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the "ligandless" Pd°. The latter evolves in two different ways:

- An oxidative addition leading to a carbon-halogen bond, with no noticeable change in the reaction time: this is in contradiction with the experimental results (compare entries 2 and 3, 5 and 6 in Table 1).
- A combination with excess phosphine^[16, 17] before the oxidative addition.

$$PdL_{2} + L \xrightarrow{?} PdL_{3} + L \xrightarrow{?} PdL_{4}$$

$$\downarrow \qquad + 2L \qquad ? \qquad \uparrow$$

The second scenario is more realistic.

The coupling of 6a with benzeneboronic acid affords diethanolaminobiphenyl within 30 min in high yield (85%) according to the conditions described in Table 1, entry 2. The synthesis of 9 via Run B has also been studied (Scheme 4).

$$\begin{bmatrix} RO & N & O & HO_2 B & O & Br \\ 2 & 6 & 8 & 9 \end{bmatrix} = \begin{bmatrix} RO & N & O & Br \\ 2 & 9 & 0 & 0 \end{bmatrix} = \begin{bmatrix} RO & N & O & O & Br \\ 2 & 9 & 0 & 0 \end{bmatrix}$$

Scheme 4. 6a: R = H, X = Br. 6b: R = Ac, X = Br. 6c: R = Ac, X = I. 9a: R = H. 9b: R = Ac.

When 6a is employed (Table 2, entry 1), after a 3 day refluxing period, there is no catalyzed reaction and a polymeric compound is obtained, while 6a is recovered. We as-

Table 2.

| Entry | Compound | Temp. | Time | Yield [%] |
|-------|----------|------------|--------|-----------|
| 1 | 6a | reflux | 3 days | [a] |
| 2 | 6c | reflux | 3 h | 65 |
| 3 | 6c | room temp. | 10 h | 85 |

[a] Not determined: the starting material 6a is recovered.

sume that the catalytic activity of the palladium with fewer ligands is unchanged, and that the oxidative addition of Pd° occurs into the carbon-halogen bond of the boronic acid **8**. This consideration implies the formation of paraphenylene, and is similar to Rehahn's results.^[18] The use of the iodo

$$\begin{bmatrix} RO \xrightarrow{N} O \xrightarrow{-1} & \stackrel{i}{\longrightarrow} & \begin{bmatrix} RO \xrightarrow{N} O & O & Br & \stackrel{ii}{\longrightarrow} \\ RO \xrightarrow{N} O & O & -CN & \stackrel{iii}{\longrightarrow} & \begin{bmatrix} HO \xrightarrow{N} O & O & -CN \\ 2 & 0 & 0 & -CN \end{bmatrix}$$

Scheme 5. i) See Table 2, entry 3. ii) CuCN/DMF, reflux, 12 h (80 %). iii) MeONa/MeOH (2%), room temperature (100%).

derivative 6c gives 2 in three steps (68% overall yield) (Scheme 5).^[19]

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- [1] For a pertinent review see D. J. Williams, Angew. Chem. Int. Ed. Engl. 1984, 23, 690. D. S. Chemla, J. Zyss, Nonlinear Optical Properties of Molecules and Crystals, Academic Press, N.Y., 1987. C. N. Prasad, D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley, Chichester, 1991. K. D. Singer, J. E. Sohn, Electroresponsive Molecular and Polymeric Systems (Ed.: T. Skotheim), Marcel Dekker, N.Y., 1991.
- [2] J. F. Fauvarque, V. Ratovelomanana, A. Jutand, C. Amatore, French Patent Demande Alcatel N.V. 9109180, 1989. C. Amatore, J. F. Fauvarque, A. Jutand, S. Negri, French Patent Demande: Alcatel N.V. 9109180, 1989.
- [3] J. Zyss, I. Ledoux, M. Bertault, E. Toupet, *Chem. Phys.* 1991, 150, 125.
 [4] R. Hytel, G. F. Lipscomb, M. Stiller, J. I. Thackara, A. J. Ticknor, *Nonlin*or Control of the second s
- ear Optical Effects in Organic Polymers (Eds.: J. Messier et al.), 1989,
 p. 277. B. K. Nayar, C. S. Whinter, Opt. Quantum Electron. 1990, 20, 297.
 [5] J. Y. Barraud, S. Gervat, J. F. Fauvarque, V. Ratovelomanana, French
- [5] J. Darrado, S. Cervat, J. F. Padvarduć, V. Ratoverolinanana, French Patent Demande: Alcatel N.V. 9109180, 1991.
- [6] A. K. Tamao, H. Kumada, Organometallic Reactions and Synthesis (Eds.: E. I. Becker, M. Tsutsui), Plenum, N.Y., 1986. R. F. Norton, R. G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Baley, C.A., 1987. R. F. Heck, Palladium Reagents in Organic Synthesis, Academic Press, N.Y., 1985.
- [7] S. Sibille, V. Ratovelomanana, J. Périchon, J. Chem. Soc. Chem. Commun. 1992, 283. E. I. Negishi, A. King, N. Okukado, J. Org. Chem. 1977, 42, 1821.
- [8] E. I. Negishi, Current Trends in Organic Synthesis (Ed. H. Nozaki), Pergamon, Oxford, 1983, p. 269.
- [9] A. M. Echavarren, J. K. Stille, J. Am. Chem. Soc. 1987, 109, 5478. J. P. Beleskaya, J. Organomet. Chem. 1983, 250, 551. V. Farina, B. Krishnan, J. Am. Chem. Soc. 1991, 113, 9585.
- [10] Y. Hatanaka, T. Hiyama, Synlett 1991, 845.
- [11] a) N. Miyaura, T. Yanaki, A. Suzuki, Synth. Commun. 1981, 11, 583;
 b) W. J. Thomson, J. Gaudino, J. Org. Chem. 1984, 84, 5237; c) W. A. Cristofoli, B. A. Keay, Tetrahedron Lett. 1991, 5880.
- [12] H. Matsubara, K. Seto, T. Tahara, S. Takahashi, Bull. Chem. Soc. Jpn. 1989, 62, 3896.
- [13] L. Friedman, H. Shechter, J. Org. Chem. 1961, 26, 2522. M. S. Newman, H. Boden, *ibid.* 1961, 26, 2525.
- [14] J. Venishi, J. M. Beau, R. W. Armstrong, Y. Kishi, J. Am. Chem. Soc. 1987, 109, 4759. Y. Hoshino, N. Miyama, A. Suzuki, Bull. Chem. Soc. Jpn. 1988, 61, 3008.
- [15] J. K. Stille, Angew. Chem. Int. Ed. Engl. 1983, 25, 551.
- [16] E. Negishi, T. Takahashi, K. Akiyoshi, J. Chem. Soc. Chem. Commun. 1986, 1338.
- [17] Surprisingly, the use of four equivalents of triphenylphosphine requires a longer reaction time (compare entries 1 and 3 in Table 1). Kinetic and spectroscopic studies are in progress.
- [18] M. Rehahn, A. D. Schlüter, G. Wegner, Makromol. Chem. 1990, 191, 1991.
- [19] The nonlinear optical properties of various polymers functionalized with 2 will be published elsewhere.

Electrochemical Deposition and Characterization of Poly(2,5-dimethoxyaniline): A New Highly Conducting Polyaniline with Enhanced Solubility, Stability and Electrochromic Properties

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Since the discovery of the unusual properties of polyaniline (PANI), much work has been devoted to the synthesis of

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substituted polyanilines aimed mainly at obtaining soluble (and hence processible) polymers because polyaniline itself is almost insoluble. Soluble substituted polyanilines such as those based on 2-alkyl⁽¹⁻⁵⁾ and 2-alkoxyanilines^(6, 7) have been produced and characterized but substitution has generally resulted in a severe decrease of conductivity. With the intent of obtaining even more soluble polyanilines while preserving a high conductivity and at the same time improving the stability of the materials towards nucleophilic attack on the fully oxidized (pernigraniline) form of the polymer, we have investigated the electropolymerization of 2,5-dimethoxyaniline (DMA), in which the presence of two electron-rich methoxy substituents were expected both to favor electropolymerization⁽²⁾ and to produce an easily oxidizable and soluble polymer.

Electrosynthesis of the polymer: Cycling of the potential between -0.6 and 0.6 V in 1.0 M NaHSO₄ + 0.1 M DMA results initially in the development of a double redox cycle at 0.1 and 0.3 V, due to the head-to-tail coupled (N-phenyl-pphenylenediamine) and tail-to-tail coupled (benzidine) dimers respectively as found for PANI.^[8] With subsequent cycling, side redox cycles at -0.1 and 0.45 V, attributable to electrodeposited poly(2,5-dimethoxyaniline) (PDMA), are observed. Analysis of the stationary current during growth shows a sigmoidal relation with potential (as for PANI^[9]) with $E_{1/2} = 0.45$ V, i.e. the potential of the second redox cycle of PDMA. The maximum current density was 2.4 mA/ cm², vs 2 for the monosubstituted poly(2-methoxyaniline) and 7.5 for PANI under the same conditions. This indicates that PDMA growth occurs from the fully oxidized form of the polymer as for PANI, with a lower but still high rate and that the presence of an additional substituent group in the five position does not appear to provide a barrier to polymerization.

Bulk polymer is produced by electrolysis at 0.6 V. The electrodeposited crude material is filtered off, washed with 1.0 M NaHSO₄, water and 1.0 M NH₃ and dried under vacuum; after washing with acetone, to dissolve side products and oligomeric species, the dark solid base polyemeraldine is obtained with a coulombic yield of approximately 0.7 mg/C. The polymer has the expected high solubility (up to 30 g/l in CHCl₃). The degree of polymerization of the fraction soluble in *N*-methylpyrrolidone (ca. 50%) is 50.

Redox behavior of the polymer: The cyclic voltammogram of as-deposited PDMA in blank solution exhibits the redox cycles due to the polymer and the incorporated dimers. After neutralization with ammonia in the oxidized form, the electrode deposit releases in acetone the codeposited dimers and the residual deposit displays only the redox cycles of the polymer (Fig. 1). Dimer-free polymer deposits may also be produced directly by cycling the potential under stirring which removes the soluble dimers as they are formed. PDMA films are very stable to oxidation as no degradation is observed up to 0.8 V.

Characterization of the polymer: The IR spectrum of PDMA in the neutral state shows the bands of the monomer,



Fig. 1. Cyclic voltammogram of PDMA in 1.0 μ NaHSO₄. Scan rate: 0.1 V/s; reversible charge: 20 mC/cm².

with the only exception being that of the two CH out-ofplane deformation bands of the monomer at 835 and 780 cm⁻¹. The latter is absent, which supports predominant head-to-tail coupling. In the fully oxidized and neutralized polymer (pernigraniline base) the IR spectrum shows the disappearance of the NH stretching band at 3400 cm⁻¹ and the appearance of a strong signal at 1570 cm⁻¹, due to C=N stretching, as for PANI.^[10]

In-situ conductivity (Fig. 2) indicates that the polymer becomes conducting at the intermediate (emeraldine) oxidation state, with a maximum of 5 S/cm at the intermediate potential of 0.2 V. This value is high compared to those of the



Fig. 2. In-situ conductivity of PDMA in 1.0 м NaHSO₄.

majority of substituted polyanilines and comparable to that of PANI itself. Thus, the goal of producing a soluble and still highly conducting polymer has been achieved. Conductivity measured on pressed pellets is lower (0.2 S/cm), due to the fact that the doping level may not be the optimum and that the sample is rather dry, but it is still considerable.

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In-situ ESR, performed in acetonitrile + 0.1 M TEAP (tetraethylammonium perchlorate) due to the low oxidation potential of PDMA which prohibits the use of the acid medium, upon oxidation shows the appearance of a strong signal 1 G wide at the first oxidation process. From the relationship between the ESR signal intensity and the redox charge it appears that the maximum spin concentration is displayed at around 1/4 of the oxidation charge, in analogy with PANI in which the polaron species is intermediate between the leuco and emeraldine states.^[11]

Spectroelectrochemistry (Fig. 3) shows that upon oxidation the maximum absorption at 365 nm (with an additional peak at 500 nm) changes to a peak at 450 nm at half-oxidation (emeraldine form). Further oxidation to the pernigraniline form causes the decrease of the band at 450 nm and the appearance of a broad band at around 800 nm.



Fig. 3. Spectroelectrochemistry of PDMA in 1.0 M NaHSO_{4.}

The most unusual feature of PDMA is the presence in the neutral form of the additional low energy band (at 500 nm), with an intensity which may be as high as 30% of the maximum at 360 nm and which gives a yellow-orange color to the otherwise colorless polymer. This cannot be attributed to either oligomeric (and possibly altered) species, as it is still present in films cast-deposited from the chloroform-soluble high-molecular-weight polymer, or to ortho coupling, as the maximum absorption of o-phenylenediamine is at 298 nm against 322 nm for the para isomer, which indicates that ortho coupling produces an hypsochromic effect. Instead it could be due to the presence of azo groups which are sometimes, particularly in non-acidic media, produced in aniline oxidation.^[12] It is reported that *p*-aminoazobenzene, which is the model unit for an azo group in the polyaniline backbone, displays a maximum absorption at 500 nm in acid, which moves reversibly to 380 nm upon neutralization.^[13] Accordingly, neutralization of PDMA film in the leuco form causes the disappearance of the band at 500 nm (and increase with broadening of the band at 360 nm) while acid restores it.

The presence of the azo group has been confirmed and its concentration estimated by demonstrating its reversible reduction in acetonitrile by cyclic voltammetry.^[14] The poly-

mer film displays a reduction peak with some degree of reversibility at around -1.7 V vs Ag/Ag[®]. The relevant charge corresponds to an azo content of about 5-10% for films storing a reversible charge of around 12 mC/cm², i.e. with a thickness typical for spectroelectrochemistry. The fact that the amount is lower than that expected on the basis of the intensity of the electronic absorption is explained by the higher extinction coefficient for the azo linkage, which is $28000 \text{ M}^{-1}\text{ cm}^{-1}$ for 4-aminoazobenzene^[13] vs. $8600 \text{ M}^{-1}\text{ cm}^{-1}$ for aniline.^[15] It is possible that the 5-substituent favors head-to-head coupling and subsequent azo production and insertion in the polymer. Spin-density calculations are in progress to support this suggestion.

Conclusions: Electrooxidation of 2,5-dimethoxyaniline in 1.0 M NaHSO₄ results in deposition of the head-to-tail coupled polymer PDMA. This is the second reported disubstituted polyaniline, after the 2,5-dimethyl substituted polymer,^[16] which is soluble but exhibits low conductivity (ca. 10^{-6} S/cm). Due to the presence of two electron-rich substituents, PDMA is oxidized at lower potentials which makes it stable in the fully oxidized form. This result is of importance for the investigations that are currently being performed on pernigranilines.^[17] The double alkoxy-substitution gives polyaniline a high solubility without depressing its conductivity, which may be attributed to the lower steric hindrance created by the methoxy groups in comparison with the methyl groups, as previously observed in polythiophenes.^[18] Finally, the polymer contains some head-to-head coupled units (azo groups) which, apparently without influence on the conductivity, add an orange nuance to the color of the leuco polymer. These properties (solubility, stability and color) are of great value for the performance of this material in electrochromic devices.

Experimental

Reagent grade 2,5-dimethoxyaniline (DMA) from C. Erba (Italy) was purified by sublimation. Experiments were performed at 25 °C under nitrogen in 1 M NaHSO₄ (pH = 1). The counter electrode was platinum; the reference electrode was SCE. The working electrode for cyclic voltammetry was a glassy carbon disc (0.2 cm²). For electronic spectroscopy a 0.8×2.5 cm indium-tin-oxide (ITO) sheet (ca. 80% transmittance, resistance ca. $300 \,\Omega/\Box$, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm²) was used in preparative electrolyses.

The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra with a Perkin Elmer 682 spectrometer. In-situ ESR spectra were run on a X-band ER 100D Bruker spectrometer following the procedure previously described [19]. In-situ conductivity measurements were performed with a two-band microelectrode calibrated with poly(3-methylthiophene) [20]. Molecular weight measurements were performed by GPC N-methylpyrrolidone +1% LiCl using polystyrene as calibration standard.

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- [1] W. Shenlong, W. Fosong, G. Xiaohui, Synth. Met. 1986, 16, 99.
- [2] S. Cattarin, L. Doubova, G. Mengoli, G. Zotti, *Electrochim. Acta* 1988, 33, 1077.
- [3] M. Leclerc, J. Guay, L. H. Dao, J. Electroanal. Chem. 1988, 251, 21. M. Leclerc, J. Guay, L. H. Dao, Macromolecules, 1989, 22, 649.
- [4] G. Bidan, E. M. Genies, J. Electroanal. Chem. 1989, 271, 59.

ADVANCED MATERIALS

- [5] Y. Wei, W. W. Focke, G. E. Wnek, A. Ray, A. G. MacDiarmid, J. Phys. Chem. 1989, 93, 495.
- [6] D. Macinnes jr., B. L. Funt, Synth. Met. 1988, 25, 235.
- [7] J. C. Lacroix, P. Garcia, J. P. Audiere, R. Clement, O. Kahn, Synth. Met. 1991, 44, 117.
- [8] J. Bacon, R. N. Adams, J. Am. Chem. Soc. 1968, 90, 6596.
- [9] G. Zotti, S. Cattarin, N. Comisso, J. Electroanal. Chem. 1988, 239, 387.
 [10] H. Neugebauer, A. Neckel, N. S. Sariciftci, H. Kuzmany, Synth. Met. 1989, 29, E185.
- [11] S. H. Glarum, J. H. Marshall, J. Electrochem. Soc. 1987, 134, 2160.
- [12] G. Mengoli, M. T. Munari, P. Bianco, M. M. Musiani, J. Appl. Polym. Sci. 1981, 26, 4247.
- [13] G. Cilento, E. C. Miller, A. J. Miller, J. Org. Chem. 1956, 78, 1718.

- [14] J. P. Stradins, V. T. Glezer in *Encyclopedia of Electrochemistry of the Elements*, (Eds.: H. Lund, A. J. Bard), Marcel Dekker, New York 1979, Vol. 13, p. 163.
- [15] R. M. Silverstein, G. C. Bassler in Spectrometric Identification of Organic Compounds, Wiley, New York, 1967, 2nd edition, p. 164.
- [16] E. M. Genies, P. Noel, J. Electroanal. Chem. 1990, 296, 473
- [17] J. M. Ginder, A. J. Epstein, *Phys. Rev. B* 1991, 41, 10674. J. M. Leng, R. P. McCall, K. R. Cromak, J. M. Ginder, H. J. Ye, A. J. Epstein, *Phys. Rev. Lett.* 1992, 68, 1184. K. A. Coplin, R. P. McCall, A. J. Epstein, S. K. Manohar, Y. Sun, A. G. McDiarmid, *Bull. Am. Phys. Soc.* 1992, 37, 506.
- [18] M. Leclerc, G. Daoust, J. Chem. Soc., Chem. Commun. 1990, 273.
 [19] G. Zotti, G. Schiavon, Synth. Met. 1989, 31, 347.
- [20] G. Schiavon, S. Sitran, G. Zotti, *Synth. Met.* **1989**, *32*, 209.

The Evil Referee

By Richard L. Harlow*

Time is of the essence, your supervisor's pressing. Your professor paces nervously, "Does the structure have your blessing?"

The *R*-factor is not so good; the ellipsoids are rather strange. The bond angles are kinda funny and the lengths are out of range.

"What's the problem?", says your mentor, an older and wiser hand. "I need a publication here, you've just got to understand."

"Let's throw away the worst reflections. See how the *R*-factor falls! Now let's beat it down with DIFABS and turn the ellipsoids into balls."

"Throw the ORTEP in the trash, we'll fool that Referee. A PLUTO drawing we'll provide ('twill be done for clarity)."

"Those bond lengths need not bother us, for averages we'll take. That Referee won't have the time the calculations to remake!"

"Leave out the structure details. Don't confuse Him with the facts. We'll call it a communication and send it off to JACS!" "What's important, after all, is that the chemistry is right. Who cares if the structure would give old man Bragg a fright!"

But listen up dear colleagues, a warning take from me; in the cold of publication land lurks the Evil Referee!

Your paper He will scrutinize, every detail He'll review. With X-ray vision He's equipped, and He's coming after you!

A rejection stamp is on His desk: a red inkpad nearby. He's used it so many times the link is nearly dry!

Of every trick He is aware. (He's seen/done them all already.) Your paper will be torn to shreds and sent back as confetti!

So listen up dear colleagues, a warning take from me. Only communicate your results if the work has QUALITY.

Yes, you can stick it to this Ref. so evil, your paper he'll have to pass. Put QUALITY into your structures. Only QUALITY will save your ...!

[*] Dr. R. L. Harlow

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