

Synthesis and characterization of N-t-BOC protected pyrrole-sulfur oligomers and polymers

Citation for published version (APA):

Groenendaal, L., Pieterse, K., Vekemans, J. A. J. M., & Meijer, E. W. (1997). Synthesis and characterization of N-t-BOC protected pyrrole-sulfur oligomers and polymers. *Synthetic Communications*, 27(2), 257-266.
<https://doi.org/10.1080/00397919708005026>

DOI:

[10.1080/00397919708005026](https://doi.org/10.1080/00397919708005026)

Document status and date:

Published: 01/01/1997

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

SYNTHESIS AND CHARACTERIZATION OF *N-t*-BOC PROTECTED PYRROLE-SULFUR OLIGOMERS AND POLYMERS

L. Groenendaal, K. Pieterse, J.A.J.M. Vekemans, and E.W. Meijer*

Laboratory of Organic Chemistry

Eindhoven University of Technology

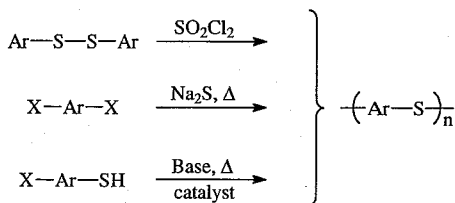
P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Abstract: The synthesis and characterization of a new class of pyrrole-sulfur compounds is described. These compounds are designed to be precursors for an organic analogue of poly(sulfur nitride). Poly(*N-t*-BOC-2,5-pyrrolyl sulfide) was prepared from *N-t*-BOC-2,5-dibromopyrrole by first lithiating this compound with *n*-BuLi, followed by the addition of bis(*p*-tosyl) sulfide. Similarly, bis(*N-t*-BOC-2-pyrrolyl) sulfide was prepared starting from *N-t*-BOC-2-bromopyrrole. Subsequent selective oxidation with one or two equivalents of *m*-CPBA quantitatively gave bis(*N-t*-BOC-2-pyrrolyl) sulfoxide and -sulfone, respectively. Thermal deprotection of the *t*-BOC groups of the oligomers and the polymer resulted in decomposition of these compounds; the latter is presumably due to a combination of sulfur-extrusion and polymerization.

Introduction

During the past decades polyarene sulfides have become a topic of research. This interest relies on the expectation that these combined organic/inorganic polymers may exhibit interesting properties, including electronic conductivity. Two well-known examples are poly(*p*-phenylene sulfide) (PPS)^{1,2} and poly(2,5-thienyl sulfide) (PTS).³ PPS is a widely

* To whom correspondence should be addressed



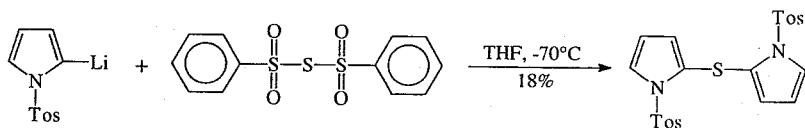
Scheme 1: Synthetic routes towards polyarene sulfides (X = halogen).

used nonrigid and processable engineering polymer that possesses in the undoped form good insulator properties (electronic conductivity $\sigma = 10^{-16} \text{ Scm}^{-1}$). However, when doped, conductivities of $\sigma = 1 \text{ Scm}^{-1}$ can be obtained in pressed pellets¹, whereas in AsF₅-doped PPS films, casted from a AsF₃ solution, values as high as $\sigma = 200 \text{ Scm}^{-1}$ have been reported for this polymer.² PTS, a heteroaromatic polymer, has also been investigated for its conducting and optical properties.³ Here, conductivities up to $\sigma = 2 \times 10^{-5} \text{ Scm}^{-1}$ have been obtained upon doping with I₂.

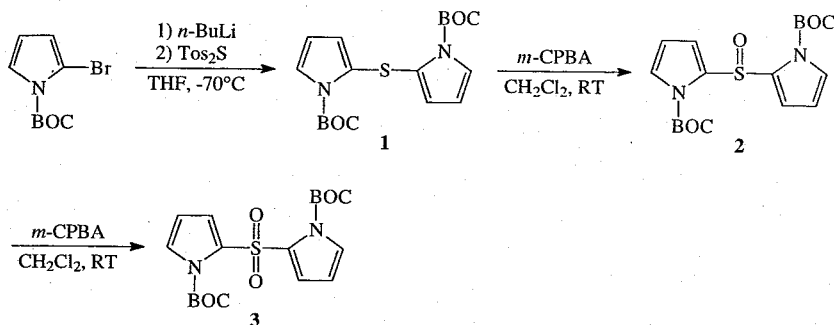
Polyarene sulfides can be prepared by a number of strategies. Well-known are the reaction between a diaryl disulfide and sulfuryl chloride⁴, the condensation of a (hetero)aromatic dihalide with Na₂S^{3,5} and the self-condensation of a halogenated (hetero)aromatic thiol⁶ (Scheme 1).

Up to now, no reports have been published on the synthesis of pyrrole-sulfur polymers. These polymers might be regarded as precursors for organic analogues of poly(sulfur nitride). Since we are interested in the electronic properties of such a polymer, new routes towards this polymer have been investigated. Unfortunately, the strategies as used for PPS and PTS (scheme 1) are not or only partially applicable for pyrroles. The high reactivity of the electron-rich pyrrole ring towards electrophiles prevents the use of reagents such as SO₂Cl₂, unless the ring carries several substituents, including electron-withdrawing groups.⁷ The well-known instability of pyrrole thiols⁸ on the one hand, and the reluctance of pyrrole to undergo nucleophilic substitutions, on the other hand, prevent reactions between thiolates and halogenated pyrroles.

In this paper we will discuss the synthesis and characterization of poly(N-*t*-BOC-2,5-pyrrolyl sulfide) (4) and bis(N-*t*-BOC-2-pyrrolyl) sulfide (1), the smallest pyrrole-sulfur oligomer. Therefore, we adapted a method developed by Berlin *et al.*⁹, who were the first and



Scheme 2: Synthesis of *N*-protected bis(2-pyrrolyl) sulfide as reported by Berlin et al.⁹

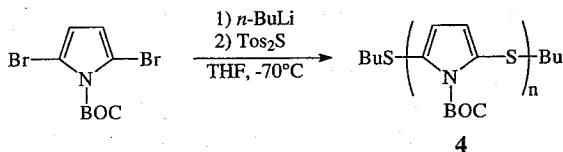


Scheme 3: Synthesis of bis(*N*-*t*-BOC-2-pyrrolyl) sulfide, -sulfoxide and -sulfone.

only to prepare an *N*-protected bis(2-pyrrolyl) sulfide up to now (Scheme 2). Their method consisted of a reaction between a lithiopyrrole and bis(phenylsulfonyl) sulfide in THF at -70°C , giving the desired product in 18% yield. Our adapted strategy makes use of the *t*-BOC protecting group^{10,11} in combination with α -brominated pyrrole derivatives. Furthermore, we synthesized the sulfur-oxidized representatives of compound **1**, being *N*-*t*-BOC protected bis(2-pyrrolyl) sulfoxide (**2**) and -sulfone (**3**), and investigated the deprotection of all synthesized structures.

Results

The synthesis of bis(*N*-*t*-BOC-2-pyrrolyl) sulfide (**1**) started from *N*-*t*-BOC-2-bromopyrrole, which, in itself, was prepared by the stannyl-bromo exchange reaction.¹² The latter was first selectively α -lithiated with *n*-BuLi in THF at -70°C , and then treated with 0.5 eq. of bis(*p*-tosyl) sulfide (Tos_2S) (Scheme 3). After work-up procedures and subsequent distillation, in order to remove low-boiling impurities, pure **1** was obtained as a dark oil (yield



Scheme 4: The synthesis of poly[(*N-t*-BOC-2,5-pyrrolyl) sulfide].

96%). Attempts to transform this oil into a more convenient appearance by decoloration with activated carbon and subsequent precipitation in methanol, yielded **1** as a slightly orange solid; however, a significant amount of material was lost.

A similar strategy towards bis(*N-t*-BOC-2-pyrrolyl) sulfoxide (**2**), using thionyl chloride instead of the sulfurating agent Tos_2S , resulted in a mixture containing **2** and a number of by-products. Therefore, purification by column chromatography was necessary, which finally gave pure **2** in 52% yield. In order to increase the yield an alternative route towards **2** was investigated: oxidation of **1** (Scheme 3). Using one equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 , resulted in the quantitative formation of bis(*N-t*-BOC-2-pyrrolyl) sulfoxide (**2**) within one hour. Similarly, **2** could be transformed into bis(*N-t*-BOC-2-pyrrolyl) sulfone (**3**) although this oxidation step proceeds significantly slower. All three compounds were fully characterized (NMR (^1H and ^{13}C), UV-Vis, IR, elemental analysis). Attempts to deprotect these compounds by thermolysis¹³ or under acidic conditions¹⁴, resulted in polymerization and sulfur-extrusion, a phenomenon earlier observed for sulfur-containing porphyrins.¹⁵

N-t-BOC protected poly(pyrrolyl sulfide) was prepared in a similar fashion as described for **1**, starting from *N-t*-BOC-2,5-dibromopyrrole.^{10,16} This compound was first lithiated at the α -positions using *n*-BuLi in THF at -70°C , after which an equimolar amount of Tos_2S was added (scheme 4). From NMR analysis of the obtained dark oil it was deduced that this oil contained *n*-butyl sulfide terminated oligomers (**4**), which is in agreement with the use of an excess of *n*-BuLi. The smaller oligomers were separated by column chromatography over silica gel, eluting with a gradient of dichloromethane/hexane (1:3) to pure dichloromethane. In order to isolate the higher molecular weight oligomers, the column was flushed with chloroform. The fractions were characterized (^1H - and ^{13}C -NMR) and size exclusion chromatographic (SEC) analyses were performed on these fractions as well as on the crude oil (Figure 1). Deprotection of these fractions by thermolysis resulted in the formation of insoluble black solids, presumably due to polymerization and sulfur-extrusion.

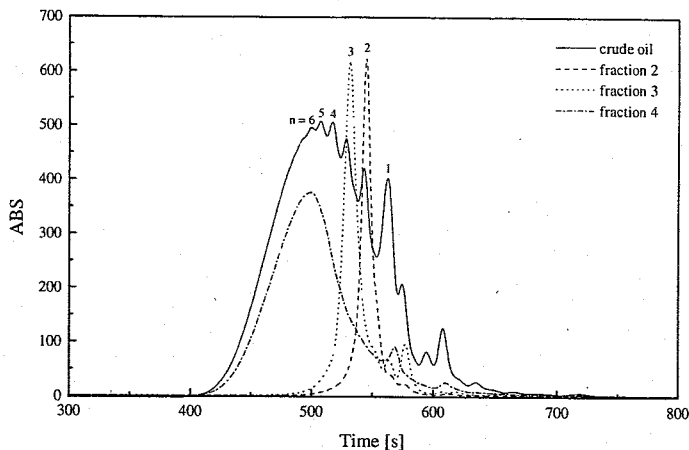


Figure 1: SEC spectra of the crude oil and the fractions 2,3 and 4.

Discussion

Adaptation of the strategy developed by Berlin⁹, has opened the way to new pyrrole-sulfur compounds. Since selective α -lithiation of *N-t*-BOC-2-bromopyrrole with *n*-BuLi proceeds much easier, bis(*N-t*-BOC-2-pyrrolyl) sulfide (**1**) can be prepared in favorable yields as compared to Berlin's bis(*N*-tosyl-2-pyrrolyl) sulfide (96% vs. 18%). This is most probably due to the higher stability of the *t*-BOC group. With this simple adaptation, we were able to synthesize poly[*(N-t*-BOC-2,5-pyrrolyl) sulfide] (**4**) starting from *N-t*-BOC-2,5-dibromopyrrole.

Oxidation of bis(*N-t*-BOC-2-pyrrolyl) sulfide (**1**) with one or two equivalents of *m*-CPBA, gives the sulfoxide (**2**) and sulfone (**3**) analogues in quantitative yields, respectively. ¹H-NMR spectroscopy of **2** shows an unusual appearance for the signal attributed to H-3 (Figure 2): instead of a sharp double doublet, a broad singlet is observed.

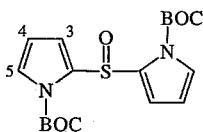


Figure 2: Bis(*N-t*-BOC-pyrrolyl) sulfoxide.

This is presumably caused by a limited rotational freedom of the pyrrole unit around its carbon-sulfur bond. Upon heating of the NMR sample, the H-3 signal gradually changes into the expected double doublet

whereas on cooling new peaks emerge, indicating the presence of several conformations. In contrast, sulfone **3** does not show any broadening of the H-3 signal but a sharp double doublet

at room temperature. This can be explained by the symmetry of the sulfone group compared to the asymmetry of the sulfoxide group.

Despite the fact that the synthesis and isolation of the first series of N-protected pyrrole-sulfur models and polymers is now well under control, deprotection of the N-*t*-BOC group is not possible with the compounds made here. The inherent instability of the electron-rich molecules hampers the isolation of the unprotected models and polymer, since polymerization and sulfur extrusion occur during removal of the *t*-BOC groups. Even the sulfoxide and sulfone model compounds decompose upon deprotection. Since the *t*-BOC group is regarded as one of the most subtle protecting groups for pyrrole, the synthesis of the parent poly(2,5-pyrrolyl sulfide) seems to be difficult.

Conclusions

The synthesis of pyrrole-sulfur compounds was accomplished by adapting the strategy developed by Berlin *et al.*⁹ Using the N-*t*-BOC protecting group and α -brominated pyrrole derivatives, the synthesis and characterization of the first pyrrole-sulfur polymer, being poly(N-*t*-BOC-2,5-pyrrolyl sulfide), was achieved. The N-*t*-BOC group also allows the oxidation of bis(N-*t*-BOC-2-pyrrolyl) sulfide into its corresponding sulfoxide and sulfone. In order to transform the polymer into an organic analogue of the well-known poly(sulfur nitride), removal of the *t*-BOC protecting groups is required. Since deprotection of the new compounds by thermolysis or under acidic conditions was unsuccessful, due to the inherent instability of these pyrrole-sulfur compounds, we are now focusing our attention on other pyrrole-sulfur polymers. It is expected that the polymerization, as presented here, can also be used for a large variety of other polymers with both a sulfide and a pyrrole unit in the main chain.

Experimental

Tetrahydrofuran (THF) was distilled over sodium/benzophenone prior to use. For column chromatography Merck silica gel 60 and Merck aluminum oxide 90 (activity II-III, additionally deactivated before use with 7 w% of water) were used. ¹H and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer at frequencies of 400.1 (¹H) and 100.6 (¹³C) MHz, respectively, using tetramethylsilane (TMS) as internal standard. UV-Vis spectra were recorded on a Perkin-Elmer Lambda 3B spectrophotometer, whereas infrared spectra were

recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Size Exclusion Chromatography (SEC) was performed on a PLgel 5 μ m 500Å column, using chloroform as eluent (flow rate of 1.0 ml/min) and UV detection at 254 nm.

Bis(*N*-*tert*-butoxycarbonyl-2-pyrrolyl) sulfide (1): *N*-*t*-BOC-2-bromopyrrole (2.72 g, 11.1 mmol) was dissolved in THF (40 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 7.5 ml, 12 mmol) was slowly added after which the solution was stirred for 15 min at -70°C. Then bis(*p*-tosyl) sulfide (1.89 g, 5.52 mmol) was added in small portions and the mixture was stirred for another 15 min at -70°C. The mixture was allowed to warm to RT, poured into water (200 ml) and extracted with Et₂O (3 × 80 ml). The combined organic fractions were washed with 0.25 M Na₂CO₃-solution (150 ml) and water (2 × 150 ml), dried (MgSO₄), filtered and concentrated, yielding a black oil (2.18 g). Distillation by means of Kügelrohr (100°C, 0.2 mbar, 1 h) removed all volatile impurities, whereas the residual black oil contained pure **1** (1.94 g, 5.32 mmol, 96%).

Decoloration with activated carbon and precipitation in methanol, yielded **1** as a slightly orange solid (0.84 g, 2.30 mmol, 42%). M.p. = 88-89°C.

¹H-NMR (CDCl₃): δ 7.37 (dd, *J* = 3.5 and 1.9 Hz, 2H, H-5), 6.16 (t, *J* = 3.4 Hz, 2H, H-4), 5.98 (dd, *J* = 3.5 and 1.9 Hz, 2H, H-3), 1.51 (s, 18H, H-methyl). ¹³C-NMR (CDCl₃): δ 148.9 (C=O), 124.7 (C-2), 123.2 (C-5), 117.7 (C-3), 111.2 (C-4), 84.4 (C-q (BOC)), 27.8 (C-methyl). UV (CH₃CN): λ_{\max} = 228 nm. IR (KBr): ν = 2977, 2934, 1758, 1733, 1455, 1394, 1370, 1336, 1318, 1284, 1154, 1099, 1056, 994, 845, 736 cm⁻¹. Anal. calcd. for C₁₈H₂₄N₂O₄S: C, 59.32; H, 6.64; N, 7.69. Found: C, 59.45; H, 6.54; N, 7.36.

Bis(*N*-*tert*-butoxycarbonyl-2-pyrrolyl) sulfoxide (2) from thionyl chloride: A solution of *N*-*t*-BOC-2-bromopyrrole (2.43 g, 9.87 mmol) in THF (40 ml) was cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 6.6 ml, 10.6 mmol) was slowly added after which the solution was stirred for 10 min at -70°C. Thionyl chloride (0.36 ml, 4.96 mmol) was added dropwise and the solution was stirred for another 15 min at -70°C. Then, the solution was allowed to warm to RT, poured into water (200 ml) and extracted with Et₂O (2 × 80 ml). The combined organic fractions were washed with 0.25 M Na₂CO₃-solution (150 ml) and water (2 × 150 ml), dried (Na₂SO₄), filtered and concentrated, yielding a black oil (1.93 g). After column chromatography (200 g Al₂O₃, CH₂Cl₂, *R*_f = 0.31), pure **2** was obtained as a colorless oil which slowly crystallized (0.97 g, 2.55 mmol, 52%). M.p. = 119-120°C.

¹H-NMR (CDCl₃): δ 7.44 (dd, *J* = 3.2 and 1.9 Hz, 2H, H-5), 6.49 (s, 2H, H-3), 6.27 (t, *J* = 3.4 Hz, 2H, H-4), 1.54 (s, 18H, H-methyl). ¹³C-NMR (CDCl₃): δ 147.8 (C=O), 135.0 (C-2), 124.8 (C-5), 118.0 (C-3), 111.3 (C-4), 86.0 (C-q (BOC)), 27.7 (C-methyl). UV (CH₃CN): λ_{\max} = 234 nm. IR (KBr): ν = 3129, 2981, 2935, 1748, 1396, 1372, 1320, 1260, 1154, 1099, 1054, 992, 842, 739 cm⁻¹. Anal. calcd. for C₁₈H₂₄N₂O₅S: C, 56.82; H, 6.36; N, 7.36. Found: C, 56.70; H, 6.60; N, 6.92.

Bis(*N*-*tert*-butoxycarbonyl-2-pyrrolyl) sulfoxide (2) via oxidation: To a solution of bis(*N*-*t*-BOC-2-pyrrolyl) sulfide (**1**, 0.4237 g, 1.163 mmol) in CH₂Cl₂ (4 ml), *m*-chloroperbenzoic acid (techn. 70%, 0.2902 g, 1.177 mmol) was slowly added. After stirring for 45 min at RT, the solution was poured into water (50 ml) and extracted with Et₂O (3 × 25 ml). The combined organic fractions were washed with Na₂CO₃-solution (50 ml) and water (2 × 50 ml), dried (Na₂SO₄), filtered and concentrated, yielding pure **2** as a slightly orange oil which slowly crystallized (0.45 g, 1.163 mmol, 100%).

Bis(*N*-*tert*-butoxycarbonyl-2-pyrrolyl) sulfone (3) via oxidation: Bis(*N*-*t*-BOC-2-pyrrolyl) sulfoxide (**2**, 0.45 g, 1.163 mmol) was dissolved in CH₂Cl₂ (4 ml) and *m*-chloroperbenzoic acid (techn. 70%, 0.2880 g, 1.17 mmol) was slowly added. After stirring for 3 h at RT, the solution was poured into water (50 ml) and extracted with Et₂O (3 × 25 ml). The combined organic fractions were washed with Na₂CO₃-solution (50 ml) and water (2 × 50 ml), dried (Na₂SO₄), filtered and concentrated, yielding **3** as a slightly orange oil which slowly crystallized (0.45 g, 1.14 mmol, 98%). M.p. = 134-135°C.

¹H-NMR (CDCl₃): δ 7.49 (dd, *J* = 3.1 and 2.0 Hz, 2H, H-5), 6.79 (dd, *J* = 3.7 and 2.0 Hz, 2H, H-3), 6.23 (t, *J* = 3.4 Hz, 2H, H-4), 1.52 (s, 18H, H-methyl). ¹³C-NMR (CDCl₃): δ 146.9 (C=O), 131.2 (C-2), 127.0 (C-5), 123.5 (C-3), 109.6 (C-4), 86.1 (C-q (BOC)), 27.3 (C-methyl). UV (CH₃CN): λ_{max} = 232 nm. IR (KBr): ν = 3130, 2975, 2934, 1764, 1401, 1374, 1341, 1290, 1264, 1216, 1149, 1116, 1096, 1065, 1004, 840, 766, 742, 647, 625 cm⁻¹. Anal. calcd. for C₁₈H₂₄N₂O₆S: C, 54.53; H, 6.10; N, 7.10. Found: C, 55.41; H, 5.85; N, 6.71. (N.B. From ¹H-NMR it was deduced that **3** contained 7% of **2**; the presence of the latter can be prevented by using a small excess of *m*-CPBA. Analyses were performed on pure **3**).

Poly[(*N*-*tert*-butoxycarbonyl-2,5-pyrrolyl) sulfide] (4): *N*-*t*-BOC-2,5-dibromopyrrole (2.32 g, 7.14 mmol) was dissolved in THF (36 ml) and cooled to -70°C, blanketed by argon. *n*-BuLi (1.6 M in hexane, 10.7 ml, 17.1 mmol) was slowly added, after which the solution was stirred for 1 h at -70°C. Bis(*p*-tosyl) sulfide (2.46 g, 7.18 mmol) was added in small portions and the mixture was stirred for another hour at -70°C. The mixture was then allowed to warm to RT, stirred for 2 h, poured into water (300 ml) and extracted with Et₂O (3×200 ml). The combined organic layers were then washed with water (2×300 ml), dried over MgSO₄ and concentrated, yielding 1.82 g of a black oil, **4**. The smaller oligomers present in the oil were separated by column chromatography (130 g SiO₂, gradient CH₂Cl₂:hexane (1:3) via CH₂Cl₂ to CHCl₃), affording four fractions: fraction 1 (0.05 g) monomer **4a**, fraction 2 (0.01 g) dimer **4b**, fraction 3 (0.02 g) trimer **4c** and fraction 4 (0.76 g, ~50%) containing the higher oligomers **4d**.

***N*-*tert*-Butoxycarbonyl-2,5-bis(*n*-butyl sulfide)pyrrole (4a):** ¹H-NMR (CDCl₃) δ: 6.17 (s, 2H, H-3,4), 2.78 (t, *J* = 7.5 Hz, 4H, -S-CH₂-), 1.70-1.54 (m, 4H, -S-CH₂-CH₂-), 1.65 (s, 9H, H-methyl (BOC)), 1.54-1.36 (m, 4H, -CH₂-CH₃), 0.90 (t, *J* = 7.5 Hz, 6H, -CH₂-CH₃).

Bis(N-tert-butoxycarbonyl-5-(n-butyl sulfide)-2-pyrrolyl) sulfide (4b): $^1\text{H-NMR}$ (CDCl_3) δ : 6.12 (d, $J = 3.6$ Hz, 2H, H-4), 6.01 (d, $J = 3.6$ Hz, 2H, H-3), 2.80 (t, $J = 7.5$ Hz, 4H, $-\text{S}-\underline{\text{CH}_2}$ -), 1.70-1.54 (m, 4H, $-\text{S}-\text{CH}_2-\underline{\text{CH}_2}$ -), 1.55 (s, 18H, H-methyl (BOC)), 1.54-1.35 (m, 4H, $-\text{CH}_2-\text{CH}_3$), 0.93 (t, $J = 7.5$ Hz, 6H, $-\text{CH}_2-\underline{\text{CH}_3}$). $^{13}\text{C-NMR}$ (CDCl_3) δ : 149.0 (C=O), 129.3 (C-5), 125.6 (C-2), 117.4 (C-3/C-4), 114.9 (C-3/C-4), 85.4 (C-q (BOC)), 34.7 ($-\text{S}-\underline{\text{CH}_2}$ -), 30.6 ($-\text{S}-\text{CH}_2-\underline{\text{CH}_2}$ -), 27.8 (C-methyl (BOC)), 22.0 ($-\underline{\text{CH}_2}-\text{CH}_3$), 13.6 ($-\text{CH}_2-\underline{\text{CH}_3}$).

N-tert-Butoxycarbonyl-2,5-bis[N-tert-butoxycarbonyl-5-(n-butyl sulfide)-2-pyrrolyl sulfide] pyrrole (4c): $^1\text{H-NMR}$ (CDCl_3) δ : 6.12 (d, $J = 3.6$ Hz, 2H, H-3'/4'), 6.10 (d, $J = 3.6$ Hz, 2H, H-3'/4'), 5.93 (s, 2H, H-3,4), 2.80 (t, $J = 7.5$ Hz, 4H, $-\text{S}-\underline{\text{CH}_2}$ -), 1.70-1.54 (m, 4H, $-\text{S}-\text{CH}_2-\underline{\text{CH}_2}$ -), 1.55 (s, 18H, H-methyl (BOC')), 1.54-1.35 (m, 4H, $-\text{CH}_2-\text{CH}_3$), 1.48 (s, 9H, H-methyl (BOC)), 0.93 (t, $J = 7.5$ Hz, 6H, $-\text{CH}_2-\underline{\text{CH}_3}$). $^{13}\text{C-NMR}$ (CDCl_3) δ : 148.9 (C=O (BOC,BOC')), 129.8 (C-5'), 127.8 (C-2'), 125.0 (C-2,5), 118.2 (C-4'), 116.9 (C-3'), 114.5 (C-3,4), 85.4 (C-q (BOC,BOC')), 34.8 ($-\text{S}-\underline{\text{CH}_2}$ -), 30.6 ($-\text{S}-\text{CH}_2-\underline{\text{CH}_2}$ -), 27.8 (C-methyl (BOC')), 27.7 (C-methyl (BOC)), 22.0 ($-\underline{\text{CH}_2}-\text{CH}_3$), 13.6 ($-\text{CH}_2-\underline{\text{CH}_3}$).

Poly[(N-tert-butoxycarbonyl-2,5-pyrrolyl) sulfide] (4d): $^1\text{H-NMR}$ (CDCl_3) δ : 6.5-5.8 (m, Py-H), 2.9-2.7 (m, $-\text{S}-\underline{\text{CH}_2}$ -), 1.8-1.1 (m, BOC, $-(\underline{\text{CH}_2})_2-\text{CH}_3$), 1.1-0.8 (m, $-\text{CH}_2-\underline{\text{CH}_3}$). $^{13}\text{C-NMR}$ (CDCl_3) δ : 149 (C=O), 132-126 (C- α (Py)), 120-114 (C- β (Py)), 86 (C-q (BOC)), 35 ($-\text{S}-\underline{\text{CH}_2}$ -), 31 ($-\text{S}-\text{CH}_2-\underline{\text{CH}_2}$ -), 29-27 (C-methyl (BOC)), 22 ($-\underline{\text{CH}_2}-\text{CH}_3$), 14 ($-\text{CH}_2-\underline{\text{CH}_3}$).

Acknowledgment

The authors thank E.E. Havinga for valuable discussions, J.L.J. van Dongen for performing the SEC analyses and Philips Research for an unrestricted research grant.

References

1. Elsenbaumer, R.L.; Shacklette, L.W. in *Handbook of Conducting Polymers Vol 1.* (Edt.: Skotheim, T.A.); Marcel Dekker Inc.; New York, **1986**.
2. Frommer, J.E.; Elsenbaumer, R.L.; Chance, R.R. *ACS Symp. Ser.* **1984**, 242, 447.
3. Ford, W.T.; Gutierrez, M.; Pohl, H.A. *Polymer Preprints* **1983**, 24, 332.
4. Cava, M.P.; Lakshmikantham, M.V.; Jen, K.-Y.; Benfaremo, N.; Huang, W.S.; MacDiarmid, A.G. *Polymer Preprints* **1983**, 24, 251.
5. Edmonds, J.T., Jr.; Hill, H.W., Jr. U.S. Patent 3354129, **1967**.
6. Lenz, R.W.; Handlovits, C.E.; Smith, H.A. *J. Polym. Sci.* **1962**, 58, 351.
7. Fisher, H.; Csukas, Z. *Liebigs Ann. Chem.* **1934**, 508, 167. Harris, R.L.N. *Tetrahedron Lett.* **1968**, 4045. Beveridge, S.; Harris, R.L.N. *Aust. J. Chem.* **1971**, 24, 1229. Treies, A.; Schulze, L.; Kreuzer, F.H.; Kolm, H.G. *Liebigs Ann. Chem.* **1973**, 207.

8. Harris, R.L.N. *Aust. J. Chem.* **1972**, 25, 985.
9. Berlin, A.; Ferraccioli, R.; Pagani, G.A. *Gazz. Chim. Ital.* **1987**, 117, 507.
10. Carpino, L.A.; Barr D.E. *J. Org. Chem.* **1966**, 31, 764.
11. Martina, S.; Enkelmann, V.; Wegner, G.; Schlüter, A.-D. *Synthesis* **1991**, 613.
12. Groenendaal, L.; Van Loo, M.E.; Vekemans, J.A.J.M.; Meijer, E.W. *Synth. Commun.* **1995**, 25, 1589.
13. Rawal, V.H.; Cava, M.P. *Tetrahedron Lett.* **1985**, 26, 6141.
14. Kocienski, P.J. in "Theme foundations of organic chemistry series: Protecting groups", Georg Theme Verlag: Stuttgart, 1994.
15. Broadhurst, M.J.; Grigg, R.; Johnson, A.W. *J. Chem. Soc. Perkin 1* **1972**, 1124.
16. Groenendaal, L.; Peerlings, H.W.I.; Van Dongen, J.L.J.; Havinga, E.E.; Vekemans, J.A.J.M.; Meijer, E.W. *Macromolecules* **1995**, 28, 116.

(Received in The Netherlands 16 July 1996)