# Notes

## Synthesis of End-Functionalized Polyanilines

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### Introduction

Growing interest in the incorporation of conducting polymers into optoelectronic devices, on surfaces,[1] in polymer−inorganic composites,[2] in block copolymeric materials,[3] in single-molecule systems,[4] and in biological arrays[5] calls for the ability to synthesize well-defined polymeric and oligomeric materials with suitable terminal functionalities for covalent connection to the desired structure. In the course of our work on insulated molecular wires and encapsulated dyes,[6] we set out to synthesize insulated polyaniline polyrotaxane molecular wires, with the ultimate goal of applying them as advanced materials, in photovoltaic devices and light-emitting diodes.[7,8] Preliminary results showed that encapsulation of a short monodisperse oligoaniline in a cucurbituril macrocycle drastically enhances the stability of the radical cation oxidation state, which has the same spin stoichiometry as the conducting emeraldine salt form of polyaniline.[7] The next goal is to apply these principles to larger, polydisperse systems, which should have better materials properties for device fabrication and stability. For this purpose, it is essential to have a soluble polyaniline (PANI) of low polydispersity, functionalized *on both ends* with groups that allow efficient stopper attachment under conditions favoring macrocycle threading. Because commercially available PANI has an unreactive phenyl group on one end of the polymer chain,[9] we chose to construct an α,ω-bis-benzylamine-substituted polyaniline through synthesis and subsequent deprotection of a *tert*-butoxycarbonyl (Boc) protected PANI precursor using Pd-catalyzed Buchwald−Hartwig[10] polymerization. The terminal benzylic amines can then be covalently attached to stoppers, or other groups, using a wide range of chemistry.

Investigations by Buchwald and co-workers have shown that Pd-catalyzed amination can be used to synthesize discrete end-functionalized low molecular weight oligoanilines through multistep synthesis.[11,12] This methodology has found application in the synthesis of electroactive hexaaniline−amide copolymers,[13] regiospecific copolyanilines,[14] electron-acceptor-substituted oligoanilines,[15] oligoaniline-grafted PMMA,[16] and monodisperse thiol- and diazonium-substituted oligoanilines for monolayer self-assembly.[17] Buchwald and co-workers used a similar protocol for the synthesis of polymeric high molecular weight polyaniline through step-growth polymerization of an α-bromo-ω-amino-functionalized AB monomer.[18] Although highly efficient, this approach is not suitable to our needs, as it leads to polymers with two different (undesired) end groups, and the molecular weight of the reported polymers is generally too high to allow for subsequent solution-phase chemistry on the deprotected PANI. We therefore opted for a three-component step-growth polymerization, using diamine **1** and dibromide **2** monomers and a monobromide chain stopper **3** with a protected benzylamine functionality (Scheme 1). This approach gives symmetrical end-functionalized polymer **P1**, with control over the molecular weight through the stoichiometry of the monomer feed ratio. Because of the difference in reactivity between the end groups and the unprotected polymer backbone NHs that are formed in the polymerization, this polymer structure allows for orthogonal postpolymerization functionalization of the polymer backbone and the polymer termini. Buchwald and co-workers reported that Boc protection is necessary for efficient step-growth polymerization and that it facilitates the purification of the polyaniline products;[11b,18] our preliminary experiments with monomers lacking Boc protecting groups confirmed both these observations.

### Results and Discussion

Monomers **1**, **2**, and **3** were synthesized in high yield and purity in three steps or less from commercially available starting materials, without any chromatography.[19] Initial polymerization experiments using the originally reported reaction conditions[18] (ligand **L1**, $Pd_2dba_3$, 80 °C, NaO*t*Bu, THF (tetrahydrofuran), 1.5 h) showed an efficient polymerization of monomers **1** and **2** to give **P2** (ratio **1**/**2** = 5/4; number-average molecular mass: $M_n = 5.6 \times 10^3$ g mol$^{-1}$; polydisersity index, $M_w/M_n$: PDI = 2.0; 61% isolated yield). However, when these conditions were applied to the three-component mixture, we observed exclusive degradation of monobromide **3**, possibly by the removal or migration of one of the Boc protecting groups,[20] in parallel with polymerization. We confirmed that this side reaction is caused by the base (NaO*t*Bu) and therefore attempted to perform the polymerization using various weaker bases. As a screening reaction, the Pd-catalyzed formation of bisadduct **4** from **3** and **1** was monitored (Scheme 2), using KOH, $K_3PO_4$, $K_2CO_3$, or $Cs_2CO_3$ as base. In all cases *t*BuOH had to be added as a cosolvent, possibly to increase the solubility of the base. Whereas KOH still showed some degradation of **3**, the other bases, especially $Cs_2CO_3$, showed a slow but clean conversion to the desired product **4** (85% conversion in 16 h). In an attempt to accelerate the reaction, ligands **L2** and **L3** were tested (Figure 1). Both gave considerably higher reaction rates, with **L2** being the most efficient (100% conversion in less than 3 h). These new conditions were applied in the polymerization of **1**, **2**, and **3** in various ratios, giving benzylamine end-functionalized polymers **P1** with $M_n$ between $2.2 \times 10^3$ g mol$^{-1}$ (ratio **1**:**2**:**3** = 2:1:2) and $6.6 \times 10^3$ g mol$^{-1}$ (ratio **1**:**2**:**3** = 15:14:2), $M_w/M_n$ between 1.5 and 2, and yields up to 96% (Figure 2). In all cases the polymer end groups could be clearly distinguished by $^1$H and $^{13}$C NMR spectroscopy (Figure 3).[19] The two small

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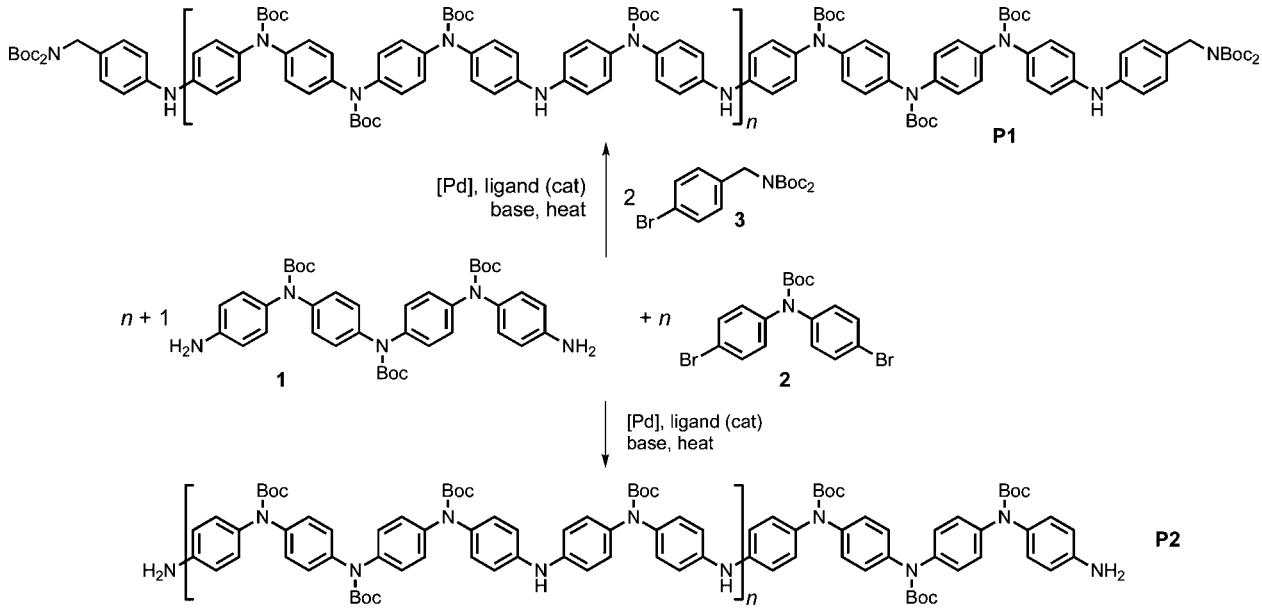
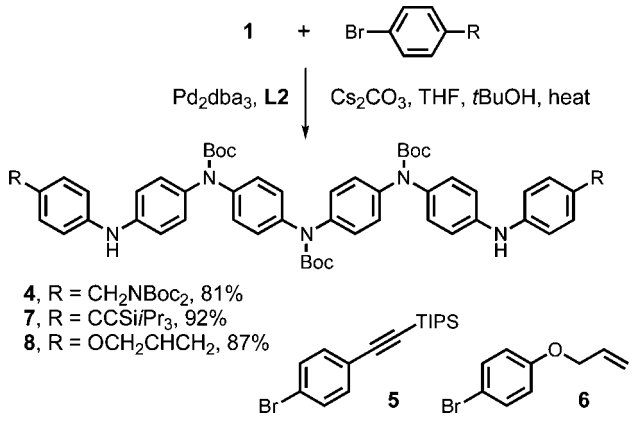
**Scheme 1. Pd-Catalyzed Polymerization (Boc = $CO_2t$-Bu)**




**Scheme 2. Incorporation of Various Functional End Groups by Pd-Catalyzed Amination**




signals at 6.83 and 6.50 ppm in the $^1$H NMR spectrum of **P2** are due to the electron-rich terminal aniline aromatic protons. The absence of these peaks (and of the $NH_2$ peak at 5.09 ppm) from the spectrum of **P1** shows that all polymer termini are capped with **3** in this material.

Covalent incorporation of conjugated polymers in organic, inorganic, or biological systems may require a range of terminal functionalities, depending on the desired method of covalent connection. Several widely applied functional groups were tested for their compatibility with our optimized polymerization conditions. Besides the protected primary amine **3**, which can be used for amide coupling, reductive amination, imine metathesis,[21] addition to isocyanates, or nucleophilic aromatic substitution,[22] we found that it is possible to couple protected acetylene **5** and *O*-allylphenol **6**. The acetylene-terminated PANI could be used in Cu-catalyzed 1,3-dipolar alkyne−azide coupling,[23] Sonogashira−Hagihara cross-coupling,[24] or Cadiot−Chodkiewicz alkyne−alkyne heterodimerization.[25] Likewise, the *O*-allyl functionality could serve as a protected phenol[26]

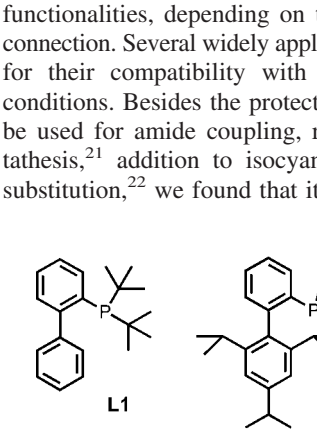



**Figure 1.** Structures of phosphine ligands **L1**, **L2**, and **L3**.

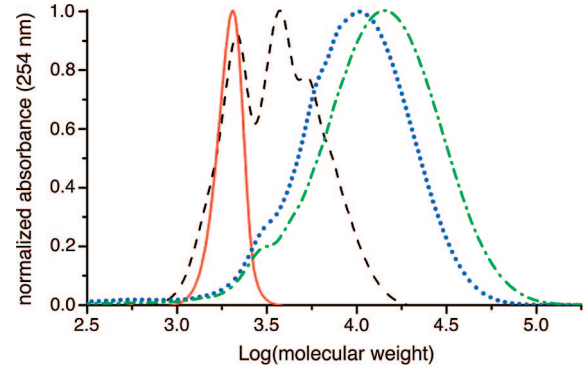



**Figure 2.** Molecular weight distribution depending on starting monomer ratio, as determined by gel-permeation chromatography (GPC). Red/solid, **4**; black/dashed, **P1** (ratio **1**:**2**:**3** = 2:1:2); blue/dotted, **P1** (ratio **1**:**2**:**3** = 6:5:2); green/dot-dashed, **P1** (ratio **1**:**2**:**3** = 15:14:2). GPC conditions: THF, 20 °C, PL Mixed D column, narrow polystyrene calibration standards.

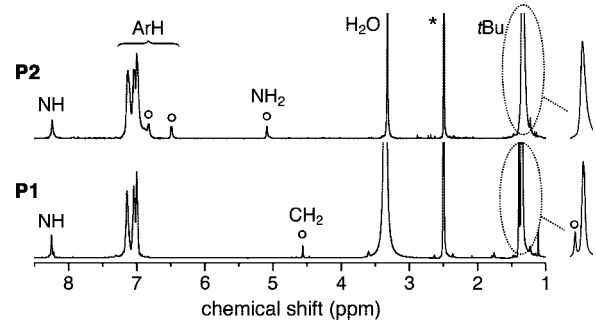
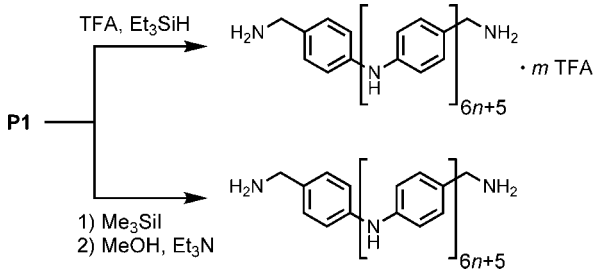



**Figure 3.** $^1$H NMR spectra (500 MHz, DMSO-$d_6$, 300 K) of polymers **P1** (bottom, ratio **1**:**2**:**3** = 5:4:2; heavy fraction, $M_n$ = 4.3 × $10^3$ g mol$^{-1}$, PDI = 1.6) and **P2** (top, ratio **1**:**2** = 5:4; $M_n$ = 5.6 × $10^3$ g mol$^{-1}$, PDI = 2.0). The resonances caused by the end groups are clearly visible (indicated by circles, o); the magnified peaks (right) show the *tert*-butyl resonances; ∗ = DMSO-$d_5$.

**Scheme 3. Deprotection of Boc-Polymer P1 under Mild Conditions**




and might be applied in olefin polymerization or Ru-catalyzed cross-metathesis.[27] All three products, **4**, **7**, and **8**, were obtained in high yield, and in no case were any mono- or trifunctionalized oligoanilines detected by $^1$H NMR spectroscopy or ESI-MS.

Deprotection of Boc-protected PANI is generally achieved by thermal elimination of the Boc group at around 150 °C.[14] Because these conditions are not compatible with many functional groups, we attempted to develop a milder deprotection protocol. Trifluoroacetic acid (TFA) is a standard reagent for deprotection of Boc-protected amines in biological and organic systems,[26] which prompted us to also apply it to these protected polymers. We found that the use of TFA (neat or in dichloromethane) leads to severe oxidation and possibly cross-linking of the polymer, as an NMP-insoluble dark blue material was obtained instantaneously upon reaction of **P2** ($M_n = 3.6 \times 10^3$ g mol$^{-1}$, $M_w/M_n = 1.7$) with TFA in dichloromethane at 0 °C. For shorter polymers (**P2**, $M_n = 1.8 \times 10^3$ g mol$^{-1}$, $M_w/M_n = 1.7$) soluble materials were obtained that showed additional *tert*-butyl signals on $^1$H, indicating alkylation of the polymer backbone. This is indicative of the high reactivity of the electron-rich leucoemeraldine (reduced) PANI toward the generated *tert*-butyl cations. To overcome this problem, the reaction was carried out in the presence of triethylsilane as a cation scavenger, eliminating the observed oxidation. The deprotected polyaniline was isolated as its TFA salt, as indicated by $^{13}$C NMR and IR spectroscopy. Alternatively, the complete removal of Boc protecting groups was achieved by reaction with trimethylsilyl iodide (TMSI) and subsequent methanolysis of the formed TMS-carbamate, leading to the formation of the leucoemeraldine PANI as a free base (Scheme 3).[11,28]

In conclusion, we have demonstrated an effective methodology for the synthesis of α,ω-end-functionalized protected polyanilines. Soluble, protected polyanilines can be synthesized in high yield and narrow molecular weight distributions, using Pd-catalyzed amination polymerization. The use of a mild base and a highly active catalyst allows for the incorporation of several useful reactive end groups for further functionalization and hybridization. Clean and mild deprotection was achieved using either TFA and triethylsilane or TMSI followed by methanol, leading to end-functionalized deprotected leucoemeraldine polyanilines. The differences between this polymerization system and that previously reported by Buchwald and co-workers[18] are (a) use of a milder base, $Cs_2CO_3$ (in *t*BuOH/THF), rather than NaO*t*Bu (in THF), (b) use of ligand **L2** (XPhos) rather than ligand **L1** (JohnPhos), and (c) use of symmetric, instead of unsymmetric, monomers. This allows us to prepare symmetric polymers with base-sensitive end groups and gives lower polydispersities than previously reported.[18] The polyanilines with aliphatic primary amine terminals are valuable intermediates for the synthesis of a wide range of hybrid materials, including insulated molecular wires.

**Experimental Procedure for the Synthesis of Polymer P1.** Diamine **1** (229 mg, 0.336 mmol), dibromide **2** (115 mg, 0.269 mmol), bromide **3** (52 mg, 0.13 mmol), $Pd_2dba_3$ (3.1 mg, 3.4 μmol), and ligand **L2** (9.6 mg, 20 μmol) were added to a flame-dried Schlenk tube. After addition of THF (4 mL) and *t*-BuOH (2 mL), the mixture was degassed by four vacuum cycles. $Cs_2CO_3$ (438 mg, 1.35 mmol) was added, and the mixture was stirred at 85 °C overnight and then allowed to cool to room temperature. The solvent was removed, and the mixture was filtered over silica (pet. ether 40−60/EtOAc/acetone/$Et_3N$ 4:1:0:0 → 0:100:10:5 gradient) to remove the ligand and a small low molecular weight fraction, yielding polymer **P1** as a yellow solid (865 mg, 96%); $M_n = 2.2 \times 10^3$ g mol$^{-1}$, PDI = 1.5 (GPC). $^1$H NMR (400 MHz, DMSO-$d_6$) δ: 8.25 (NH), 8.22 (NH), 7.15, 7.13, 7.10, 7.05, 7.04, 7.03, 7.01, 6.99, 4.57 (end group $CH_2$), 1.40 (end group Boc-$CH_3$), 1.36, 1.36. $^{13}$C NMR (126 MHz, DMSO-$d_6$) δ: 153.5, 153.2, 152.9, 152.2, 142.2, 141.6, 141.5, 140.8, 140.7, 140.7, 139.6, 135.3, 134.3, 134.3, 129.5, 128.4, 128.3, 127.8, 127.1, 126.6, 116.9, 116.8, 116.5, 116.4, 81.9, 80.5, 80.2, 80.1, 79.7, 48.5 (end group $CH_2$), 27.9, 27.8, 27.8, 27.6. Anal. Calcd for $C_{129}H_{155}N_{13}O_{22}$ (2:1:2 oligomer): C, 69.18; H, 6.98; N, 8.13%. Found: C, 68.99; H, 7.11; N, 8.13%. IR (KBr disk, cm$^{-1}$) ν: 3355, 3033, 2975, 2929, 1701, 1604, 1503, 1475, 1453, 1427, 1390, 1364, 1294, 1251, 1221, 1150, 1109, 1063, 1013, 1012, 954, 848, 826, 765, 521.

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**Supporting Information Available:** Complete experimental procedures and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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