Synthesis and characterization of a tetra-alkylated alpha-conjugated duodecithiophene

6 AUTHORS, INCLUDING:

Abderrahim Yassar
École Polytechnique
132 PUBLICATIONS **5,789** CITATIONS

SEE PROFILE

M. Hmyene
Université Hassan 1er Faculté des Scienc…
22 PUBLICATIONS **680** CITATIONS

SEE PROFILE

Belkacem Nessark
Ferhat Abbas University of Setif
44 PUBLICATIONS **368** CITATIONS

SEE PROFILE

Gilles Horowitz
French National Centre for Scientific Rese…
236 PUBLICATIONS **11,262** CITATIONS

SEE PROFILE

Communications

Synthesis and Characterization of a Tetra-Alkylated Alpha-Conjugated Duodecithiophene

By *Abderrahim Yassar, Didier Delabouglise, Mohamed Hmyene, Belkassem Nessak, Gilles Horowitz,** and *Francis Garnier*

The synthesis and characterization of well-defined oligomers as models of the conjugated ("conducting") polymers have recently received increased attention. Among the various compounds studied, the thiophene oligomers hold a leading position probably because of their high stability both in their neutral and oxidized state. Over the last few years, work carried out in this laboratory has provided a thorough electrochemical,[1] spectroscopic[2] and electrical[3] characterization of the unsubstituted thiophene oligomers, from terthiophene (3T) up to the octithiophene (8T). Furthermore, we have shown that solutions of quinquethiophene (5T) and sexithiophene (6T) can be oxidized to their respective cation and dication, and can thus help in modeling the doping process of polythiophene (PT).[4]

However, because the solubility of thiophene oligomers decreases dramatically as their chain length increases, oligomers longer than 6T are very difficult to synthesize and purify, and virtually impossible to characterize. Although we have performed an electrochemical synthesis of octithiophene (8T) and decithiophene (10T), the purity of the products was poor, and their characterization limited to the measurement of their solid-state UV-visible absorption spectrum.[11] This problem can be overcome by substituting solubilizing groups into the oligomer chains. α-Substitution presents the advantage of preserving most of the properties of the unsubstituted molecule. For instance, it has been shown that dialkylated thiophene oligomers crystalize with the same structure as the unsubstituted oligomers.[5] More recently, "end-capped" oligothiophenes—up to the heptamer—have been synthesized.[6] The solubility of thiophene oligomers (as well as polythiophene) can also be greatly enhanced by β-substitution of alkyl chains. As an example, the solubility of didecyl-6T (2D6T) in chloroform is higher than 400 g/l (1 mol/l), whereas that of unsubstituted 6T is lower than 0.05 g/l (10^{-4} mol/l).[7] This solubility gives an opportunity to synthesize much longer oligomers. The synthesis of alkyl-substituted undecithiophene (11T) has been reported recently.[8]

In the present paper, we describe the synthesis of a substituted duodecithiophene (12T) with four lateral decyl groups,

[*] Dr. G. Horowitz, Dr. A. Yassar,[+] Dr. D. Delabouglise,[*]
Dr. M. Hmyene, Dr. B. Nessak, Dr. F. Garnier
Laboratoire des Matériaux Moléculaires, C.N.R.S.
2 rue Henry Dunant, F-94320 Thiais (France)
[+] Permanent address: Department of Physics, University Ibno Zohr, Agadir (Morocco)
[*] Present address: L.I.E.S.G./E.N.S.E.F.G., 1130 rue de la Piscine, Domaine Universitaire, B. P. 75, F-38402 Saint Martin d'Heres (France)

hereafter designated as tetradecyl-duodecithiophene (4D12T, Scheme 1). This compound has been characterized spectroscopically and electrochemically. Furthermore, 4D12T can be oxidized in solution and in the solid state, and seems to provide an improved model for the doping mechanism of polythiophene.
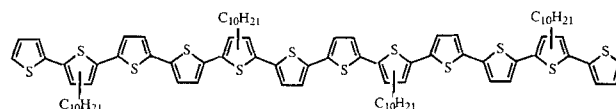
Scheme 1. The structure of tetradecylduodecithiophene (4D12T).

The synthesis of the fully conjugated $\beta'\beta''''$-didecylsexithiophene 2D6T has been described previously.[7] It proceeds by homocoupling of the α-monolithiated derivative of 3'-decyl-2,2':5',2''-terthiophene. A dimerization to 4D12T had to be expected when repeating the same procedure on the isolated 2D6T. However, the selectivity of the lithiation reaction strongly decreases when the oligomer chain length increases, and a substantial amount of dilithiated 2D6T is
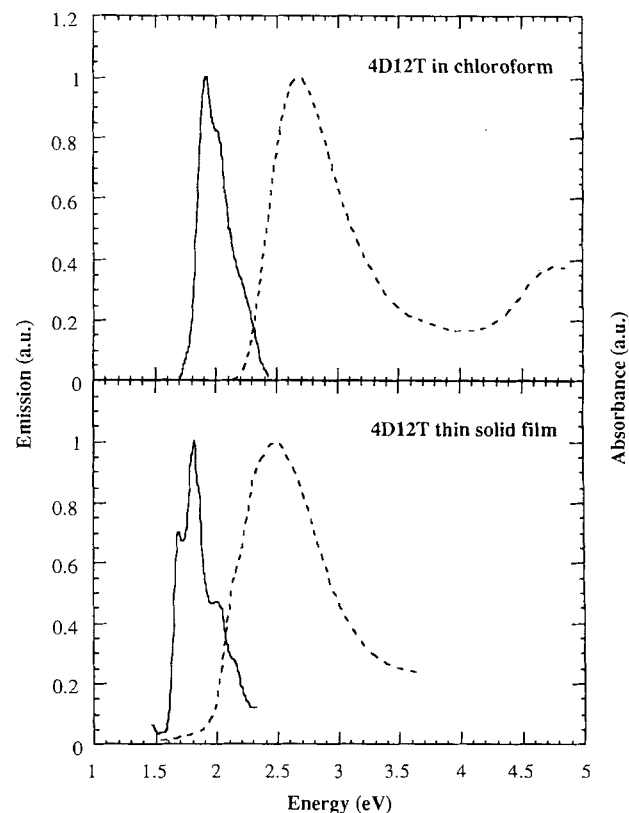

Fig. 1. Absorption (dotted lines) and emission (solid lines) spectra of 4D12T recorded in chloroform solution (upper curves) and in a thin solid film (lower curves).

formed during the reaction. Nevertheless, the specific solubility of the different molecular structures obtained after the oxidative coupling (6T, 12T, 18T...) allows the separation, by liquid chromatography, of 2D6T from 4D12T, which is then subsequently eluted with another solvent whereas the longer chains remain tightly bound to the chromatographic phase. 4D12T appears as a deep red solid that exhibits a low fusion point (80 °C) and reasonable solubility in chloroform (4.5 g/l, 3×10^{-3} mol/l).

The optical absorption and emission spectra of 4D12T in solution (chloroform) and thin solid film (spin-coated from a chloroform solution on a glass slide) are shown in Figure 1. Results of optical and electrical measurements on various alkyl-substituted oligothiophenes are collected in Table 1.

Table 1. Optical and electrical properties of β-substituted thiophene oligomers.

Oligomer [a]	λ_{cm} [b] [nm]	λ_{max} [b] [nm]	ε_{max} [b] [L mol^{-1}cm^{-1}]	Conductivity [S/cm] [c] Neutral	I$_2$-doped	Reference
1Dd3T		345				[8]
1D3T		347				This work
1B5T		412			0.01	[8]
2Dd6T		423				[8]
2D6T	520	424	45 000	10^{-13}		[7] This work
2D7T		440			0.20	[8]
1Dd9T		455				[8]
3Dd11T		462			20	[8]
4D12T	647	465	110 000	10^{-9}	5	This work

[a] The notation used here reads as follows: the first digit gives the number of alkyl side chains; B stands for butyl, D for decyl and Dd for dodecyl; the second digit corresponds to the number of thiophene rings. [b] Emission and absorption maximum in chloroform. [c] Conductivity from two-probe measurement on sandwich cells for undoped, and four-probe measurement on I$_2$-doped thin films.

Figure 2 shows the variation of the energy of the maximum of absorption as a function of the inverse of the chain length n (i.e. the number of thiophene rings). The extrapolation to an infinite chain gives $E_{max}(n \to \infty) = 2.31$ eV (or $\lambda_{max}(n \to \infty)$
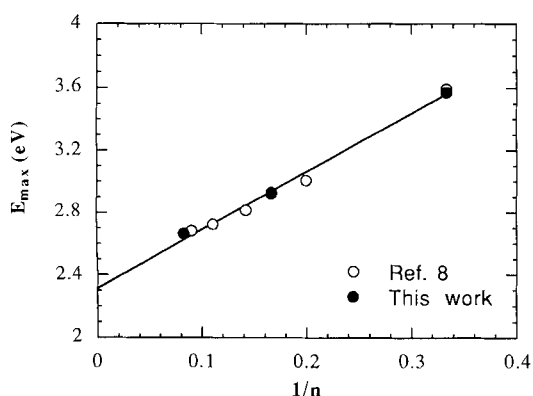

Fig. 2. Variation of the energy of the absorption peak of β-substituted oligothiophenes as a function of the inverse chain length. Extrapolation to $n \to \infty$ is 2.31 eV (537 nm).

= 537 nm), a value very close to the one reported by Bäuerle on end-capped oligothiophenes.[6]

The solid-film absorption and emission spectra differ from those in solution by a red shift (from 465 nm to 500 nm in absorption, and from 647 nm to 682 nm in emission), and the appearance of equally spaced maxima, mainly visible in the emission spectrum. The latter behavior is also found for shorter oligomers, and has been attributed to vibrational coupling with the electronic transition involving the C=C ring stretching, indicated by the coincidence between the energy spacing of the peaks and the frequency of this mode as observed by resonance Raman spectroscopy.[2] It should be noted, however, that the structure in the absorption spectrum is less marked than in shorter oligomers.[8] As a matter of fact, the absorption spectrum of 4D12T thin films strongly resembles that of poly-3-alkylthiophene (P3AT) films.[9] This last remark also includes the position of the maximum, namely 500 nm (2.48 eV).

Also given in Table 1 are the conductivity of undoped and I$_2$-doped oligothiophenes. The conductivity of undoped 2D6T and 4D12T are significantly lower than that of the unsubstituted sexithiophene (10^{-7} S/cm).[10] Obviously, the pendant alkyl chains tend to move the conjugated chains apart from each other, which leads to the decrease of the interchain charge transfer rate, thus lowering the conductivity. The measurement of the conductivity of short (up to the octithiophene) doped oligothiophenes is hampered by their tendency to dimerize in the solid state.[1, 8] As will be shown, such a reaction does not occur with 4D12T, the conductivity of which in a doped film approaches that of P3AT. It must be noted, however, that I$_2$-doped 4D12T spontaneously undopes in air, the complete undoping of a 5 μm thick film occurring within two or three days.

Figure 3 shows a cyclic voltammogram (CV) recorded on a platinum disk electrode dipped into a solution of 4D12T in nitrobenzene. Like that of 2D6T,[11] it shows two quasi-reversible couples (1) and (2). Table 2 gives the positions of the anodic and cathodic peak potentials measured on 2D6T and 4D12T. It can be seen that the first redox couple (1) is shifted towards lower potentials as the chain length increases, whereas the second one (2) remains practically unchanged. This behavior is markedly different from that reported on end-capped oligothiophenes,[6] where the difference between couples (1) and (2) decreases when the chain length increases. Moreover, a peak separation of ca. 60 mV, which indicates a reversible one-electron process, is observed on end-capped oligothiophenes. This behavior seems to degrade in the presence of alkyl side chains: the peak separation of β-substituted 6T and 12T ranges from 140 to 170 mV, indicating that the presence of alkyl chains introduces some irreversible steps during the electrochemical process. Importantly, whereas continuous cycling in a 2D6T solution leads to the formation of a solid film on the electrode, which we can now identify as being mainly 4D12T (see below) whose formation is accompanied by a gradual change of the corresponding CV,[7] the CV of a 4D12T solution
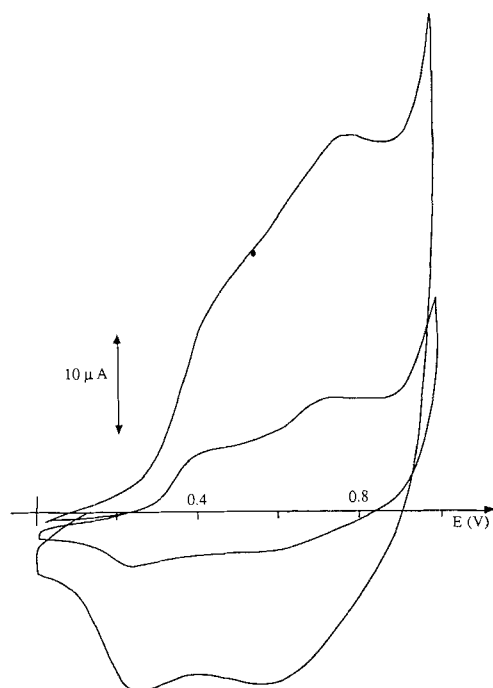
Fig. 3. Cyclic voltammogram of 2.7×10^{-5} M 4D12T in nitrobenzene. Reference: Ag/Ag⊕. Scan rate: 10 mV/s (inner curve) and 50 mV/s (outer curve).

Fig. 4. Cyclic voltammogram of a 4D12T solid film on a platinum electrode in acetonitrile 0.1 M LiClO₄. Reference: Ag/Ag⊕. The different curves correspond to scan rates increasing from 10 to 100 mV/s.

remains stable, indicating that the coupling of this molecule does not occur.

Table 2. Anodic (E_{pa}) and cathodic (E_{pc}) peak potentials (in V vs Ag/Ag⊕) of the two quasi-reversible redox couples measured on 2D6T and 4D12T nitrobenzene solution.

Oligomer	E_{pa1}	E_{pc1}	E_{pa2}	E_{pc2}
2D6T	0.55	0.40	0.72	0.58
4D12T	0.40	0.24	0.71	0.54

The CV of a 4D12T solid film recorded in acetonitrile—where it is poorly soluble—is shown in Figure 4. The film was obtained by depositing some drops of a chloroform solution onto a platinum disk electrode and letting the solvent evaporate. This CV is typical of a P3AT solid film, with one anodic (E_{pa} = 0.35 V) and one cathodic (E_{pc} = 0.20 V) peak, the potentials of which are very close to those measured for electrochemically coupled 2D6T.[7] The absorption spectra (measured on an ITO–glass electrode) of neutral and oxidized 4D12T are shown in Figure 5. Once again, they strongly resemble those corresponding to coupled 2D6T. These results lead us to suggest that electrochemically coupled 2D6T consists mainly in 4D12T.

Also shown in Figure 5 are the absorption spectra of neutral and oxidized 4D12T in dichloromethane. Oxidized 4D12T was obtained by adding $FeCl_3$ to the solution. The concentration of 4D12T in the solution was low (ca. 10^{-5} mol l^{-1}) in order to prevent bimolecular reactions. The quasi-similar-

Fig. 5. Absorption of neutral (dotted lines) and doped (solid lines) 4D12T. Upper curves: thin film on ITO-glass slide, electrochemically doped. Lower curves: solution in CH_2Cl_2 chemically doped with $FeCl_3$.

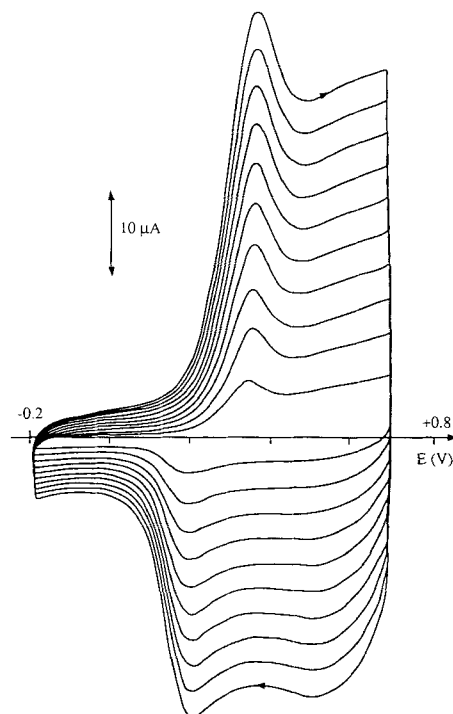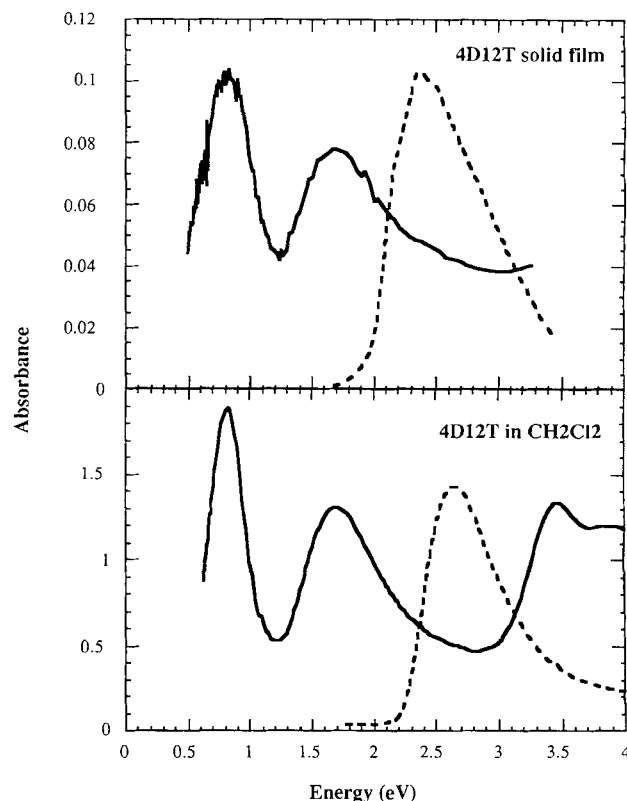ity of the two spectra in Figure 5 is further evidence that the dimerization of 4D12T does not occur in the solid state.

Previous work from this laboratory[4] has shown that the chemical oxidation of short oligomers nT (n = 5 or 6) can be studied in very dilute solutions, where bimolecular reactions are avoided. The successive generation of the radical cation and dication can be followed by UV-visible-near-IR spectroscopy. During a first step, the visible absorption peak of the neutral form (located at 432 nm for 6T) gradually disappears as $FeCl_3$ is added, and two near-IR peaks grow (780 nm and 1473 nm for 6T), attributed to the cation radical $nT^{\ominus\oplus}$. When more $FeCl_3$ is added, these two peaks are gradually replaced by a single peak (1003 nm for 6T), corresponding to the dication $nT^{\oplus\oplus}$. The presence of isosbestic points confirmed the successive interconversion of nT to $nT^{\ominus\oplus}$, and $nT^{\ominus\oplus}$ to $nT^{\oplus\oplus}$. These results were confirmed by ESR spectroscopy, which first showed the appearance of a narrow signal ($\Delta H_{pp} \approx 4$ G) centered near g = 2 (corresponding to the radical cation), and then the disappearance of this signal during the second step leading to the formation of the spinless dication. These results have been confirmed by others on α-alkylated[5] and end-capped[6] short oligothiophenes.

The spectroscopic behavior of 4D12T is quite different, in that its oxidation is a one-step reaction. Figure 6 shows that as $FeCl_3$ is added to the solution, only the gradual growth of two near-IR peaks seen on the solid line spectra and the concomitant disappearance of the visible peak are observed.

Fig. 6. Absorption spectra of 4D12T, 1.96×10^{-5} M, in CH_2Cl_2, gradually doped with $FeCl_3$. y: number of charges per thiophene ring, calculated by assuming two molecules of $FeCl_3$ for one charge.

The isosbestic point at 2.15 eV clearly shows the interconversion from neutral to doped 4D12T. The doping level y corresponds to the number of charges per thiophene ring, and was calculated by assuming that two $FeCl_3$ molecules are needed to generate one charge.[4] The absorption at hv > 3 eV observed on the curve corresponding to y = 0.25 corresponds to unreacted $FeCl_3$, indicating that the maximum doping level has been reached. ESR measurements carried out under the same experimental conditions and identical concentration (2×10^{-5} M in CH_2Cl_2) than those that lead to a clear

signal with 6T and 4D6T solutions only gave a very weak signal that could hardly be extracted from the background noise. Furthermore, the absorption peaks of the oxidized state of 4D12T are located at 0.8 and 1.7 eV. These values are close to those measured on electrochemically doped PT[11] and P3AT.[10] It can then been deduced that unlike in the shorter oligomers, where the radical cationic (polaronic) state of which are stable, the more stable configuration of oxidized 4D12T is the spinless bipolaron. This result is similar to what is observed on P3AT,[9] and confirms the theoretical predictions for long polythiophene chains.[12, 13]

In conclusion, β-substituted oligothiophenes offer the possibility to synthesize very long oligomers. Duodecithiophene models the doping process of polythiophene better than shorter oligomers. It appears that the more stable oxidized state of 4D12T corresponds to the spinless bipolaron, a behavior that differentiates it from the shorter oligomers where cations radicals (polarons) are stable. The polaronic signal often detected during the oxidation of PT could thus arise from the presence in the polymer of short oligomers. A similar explanation has recently been put forward based on spectroelectrochemical measurements on highly conjugated polypyrrole.[14] Work is in progress in order to determine the exact amount of spins in doped 4D12T, both in solution and in the solid state.

Experimental

sandwich structures, with sputtered gold back and front contacts, by using a Hewlett-Packard 4140B picoammeter-dc voltage source.

[1] a) Z. G. Xu, D. Fichou, G. Horowitz, F. Garnier, *J. Electroanal. Chem.* **1989**, *267*, 339; b) Z. G. Xu, G. Horowitz, *J. Electroanal. Chem.* **1992**, in press.
[2] D. Fichou, G. Horowitz, B. Xu, F. Garnier, *Synth. Met.* **1992**, *48*, 167.
[3] G. Horowitz, D. Fichou, X. Z. Peng, P. Delannoy, *J. Phys. France* **1990**, *51*, 1489.
[4] a) D. Fichou, G. Horowitz, F. Garnier, *Synth. Met.* **1990**, *39*, 125; b) D. Fichou, G. Horowitz, B. Xu, F. Garnier, *Synth. Met.* **1990**, *39*, 243.
[5] S. Hotta, K. Waragai, *J. Mater. Chem.* **1991**, *1*, 835.
[6] P. Bäuerle, *Adv. Mater.* **1992**, *4*, 102.
[7] D. Delabouglise, M. Hmyene, G. Horowitz, A. Yassar, F. Garnier, *Adv. Mater.* **1992**, *4*, 107.
[8] a) E. E. Havinga, I. Rotte, A. W. Meijer, W. ten Hoeve, H. Wynberg, *Synth. Met.* **1991**, *41*, 473; b) W. ten Hoeve, H. Wynberg, E. E. Havinga, E. W. Meijer, *J. Am. Chem. Soc.* **1991**, *113*, 5887.
[9] M. J. Nowak, S. D. D. V. Rughooputh, S. Hotta, A. J. Heeger, *Macromolecules* **1987**, *20*, 965.
[10] G. Horowitz, D. Fichou, X. Z. Peng, P. Delannoy, *J. Phys. France* **1990**, *51*, 1489.
[11] K. Kaneto, Y. Kohno, K. Yoshino, *Solid-State Commun.* **1984**, *51*, 267.
[12] J. L. Brédas, G. B. Street, *Acc. Chem. Rs.* **1985**, *18*, 309.
[13] D. Bertho, C. Jouanin, *Phys. Rev. B* **1987**, *35*, 626.
[14] S. Skaarup, K. West, B. Zachau-Christiansen, T. Jacobsen, *Symposium on Polyconjugated Materials: Chemistry, Physics, and Tehnology, E-MRS Fall Meeting*, Strasbourg (France), November 4–8. **1991**. To be published in *Synth. Met.*

# A Route to Boron Nitride via New BN Precursors

By *Günter Schmid** and *Thorsten Piontek*

Although numerous methods for the preparation of boron nitride exist, a better approach to this kind of non-oxidic ceramic is still of considerable interest. Especially the production of BN films is of increasing importance, as numerous promising applications seem possible. BN films prevent destruction of material surfaces by chemical reactions or by mechanical strain. Boron nitride is an electric insulator and it possesses a high specific resistance. Its hardness depends on its structure and, of course, the diamond-like cubic modification (c-BN) is of special interest. However, the hexagonal modification (h-BN) is of industrial interest too, namely for its properties as a lubricant.

The generation of thin BN films is usually connected with energetically intensive and apparatively expensive methods:[11] sputter deposition (rf sputtering) is used, if one of the educt components is volatile. Physical vapor deposition (PVD) is achieved through the bombardment of a boron film (produced by an electron beam) using 100 keV nitrogen ions. The implantation of nitrogen ions into a boron film is also

[*] Prof. G. Schmid, T. Piontek
Institut für Anorganische Chemie der Universität Essen
Universitätsstraße 5–7, W-4300 Essen 1 (FRG)

used in reactive-ion-beam-assisted deposition (RIBAD), whereas in the dynamic mixing process (IVD) gaseous boron is reacted with a 200 eV–40 keV nitrogen-ion beam. Direct ion-beam deposition is based on a borazine plasma beam, which condenses to a BN film on substrate surfaces. Chemical vapor deposition (CVD) makes use of the gas-phase reaction of two or more components like BCl_3, N_2, H_2 to produce BN films on various substrates. These and other procedures, which are not mentioned here, are accompanied by a considerable technological expenditure. BN films therefore have only been applied in a very limited way in economical processes. It was thererfore our aim to synthesize oligomeric precursors for boron nitride which can be used to generate BN films or BN powders under more attractive conditions.

An ideal BN precursor should consist of oligomeric BN molecules with appropriate leaving groups, forming polymeric boron nitride by heating. If Li_3N is reacted with BF_3–di-n-butyletherate in boiling di-n-butylether, a colorless precipitate of the composition $(BN)_x(BF_2)_yF_y$ is formed quantitatively over several hours. The values for x and y are limited by the solubility. In the present case the average value for x is about 75 and for y it is 15 (Eq. 1).

$$75\,Li_3N + 315\,F_3B\text{--}OBu_2 \longrightarrow$$
$$(BN)_{75}(BF_2)_{15}F_{15} + 225\,LiBF_4 + 315\,Bu_2O \quad (1)$$
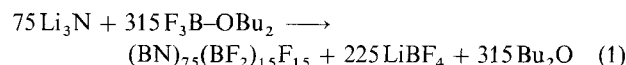
$(BN)_{75}(BF_2)_{15}F_{15}$ (f-BN)[2] is filtered off together with larger amounts of $LiBF_4$. The precipitate is washed with tetrahydrofuran (THF) till $LiBF_4$ can no longer be detected (by X-ray powder diffraction Li analysis or by ^{11}B NMR spectroscopy). The product is then dried at 270 °C to remove
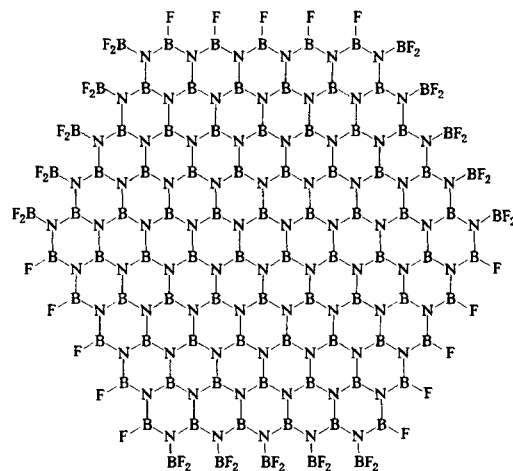

Fig. 1. A f-BN monolayer of the composition $(BN)_{75}(BF_2)_{15}F_{15}$.

the THF quantitatively. f-BN consists of hexagonally oriented BN units with BF_2 groups at the peripheral N atoms and with F substituted peripheral B atoms. Figure 1 shows such an idealized f-BN layer.