

o,p-Polyaniline: A New Form of a Classic Conducting Polymer

Rachel E. Ward, and Tara Y. Meyer

Macromolecules, **2003**, 36 (12), 4368-4373 • DOI: 10.1021/ma021343f

Downloaded from <http://pubs.acs.org> on February 9, 2009

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 4 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



o,p-Polyaniline: A New Form of a Classic Conducting Polymer

Rachel E. Ward and Tara Y. Meyer*

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

Received August 16, 2002; Revised Manuscript Received February 4, 2003

ABSTRACT: A new *o*-PANI-*co-p*-PANI copolymer was prepared in order to allow for the introduction of solubilizing and function-enhancing substituents on the conducting polymer backbone without concomitant loss of conductivity. An urea-protected trimeric aniline macromonomer with *para-ortho-para* connectivity and bromine end groups was condensed using palladium catalysis with a di-BOC-protected trimeric aniline comonomer with all *para* connectivity and amine end groups to give *5p,o*-PANI. The new polymer has a repeat unit consisting of five *para*-substituted aniline rings for every one *ortho*-substituted aniline ring. The regioregularity of *5p,o*-PANI ($M_n = 14\,000$, GPC in NMP, polystyrene standards) was established using ^1H NMR, $^{13}\text{C}\{^1\text{H}\}$ NMR, and IR spectroscopy. Analogous with *p*-PANI, the *5p,o*-PANI exhibited three distinct oxidation states. The conductivity of blends of *5p,o*-PANI and PVC was on the same order of magnitude as the conductivity of PANI films prepared under the same conditions.

Introduction

We have prepared a new copolymer of *ortho*- and *para*-substituted polyaniline that keeps the fundamental conducting backbone of polyanilines while allowing for property and functionality enhancing derivatization. The desire to tailor conducting polymers for particular applications has resulted in a variety of interesting modifications to the basic conducting chains.¹ The goals of these derivatizations include increasing solubility, optimizing processability, and introducing recognition elements to improve their performance as sensors. Polyaniline, which is unique among conducting polymers for its chemical and environmental stability, tunable electrical conductivity, and unique optical properties,² has been thus far limited in its potential for application because, relative to other well-known conducting systems such as polythiophene, it cannot be easily modified without a concomitant sacrifice in conductivity.

We hypothesized that the periodic introduction of *ortho*-substituted anilines into the main chain of *p*-polyaniline would address the functionalization problem. The fundamental challenge in modifying *p*-polyaniline is that the introduction of substituents onto the rings exacerbates the puckering caused by *ortho-ortho* interactions (Figure 1). Since conductivity is a function of π -overlap along the polymer chain, steric interactions that decrease planarity adversely affect the conductive properties. Functionalization at the 4- and 5-positions of *ortho*-substituted anilines incorporated into the chain will not introduce this type of unfavorable steric interaction.

Our approach to the synthesis of these *o*- and *p*-polyanilines relies on the elegant palladium-catalyzed amination of aryl halide reaction developed by the Buchwald and Hartwig groups.³ Since the Pd-catalyzed coupling of aryl halides and arylamines is a regiospecific reaction, it is especially useful for the controlled synthesis of PANI derivatives. To date, this coupling reaction has been used by our group and others to prepare *m*-,^{4–6} *p*-,^{6,7} and hyperbranched-PANI⁴ derivatives as well as discrete oligomers of both *m*-⁸ and *p*-PANI.⁹

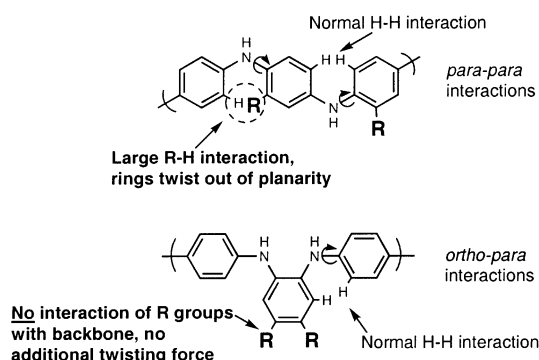


Figure 1. Steric interactions of polyaniline isomers.

Herein, we report the synthesis and characterization of a new polyaniline derivative (*para*)₅-*ortho*-polyaniline (*5p,o*-PANI) with *tert*-butoxycarbonyl (BOC) and urea protecting groups that contains five *para*-substituted aniline repeat units for every one urea-protected *ortho*-substituted unit. To our knowledge, this is the first example of polyaniline containing a regularly incorporated *ortho*-substituted ring.

Results

Synthesis and Characterization. To incorporate *ortho*-substituted repeat units into a *p*-polyaniline chain, it was necessary to construct a macromonomer containing the preformed *ortho-para* linkages. While the palladium-catalyzed coupling reaction that we use to assemble the final structure allows us to precisely control the polymer's microstructure, it is not an efficient process for *ortho* couplings. To circumvent this problem, we synthesized 1,2-di(*N-p*-bromophenylamino)benzene, which contains a built-in *o*-aniline moiety. Initial unsuccessful attempts at coupling this macromonomer with *p*-phenylenediamine established that the diamine moiety of the macromonomer could not be left unprotected, however, since its *ortho*-orientation is ideal for chelating deactivation of the palladium catalyst (Figure 2).

Protecting the diamine moiety as an imidazolone was both effective and synthetically facile. Other candidate protecting groups either led to the urea indirectly, e.g.,

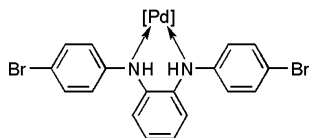
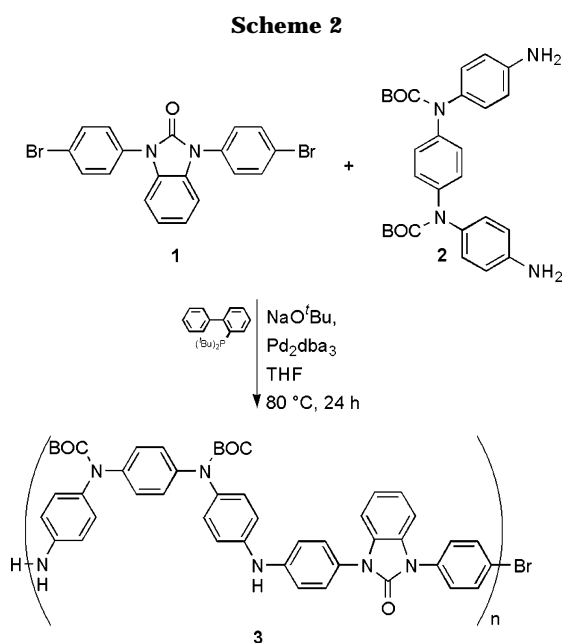
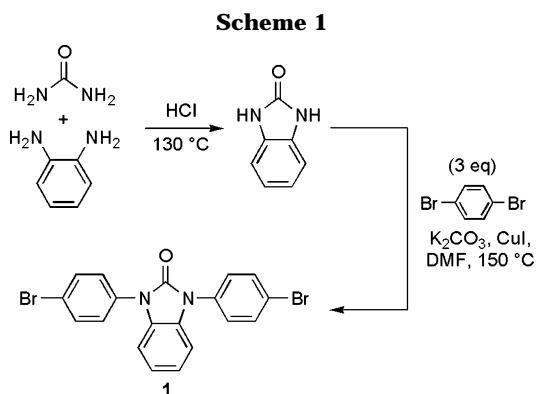
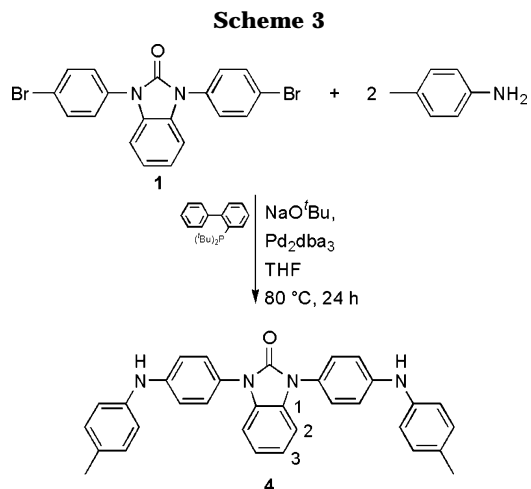


Figure 2. *Ortho* orientation of 2° amines promotes coordination of the palladium catalyst.



BOC, or were labile under the reaction conditions, e.g., alkylsilanes. Although initially we prepared macromonomer **1** by protecting the preassembled trimer, it proved synthetically easier to prepare the urea-protected species by performing an Ullmann–Goldberg coupling of 1,3-dihydrobenzimidazol-2-one with excess *p*-bromobenzene, following the procedure of Sugahara et al.¹⁰ Column chromatography allowed for effective separation of the excess *p*-dibromobenzene from the monomer and gave a 28% yield of 1,3-bis(4-bromophenyl)-1,3-dihydrobenzimidazol-2-one, **1**, as a white solid. The structure of macromonomer **1** was confirmed using ¹H NMR, ¹³C NMR, and elemental analysis.

Coupling of urea macromonomer **1** and BOC-protected PANI trimer⁹ **2** gave the copolymer **3**, 5*p*,*o*-PANI (see Scheme 2). Our initial attempts to polymerize **1** with *p*-phenylenediamine or with *p*-phenylenediamine dihydrochloride to give a 3*p*,*o*-PANI produced an insoluble material. Switching from the simple diimine to the BOC-protected trimer, **2**, resolved the problem. This monomer was originally prepared and used for the



synthesis of pure *p*-PANI oligomers by Buchwald and co-workers.⁷ A typical polymerization was performed in dry THF using 1.4 equiv of NaO^{*t*}Bu per halide with Pd₂dba₃ and 2-(di-*tert*-butylphosphino)biphenyl catalyst. The tan or pale purple copolymers were isolated after workup in 13–51% yield, depending on reaction conditions.

Catalyst loadings of 1.5 mol % gave the best results. Higher loadings produced largely insoluble materials, and lower loadings gave primarily short oligomers. Polymers prepared using the optimal loading were highly soluble in THF and NMP, slightly soluble in CDCl₃, and completely insoluble in methanol and hexanes. All other data discussed in this report correspond to reaction mixtures using 1.5 mol % catalyst loading. We speculate that the higher catalyst loadings may be promoting cross-linking by double coupling at a single N center.

Although the ¹H NMR spectrum of 5*p*,*o*-PANI exhibits the peak broadness that is typical of macromolecules, a primary amine end-group resonance (δ 4.4) is visible in the spectrum, and its integration relative to the aryl region appears to correlate with the molecular weight of the polymer. The identity of the 1° and 2° amine resonances at δ 4.46 and 7–7.4 (THF-*d*₈), respectively, was confirmed by exchange with D₂O. The polymer also exhibited the expected BOC resonance at δ 1.39. Additionally, no trace of phosphine incorporation was detected by ³¹P NMR spectroscopy, which establishes that ligand incorporation into the polymer chain by phosphine aryl exchange is not significant.¹¹

To aid in the interpretation of the complex NMR spectra of the copolymer and to establish that the coupling was efficacious, a model oligomer, **4**, was prepared by coupling macromonomer **1** with excess *p*-toluidine (Scheme 3). Model compound **4** exhibited unique spectral features in the ¹³C NMR spectrum, including the urea resonance found at δ 153 and the carbon-2 resonance of the *meta* ring which appeared distinctly upfield of all the other aryl resonances at δ 109.

The ¹³C NMR spectrum of polymer **3** establishes that the expected alternating copolymer structure is present. Collection of the ¹³C NMR data at 330 K in THF-*d*₈ greatly simplifies the spectrum relative to room temperature spectra. By comparison to the spectrum for monomers **1** and **2** and the model oligomer **4**, resonances consistent with the four different aryl ring substitution patterns (A–D) expected in the repeating unit of the polymer can be identified (Figure 3). Particularly note-

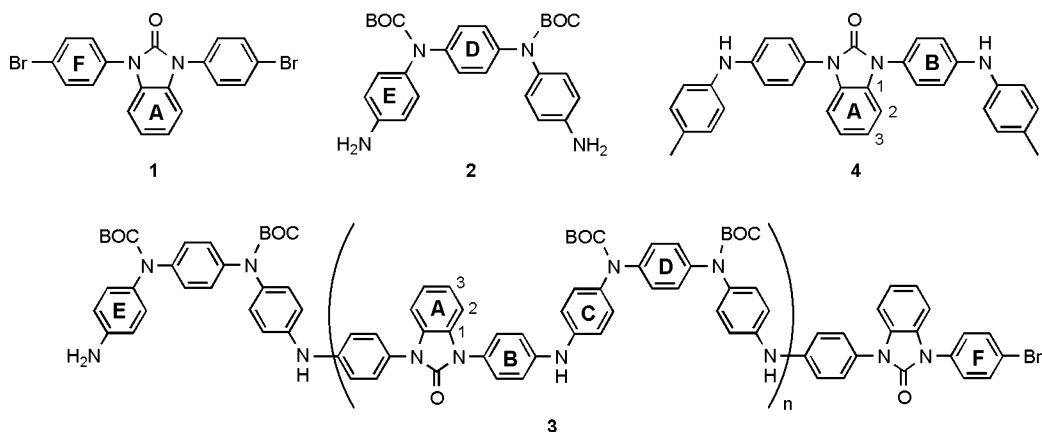


Figure 3. $^{13}\text{C}\{\text{H}\}$ NMR spectrum of **3** can be assigned by comparison to monomers **1** and **2** and to model compound **4**.

worthy are the CO resonances for the urea and BOC carbonyl carbons at δ 153 and 154, respectively, and the resonance at δ 115, which is assignable to the unsubstituted carbons of the **D** ring. Moreover, the resonances associated with the unsubstituted carbons of the *ortho*-substituted **A** ring (δ 109 and 123) and the BOC protecting group (δ 28.5) are sufficiently clean and well resolved that they can be integrated if the ^{13}C NMR data are acquired under conditions that minimize NOE. Assuming that BOC cleavage is minimal, these integrations establish that the units derived from macromonomers **1** and **2** are present in a 1:1 ratio. There were also some resonances in the spectrum that could be attributed to end-group rings (**E** and **F**), but their low intensities and overlap with repeating unit resonances make it difficult to assign them unambiguously.

The molecular weight (M_n) of the *5p,o*-PANI **3** is in the 2400–5500 range (DP = 36–85 aniline units). Although the molecular weight obtained by GPC in NMP vs polystyrene standards is significantly higher, M_n of 14 000 (PDI = 1.75), it has been reported by both us and others that this method overestimates the molecular weight of polyanilines.^{4,12} It is worth noting that, consistent with expectations for multiple couplings, there was a significant difference in the GPC retention times of the macromonomers (**1** and **2**) and polymer **3** under these conditions. A more realistic estimate of molecular weight can be obtained by end-group analysis. If we assume that the structure is in fact regioregular and that the monomers are present in a 1:1 ratio, the molecular weight is easily calculated from both the ^1H NMR spectrum (integration of the primary NH vs the entire aryl C–H region) and the chemical analysis for Br (comparing the expected C/H/N to Br percentages). The modest molecular weights of 2400–5500 thus determined are consistent with the relatively poor film-making properties that we observed for *5p,o*-PANI.

Deprotection and Oxidation of *5p,o*-PANI. Analogous to *p*-polyaniline, dramatic color changes accompany changes in the oxidation/doping state of *5p,o*-PANI as shown in Figure 4. Very thin films of polymer **3** were prepared by spin casting from THF onto glass slides using a photoresist spinner. To generate the leucoemeraldine base (LB), emeraldine base (EB), and emeraldine salt (ES) forms of *5p,o*-PANI, three separate film treatments were then applied. Buchwald and co-workers originally developed these procedures for deprotecting their *p*-polyanilines.⁷ Films placed in a 185 °C silica bath in a N_2 drybox and heated for 8 h turned from a pale

tan color to brown, consistent with the formation of the LB form of the polymer. The deep purple EB form was achieved by similarly heating fresh films to 185 °C in air for 8 h. Finally, the characteristically green ES polymer was generated by immersing a third set of films in an HCl/Et₂O solution for 30 min and allowing the films to dry in air for several hours. Similar films for FT-IR spectroscopy were also prepared on KBr salt plates by the slow evaporation of THF, followed by the appropriate oxidation/doping procedure.

The electronic spectra of oxidized samples of *5p,o*-PANI, **3**, suggest that, by analogy with spectra of similarly prepared *p*-PANI samples, it should be conducting. Notably, as the polymer is oxidized to *5p,o*-PANI-EB and *5p,o*-PANI-ES, new bands appear in the visible region of the spectrum (Figure 4). Furthermore, *5p,o*-PANI-ES exhibits a gradual increase in absorption intensity of a broad band at ca. 525 to beyond 1100 nm; the presence of this free carrier tail is consistent with the delocalization of electrons expected for a highly conjugated chain.¹³

FTIR spectra of the treated polymer films also confirmed the changes in the oxidation state of *5p,o*-PANI. The major features of the IR spectrum of polymer **3** included a 2° amine stretch at 3333 cm^{-1} , a carbonyl stretch at 1706 cm^{-1} , and aromatic (3042 cm^{-1}) and aliphatic (2975 and 2870 cm^{-1}) C–H stretches (Figure 5a). Additionally, the polymer exhibits absorptions associated with the C–H out-of-plane bending of 1,4-substituted (828 cm^{-1}) and 1,2-substituted (750 cm^{-1}) aromatic rings. The cleavage of the BOC protecting groups in the LB, EB, and ES forms of the polymer is accompanied by a significant decrease in intensity in the 2800–3000 region associated with aliphatic C–H stretches.¹⁴ The IR vibrational bands at 1606 and 1509 cm^{-1} , present in all forms of *5p,o*-PANI, can be assigned to C=C and C–C stretching and bending modes reported for polyaniline. Tang et al. have assigned the \sim 1600 cm^{-1} peak to the quinonoid ring and the \sim 1500 cm^{-1} peak to the benzenoid ring of PANI.¹⁵ As would be expected on the basis of this analysis, we observe that oxidation to the ES form produces a significant change in the 1600 cm^{-1} absorption; the band shifts to 1582 cm^{-1} and increases in intensity relative to the 1504 cm^{-1} peak. This shift indicates that when *5p,o*-PANI is treated with HCl, quinoid units are incorporated into the polymer.¹⁶ Further confirmation of the formation of the conducting ES form of *5p,o*-PANI is the long absorption tail above 2000 cm^{-1} that masks the N–H

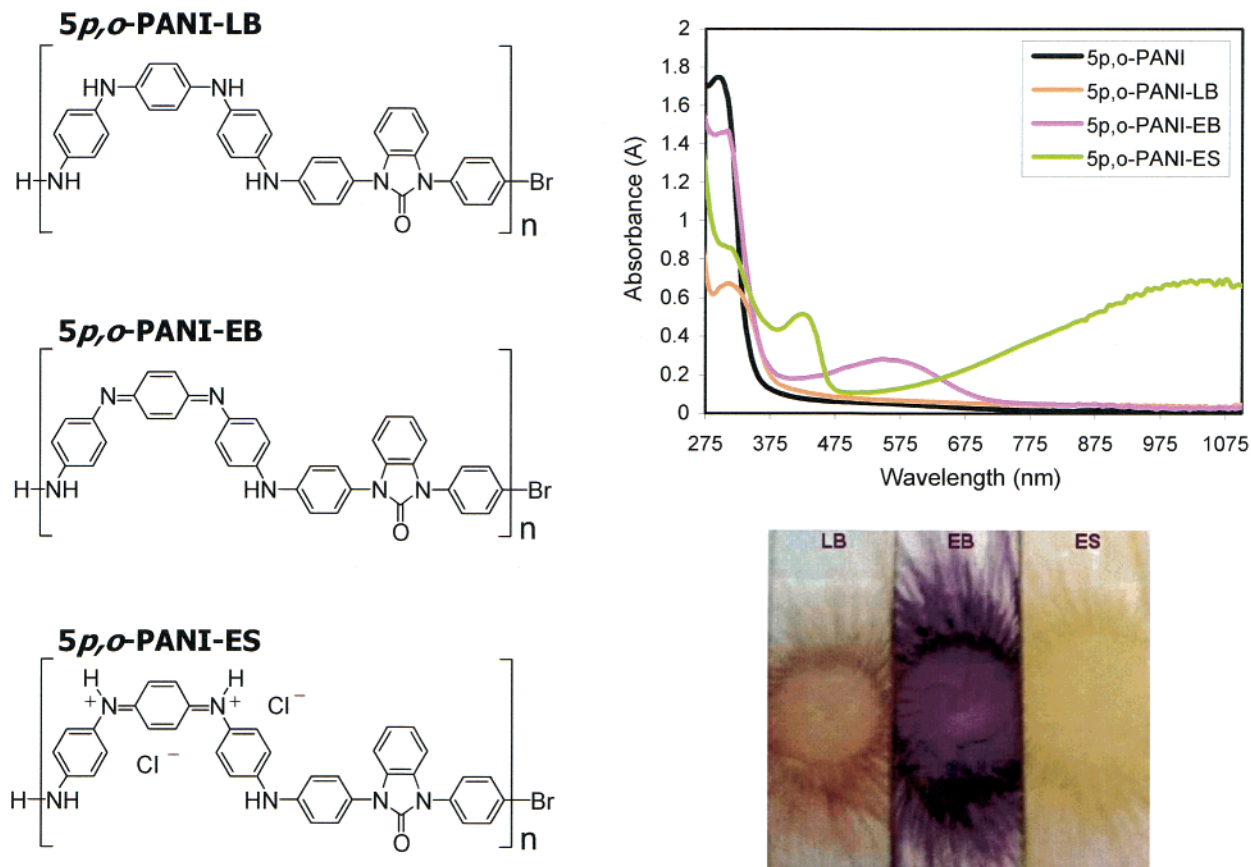


Figure 4. UV-vis spectra and films of polymer **3** and its deprotection products: *5p,o*-PANI-LB, *5p,o*-PANI-EB, and *5p,o*-PANI-ES.

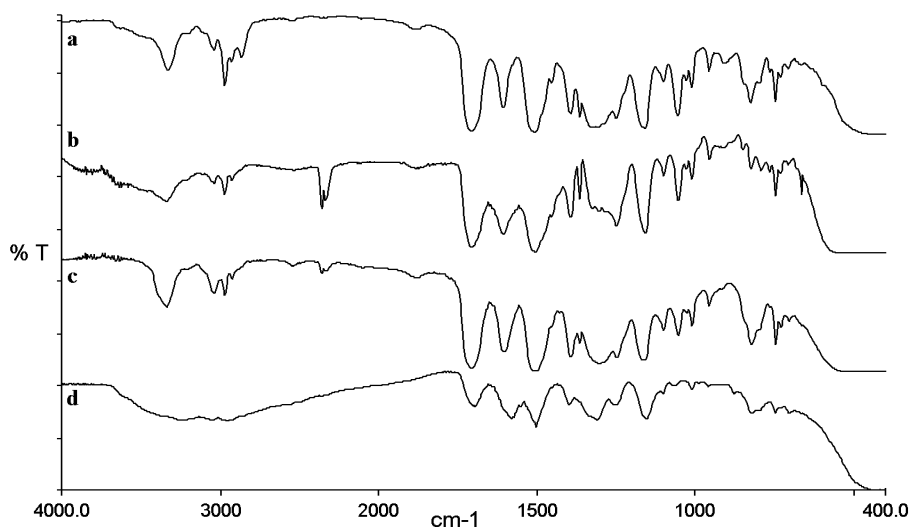


Figure 5. IR spectra of polymer **3** (a) and its deprotection and oxidation products: *5p,o*-PANI-LB (b), *5p,o*-PANI-EB (c), and *5p,o*-PANI-ES (d).

stretching frequency. This spectroscopic feature has been associated with high electrical conductivity and a high degree of electron delocalization in PANI.¹⁶

Initial studies on polymer *5p,o*-PANI-ES (blended with PVC to improve film quality) show conductivities within an order of magnitude of those measured for *p*-polyaniline in similar sample preparations (~ 0.2 S/cm). We plan to pursue more detailed studies of the conductive properties of these polymers in the future.

Discussion

We have successfully prepared an *o,p*-polyaniline derivative, *5p,o*-PANI, that contains one *ortho*-substituted aniline ring for every five *para*-substituted aniline rings. NMR and IR spectroscopy confirm the presence of an *ortho*-substituted ring and unambiguously establish the regioregularity of this polymer. Furthermore, integration of the ¹³C NMR spectrum suggests that

there is no difference in the activities of the macromonomers; they are present in a 1:1 ratio.

While the relatively modest size of the *ortho,para*-copolymers does adversely affect their film-making properties, it would not be expected to significantly inhibit conductivity. Recently, several reports on the preparation and chemical and physical properties of oligomeric anilines have appeared in the literature.^{9,17–19} Because conductivity depends on intramolecular, intermolecular, and interdomain contributions, polymer length is not the sole determining factor in the magnitude of bulk conductivity.^{18,20} Oligomers as small as 16 repeat units show conductivities in the 10^{−3} range.¹⁷ The relatively low molecular weights are likely due to the competing formation of cyclic oligomers, a phenomenon that has been observed previously in the preparation of polyanilines by Pd-catalyzed couplings.⁶

Conclusions

The *ortho–para* derivative of polyaniline, 5*p,o*-PANI, **3** exhibited the spectroscopic properties, colored oxidation states, and conductive properties associated with conducting polyaniline. These findings suggest that the presence of the *ortho*-substituted aniline ring does not critically disrupt the conjugation of the polymer or interfere significantly with interchain interactions. The effect on bulk conductivity of the urea-protecting group is not clear. Although the urea carbonyl could be acting as a spin trap and, thereby, inhibit free movement of electrons along the backbone,²¹ the imidazolone ring could also be promoting conjugation by enforcing planarity along the backbone. We intend to address this question in future studies by preparing the analogous “unprotected” 5*p,o*-PANI. Finally, we are now prepared to synthesize derivatives of 5*p,o*-PANI carrying substituents in the **A3** position of the *ortho* rings with the objective of creating polyanilines with tunable conductivity and physical properties.

Experimental Section

General. All reactions and manipulations were performed under an atmosphere of nitrogen either in a glovebox or by using standard Schlenk techniques. All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. NaO^tBu and 1,4-phenylenediamine were sublimed. 1,3-Dihydrobenzimidazol-2-one was prepared by the literature procedure.²² BOC-protected PANI trimer, **2**, was prepared using the synthetic scheme outlined by Buchwald et al.⁹ Polyaniline was prepared in its emeraldine base form by the standard procedure for the oxidation of aniline using ammonium peroxydisulfate followed by treatment with ammonium hydroxide.²³ CDCl₃ was vacuum-transferred from P₄O₁₀. THF and THF-*d*₈ were distilled from Na and Na/benzophenone, respectively.

¹H NMR and ¹³C{¹H} NMR spectra were acquired on Bruker 300 MHz instruments; the ¹³C{¹H} NMR of polymer **3** was collected on a Bruker 500 MHz spectrometer. GPC data were acquired in NMP solvent on a Waters GPC system equipped with phenogel columns and a Waters 410 differential refractometer calibrated using polystyrene standards. IR data were acquired on a Perkin-Elmer Spectrum BX FT-IR system. UV–vis data were acquired on a Perkin-Elmer Lambda 19 UV/vis/NIR spectrometer. EI-MS data were acquired on a VG-70S (+) EI-MS. Thin films were spun-cast on a Headway Research, Inc., photoresist spinner model 1-EC101D-R485. Conductivity measurements were made using the standard four-point probe method.²⁴

Synthesis of 1,3-Bis(4-bromophenyl)-1,3-dihydrobenzimidazol-2-one, 1. A round-bottomed flask was loaded with

1,3-dihydrobenzimidazol-2-one (2.00 g, 14.9 mmol), *p*-dibromobenzene (10.6 g, 44.7 mmol), potassium carbonate (4.12 g, 29.8 mmol), copper(I) iodide (0.568 g, 2.98 mmol), and dimethylformamide (48 mL). The mixture was then refluxed at 150 °C for 24 h. After cooling to room temperature, the reaction mixture was taken up in dilute ammonium hydroxide, extracted into ethyl acetate, washed with brine solution, and finally dried with magnesium sulfate according to the procedure described by Sugahara et al.¹⁰ Following purification by column chromatography in CH₂Cl₂/hexanes, 1.89 g of macromonomer **1** (28% yield) was isolated as a white powder. ¹H NMR (CDCl₃): δ 7.68 (d, 4H), 7.49 (d, 4H), 7.15 (s, 4H). ¹³C{¹H} NMR (CDCl₃): δ 152.1 (*ipso*, carbonyl), 133.6 (*ipso*), 133.0, 129.3 (*ipso*), 127.8, 122.8, 121.6 (*ipso*), 109.2. IR (film, cm^{−1}): 1726. EI-MS (*m/z*): 444 (M⁺). Anal. Calcd for C₁₉H₁₂N₂OBr₂: C, 51.38; H, 2.73; N, 6.31. Found: C, 51.21; H, 2.75; N, 6.30.

Synthesis of 5*p,o*-PANI, 3. In a glovebox were weighed *ortho–para*-macromonomer, **1** (0.222 g, 0.500 mmol), PANI trimer **2** (0.245 g, 0.500 mmol), NaO^tBu (0.135 g, 1.40 mmol), Pd₂dba₃ (0.009 g, 1.5 mol % Pd/amine), and 2-(di-*tert*-butylphosphino)biphenyl (0.018 g, 0.06 mmol). The reagents were transferred to a heavy-walled flask equipped with a Teflon-coated valve and suspended in 2.7 mL of THF. The flask was sealed and heated to 80 °C for 2 days. The reaction mixture was cooled to room temperature, and the THF was removed in vacuo. The crude product was washed by sonication using first ether (2 × 10 mL), then H₂O (2 × 10 mL), and finally methanol (2 × 10 mL). Sonication of the remaining solids in THF (15 mL) gave a homogeneous solution, which was added dropwise to 40 mL of methanol, producing a fine suspension. Collection of the precipitate gave a 45% yield of polymer **3**. The remaining 55% of the product was isolated as smaller oligomers by concentration of the filtrate. GPC (NMP): *M*_w = 24 000, *M*_n = 14 000, PDI = 1.75. ¹H NMR (THF-*d*₈): δ 7.70–6.59 (m, aryl and 2° NH), 4.46 (br, 1° NH), 1.42–1.29 (m, *t*-Bu). ¹³C{¹H} NMR (THF-*d*₈, 25 °C): δ 154.8 (*ipso*), 154.6 (*ipso*), 153.7 (*ipso*), 153.2 (*ipso*), 148.1 (*ipso*), 145.0 (*ipso*), 144.8 (*ipso*), 144.1 (*ipso*), 141.8 (*ipso*), 141.2 (*ipso*), 140.5 (*ipso*), 136.4 (*ipso*), 135.8 (*ipso*), 133.6, 131.7 (*ipso*), 131.4 (*ipso*), 130.9, 130.3, 129.6, 129.4, 128.8, 128.4, 128.0 (*ipso*), 127.4, 126.6, 125.4, 123.3, 122.6, 121.5, 121.0, 119.0, 118.3, 116.9, 116.5, 115.2, 109.5, 80.8 (*ipso*), 80.5 (*ipso*), 28.5. ¹³C{¹H} NMR (THF-*d*₈, 57 °C): δ 154.2 (*ipso*), 153.2 (*ipso*), 144.6 (*ipso*), 142.3 (*ipso*), 141.7 (*ipso*), 137.6 (*ipso*), 133.2, 131.4 (*ipso*), 129.2 (*ipso*), 129.0, 128.0, 127.0, 122.4, 119.13, 118.3, 115.0, 109.2, 80.2 (*ipso*), 28.5. IR (film, cm^{−1}): 3333, 3042, 2975, 2870, 1709, 1607, 1509, 1325, 1162, 1058, 828, 750. UV–vis (film, λ_{max}, nm): 297. Anal. Calcd for (C₄₇H₄₄N₆O₅)_n: C, 73.03; H, 5.75; N, 10.87; Br, 0.00. Found: C, 70.27; H, 5.38; N, 10.26; Br, 3.26.

Synthesis of Model Oligomer, 4. In a glovebox were weighed 0.300 g (0.676 mmol) of *ortho–para*-macromonomer, **1**, 0.148 g (1.385 mmol) of toluidene, 0.149 g (1.55 mmol) of NaO^tBu, 0.013 g (2 mol % Pd/amine) of Pd₂dba₃, and 0.017 g (0.06 mmol) of 2-(di-*tert*-butylphosphino)biphenyl. The reagents were transferred to a heavy-walled flask equipped with a Teflon-coated valve and suspended in 2.5 mL of THF. The flask was sealed and heated to 80 °C for 18 h. The reaction mixture was cooled to room temperature, diluted with CH₂Cl₂, and filtered through Celite. Hexanes were added to the filtrate to precipitate the crude product which was subsequently washed with toluene to give a 33% yield of compound **4** as a pale tan powder. ¹H NMR (THF-*d*₈): δ 7.45 (br, 2° NH, 2H), 7.41 (d, *J* = 8.8 Hz, aryl, 4H), 7.18 (d, *J* = 8.8 Hz, aryl, 4H), 7.06 (m, aryl, 12 H), 2.25 (s, CH₃, 6H). ¹³C{¹H} NMR (THF-*d*₈) δ 153.2 (*ipso*), 145.2 (*ipso*), 141.6 (*ipso*), 131.2 (*ipso*), 130.9 (*ipso*), 130.4, 127.9, 127.0 (*ipso*), 122.1, 119.7 (*ipso*), 116.9, 109.0, 20.8. EI-MS (*m/z*): 496 (M⁺).

Representative Procedure for Removal of BOC-Protecting Groups. Polymer **3** was cast into thin films by spin-casting from a THF solution. These films of the BOC-protected polymer were then heated to 185 °C for 8 h under N₂ on a silica constant-temperature bath or in an open-air oven to produce the leucoemeraldine and emeraldine base forms of the polymer, respectively. The emeraldine salt oxidation state

was formed by treating films with Et₂O/HCl solution for 30 min with subsequent air oxidation for several hours.

Thin-Film Preparation and Doping Procedure for Conduction Measurements. Films of polymer **3** and PANI-EB were drop-cast from an NMP solution containing the a 50:50 mixture of polymer and poly(vinyl chloride) (PVC). Solutions were dropped onto clean glass slides, and the NMP was removed in vacuo in a vacuum desiccator. The films were removed from the glass slide with distilled water, dried, and subsequently placed into a vial containing HCl vapors. After 3 days, the conductivity of each film was measured using a standard four-point probe apparatus. Current flow, *I*, through each film was measured in at least two separate areas on the film. The value of *I* was recorded when the applied voltage, *V*, reached a minimum value. If the measured current passing through the film was less than 1.5×10^{-8} A, the reading was excluded from the data set. Typically at least three voltage/current measurements were measured for each film and averaged. Film thicknesses were measured using an L.S. Starrett Co. caliper that was calibrated and found to measure to the nearest thousandth of an inch \pm 2%. When possible, three film thickness measurements were recorded and averaged.

Acknowledgment. This research was supported by the NSF (CHE-0091499). We thank Prof. Richard McCullough and Dr. Richard Pilston at Carnegie Mellon University for help with conductivity measurements.

Supporting Information Available: ¹H and ¹³C NMR spectra for 5p,o-PANI **3** and model oligomer **4** and GPC data for polymer **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- Goto, H.; Akagi, K. *Macromolecules* **2002**, *35*, 2545–2551. Prevost, V.; Petit, A.; Pla, F. *Synth. Met.* **1999**, *107*, 79–87. Kitani, A.; Satoguchi, K.; Tang, T.-Q.; Ito, S.; Sasaki, K. *Synth. Met.* **1995**, *69*, 131–132. Zotti, G.; LeClerc, M. *Chem. Mater.* **1995**, *7*, 33–42. Bodalia, R.; Stern, R.; Batich, C.; Duran, R. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2123–2127. Wang, X.-H.; Li, J.; Wang, L.-X.; Jing, X.-B.; Wang, F. S. *Synth. Met.* **1995**, *69*, 147–147. Mattoso, L. H. C.; Faria, R. M.; Bulhoes, L. O. S.; MacDiarmid, A. G. *J. Polym. Sci., Polym. Chem.* **1994**, *32*.
- MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27–34. Heeger, A. J. *Synth. Met.* **1993**, *55–57*, 3741. MacDiarmid, A. G.; Epstein, A. J. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317. MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 85.
- Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805. Hartwig, J. F. *Angew. Chem., Int. Ed.* **1998**, *37*, 2046. Wagaw, S.; H., Y. B.; Buchwald, S. L. *J. Organomet. Chem.* **1999**, *576*, 125.
- Spetseris, N.; Ward, R. E.; Meyer, T. Y. *Macromolecules* **1998**, *31*, 3158–3161.
- Kanbara, T.; Izumi, K.; Nakadani, Y.; Narise, T.; Hasegawa, K. *Chem. Lett.* **1997**, 1186. Kanbara, T.; Miyazaki, Y.; Hasegawa, K.; Yamamoto, T. *J. Polym. Sci., Polym. Chem.* **2000**, *38*, 4194–4199. Goodson, F. E.; Hauck, S. I.; Hartwig, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 7527–7539. Kanbara, T.; Nakadani, Y.; Hasegawa, K. *Polym. J.* **1999**, *31*, 206–209.
- Goodson, F. E.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 1700–1703.
- Zhang, X.-X.; Sadighi, J. P.; Mackewitz, T. W.; Buchwald, S. L. *J. Am. Chem. Soc.* **2000**, *122*, 7606–7607.
- Louie, J.; Hartwig, J. F. *Macromolecules* **1998**, *31*, 6737–6739.
- Sadighi, J. P.; Singer, R. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 4960–4976.
- Sugahara, M.; Ukita, T. *Chem. Pharm. Bull.* **1997**, *45*, 719–721.
- Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441–12453.
- Hsu, C.-H.; Peacock, P. M.; Flippen, R. B.; Manohar, S. K.; MacDiarmid, A. G. *Synth. Met.* **1993**, *60*, 233–237.
- MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1995**, *69*, 85–92.
- There is some residual aliphatic C–H absorption in the 2800–3000 region likely arising from a small percentage of uncleaved BOC groups. We have not yet attempted to optimize the procedure to ensure complete cleavage.
- Tang, J.; Jing, X.; Wang, F. *Synth. Met.* **1988**, *24*, 231.
- Kang, E. T.; Neoh, K. G.; Tan, K. L. *Prog. Polym. Sci.* **1998**, *23*, 277–324 and references therein.
- Zhang, W. J.; Feng, J.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1997**, *84*, 119–120.
- MacDiarmid, A. G.; Feng, J. *Synth. Met.* **1999**, *100*, 131–140.
- Lokshin, N. A.; Pyshkina, O. A.; Golubev, V. B.; Sergeev, V. G.; Zezin, A. B.; Kabanov, V. A.; Levon, K.; Piankijakul, S. *Macromolecules* **2001**, *34*, 5480–5486. Gao, J.; Zhang, W.; Wang, C.; Wu, Z.; Ji, Y.; Zhou, Y.; Shibata, M.; Yosomiya, R. *Macromol. Rapid Commun.* **1999**, *20*, 560–563.
- MacDiarmid, A. G. *Synth. Met.* **1997**, *84*, 27.
- Burke, L. A. *J. Polym. Sci., Polym. Phys. Ed.* **1984**, *22*, 1987–1989.
- Crank, G.; Mursyidi, A. *Aust. J. Chem.* **1982**, *35*, 775–784.
- Mattoso, L. H. C.; MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *68*, 1–11.
- Van der Pauw, L. J. *Phillips Res. Rep.* **1958**, *13*, 1.

MA021343F