synthesis. The ¹¹B NMR resonance at δ_{B} 2.8 lies in the region expected for amine adducts,⁸ the boron 2p orbital being occupied.

Treatment of **1a–c** with thexylborane–dimethyl sulfide complex in CH₂Cl₂ in the presence of (PPh₃)₂PdCl₂ affords, respectively, polymers **7a–c** (Scheme 1), this borane reagent being known to give linear polymers with internal diynes.³ The ¹¹B NMR resonances (δ_{B} 18–19) lie in the region expected for dimethyl sulfide adducts.⁸ The boron 2p orbital is occupied and the colours are less intense than those of **4**. SEC showed that **7b** is an oligomer of 25 units with a polydispersity index of 3.7 (polystyrene calibrants). For comparison, the analogous model



Scheme 1 Reagents and conditions: i, BCl₃, Et₃SiH, CH₂Cl₂, -78 to -40 °C; ii, **1**, Et₃SiH, -50 °C to room temp.; iii, 9-BBN, Pt(PPh₃)₄, THF, -78 to 65 °C; iv, Me₃N(CH₂)₃OH, PhMe, 110 °C; v, thexylborane–Me₂S, (PPh₃)₂PdCl₂, CH₂Cl₂, -78 °C to room temp. Only one of the various possible structural isomers is shown in each case.



Scheme 2 Reagents and conditions: i, hexylborane–Me₂S, CH₂Cl₂, –78 °C to room temp. Only one of the three possible structural isomers is shown.

monomers **8a–c** were made starting from the corresponding monoalkynylthiophene (Scheme 2). The change in colour, corresponding to an absorption red-shift, on going from the model monomers **8a** and **8b** to the polymers **7a** and **7b** indicates the presence of some additional electron delocalization in the polymers. However, the extent must be slight since the ¹¹B NMR chemical shifts for the model monomers are essentially the same as those for the polymers. This is in contrast to the case of the intensely-coloured polymers **4** with an empty boron 2p orbital, for which an ¹¹B NMR upfield shift of ca. 50 ppm is observed (*vide supra*). Work is in progress on the synthesis by hydroboration polymerization of more stable analogues of **4**.

The European Commission is thanked for a fellowship awarded to T. D. under contract no. ERBCHBGCT940539 of the Human Capital and Mobility (Institutional Fellowships) Programme. Financial support from the Deutsche Forschungsgemeinschaft (SFB 247) and the Alexander von Humboldt Stiftung (to R. J.-P. C.) is gratefully acknowledged.

Notes and References

† E-mail: douglas@crit.univ-montp2.fr

‡ Polymers **4a–c** were prepared using the following one-pot procedure. A solution of BCl₃ in CH₂Cl₂ at –78 °C was treated dropwise with a CH₂Cl₂ solution containing Et₃SiH (2 equiv.) and the starting diyne **1** (0.5 equiv.). Addition of 50% of the latter Et₃SiH/diyne solution resulted in formation of the bis(dichloroborane) intermediate **2**. At this stage excess BCl₃ was removed from the reaction mixture *in vacuo* (5 min at –78 °C followed by 5 min at –40 °C) and addition of the Et₃SiH/diyne solution was then resumed at –50 °C. After addition was complete the reaction mixture was allowed to warm to room temperature overnight, becoming intensely coloured, and the polymers were isolated by removal of the solvent.

- 1 J. Roncali, *Chem. Rev.*, 1992, **92**, 711.
- 2 Y. Chujo, I. Tomita, Y. Hashiguchi, H. Tanigawa, E. Ihara and T. Saegusa, *Macromolecules*, 1991, **24**, 345.
- 3 Y. Chujo, I. Tomita, Y. Hashiguchi and T. Saegusa, *Macromolecules*, 1992, **25**, 33.
- 4 Y. Chujo, N. Takizawa and T. Sakurai, *J. Chem. Soc., Chem. Commun.*, 1994, 227.
- 5 F. Freeman and D. S. H. L. Kim, *J. Org. Chem.*, 1992, **57**, 1722.
- 6 D. R. Rutherford, J. K. Stille, C. M. Elliott and V. R. Reichert, *Macromolecules*, 1992, **25**, 2294.
- 7 R. Soundarajan and D. S. Matteson, *Organometallics*, 1995, **14**, 4157.
- 8 H. Nöth and B. Wrackmeyer, in *NMR Basic Principles and Progress; Vol. 14, Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*, ed. P. Diehl, E. Fluck and R. Kosfeld, Springer-Verlag, Berlin, 1978.
- 9 A. Pelter, K. Smith, D. Buss and A. Norbury, *Tetrahedron Lett.*, 1991, **32**, 6239.

Received in Liverpool, UK, 26th January 1998; 8/00690C