Well-Defined Oligo(pyrrole-2,5-diyl)s by the Ullmann Reaction

L. Groenendaal, H. W. I. Peerlings, J. L. J. van Dongen, E. E. Havinga, 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

Received June 28, 1994; Revised Manuscript Received September 12, 1994®

ABSTRACT: The Ullmann coupling reaction has been used to polymerize *N*-*t*-BOC-2,5-dibromopyrrole into well-defined oligo(pyrrole-2,5-diyl)s. After optimization of the reaction conditions, i.e. using 1 wt equiv of Cu-bronze in DMF at 100 °C for 1 h, oligomers up to 25 repeating pyrrole units are obtained. Starting from 5,5′- and 5,5″-dibrominated *N*-*t*-BOC protected bi- and terpyrrole as monomers, the polymerization is slower and a lower degree of polymerization is observed, yielding oligomers with an even lower molecular weight than those resulting from *N*-*t*-BOC-2,5-dibromopyrrole. The first 20 oligomers of poly(*N*-*t*-BOC-pyrrole) have been isolated by preparative HPLC. Characterization of the individual oligomers shows that they all are hydrogen terminated and possess a perfect 2,5-linkage: oligo(pyrrole-2,5-diyl)s. The isolated oligomers have been used to study the optical and electrical properties of the oligomers as a function of chain length.

Introduction

Polypyrrole is among the most important conducting polymers in its oxidized form, and many applications are foreseen for this organic conductor.[1] However, the molecular structure of electrochemically or $FeCl_3$-oxidatively prepared polypyrrole is far from elucidated, and it is thought that many imperfections are present with respect to the ideal 2,5-linked polymer. Model studies using well-defined oligomers are of utmost importance to gain detailed insight into the structure-property relationship, as is nicely demonstrated for oligothiophenes.[2-7] In sharp contrast to the numerous studies concerning oligothiophenes, only limited research has been carried out with respect to the synthesis and characterization of well-defined oligo(pyrrole-2,5-diyl)s. In the early days Rapoport[8] and Johnson[9] have investigated in detail the synthesis of bi- and terpyrroles, being interesting building blocks for natural products, like vitamin B_{12} and prodigiosine. Years later, Kauffmann[10] synthesized and characterized a series of oligo(*N*-methylpyrrole-2,5-diyl)s up to a chain length of 16 repeating units. In order to study the structure-property relationship of conjugated, coplanar polypyrroles, however, it is a prerequisite to have oligopyrroles without a substituent or with a labile protecting group at the N-atom of pyrrole. Using the *tert*-butoxycarbonyl (*t*-BOC) group,[11] Martina, Enkelmann, Schlüter, and Wegner developed an elegant chemical synthesis for well-defined oligo- and poly(pyrrole-2,5-diyl)s.[12] In these studies Stille chemistry[13] has been applied to *N*-*t*-BOC-protected pyrrole monomers which resulted in the synthesis of a series of oligo(2,5-pyrrole)s up to nine repeating pyrrole units and polymers up to 17 repeating units per chain. Due to methyl shifts in the Stille reaction from the $Sn(CH_3)_3$ groups to the α-positions of the oligopyrroles, it is necessary to use terpyrrole monomers as building blocks to obtain reasonable molecular weights.

Fascinated by the results of Martina et al. and encouraged by the knowledge that in porphyrin chemistry the Ullmann reaction is elaborated as an effective coupling method for pyrroles,[14] we have investigated the synthesis of well-defined oligo(pyrrole-2,5-diyl)s using this Ullmann reaction. Since its discovery at the end of the nineteenth century[15] it has been used extensively in organic chemistry[16] and only rarely in macromolecular chemistry.[17] In our case, it appears to be a suitable method to create oligomers and polymers of pyrrole. The results of this investigation are given in this paper.

Results and Discussion

Synthesis and Characterization. The *N*-*t*-BOC-protected dibromopyrrole derivatives **2**, **6**, and **11** were used as the starting materials for the Ullmann polymerization; the synthesis of these monomers is depicted in Scheme 1. The synthesis of *N*-(*tert*-butoxycarbonyl)-2,5-dibromopyrrole (**2**) was performed by first protecting pyrrole with the *tert*-butoxycarbonyl group using $(BOC)_2O$, followed by the selective dibromination using the procedure described by Martina et al.[12d] Monomer **2**, which was obtained as a white solid after two crystallizations in a 42% overall yield, had to be stored under inert atmosphere at low temperatures (−20 °C). If not, it easily decomposed resulting in a black insoluble tar.

N,*N*′-Bis(*tert*-butoxycarbonyl)-5,5′-dibromo-2,2′-bipyrrole (**6**) was prepared from 2,2′-bipyrrole. The latter was synthesized in two steps from pyrrole and 2-pyrrolidinone using the method of Rapoport.[8b] The oxygen-sensitive 2,2′-bipyrrole was then protected with *tert*-butoxycarbonyl groups after which it was selectively dibrominated in an overall yield of 22% (from pyrrole).

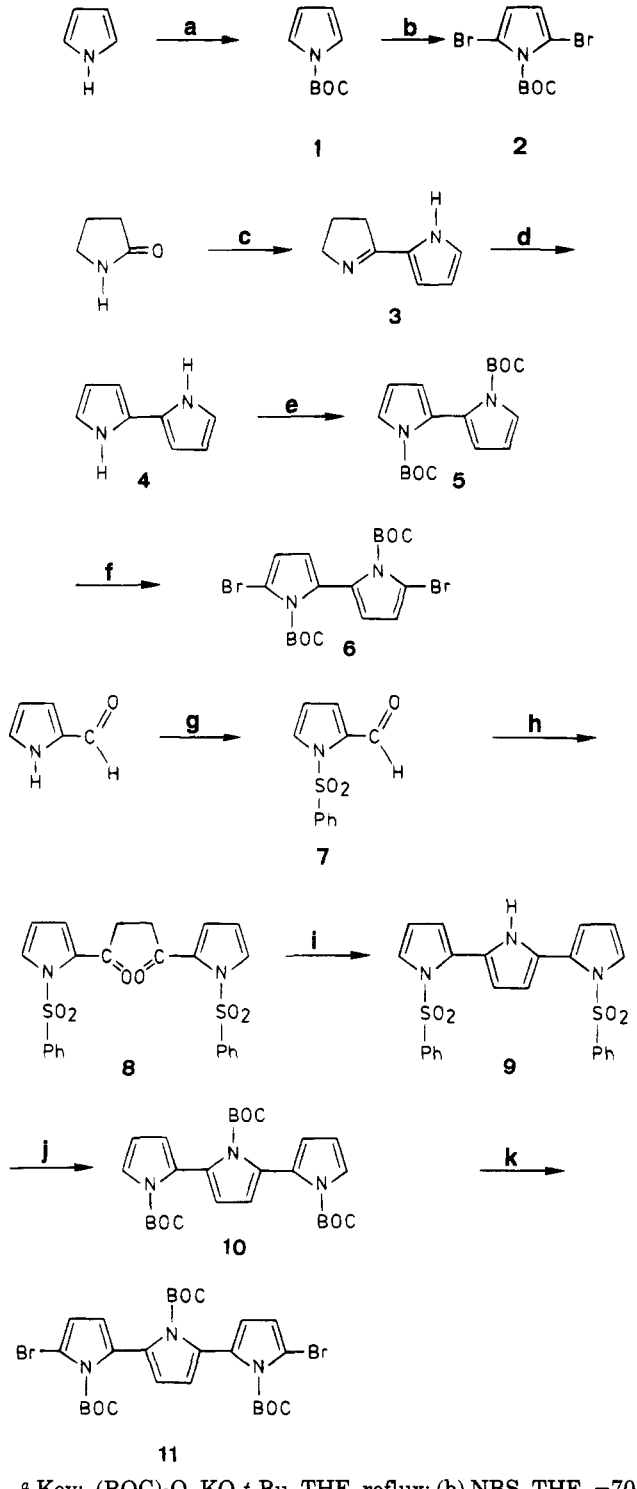
Finally, *N*,*N*′,*N*″-tris(*tert*-butoxycarbonyl)-5,5″-dibromo-2,2′:5′,2″-terpyrrole (**11**) was synthesized starting from 2-formylpyrrole[19] in a yield of 12%. In the first three steps the terpyrrole unit was synthesized. Then a deprotection of the two sulfonyl groups from the terpyrrole and a protection of the parent oxygen-labile terpyrrole with three *tert*-butoxycarbonyl groups was performed. In the last step the *t*-BOC-protected terpyrrole was selectively dibrominated using NBS.

The synthetic routes for the monomers employed in our study, most being combinations of steps published before, are thought to be the most attractive methods, although alternatives are present in a number of cases. Compound **11**, for instance, can also be prepared by a Stille reaction using the procedures of Martina et al.,[12f] however, this method is far more difficult to perform.

* Author to whom correspondence should be addressed.
® Abstract published in *Advance ACS Abstracts*, November 15, 1994.

0024-9297/95/2228-0116$09.00/0

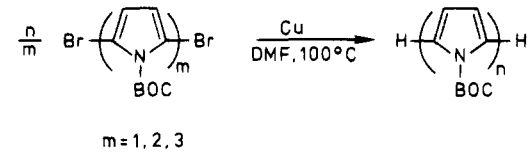
Scheme 1. Synthesis of the *N*-*t*-BOC Protected Dibromopyrrole Monomers 2, 6, and 11[a]



[a] Key: $(BOC)_2O$, KO-*t*-Bu, THF, reflux; (b) NBS, THF, −70 °C; (c) pyrrole, $POCl_3$, 0 °C; (d) Pd/C, triglyme, 200 °C; (e) $(BOC)_2O$, KO-*t*-Bu, THF, reflux; (f) NBS, THF, −70 °C; (g) 1) NaH, 2) $PhSO_2Cl$, DMF, rt; (h) divinyl sulfone, ethanol, reflux; (i) NH_4OAc, Ac_2O, propionic acid, 140 °C; (j) (1) NaOH, MeOH, rt; (2) $(BOC)_2O$, KO-*t*-Bu, THF, reflux; (k) NBS, THF, −70 °C.

All monomers obtained are pure as checked with NMR spectroscopy; no monobrominated compounds or other impurities have been detected. Although both dibrominated bi- and terpyrrole monomers prove to be much more stable than the corresponding monopyrrole monomer, it is still necessary to handle all these starting materials for the polymerization with care (inert atmosphere).

Scheme 2. Polymerization of *N*-*t*-BOC Protected Dibromopyrrole Monomers (m = 1−3) by the Ullmann Reaction.



The polymerization of the monomers using the Ullmann reaction was carried out by heating a mixture of the monomer, 1 wt equiv of Cu−bronze, and DMF (10 mL per mmol) at 100 °C under inert atmosphere (Scheme 2). After 1 h in the case of **2** and 2 h in the case of **6** and **11**, the dark reaction mixture was worked up (extraction, filtration, evaporation) which resulted in a dark green oil in all three cases. TLC analysis (Al_2O_3) showed that a large number of oligomers were formed in the reaction product of the Ullmann polymerization. After a filtration over Al_2O_3 the reaction products were analyzed in detail by analytical HPLC (reversed-phase chromatography using a gradient from methanol/water to methanol). The results of these HPLC analyses are given in Figures 1−3. These measurements revealed that in the case of **2** oligomers up to 25 pyrrole repeating units were formed, while up to 16 repeating units starting from **6** and up to 24 units starting from **11** were obtained in the Ullmann reaction. In the case of the bi- and terpyrrole monomers substantial amounts of byproducts were present as well.

In order to study the molecular structure of the oligomers obtained (e.g., what are the end groups and what are the byproducts in the case of **6** and **11**?) we performed preparative HPLC separations on the complex reaction mixtures. Although HPLC is known to be of great use in the detection of oligomers,[18] it has never been used to separate oligomers from a reaction mixture on a 2−20 mg scale. By using preparative reversed-phase chromatography we were able to isolate the first 20 individual oligomers at a milligram scale from the reaction mixture of the polymerization of **2**. The purity of the oligomers separated was checked by HPLC analysis and NMR-spectroscopy (^{1}H-NMR of all 20 isolated oligomers, ^{13}C-NMR of the first 10 oligomers, 2D-NMR to assign the peaks to the various H- and C-atoms). Up to 15 repeating units the samples featured a purity of at least 90%. In the higher oligomers a small fraction of unidentified UV absorbing impurity was detected by HPLC analysis. However, this impurity could not be detected by ^{1}H-NMR spectroscopy.

The ^{13}C-NMR spectrum of the heptamer (n = 7) and the ^{1}H-NMR spectrum of the tridecamer (n = 13) are given in Figures 4 and 5, respectively, together with the HPLC analysis of the isolated oligomers (inserts). The ^{1}H-NMR spectra revealed that the oligomers were H-terminated with the α-H-atoms at their normal position of δ = 7.40 ppm. All other H-atoms gave a multiplet at about δ = 6.2 ppm. Going to higher oligomers the ratio between the α-H-atoms and all other H-atoms changed as expected while the shape of the multiplet almost resolved into a singlet. In the ^{13}C-NMR spectrum it proved to be far more difficult to assign peaks of the pyrrole unit for the higher oligomers. However, the resonances for the *t*-BOC group (both the carbonyl and the quaternary C-group) were well-separated and the even−odd sequence could be measured as is shown in Figure 4 for the heptamer. Final proof for the molecular structure of one of the oligomers (n = 13) was obtained by electrospray mass spectros-

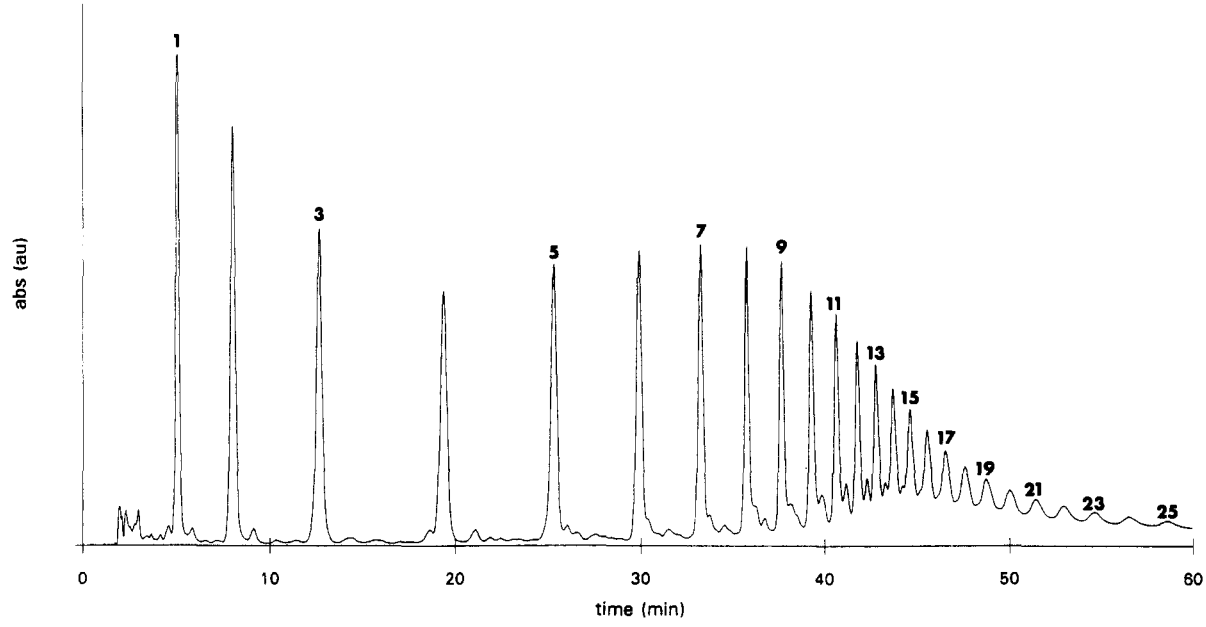


Figure 1. HPLC analysis of polymerization of **2**.

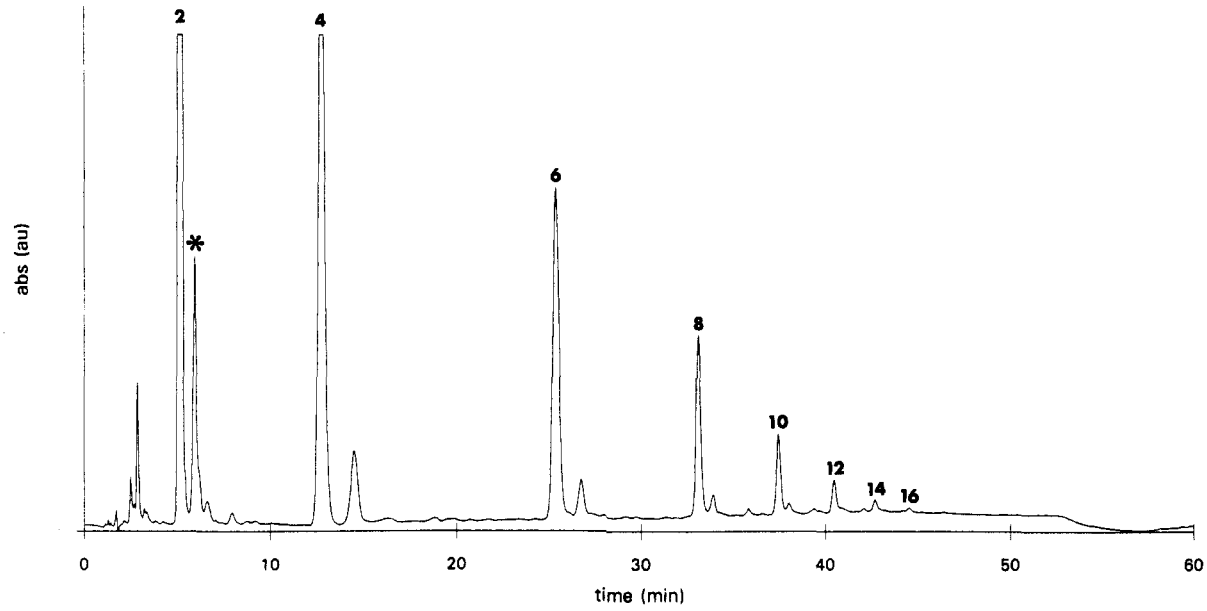


Figure 2. HPLC analysis of polymerization of **6**.

copy. A molar mass of 2186 (n = 13 (2147) plus K^+ counterion) was found.

As can be deduced from Figures 1–3, the Ullmann reactions of the bi- and terpyrrole monomers led to relatively many byproducts, in sharp contrast with the clean reaction of **2**. After 2 h of reaction time each oligomer from **6** and **11** was accompanied by a byproduct which is at least 30% of the hydrogen-terminated oligo(pyrrole-2,5-diyl). In order to investigate the structure of the byproducts, we isolated the byproducts marked with an asterisk in Figures 2 and 3 with preparative HPLC as well. From mass- and NMR-spectroscopy it was concluded that these byproducts were monobrominated bi- and terpyrrole (*N,N'*-bis(*tert*-butoxycarbonyl)-5-bromo-2,2'-bipyrrole and *N,N',N''*-tris(*tert*-butoxycarbonyl)-5–bromo-2,2':5',2''-terpyrrole), respectively. All other byproducts were by analogy proposed to be monobrominated *N-t*-BOC-protected oligo(pyrrole-2,5-diyl)s (also the very small peaks in Figure 1 are probably monobrominated oligomers; formation of non 2,5-coupled oligomers is not expected because an unlikely bromine shift should then have taken place). In contrast to N-(*tert*-butoxycarbonyl)-2-bromopyrrole, known to be unstable, these monobrominated oligomers possessed a relative high stability.

The reaction conditions applied here are the result of a study to the scope and limitations of the Ullmann polymerization of **2**. The results under different conditions are given in Table 1. From these optimization experiments, it follows that enhanced temperatures (T > 70 °C) are required to start the polymerization. However, too high temperatures result in more byproducts and in deprotection. Polymerization starting from *N*-BOC-2,5-dichloropyrrole, the use of Cu^{2+} instead of Cu–bronze, or the addition of 17% (v/v) of water in the DMF all result in a black insoluble tar.

The polymerization of the terpyrrole monomer **11** was also monitored by HPLC during polymerization. We found that during the first 20 min there was an increase of the number of oligomers with a maximum of 8. After about 5 h this number decreased until there were only 4 oligomers left after 88 h. The amount of monobrominated oligomers steadily decreased during the reaction; after 88 h there were hardly any left. The decrease of

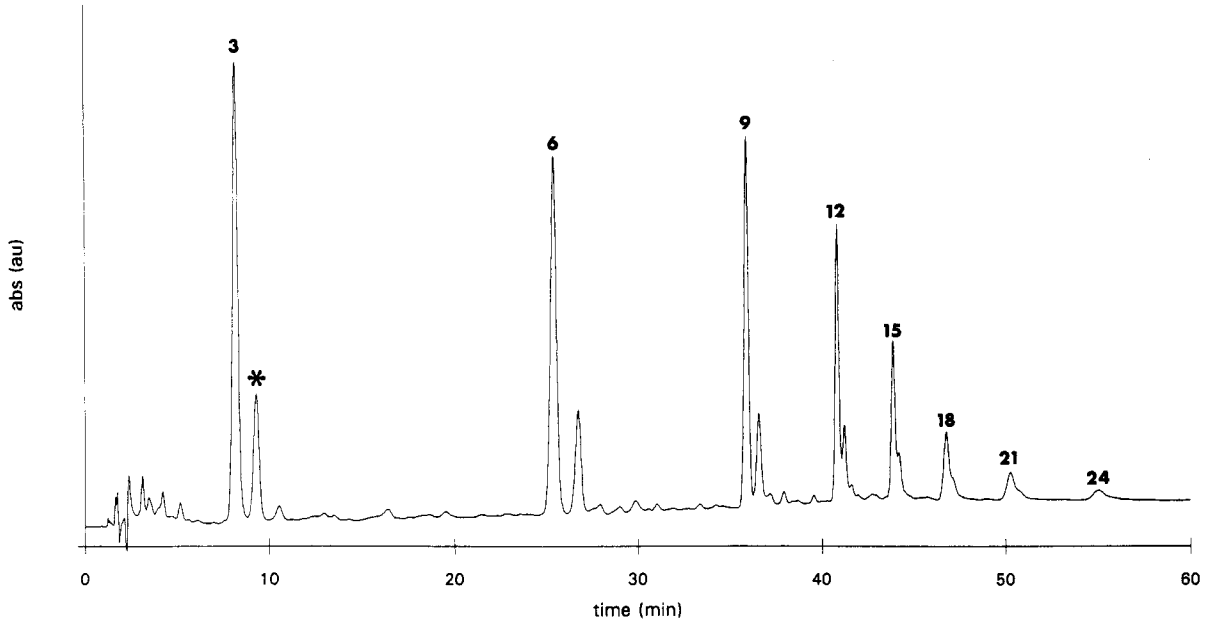


Figure 3. HPLC analysis of polymerization of **11**.

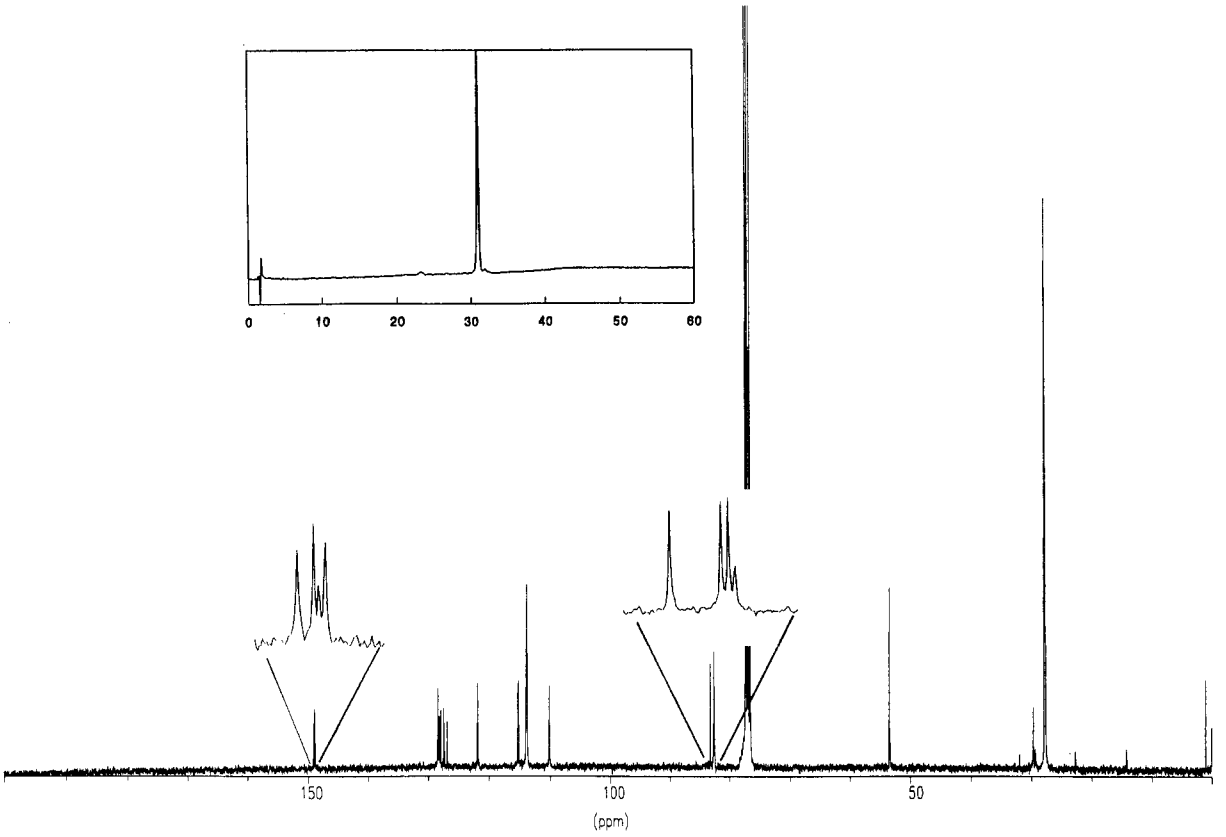


Figure 4. ^{13}C-NMR ($CDCl_3$) and HPLC analysis (inset) of the isolated heptamer (n = 7).

the number of oligomers after 5 h of reaction time is quite remarkable. This decrease may be the result of (partial) deprotection giving rise to the formation of insoluble clusters.

The NMR data of the isolated oligomers clearly show that the oligomers obtained by the Ullmann reaction possess hydrogen instead of bromine end groups at the α-positions. Evidently a reductive debromination occurs, furnishing unreactive end groups in the Ullmann reaction products. Because of the absence of water during these reactions, these hydrogen atoms must come from the solvent (DMF) which is known to be relatively unstable at higher temperatures.

In contrast to the work of Martina et al.[12] the longest oligomers are not obtained starting from the longer monomers **6** and **11** but starting from the monopyrrole monomer **2**. In the cases of **6** and **11** eight different oligomers are formed while in the case of **2** 25 different oligomers are obtained. This difference may be due to the higher stability and lower reactivity of the longer monomers compared to **2**. Extension of the time of reaction, however, leads to deprotection and insoluble products.

The experimental data presented above prompts us to propose a chain-reaction mechanism for the oligomerization of *N*-*t*-BOC-2,5-dibromopyrrole. Since the

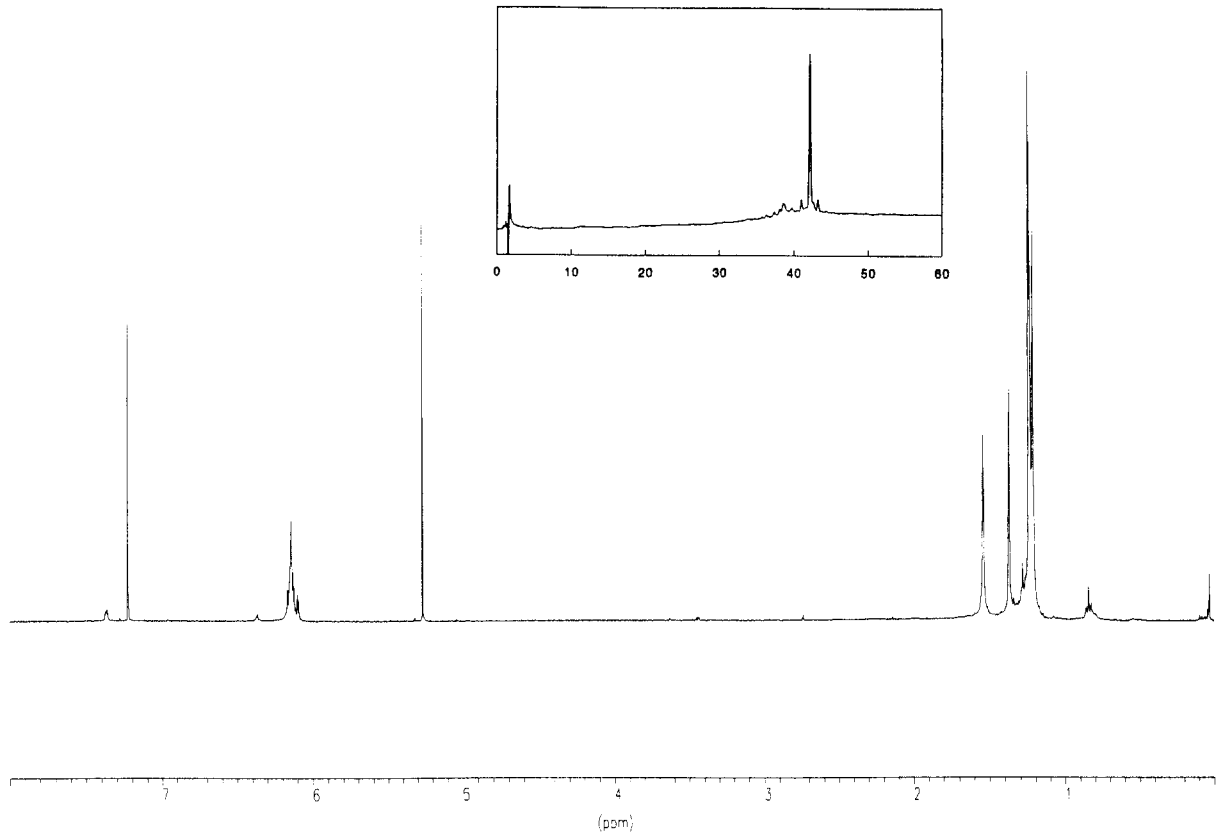


Figure 5. ^{1}H-NMR ($CDCl_3$) and HPLC analysis (inset) of the isolated tridecamer (n = 13). Signal marked (*) are from solvents.

Table 1. Optimization of the Ullmann Polymerization of 2

monomer	solvent	T (°C)	time (h)	products
2	DMF	40	7	no reaction
2	DMF	80	2	oligomers up to 12 units
2	DMF	100	1	oligomers up to 25 units
2	DMF	120	5 min	oligomers up to 15 units, also byproducts
2	THF	68	6	no reaction
2	NMP[a]	160	5 min	deprotection resulting in black insoluble tar
2	DMF/H_2O (5/1)	100	6	deprotection resulting in black insoluble tar
2	DMF[b]	100	2	deprotected monomer
2,5-dichloro	DMF	100	2	deprotection resulting in black insoluble tar

[a] *N*-Methylpyrrolidone. [b] Reaction with Cu^{2+} instead of Cu–bronze.

mechanism of the Ullmann reaction is not known with certainty, the proposal made here is speculative at this stage. First the reactive *N*-*t*-BOC-2,5-dibromopyrrole reacts with Cu under the formation of *N*-*t*-BOC-2-Cu-5-bromopyrrole. In the next step this compound reacts with the growing chain, being a dibromo- or monobromo oligopyrrole, furnishing an aryl–aryl coupling. Since the bromopyrrole unit in **2** is much more reactive than any other brominated oligomer, a new *N*-*t*-BOC-2-Cu-5-bromopyrrole intermediate is formed, which reacts with the growing chain. Concomitant with propagation, debromination can take place leading to termination. In the case of the reactive *N*-*t*-BOC-2,5-dibromopyrrole this results in the formation of 25 oligomers, while in the case of the dibrominated *N*-*t*-BOC protected bi- and terpyrrole the ratio between propagation and termination is lower resulting in only eight oligomers. Experiments in which the polymerization is followed in time to record the consumption of monomer are planned to establish the mechanism in detail.

Properties of the Oligomers. The preliminary study to the properties of the isolated oligomers showed interesting results. First, UV–vis spectra of all *t*-BOC-protected oligomers were measured. The π–π^* transition of these oligopyrroles showed a bathochromic shift from 270 to 305 nm with an increasing number of repeating units (Figure 6 (top)). A linear relation was found by plotting the bandgap energy versus 1/n (Figure 6(bottom)). Theoretical calculations on oligophenylenes showed similar results,[20] while for a number of systems, including oligothiophenes, experimental data were presented to verify this relation. Despite the bulky protecting groups at nitrogen, responsible for a torsional angle of approximately 70°,[12a] some π-overlap is still present in the N^t-BOC-protected oligo(pyrrole-2,5-diyl)s. Recently, similar data using a limited number of oligo(pyrrole-2,5-diyl)s were presented showing comparable results.[12k]

Second, UV measurements of some deprotected oligomers were established. Therefore, these oligomers were heated at 180 °C for 5 min *in vacuo*. This method leads to a complete deprotection of oligomers up to n = 6. However, for n > 6 the deprotection is not complete. Unfortunately, there are no techniques available to detect the degree of deprotection, due to insolubility and extreme sensitivity to oxidation of the (partially) unprotected oligopyroles. The UV data recorded for the completely deprotected oligomers are in good agreement with the results described by Martina et al.[12a]

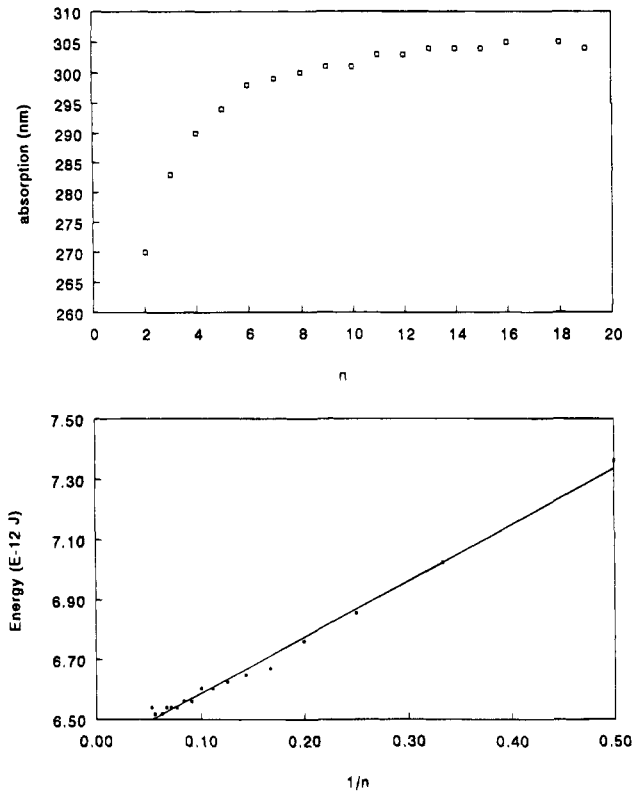


Figure 6. (Top) $\pi-\pi^*$ transition (λ_{max}) versus number of pyrrole units in the oligomer (n). (Bottom) bandgap energy (E_g) versus reciprocal number of pyrrole units in the oligomer ($1/n$).

Some of the isolated oligomers were also used for conductivity experiments. These measurements were accomplished using the pentamer ($n = 5$), the decamer ($n = 10$), and the pentadecamer ($n = 15$). Therefore, thin films of the *t*-BOC-protected oligomers were prepared which were heated at 180 °C for 1 h. Doping of the fully deprotected pentamer with I_2 afforded samples with conductivities as high as 100 S cm^{-1} (four-probe measurement). Similar conductivity experiments with the decamer and pentadecamer showed significantly lower conductivities in the range of 10^{-2} S cm^{-1}. These lower values of the longer oligomers are due to incomplete deprotection after heating (see above). The remaining *t*-BOC groups diminish the conjugation which results in lower conductivities. The experiments performed so far do not indicate whether the doped oligomers are stable or polymerize further as has been observed for a number of oligothiophenes.[5] Further research to investigate the properties of isolated oligomers is in progress.

Conclusions

We have shown that the Ullmann reaction is a good alternative for the Stille reaction in the preparation of well-defined oligo(pyrrole-2,5-diyl)s. Oligomers up to 25 repeating pyrrole units are formed starting from the most reactive monomer, *N*-*t*-BOC-2,5-dibromopyrrole. Using preparative HPLC the first 20 oligomers have been isolated on a milligram scale and characterized by NMR and UV spectroscopy. These oligomers show interesting properties such as a linear relationship between the bandgap energy and $1/n$ and a high conductivity for the oxidized deprotected pentamer. Without questioning the elegance of organic synthesis to well-defined oligomers, it is worth noting that in particular cases the relevant information on a series of oligomers is obtained much easier by the combination of oligomerization and HPLC separation.

Experimental Section

All materials and solvents were reagent grade and used as received, unless otherwise indicated. *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 at reduced pressure and stored in dark flasks over molecular sieves. Tetrahydrofuran (THF) was distilled over Na/benzophenone and directly used.

^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker AM-400 spectrometer. UV–vis spectra were recorded on a Perkin-Elmer Lambda 3B. MS data were collected using a AMD mass spectrometer/data system (Beckeln, GFR).

***N*-(*tert*-Butoxycarbonyl)pyrrole (1).**[12d] A vigorously stirred mixture of pyrrole (13.95 g, 208 mmol), di-*tert*-butyl dicarbonate (52.56 g, 241 mmol), THF (1000 mL), and potassium *tert*-butoxide (2.0 g, 18 mmol), blanketed by nitrogen, was refluxed. After 18 h the mixture was cooled to room temperature and 2-(dimethylamino)ethylamine (5.25 g, 60 mmol) was added. After continued stirring for another 30 min the solvent was evaporated. The residue was dissolved in Et_2O (600 mL) and extracted with dilute HCl (3 × 200 mL, 0.1 M) and H_2O (3 × 200 mL). This resulted in a brown liquid from which after distillation (18 mmHg, 80 °C) a colorless liquid was obtained (29.55 g, 177 mmol, 85%). ^{1}H-NMR ($CDCl_3$): δ 7.23 (t, $J = 2.2$ Hz, 2H, H-2, H-5), 6.20 (t, $J = 2.2$ Hz, 2H, H-3, H-4), 1.58 (s, 9H, H-methyl). ^{13}C-NMR ($CDCl_3$): δ 148.8 (C=O), 119.9 (C-2, C-5), 111.7 (C-3, C-4), 83.4 (C-q (BOC)), 27.9 (C-methyl).

***N*-(*tert*-Butoxycarbonyl)-2,5-dibromopyrrole (2).**[12d] *N*-(*tert*-butoxycarbonyl)pyrrole (**1**, 16.75 g, 100 mmol) was dissolved in THF (570 mL) and cooled to −70 °C, blanketed by argon. NBS (35.57 g, 200 mmol) was added in portions, and the mixture was stirred at −70 °C for another 20 min. Then it was warmed to 3 °C at which temperature it was kept for 18 h. Na_2SO_3 (15.0 g, 119 mmol) was added to the solution, and the solvent was evaporated. To the remaining residue CCl_4 (300 mL) was added, and the mixture was stirred for another 30 min after which the resulting mixture was filtered and the solvent evaporated. The resulting solid was recrystallized twice from ethanol. During the first recrystallization the temperature was maintained below 45 °C. After the second recrystallization a white solid (16.40 g, 50 mmol, 50%) was obtained which was kept at −20 °C under argon. ^{1}H-NMR ($CDCl_3$): δ 6.24 (s, 2H, H-3, H-4), 1.64 (s, 9H, H-methyl). ^{13}C-NMR ($CDCl_3$): δ 147.4 (C=O), 116.1 (C-3, C-4), 100.3 (C-2, C-5), 86.5 (C-q (BOC)), 27.8 (C-methyl).

2,2′-(1′-Pyrrolinyl)pyrrole (3).[8b] Pyrrole (40.57 g, 605 mmol) was cooled on an ice bath under nitrogen. Then phosphorus oxychloride (18.32 g, 120 mmol) was added over a 40-min period under vigorous stirring followed by the addition of pyrrolidinone (12.12 g, 142 mmol) over a 70-min period. After the last addition the dark viscous liquid was stirred for another 50 min at room temperature when CH_2Cl_2 (70 mL) was added. The mixture was poured in an ice-cold solution of NaOAc (200 mL, 3 M), and a solution of KOH (10 M) was added slowly while the temperature was maintained at 0 °C until the pH reached a value of 10. This resulted in a yellow aqueous fraction and a dark organic fraction. The organic fraction was separated and washed with H_2O (2 × 100 mL). The aqueous fraction was extracted with CH_2Cl_2 (3 × 100 mL), and the combined organic fractions were washed with H_2O (2 × 50 mL). Then the combined organic fractions were washed with a KH_2PO_4 solution in water (5 × 100 mL, 2 M), and the combined aqueous fractions were basified to pH 10 and extracted with CH_2Cl_2 (3 × 50 mL). The combined CH_2Cl_2 fractions were dried ($MgSO_4$) and filtered, and the solvent was evaporated. This resulted in a yellow solid (17.68 g). Sublimation (0.2 mmHg, 80 °C) gave a white solid (10.02 g, 75 mmol, 62%). ^{1}H-NMR ($CDCl_3$): δ 8.91 (s, 1H, N-H), 6.93 (dd, $J =$ 2.6 and 1.4 Hz, 1H, H-5), 6.53 (dd, $J = 3.5$ and 1.3 Hz, 1H, H-3), 6.23 (dd, $J = 3.5$ and 2.7 Hz, 1H, H-4), 4.03 (tt, $J = 7.2$ and 1.6 Hz, 2H, H-5′), 2.90 (tt, $J = 8.2$ and 1.7 Hz, 2H, H-3′), 2.01 (q, $J = 7.7$ Hz, 2H, H-4′). ^{13}C-NMR ($CDCl_3$): δ 166.3 (C-2′), 127.9 (C-2), 121.9 (C-5), 112.8 (C-3), 109.2 (C-4), 60.5 (C-5′), 34.8 (C-3′), 22.6 (C-4′).

2,2′-Bipyrrole (4).[8b] A mixture of 2,2′-(1′-pyrrolinyl)pyrrole (**3**, 2.17 g, 16 mmol), 10% Pd/C (7.50 g, 16 mmol Pd), and triglyme (125 mL) was heated at 200 °C with vigorous stirring for 2.5 h, continuously sweeping with nitrogen. The hot mixture was filtered, and the solvent was evaporated. The resulting dark green oil (1.9 g) was purified by chromatography (60 g SiO_2, CH_2Cl_2 as eluent, R_f = 0.28) which gave a green solid (1.11 g, 8.3 mmol, 54%). ^{1}H-NMR ($CDCl_3$): δ 8.23 (s, 1H, N-H), 6.77 (td, J = 2.6 and 1.5 Hz, 2H, H-5, H-5′), 6.24 (dd, J = 6.1 and 2.7 Hz, 2H, H-4, H-4′), 6.21 (td, J = 2.5 and 1.5 Hz, 2H, H-3, H-3′). ^{13}C-NMR ($CDCl_3$): δ 125.9 (C-2, C-2′), 117.6 (C-5, C-5′), 109.4 (C-3, C-3′), 103.5 (C-4, C-4′).

***N,N′*-Bis-*tert*-(butoxycarbonyl)-2,2′-bipyrrole (5).** A mixture of 2,2′-bipyrrole (**4**, 0.26 g, 2.0 mmol), THF (12 mL), di-*tert*-butyl dicarbonate (0.88 g, 4.0 mmol), and potassium *tert*-butoxide (0.06 g, 0.5 mmol) was heated at reflux temperature for 4.5 h, argon blanketed. Then the reaction mixture was cooled to room temperature, and 2-(dimethylamino)ethylamine (45 mg, 0.5 mmol) was added. The mixture was stirred for another 15 min and the solvent was evaporated. The resulting oil was dissolved in Et_2O (40 mL) and washed with water (3 × 30 mL). The organic fraction was dried ($MgSO_4$) and filtered, and the solvent was evaporated to afford a black oil. Column chromatography (25 g SiO_2, CH_2Cl_2:hexane =1:1, R_f = 0.24) gave a colorless oil (0.43 g, 1.3 mmol, 66%). ^{1}H-NMR ($CDCl_3$): δ 7.40 (t, J = 2.6 Hz, 2H, H-5, H-5′), 6.20 (d, J = 2.6 Hz, 4H, H-3, H-3′, H-4, H-4′), 1.39 (s, 18H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1 (C=O), 126.0 (C-2, C-2′), 121.9 (C-5, C-5′), 115.3 (C-3, C-3′), 110.1 (C-4, C-4′), 83.0 (C-q (BOC)), 27.8 (C-methyl).

***N,N′*-Bis(*tert*-butoxycarbonyl-5,5′-dibromo-2,2′-bipyrrole (6).** *N,N′*-Bis(*tert*-butoxycarbonyl)-2,2′-bipyrrole (**5**, 85.0 mg, 0.256 mmol) was solved in THF (4.5 mL) and cooled to −70 °C. NBS (91.0 mg, 0.511 mmol) was added and the mixture was stirred for 30 min at −70 °C. Then it was warmed to 3 °C at which temperature it was kept for 3 h. Na_2SO_3 (a few mg) was added, and the solvent was evaporated. CCl_4 (10 mL) was added to the residue, and the mixture was stirred for 10 min and filtered. The solvent was then evaporated resulting in a slightly red oil (132.5 mg) which was used directly in an Ullmann coupling reaction. ^{1}H-NMR ($CDCl_3$): δ 6.31 (d, J = 3.5 Hz, 2H, H-4, H-4′), 6.13 (d, J = 3.5 Hz, 2H, H-3, H-3′), 1.36 (s, 18H, H-methyl). ^{13}C-NMR ($CDCl_3$): δ 148.0 (C=O), 128.1 (C-2, C-2′), 115.7−115.1 (C-3, C-3′, C-4, C-4′), 102.5 (C-5, C-5′), 84.9 (C-q (BOC)), 27.5 (C-methyl).

N-(Phenylsulfonyl)-2-formylpyrrole (7).[19] 2-Formylpyrrole (4.76 g, 50.1 mmol) was dissolved in DMF (25 mL) under nitrogen at room temperature. NaH (1.56 g, 65.0 mmol) was added in portions, and after addition the mixture was stirred for another 15 min. Then benzenesulfonyl chloride (9.03 g, 51.1 mmol) was added dropwise over a 15-min period, and after addition the mixture was stirred for another 60 min. The mixture was then poured into ice−water (250 mL) and extracted with Et_2O (3 × 100 mL). The combined organic fractions were dried ($MgSO_4$) and filtered, and the solvent was evaporated. The resulting beige solid (8.81 g, 37.5 mmol, 75%) was used directly for the diketone (**8**) synthesis. ^{1}H-NMR ($CDCl_3$): δ 9.96 (s, 1H, H-ald.), 7.93 (d, J = 8.2 Hz, 2H, H-ortho), 7.65 (m, 2H, H-para, H-5), 7.55 (t, J = 7.8 Hz, 2H, H-meta), 7.17 (dd, J = 3.8 and 1.7 Hz, 1H, H-3), 6.43 (t, J = 3.4 Hz, 1H, H-4). ^{13}C-NMR ($CDCl_3$): δ 178.8 (C=O), 138.1 (C-ipso (phenyl)), 134.5 (C-para), 133.5 (C-2), 129.5 (C-ortho and C-5), 127.4 (C-meta), 124.9 (C-3), 112.5 (C-4).

1,4-Bis(*N*-(phenylsulfonyl)-2-pyrryl)-1,4-butanedione (8).[19] A mixture of *N*-(phenylsulfonyl)-2-formylpyrrole (**7**, 7.06 g, 30.0 mmol), 3-benzyl-5-(2-hydroxyethyl)-4-methyl-1,3-thiazolium chloride (1.23 g, 4.6 mmol), NaOAc (0.63 g, 7.7 mmol), and ethanol (40 mL) was heated at reflux temperature under argon. Divinyl sulfone (1.76 g, 14.9 mmol) was added dropwise, and the mixture was refluxed for another 17 h. The resulting precipitate was filtered, washed with ethanol, water, and Et_2O (each 25 mL), and dried. A slightly brown solid was obtained (3.34 g, 6.7 mmol, 45%). ^{1}H-NMR ($CDCl_3$): δ 7.96 (d, J = 7.4 Hz, 4H, H-ortho), 7.80 (dd, J = 3.2 and 1.7 Hz, 2H, H-5), 7.58 (t, J = 7.4 Hz, 2H, H-para), 7.50 (t, J = 7.3 Hz, 4H, H-meta), 7.12 (dd, J = 3.8 and 1.7 Hz, 2H, H-3), 6.35 (t, J = 3.6 Hz, 2H, H-4), 3.04 (s, 4H, CH_2). ^{13}C-NMR ($CDCl_3$): δ 186.6 (C=O), 138.8 (C-ipso (phenyl)), 133.6 (C-para), 132.7 (C-2), 130.3 (C-5), 128.7−128.0 (C-ortho, C-meta), 123.9 (C-3), 110.5 (C-4), 32.9 (CH_2).

2,5-Bis(1-(phenylsulfonyl)-2-pyrryl)pyrrole (9). A mixture of 1,4-bis(1-(phenylsulfonyl)-2-pyrryl)-1,4-butanedione (**8**, 2.57 g, 5.2 mmol), propionic acid (37 mL), acetic anhydride (7.5 mL, 79.4 mmol), and NH_4OAc (10.97 g, 142 mmol) was refluxed under nitrogen. After 18 h it was cooled to room temperature and the solvent was evaporated. H_2O (100 mL) was added to the residue, and this mixture was neutralized with NaOH (2 M). The aqueous fraction was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic fractions were washed with $NaHCO_3$ (2 × 50 mL, 1 M) and brine (2 × 50 mL) and dried ($MgSO_4$). After evaporation of the solvent a black solid was obtained. Column chromatography (50 g SiO_2, CH_2Cl_2:hexane = 3:1, R_f = 0.47) afforded a nice smelling, slightly green solid (1.57 g, 3.3 mmol, 63%). ^{1}H-NMR ($CDCl_3$): δ 9.22 (s, 1H, N-H), 7.53 - 7.46 (m, 6H, H-ortho, H-para), 7.42 (dd, J = 3.1 and 2.0 Hz 2H, H-5, H-5″), 7.34 (t, 7.6 Hz, 4H, H-meta), 6.33 - 6.31 (m, 4H, H-3, H-3″, H-4, H-4″), 6.09 (d, J = 2.6 Hz, 2H, H-3′, H-4′). ^{13}C-NMR ($CDCl_3$): δ 137.9 (C-ipso (phenyl)), 133.8 (C-para), 128.9−127.1(C-ortho, C-meta), 127.3 (C-2, C-2″), 123.8 (C-5, C-5″), 122.1 (C-2′, C-5′), 115.7 (C-3, C-3″), 112.1−111.7 (C-3′, C-4′, C-4, C-4″).

***N,N′,N″*-Tris(*tert*-butoxycarbonyl)-2,2′:5′,2″-terpyrrole (10).** A deaerated solution of NaOH (1.05 g, 26 mmol) in methanol (20 mL) was charged with 2,5-bis(1-(phenylsulfonyl)-2-pyrryl)pyrrole (9, 0.80 g, 1.7 mmol) and refluxed for 2.5 h under argon. The mixture was cooled to room temperature and extracted from an NH4Cl solution in water (sat, 30 mL) with CH2Cl2 (3 × 15 mL). The combined organic fractions were washed with H2O (2 × 20 mL) and dried (MgSO4), and the solvent was evaporated. The resulting black solid (0.25 g) was directly used. Together with di-*tert*-butyl dicarbonate (1.50 g, 6.9 mmol), THF (12 mL), and potassium *tert*-butoxide (50 mg) it was refluxed for 18 h under argon. Then (dimethylamino)ethylamine (0.20 g, 2.3 mmol) was added, the mixture was stirred for another 15 min, the solvent was evaporated, and Et2O (25 mL) was added. Extraction with dilute HCl (2 × 1 mL) and H2O (2 × 10 mL) followed by drying (MgSO4) of the organic fraction and evaporation of the solvent resulted in a dark oil. Column chromatography (50 g SiO2, CH2Cl2: hexane = 2:1, Rf = 0.22) gave pure product **10** (0.46 g, 0.9 mmol, 55%). ^{1}H ($CDCl_3$): δ 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-5, H-5″), 6.20 (t, J = 3.3 Hz, 2H, H-4, H-4″), 6.15 (s, 2H, H-3′, H-4′), 6.14 (dd, J = 3.3 and 1.9 Hz, 2H, H-3, H-3″), 1.39 (s, 18H, H-methyl (BOC and BOC″)), 1.21 (s, 9H, H-methyl (BOC′)). ^{13}C-NMR ($CDCl_3$): δ 149.1 (C=O and C=O″), 149.0 (C=O′), 127.6−126.7 (C-2, C-2′, C-5′, C-2″), 121.9 (C-5, C-5″), 115.3 (C-3, C-3″), 113.8 (C-3′, C-4′), 110.3 (C-4, C-4″), 83.3 (C-q (BOC), C-q (BOC″)), 82.5 (C-q (BOC′)), 27.8 (C-methyl, C-methyl″), 27.6 (C-methyl′).

***N,N′,N″*-Tris(*tert*-butoxycarbonyl)-5,5″-dibromo-2,2′:5′,2″-terpyrrole (11).** *N,N′,N″*-Tris(*tert*-butoxycarbonyl)-2,2′:5′,2″-terpyrrole (**10**, 108.9 mg, 0.219 mmol) was solved in THF (3 mL) and cooled to −70 °C under argon. NBS (78.0 mg, 0.438 mmol) was added and the mixture was stirred for another 30 min at −70 °C. Then the solution was warmed to 3 °C at which temperature it was kept for 3.5 h. Na_2SO_3 (a few mg) was added to the solution, and the solvent was evaporated. CCl_4 (10 mL) was added, and the mixture was stirred for another 15 min and filtered. After evaporation of the solvent a gray solid remained (141.1 mg) which was used directly in an Ullmann coupling reaction. ^{1}H-NMR ($CDCl_3$): δ 6.32 (d, J = 3.6 Hz, 2H, H-4, H-4″), 6.17 (s, 2H, H-3′, H-4′), 6.10 (d, J = 3.6 Hz, 2H, H-3, H-3″) 1.37 (s, 18H, H-methyl, H-methyl″), 1.26 (s, 9H, H-methyl′). ^{13}C-NMR ($CDCl_3$): δ 148.5 (C=O, C=O″), 148.0 (C=O′), 128.5−127.7 (C-2, C-2′, C-5′, C-2″), 115.6 - 114.2 (C-3, C-4, C-3′, C-4′, C-3″, C-4″), 102.2 (C-5, C-5″), 84.3 (C-q (BOC), C-q (BOC″)), 83.7 (C-q (BOC′)), 27.6 (C-methyl, C-methyl″), 27.5 (C-methyl′).

Polymerization of the Monomers. The Ullmann polymerization of the three monomers (**2**, **6** and **11**) was performed by heating a mixture of the monomer, DMF (10 mL/g monomer), and 1 wt equiv of Cu−bronze under argon at 100 °C. After the reaction time (1 h in the case of **2**, 2 h in the case of **6** and **11**) the dark green mixture was poured into ice−water

and extracted with Et_2O. The organic fractions were dried ($MgSO_4$) and the solvent was evaporated resulting in dark oils which were filtered over Al_2O_3, using CH_2Cl_2 as eluent, before HPLC analysis.

HPLC Separations. A Pharmacia/LKB HPLC system was used consisting of a Model 2252 LC-controller, two Model 2248 pumps, a Model 2510 uvicord SD detector operating at 276 nm, a Model 2211 superrac fraction collector, and a Spark marathon autosampler.

The stainless-steel analytical (150 × 4.6 mm) and preparative (100 × 16 mm) columns were self-packed with Lichrosorb RP-18 (5 μm, Merck, Darmstadt, F. R. G.). The column temperature was 40 °C, and the samples were dissolved in a mixture of methanol and dichloromethane (9/1).

Eluent A was methanol (HPLC-grade, Biosolve, Barneveld, Holland) and eluent B was water (milli-Q, Bedford, U.S.A.) with the following linear gradient profile: t = 0, 85% A, 15% B; t = 5 min, 85% A, 15% B; t = 40 min, 100% A; t = 60 min, 100% A; t = 65 min, 85% A, 15% B. This profile was slightly adjusted for the analysis of the oligomerization of the dibrominated bi- and terpyrrole (e.g. 80% A, 20% B instead of 85% A, 15% B). In this way a better separation was obtained.

The flow rate was 1 mL/min for the analytical column and 6 mL/min for the preparative column.

NMR Data of the Isolated Oligomers. n = 1: ^{1}H-NMR ($CDCl_3$): 7.23 (t, J = 2.2 Hz, 2H, H-2, H-5), 6.20 (t, J = 2.2 Hz, 2H, H-3, H-4), 1.58 (s, 9H, H-methyl). ^{13}C-NMR ($CDCl_3$): 148.8 (C=O), 119.9 (C-2, C-5), 111.7 (C-3, C-4), 83.4 (C-q (BOC)), 27.9 (C-methyl).

n = 2; ^{1}H-NMR ($CDCl_3$): 7.40 (t, J = 2.6 Hz, 2H, H-5, H-5′), 6.20 (d, J = 2.6 Hz, 4H, H-3, H-4, H-3′, H-4′), 1.39 (s, 18H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1 (C=O), 126.0 (C-2, C-2′), 121.9 (C-5, C-5′), 115.3 (C-3, C-3′), 110.1 (C-4, C-4′), 83.0 (C-q (BOC)), 27.6 (C-methyl).

n = 3: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-5, H-5″), 6.20 (t, J = 3.3 Hz, 2H, H-4, H-4″), 6.15 (s, 2H, H-3′, H-4′), 6.14 (dd, J = 3.3 and 1.9 Hz, 2H, H-3, H-3″), 1.39 (s, 18H, H-methyl (BOC and BOC″)), 1.21 (s, 9H, H-methyl (BOC′)). ^{13}C-NMR ($CDCl_3$): 149.1 (C=O and C=O″), 149.0 (C=O′), 127.6–126.7 (C-2, C-2′, C-2″, C-5), 121.9 (C-5, C-5″), 115.3 (C-3, C-3″), 113.8 (C-3′, C-4′), 110.3 (C-4, C-4″), 83.3 (C-q (BOC and BOC″)), 82.5 (C-q (BOC′), 27.8 (C-methyl (BOC and BOC″)), 27.6 (C-methyl (BOC′)).

n = 4: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.22–6.13 (m, 8H, H-3,4), 1.42 (s, 18H, H-methyl (BOC and BOC‴), 1.26 (s, 18H, H-methyl (BOC′ and BOC″)). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9, 128.2, 127.5, 126.8, 121.9, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 27.8, 27.7.

n = 5: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.1 and 2.0 Hz, 2H, H-α), 6.21–6.14 (m, 10H, H-3,4), 1.41–1.24 (45H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.0, 148.9, 148.8, 128.3, 128.2, 127.5, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.1, 82.8, 82.5 27.8, 27.7, 27.5.

n = 6: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.22–6.15 (m, 12H, H-3,4), 1.43–1.25 (54H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9, 148.8, 128.4, 128.3, 128.1, 127.4, 126.9, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.6, 82.5, 27.8, 27.7 (2 peaks).

n = 7: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.3 and 1.9 Hz, 2H, H-α), 6.23–6.15 (m, 14H, H-3,4), 1.43–1.27 (63H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9 (2 peaks), 148.8, 128.4, 128.2, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.6 (2 peaks), 82.5, 27.8 (2 peaks), 27.7.

n = 8: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23–6.15 (m, 16H, H-3,4), 1.43–1.27 (72H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9, 148.8 (2 peaks), 128.4, 128.3, 128.1, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 82.5 (2 peaks), 27.8, 27.7 (2 peaks), 27.6.

n = 9: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23–6.15 (m, 18H, H-3,4), 1.41–1.25 (81H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9, 148.8 (2 peaks), 128.4, 128.3, 128.2, 128.1, 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 113.8, 110.2, 83.2, 82.7, 82.5 (2 peaks), 27.8, 27.7.

n = 10: ^{1}H-NMR ($CDCl_3$): 7.40 (dd, J = 3.2 and 1.9 Hz, 2H, H-α), 6.23–6.15 (m, 20H, H-3,4), 1.41–1.23 (90H, H-methyl). ^{13}C-NMR ($CDCl_3$): 149.1, 148.9, 148.8, 128.4, 128.3, 128.2 (2 peaks), 128.0, 127.4, 126.8, 121.8, 115.3, 113.9, 110.2, 83.2, 82.7, 82.5, 27.8, 27.7.

From n = 11 to n = 20 only ^{1}H-NMR spectra were measured. These proton spectra were comparable to that of n = 10; just the ratios changed in the expected way.

Acknowledgment. An unrestricted grant from Philips Research Laboratories, Eindhoven, The Netherlands, is greatly appreciated.

References and Notes

(1) Street, G. B. *Handbook of conducting polymers* Marcel Dekker: New York, 1986.
(2) (a) Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mat.* **1992**, *4*, 107. (b) Garnier, F.; Yassar, A.; Hajlaoui, R.; Horowitz, G.; Deloffre, F.; Servet, B.; Ries, S.; Alnot, P. *J. Am. Chem. Soc.* **1993**, *115*, 8716.
(3) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.
(4) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mat.* **1993**, *5*, 430, 620.
(5) (a) Havinga, E. E.; Rotte, I.; Meijer, E. W.; ten Hoeve, W.; Wynberg, H. *Synth. Met.* **1991**, *41*–43, 473. (b) ten Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W. *J. Am. Chem. Soc.* **1991**, *113*(15), 5887.
(6) van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B.; Zimmer, H. *Phosphorus, Sulfur Silicon* **1989**, *46*, 153.
(7) (a) Bäuerle, P.; Pfau, F.; Schlupp, H.; Würthner, F.; Gaudl, K.-U.; Caro, M. B.; Fischer, P. *J. Chem. Soc., Perkin Trans. 2* **1993**, 489. (b) Bäuerle, P.; Würthner, F.; Gölz, G.; Effenberger, F. *Synthesis* **1993**, 1099.
(8) (a) Rapoport, H.; Holden, K. G. *J. Am. Chem. Soc.* **1962**, *84*, 635. (b) Rapoport, H.; Castagnoli, N., Jr. *J. Am. Chem. Soc.* **1962**, *84*, 2178. (c) Rapoport, H.; Castagnoli N., Jr.; Holden, K. G. *J. Org. Chem.* **1964**, *29*, 883.
(9) (a) Grigg, R.; Johnson, A. W.; Wasley, J. W. F. *J. Chem. Soc.* **1963**, 359. (b) Grigg, R.; Johnson, A. W. *J. Chem. Soc.* **1964**, 3315.
(10) Kauffmann, T.; Lexy, H. *Chem. Ber.* **1981**, *114*, 3674.
(11) (a) Grehn, L.; Ragnarsson, U. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 296. (b) Chen, W.; Stephenson, E. K.; Cava, M. P.; Jackson, Y. A. *Org. Synth.* **1991**, *70*, 151. (c) Rawal, V. H.; Cava, M. P. *Tetrahedron Lett.* **1985**, *26*, 6141. (d) Chen, W.; Cava, M. P. *tetrahedron Lett.* **1987**, *28*, 6025.
(12) (a) Martina, S. Dissertation, University of Mainz, Mainz, Germany, 1992. (b) Martina, S.; Enkelmann, V.;Schlüter, A.-D.; Wegner, G. *Synth. Met.* **1991**, *41*, 403. (c) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32(3)*, 215. (d) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G. *Synthesis* **1991**, 613. (e) Martina, S.; Schlüter, A.-D. *Macromolecules* **1992**, *25*, 3607. (f) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G. *Synth. Met.* **1992**, *51*, 299. (g) Zotti, G.; Martina, S.; Schlüter, A.-D.; Wegner, G. *Adv. Mat.* **1993**, *4*(12), 798. (h) Zerbi, G.; Veronelli, M.; Martina, S.; Schlüter, A.-D.; Wegner, G. *J. Chem. Phys.* **1994**, *100*(2), 978. (i) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G.; Zotti, G.; Zerbi, G. *Synth. Met.* **1993**, *55*(2–3), 1096 (j) Schlüter, A.-D.; Wegner, G. *Acta Polymerica* **1993**, *44*, 59. (k) Zerbi, G.; Veronelli, M.; Martina, S.; Schlüter, A.-D.; Wegner, G. *Adv. Mat.* **1994**, *6*(5), 385.
(13) Stille, J. K. *Angew. Chem.* **1986**, *98*, 504.
(14) (a) Webb, J. L. A.; Threlkeld, R. R. *J. Org. Chem.* **1953**, *18*, 1406. (b) Bauer, V. J.; Woodward, R. B. *J. Am. Chem. Soc.* **1983**, *105*, 6429. (c) Sessler, J. L.; Cyr, M.; Burrell, A. K. *Tetrahedron* **1992**, *48*(44), 9661. (d) Ikeda, H.; Sessler, J. L. *J. Org. Chem.* **1993**, *58*, 2340.
(15) (a) Ullmann, F. *Ber.* **1896**, 1878. (b) Ullmann, F. *Annalen* **1904**, *332*, 38.
(16) (a) Fanta, P. E. *Chem. Rev.* **1946**, *38*, 139. (b) Fanta, P. E. *Chem. Rev.* **1964**, *64*, 613. (c) Fanta, P. E. *Synthesis* **1974**, 9. (d) Goshaev, M.; Otroshchenko, O. S.; Sadykov, A. S. *Russ. Chem. Rev.* **1972**, *41*(12), 1046.
(17) (a) Noren, G. K.; Stille, J. K. *Macromol. Rev.* **1971**, *5*, 385. (b) Tour, J. M. *Adv. Mat.* **1994**, *6*(3), 190. (c) Brockmann, T. W.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 7435. (d) Polis, D. W.; Young, C. L.; McLean, M. R.; Dalton, L. R. *Macromolecules* **1990**, *23*, 3231.
(18) (a) Lewis, J. J.; Rogers, L. B.; Pauls, R. E. *J. Chromatogr.* **1983**, *264*, 339. (b) Glöckner, G.; van den Berg, J. H. M. *J. Chromatogr.* **1987**, *384*, 135.
(19) Merrill, B. A.; LeGoff, E. *J. Org. Chem.* **1990**, *55*, 2904.
(20) Brédas, J. L.; Baughman, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 475.

MA940927H