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Soluble Polyarylenes with Alternating Sequences of Alkyl-Substituted Phenylene and Pyrrolic or Terpyrrolic Units

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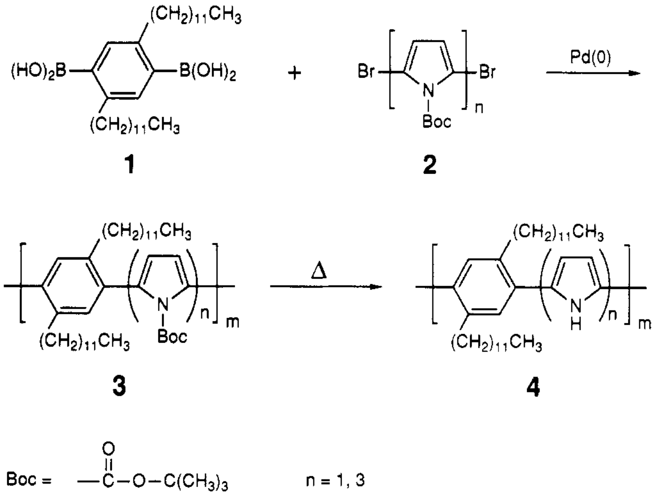
The Pd-catalyzed polycondensation[1] of aromatic monomers carrying either bromo/boronic acid or bromo/trialkyltin substituents has been developed by us and is currently the best method for the synthesis of polyarylenes and related polymers.[2,3] Important advantages of this polymerization method are its regiospecificity and its high tolerance toward functional groups such as carbonyls, amides, and carboxylic acids. One of the few remaining challenges is to apply this reaction to electron-rich aromatic monomers which are notoriously difficult candidates for low-valent transition-metal-catalyzed cross couplings. In this regard, we are presently exploring the pyrrole monomer in a number of variations.[4] The ultimate goal of this effort is the synthesis of poly(2,5-pyrrole), an extremely interesting but still unknown polymer. Here we give a preliminary account of the Pd-catalyzed cross-coupling polycondensation of the benzenediboronic acid derivative **1** with the *N*-Boc-protected (Boc = *tert*-butoxycarbonyl) dibromopyrrolic monomers **2** ($n = 1, 3$) which yields the alternating copolymers **3** ($n = 1, 3$)[5] (Scheme I). A description of the procedure for deprotection of **3** to **4** is also presented. Polymers like **4** are potentially interesting for their electrical and nonlinear optical properties.[6]

Because of the observation that *N*-(*tert*-butoxycarbonyl)pyrrolyl-2-boronic acid loses 50% of its functional group merely upon heating to 50 °C in toluene/2 M Na_2CO_3 for 24 h (no coupling partner or catalyst present),[7] efforts were concentrated on coupling reactions in which the pyrrole moiety carries the halogen functionalities. At first, a model study was performed. The reaction of **2**(n=1) with 2 mol of benzeneboronic acid under standard coupling conditions ($Pd(PPh_3)_4$, 1 mol % per coupling step, toluene/2 M Na_2CO_3, 100 °C, under N_2) was monitored by ^1H NMR spectroscopy using dichloromethane as an internal integration standard. An analysis of the NMR spectrum of the reaction mixture after 4 h yielded the following results: **2**(n=1), 6%; 2-bromo-5-phenyl-*N*-(*tert*-butoxycarbonyl)pyrrole, 70.5%; 2,5-diphenyl-*N*-(*tert*-butoxycarbonyl)pyrrole, 21.5%. After 24 h, the conversion to the latter product was 85% and after 45 h 96% (all data with an estimated error of about ±5%). Some doubts remained, however, as to whether this very high conversion was indicative of a quantitative coupling. Upon expansion of the ^1H NMR spectrum of the raw reaction mixture (after 45 h) to the extent that the ^{13}C satellites were easily observed, some signals of minor intensity between δ 6.4 and 6.6 were detected, the identity of which was not clarified.

The synthesis and purification of monomers **1** and **2**(n=1) have been described elsewhere.[2b,8] The terpyrrolic monomer **2**(n=3) was obtained in 5–10-g quantities from the Pd-catalyzed coupling of **2**(n=1) with 2-(trimethylstannyl)-*N*-(*tert*-butoxycarbonyl)pyrrole[8] followed by bromination with NBS and purification by repeated recrystallization from EtOH. The copolymerizations were performed similarly to the above-mentioned model reaction, except that refluxing benzene was used instead of toluene to give a better temperature control. Typical reaction times are 2–3 days, after which period the reactions tend to become dark and no further coupling is observed (TLC). Standard workup yielded a dark residue which was dissolved in dichloromethane and filtered through silica gel to remove the catalyst. The molecular weight of the product before and after filtration remained unchanged (GPC). This filtration did not render the materials colorless. Copolymers **3**(n=1) and **3**(n=3) were obtained on the gram scale as dark, highly viscous oil (typical yield = 55–70%) and as a gray-greenish powder (~90%), respectively. All attempts to further purify the products by reprecipitation failed.

Scheme I



The structures of **3** (n = 1, 3) were confirmed by analyzing their high-resolution ^1H, ^{13}C, and ^{13}C DEPT NMR spectra.[9] Specifically characteristic are the signals of the β hydrogens of the pyrrolic rings that appear as a singlet for **3**(n=1) as a singlet and an AB system for **3**(n=3). Both the ^1H and ^{13}C NMR spectra of the copolymers showed signals with low intensity whose chemical shifts varied slightly from experiment to experiment and were therefore assigned to the above-mentioned impurities. Others remain unchanged and seem to be due to end groups. The molecular weights were determined by GPC (standard, PS; solvent, THF). The results for the various independent runs were similar for the two copolymers and fell within the following ranges: $5000 < M_n \leq 8000$, $17\,000 < M_{peak} \leq 20\,000$, $18\,000 < M_w \leq 23\,000$, $2.5 < D < 4$. HPLC traces of the products (reverse-phase Merck LiChroCart RP 18 column, CH_2Cl_2/CH_3CN gradient) showed regular peak patterns whose maximum appears approximately at a DP ≅ 30, which is in good agreement with the GPC data.[10]

The Boc group was chosen to protect the pyrrole and terpyrrole fragment during polymerization because it is readily removed upon thermal treatment to give only gaseous products.[11] This is of crucial importance considering the sensitivity of the unprotected pyrrole oligomers. To achieve deprotection, the neat copolymers **3** (n = 1, 3) were heated to 190 °C under a dynamic vacuum ($\leq 10^{-3}$ mbar) for 1.5 h. At the end of the process the color of the material had changed to almost black. For **3**(n=1), the deprotection proceeded cleanly and reproducibly. The deprotected copolymer **4**(n=1) is an air-stable and soluble material. Reprecipitation from benzene using acetone as nonsolvent furnished a yellow–green material which was

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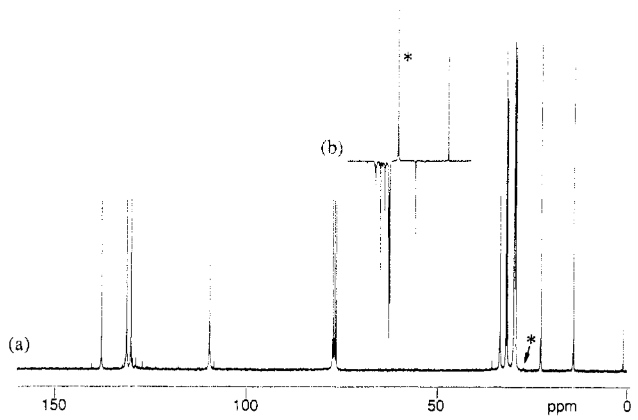

Figure 1. (a) ^{13}C NMR spectrum of $\mathbf{4}(n=1)$. (b) Aliphatic region of the ^{13}C DEPT NMR spectrum of $\mathbf{3}(n=1)$. The signal for the methyl groups of the Boc is marked (*).

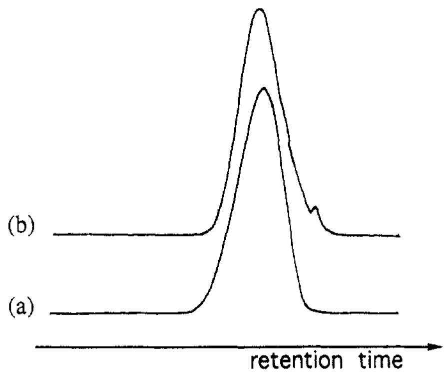

Figure 2. GPC traces of $\mathbf{4}(n=1)$ (a) and of $\mathbf{3}(n=1)$ (b).

then freeze dried (benzene). The yield of the two steps, deprotection and purification, was approximately 86%. The NMR spectra of the product[12] show that deprotection is quantitative and that the main structure is retained. No degradation of the backbone occurred (Figure 1). GPC analysis (Figure 2) confirms this observation. The values obtained after deprotection are M_n = 11 000, M_{peak} = 15 000, M_w = 25 000, and D = 2.3. The fact that these values are slightly higher than the ones of the corresponding protected copolymer probably reflects a somewhat different behavior on the column and the absence of low molecular weight impurities.

A wide-angle X-ray powder diffractogram of $\mathbf{4}(n=1)$ after 2 days annealing at 80 °C shows the pattern often observed for rigid-rod polymers with flexible side chains.[13] DSC analysis shows a sharp endothermic peak on the heating curve between 105 and 125 °C, that remains nearly unchanged by cycling, and a sharp exothermic peak on cooling, between 65 and 45 °C. Complete deprotection of $\mathbf{3}(n=1)$ can also be achieved by treatment of this copolymer with a 5-fold excess of MeONa in THF solution at reflux for 12 h.[14] The NMR spectra and GPC data obtained for $\mathbf{4}(n=1)$ are almost identical with those of the thermally deprotected material.

The deprotection of $\mathbf{3}(n=3)$ yielded an almost insoluble material. Therefore, it is not certain that the deprotection proceeded cleanly. However, the IR spectrum shows almost no carbonyl absorption. In this context, it is interesting to note that deprotection studies performed on *N*-(*tert*-butyoxycarbonyl)pyrrolic oligomers with up to five pyrrole units gave fully satisfactory results.[15] It should also be noted that α,ω-dibromopyrrolic monomers of type **2** with n up to 7 can also be prepared[15] and could be used for the synthesis of copolymers using the cross-coupling reaction described here.

In summary, we have shown that the Pd-catalyzed polycondensation allows the incorporation of *N*-Boc-protected pyrrolic units into a polymer structure. The Boc protecting group proved to be optimal in that it does not interfere with the polymerization and can be completely removed. The molecular weights seem to be in the range typical for these kinds of polycondensations.

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References and Notes

(1) For application of this coupling reaction in low molecular weight chemistry, see, for example: (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Gronowitz, S.; Hörnfeldt, A. B.; Yang, Y. In *Organic Synthesis*: *Modern Trends*; Chizhov, O., Ed.; Blackwell Scientific Publications: Oxford, U.K., 1987; pp 253. (c) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314. (d) Snieckus, V. *Chem. Rev.* **1990**, *90*, 879.

(2) (a) Rehahn, M.; Schlüter, A.-D.; Wegner, G.; Feast, W. J. *Polymer* **1989**, *30*, 1060. (b) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem.* **1990**, *191*, 1991. (c) Rehahn, M.; Schlüter, A.-D.; Wegner, G. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 535.

(3) (a) Fahnenstich, U.; Koch, K.-H.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 563. (b) Scherf, U.; Müllen, K. *Makromol. Chem., Rapid Commun.* **1991**, *12*, 489. (c) Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1991**, *113*, 7411.

(4) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, in press.

(5) A route to similar copolymers using conventional chemistry has been described: Pouwer, K. L.; Vries, T. R.; Havinga, E. E.; Meijer, E. W.; Wynberg, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1432.

(6) See, for example: (a) Skotheim, T. A., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (b) Brédas, J. L., Chance, R. R., Eds. *Conjugated Polymeric Materials*: *Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1990.

(7) Loss of the boronic function has also been observed by other investigators; see: Reference 1b.

(8) Martina, S.; Enkelmann, V.; Wegner, G.; Schlüter, A.-D. *Synthesis* **1991**, 613.

(9) NMR data for copolymers **3** ($CDCl_3$, 300 MHz). ^{1}H NMR ($CHCl_3$ = 7.24 ppm): $\mathbf{3}(n=1)$, δ 0.86 (t, 6 H, J = 7 Hz, CH_2CH_3), 0.9–1.7 (m, 49 H, $-CH_2-$ and CCH_3), 2.54 (unresolved, 4 H, $C_{ar}CH_2-$), 6.13 (s, 2 H, β), 7.14 (s, 2 H, $C_{ar}H$); $\mathbf{3}(n=3)$, δ 0.86 (t, 6 H, J = 7 Hz, CH_2CH_3), 0.9–1.7 (m, 49 H, $-CH_2-$ and CCH_3), 2.51 (unresolved, 4 H, $C_{ar}CH_2-$), 6.06 and 6.23 (AB system, 4 H J = 3 Hz, β outer rings), 6.25 (s, 2 H, β central ring), 7.08 (s, 2 H, $C_{ar}H$). ^{13}C NMR ($CDCl_3$ = 77.0 ppm): $\mathbf{3}(n=1)$, δ 14.2 (CH_2CH_3), 22.7 and 29.4–33.3 (CH_2 aliphatic), 27.3 (CCH_3), 83.0 (CCH_3), 112.5 (β), 130.6 ($C_{ar}H$), 133.9, 134.1, 138.9 (other aromatic), 149.4 (C=O); $\mathbf{3}(n=3)$, δ 14.1 (CH_2CH_3), 22.7 and 29.3–32.8 (CH_2 aliphatic), 27.5 and 27.8 (CCH_3), 82.3 and 82.7 (CCH_3), 112.5, 113.7, 114 (β), 130.2 ($C_{ar}H$), 127.8, 128.1, 134.0, 135.0, 138.3 (other aromatic), 149.0 (C=O).

(10) VPO measurements were not carried out because of the presence of impurities.

(11) Rawal, V. H.; Cava, M. P. *Tetrahedron Lett.* **1985**, *26*, 6141.

(12) NMR data for copolymer $\mathbf{4}(n=1)$ ($CDCl_3$, 300 MHz). ^{1}H NMR ($CHCl_3$ = 7.24 ppm): all signals unresolved, δ 0.9 (6 H, CH_2CH_3), 0.9–2.1 (m, 40 H, $-CH_2-$), 2.85 (4 H, $C_{ar}CH_2-$), 6.4 (2 H, β), 7.35 (2 H, $C_{ar}H$), 8.27 (1 H, NH). ^{13}C NMR ($CDCl_3$ = 77.0 ppm): δ 14.1 (CH_2CH_3), 22.7 and 29.4–33.6 ($-CH_2-$), 109.5 (β), 130.3 ($C_{ar}H$), 131.37, 131.41, 137.9 (other aromatic).

(13) See, for example: Ballauff, M.; Schmidt, G. F. *Mol. Cryst. Liq. Cryst.* **1987**, *147*, 163.

(14) Hasan, I.; Marinelli, E. R.; Lin, L.-C. C.; Fowler, F. W.; Levy, A. B. *J. Org. Chem.* 1981, *46*, 157.

(15) Martina, S.; Enkelmann, V.; Schlüter, A.-D.; Wegner, G., in preparation.