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Macromolecules, **2001**, 34 (4), 812-816 • DOI: 10.1021/ma000771n

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Regiospecific Copolyanilines from Substituted Oligoanilines: Electrochemical Comparisons with Random Copolyanilines

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Received May 4, 2000; Revised Manuscript Received November 6, 2000

ABSTRACT: Regiospecific substituted polyanilines have been assembled via electropolymerization of methoxy-substituted dimeric and trimeric oligoanilines. The oligoaniline monomers were synthesized utilizing Pd-catalyzed aryl amination cross-coupling chemistry. The single-crystal X-ray structure of one of the oligomers is presented. The oligoaniline monomers were electropolymerized in 1 M H_2SO_4, and the electrochemical behavior and potential-dependent in situ conductivities of the regiospecific polyaniline films were compared to those of random copolymers polymerized from solutions of aniline and *o*-anisidine of the same molar ratio. The regiospecific polyanilines exhibited higher conductivities, which may be attributed to a more crystalline and regular structure. Differences in the oxidation potential of the polymers are observed depending on the degree of methoxy substitution.

Introduction

Various pre- and post-polymerization methods have been employed to synthesize derivatized polyanilines. Functionalized homopolyanilines have been assembled with substituents on every phenyl ring[1] or amine[2] from derivatized aniline monomers. Also, random copolymers have been chemically and electrochemically synthesized from solutions containing different amounts of aniline and/or various derivatized aniline monomers.[3]

A fewer number of post-polymerization methods have been utilized. Most notably, Yue and Epstein submitted the emeraldine base form of polyaniline to fuming sulfuric acid to produce the first protonic acid, self-doped conducting polymer.[4] Wrighton and group showed how to derivatize the amine groups of polyaniline.[5] Recently, Han and co-workers have reported the derivatization of electropolymerized films of polyaniline with dialkylamino- and alkylthio-based groups via concurrent reduction and substitution chemistry.[6] In all cases, except when forming a homopolymer, regiospecificity could not be controlled yielding randomly substituted polyanilines or copolyanilines. Employing Pd-catalyzed amination chemistry of aryl halides,[7] substituted dimeric and trimeric oligoanilines have been synthesized and subsequently polymerized to assemble regiospecific polyanilines. The utility of this approach for the synthesis of linear oligoanilines has been established.[8] Herein we present the synthesis and characterization of regiospecific functionalized copolyanilines from derivatized oligoanilines and compare their electrochemical and potential-dependent in situ conductivity properties to their random copolymer counterparts.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were completed using a Varian UN-300 or Mercury 300 spectrometer and referenced with respect to TMS and solvent, respectively. High-resolution mass spectra were completed using a Finnigan MAT 8200, and a 3-nitrobenzyl alcohol matrix was used for FAB measurements. Elemental analyses were obtained at Desert Analytics (Tuscon, AZ). Compounds **1** and **2** were prepared according to ref 7a. Pd_2dba_3 and *rac*-BINAP were obtained from Strem Chemical Co. while all other compounds were purchased from Aldrich.

Methoxy Derivatized Protected Dimer Aniline (3). A solution of 1.00 g (8.10 mmol) of *o*-anisidine, 2.82 g (8.40 mmol) of **1**, 0.0740 g (0.0810 mmol) of $Pd_2(dba)_3$, 0.126 g (0.200 mmol) of BINAP, and 1.09 g (11.3 mmol) of NaOtBu in 35 mL of THF was heated at reflux for 24 h. The mixture was then cooled to room temperature and the THF removed. The residue was taken up in 25 mL of CH_2Cl_2, washed with 20 mL of 2.0 M NaOH and 20 mL of a saturated aqueous solution of NaCl, and dried over Na_2SO_4, and the solvent was removed. The oily, dark orange residue was purified via column chromatography (2:1 hexane/$CHCl_3$) and recrystallized in MeOH to yield dark orange, chunklike crystals. Yield 86%; Mp 119−120 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.74 (dt, $J = 6.6$, 1.5 Hz, 2H), 7.42 (m, 3H), 7.30 (d, $J = 2.1$ Hz, 2H), 7.29 (d, $J = 1.5$ Hz, 1H), 7.16 (d, $J = 2.1$ Hz, 1H), 7.14 (m, 2H), 6.95 (dt, $J = 8.4$, 2.1 Hz, 2H), 6.80 (m, 3H), 6.69 (dt, $J = 8.4$, 2.1, 2H), 6.02 (bs, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.79, 147.98, 145.39, 140.23, 138.38, 136.86, 133.78, 130.69, 129.82, 129.40, 128.70, 128.36, 128.22, 122.76, 121.00, 119.70, 119.39, 113.96, 110.48, 55.74. HRMS (EI) *m*/*z* 378.1725 (378.1732 calcd for $C_{26}H_{22}N_2O$, M^+). Anal. Calcd $C_{26}H_{22}N_2O$: C, 82.51; H, 5.86; N, 7.40. Found: C, 82.31; H, 5.95; N, 7.41.

Methoxy Derivatized Dimer Aniline (4). A solution of 0.300 g (0.793 mmol) of **3**, 0.168 g (0.159 mmol) of 10% palladium on carbon, 1.00 g (15.9 mmol) of $(NH_4)HCO_2$, 20 mL of THF, and 10 mL of EtOH was heated at reflux for 4 h. The solution was cooled to room temperature and filtered thru Celite. The solvent was removed, and the residue was taken up in 30 mL of CH_2Cl_2, washed with 15 mL of 2 M NaOH and 15 mL of a saturated NaCl solution, and dried. The residue was purified via flash chromatography (2:1 $CHCl_3$/ethyl acetate) to yield a white solid. Yield 93%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.01 (dt, $J = 8.7$, 2.1 Hz, 2H), 6.96 (dd, $J = 7.5$, 1.8 Hz, 1H), 6.82 (dt, $J = 7.5$, 1.8 Hz, 2H), 6.76 (dt, $J = 7.5$, 1.8 Hz, 1H), 6.67 (dd, $J = 6.6$, 2.1 Hz, 2H), 5.85 (bs, 1H), 3.89 (s, 3H), 3.51 (bs, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.19, 142.16, 135.83, 133.59, 123.87, 121.06, 118.11, 116.23, 112.26, 110.19, 55.72. HRMS (EI) *m*/*z* 214.1102 (214.1106 calcd for $C_{13}H_{14}N_2$, M^+).

Methoxy Derivatized Protected Trimer Aniline (5). A solution of 0.350 g (2.84 mmol) of *o*-anisidine, 1.50 g (2.84 mmol) of **2**, 0.0710 g (0.114 mmol) of BINAP, 0.0520 g (0.0568 mmol) of Pd_2dba_3, 0.382 g (3.98 mmol) of NaOtBu, and 40 mL of THF was heated at reflux for 24 h. The solution was cooled to room temperature and the solvent removed. The residue was taken up in 40 mL of CH_2Cl_2, washed with 20 mL of 2 M NaOH and 20 mL of a saturated aqueous NaCl solution, dried over Na_2SO_4, and filtered. The solvent was removed to yield a deep red oily residue. The residue was purified via column

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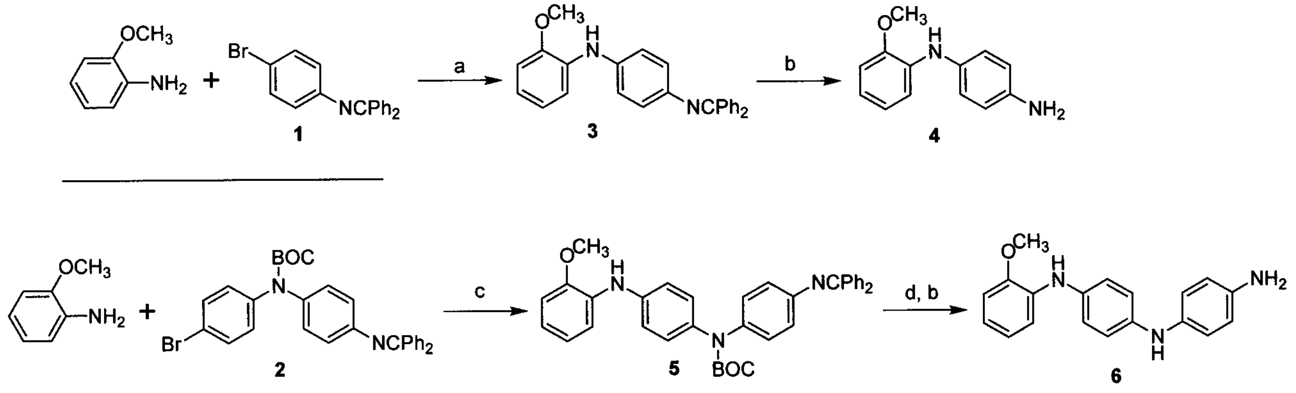
10.1021/ma000771n CCC: $20.00

Scheme 1[a]



[a] (a) Pd$_2$dba$_3$, *rac*-BINAP, NaOtBu, THF, reflux; (b) 10% Pd/C, NH$_4$HCO$_2$, THF, EtOH, 60 °C; (c) Pd$_2$dba$_3$, *rac*-BINAP, NaOtBu, THF, reflux; (d) 150 °C.

chromatography (2:1 hexanes/ethyl acetate) to yield a thick orange oil. Yield: 79%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.73 (dt, J = 6.9, 1.8 Hz, 2H), 7.42 (m, 3H), 7.25 (m, 4H), 7.10 (m, 2H), 7.05 (m, 4H), 6.99 (dt, J = 8.7, 2.1 Hz, 2H), 6.86 (m, 3H), 6.66 (dt, J = 8.7, 2.1 Hz, 2H), 6.11 (s, 1H), 3.88 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 155.45, 154.08, 149.74, 139.83, 138.71, 136.27, 132.00, 130.70, 129.57, 129.31, 128.64, 128.20, 128.03, 125.81, 122.62, 122.16, 120.79, 119.48, 113.84, 111.95, 110.36, 106.63, 80.31, 55.60, 28.22.

Methoxy Derivatized Trimer Aniline (6). In a 25 mL round-bottom flask was placed 2.00 g (3.51 mmol) of **5** and heated at 150 °C in an argon atmosphere for 3 h. The black residue was taken up in 45 mL of THF and 30 mL of EtOH. To the solution was added 0.744 g (0.702 mmol) of 10% palladium on carbon and 4.43 g (70.2 mmol) of (NH$_4$)HCO$_2$ and heated to 60 °C for 4 h. The mixture was cooled to room temperature and filtered thru Celite, and the solvent was removed. The residue was quickly purified via flash chromatography (5% MeOH/CH$_2$Cl$_2$) to yield a light red oil which rapidly oxidizes in air to a purple-black oil. The product was stored in an inert atmosphere in the absence of light. Yield: 70%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.58 (d, J = 6.6 Hz, 1H), 7.60 (dt, J = 7.5, 2.1 Hz, 1H), 7.49 (dt, J = 7.8, 2.1 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 7.25 (m, 2H), 7.19 (dt, J = 6.6, 1.8 Hz, 1H), 7.00 (dt, J = 8.4, 2.1 Hz, 2H), 6.42 (s, 1H), 5.75 (bs, 1H), 4.25 (s, 3H), 3.87 (bs, 2H). ^{13}C NMR (75 MHz, CDCl$_3$): δ 147.13, 141.28, 140.77, 135.12, 134.74, 134.19, 128.84, 128.37, 122.72, 121.72, 120. 87, 118.20, 117.02, 116.14, 112.43, 110.12, 55.51.

X-ray Measurements. An orange block of dimensions 0.24 × 0.24 × 0.24 mm^3 was afixed with oil to a glass fiber and transferred to a Bruker SMART/CCD diffractometer system. A standard hemisphere of data were collected. The structure was solved by direct methods and difference Fourier techniques. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were placed in idealized positions. Full tables of crystallographic data have been placed in the Supporting Information.

Electrochemistry. Cyclic voltammetry was carried out on an EcoChemie B.V. bipotentiostat using GPES v.4.4 software. A platinum coil was used as a counter electrode, and 5 μm spaced interdigitated microelectrodes purchased from ABTECH were used as working electrodes. Measurements were performed using a SCE reference in 1 M H$_2$SO$_4$ under an argon atmosphere. Films were grown cycling in a monomer solution at 100 mV/s. The films were rinsed in distilled water followed by methanol and placed in a monomer-free solution. In situ conductivity measurements, obtained as previously explained,[9] were run at 5 mV/s with a 40 mV offset potential between the working electrodes. Film thicknesses were obtained with a Tencor P10 surface profilometer and ranged from 1500 to 5500 Å for all polymers studied.

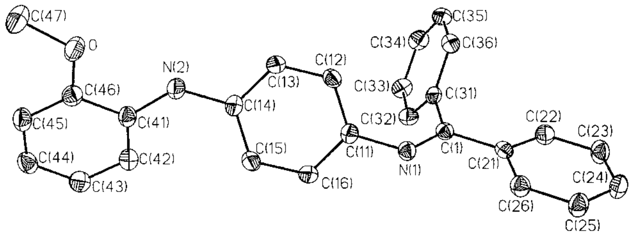


Figure 1. Single-crystal X-ray structure of protected oligomer **3**. Selected bond lengths and angles: O–C(46) 1.373(3), O–C(47) 1.428(3), N(2)–C(41) 1.389(3), N(2)–C(14) 1.402(3), N(1)–C(11) 1.420(3), N(1)–C(1) 1.281(3) Å; C(46)–O–C(47) 117.3(2), O–C(46)–C(45) 125.5(3), C(14)–N(2)–C(41) 129.2(2), C(1)–N(1)–C(11) 124.0(2)°.

Results and Discussion

Monomer Syntheses. The syntheses of the methoxy derivatized dimeric and trimeric oligoanilines **4** and **6** are shown in Scheme 1. *o*-Anisidine was cross-coupled with **1** and **2** using Pd$_2$dba$_3$/BINAP[7,8] catalyst system to give the monomethoxy derivatized dimer (**3**) and trimer anilines (**5**) in 86% and 79% yields, respectively. The single-crystal X-ray structure of **3** is shown in Figure 1. The diphenyl imine protected compounds **3** and **5** exhibited intense orange-red colors. The terminal amine groups were deprotected using 10% Pd/C and an excess of (NH$_4$)HCO$_2$. The BOC protected amine group of **5** was deprotected by heating to 160 °C over a period of 7 h. This deprotection procedure proceeded for compounds **3** and **5** in 70–95% yields. The resulting deprotected oligoanilines were found to be air sensitive as the products darkened during purification steps and storage. As a result, the oligoanilines were stored in their respective protected forms, and electrochemical studies were performed immediately after deprotection.

Electrochemistry and in Situ Conductivity. Table 1 lists redox potentials and in situ conductivity data for all systems studied. It is well-known that the electrochemical properties of conducting polymers, in particular polyaniline, are sensitive to the polymerization conditions.[10] Therefore, despite the tremendous amount of literature published on the random copolymers and homopolymers of aniline and *o*-anisidine, we also have electropolymerized these same systems in identical conditions as the oligoanilines **4** and **6** for optimal comparison. They were found to be consistent with previous reports.[1–3,10,11] Polymerization of oligoaniline monomers **4** (Figure 2) and **6** (Figure 3) was initiated by scanning the working electrodes to potentials greater than 0.60 V. All polymer films were studied over the potential range of −0.20 to 0.70 V. Scan rate dependence studies of films of poly(**4**) and poly(**6**) in monomer-free electrolyte showed the peak currents to scale with scan

Table 1. Cyclic Voltammetry (vs SCE) and in Situ Conductivity Data

	cyclic voltammetry		conductivity	
polymer	$E_{\mathrm{p,a}}$	$E_{\mathrm{p,c}}$	$E_{\max}$[a]	$\sigma_{\max}$ (S/cm)[b]
o-anisidine	0.15	−0.06	0.17	0.8
	0.42	0.35		
	0.69	0.65		
aniline	0.24	0.01	0.25	12.4
	0.52	0.43		
poly(**7**)	0.17	−0.05, 0.08	0.20	1.1
	0.41	0.34		
poly(**4**)	0.19	−0.03	0.19	3.2
	0.34	0.31		
	0.49	0.43		
poly(**8**)	0.15	−0.05, 0.06	0.31	6.8
	0.37	0.32		
poly(**6**)	0.18	0.02	0.27	9.1
	0.35	0.31		
	0.46	0.40		

[a] Potential at which polymer exhibits highest conductivity. [b] Average of conductivity maxima of several sample films.

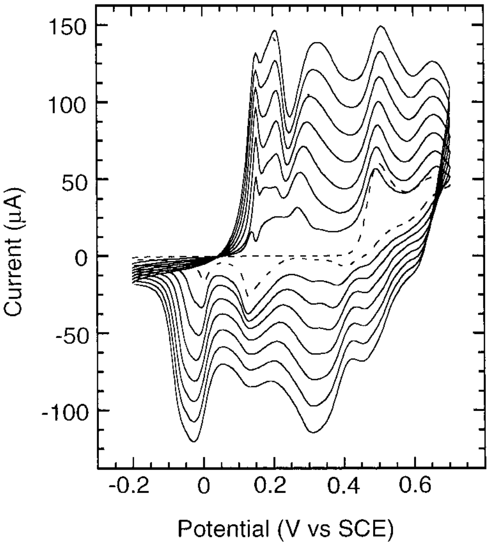


Figure 2. Electropolymerization of oligomer **4**. The dotted line represents the initial scan. Conditions: 1 M H_2SO_4, Pt interdigitated micro working electrode, Pt coil counter electrode, SCE reference electrode, and scan rate of 100 mV/s.

rate as expected for a surface confined electroactive species. Figure 4 exhibits the cyclic voltammetric (CV) curves and potential-dependent in situ conductivity traces for films of regiospecifically substituted poly(**4**) and poly(**6**). Figure 5 shows the CV and in situ conductivity traces for random copolymer poly(**7**), electropolymerized from a solution containing equimolar amounts of aniline and *o*-anisidine, and poly(**8**), which was electropolymerized from a solution containing a 2:1 molar feed ratio of aniline/*o*-anisidine.

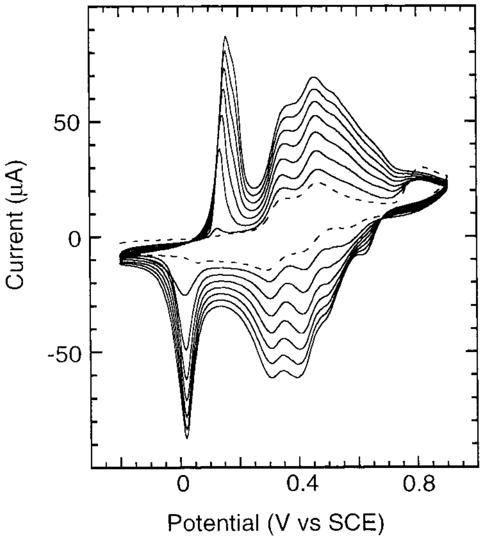


Figure 3. Electropolymerization of oligomer **6**. The dotted line represents the initial scan. Conditions: same as described in Figure 2 caption.

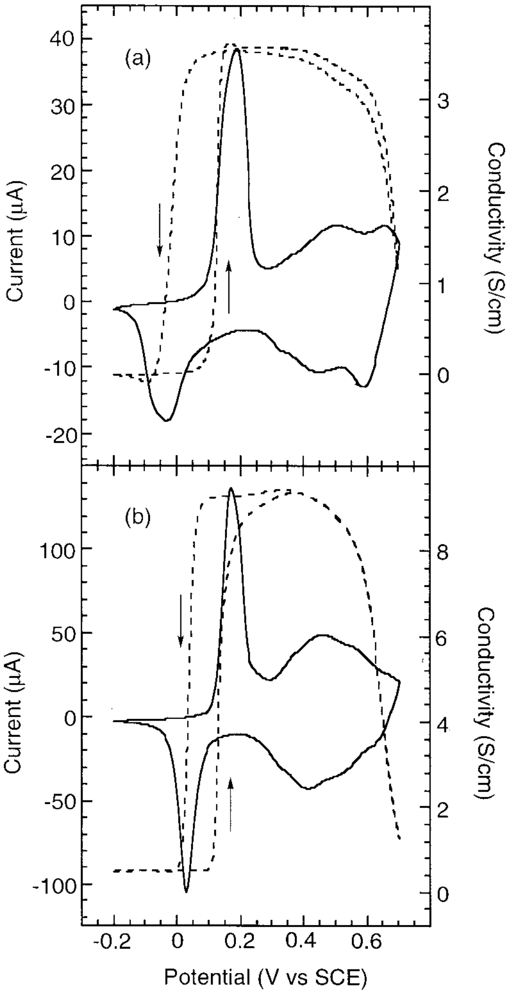


Figure 4. Cyclic voltammetric and in situ conductivity measurements (dotted line) of films of regiospecific polymers (a) poly(**4**) and (b) poly(**6**). Conditions: 1 M H_2SO_4, Pt interdigitated micro working electrode, Pt coil counter electrode, and SCE reference electrode. Scan rate: 100 mV/s for CV and 5 mV/s for conductivity measurements.

A study by Leclerc and associates explained how both structural and electronic effects should be considered when attempting to understand the electrochemistry of alkoxy-substituted polyanilines.[1c] In our experimental conditions we found that polyaniline has a higher oxidation potential for the first major redox wave (0.24 V) than poly(*o*-anisidine) (0.15 V). This can be attributed to the electron-donating effect of the methoxy groups in poly(*o*-anisidine) and not from a structural effect of the anisidine units being more twisted out of plane, resulting in increased localized electronic density. Polyaniline's peak conductivity is more than an order of magnitude higher, and this fact can be attributed to its ability to form a more coplanar backbone than substituted analogues. This is supported by a comparison in X-ray crystal structures of a tetrameric aniline oligomer

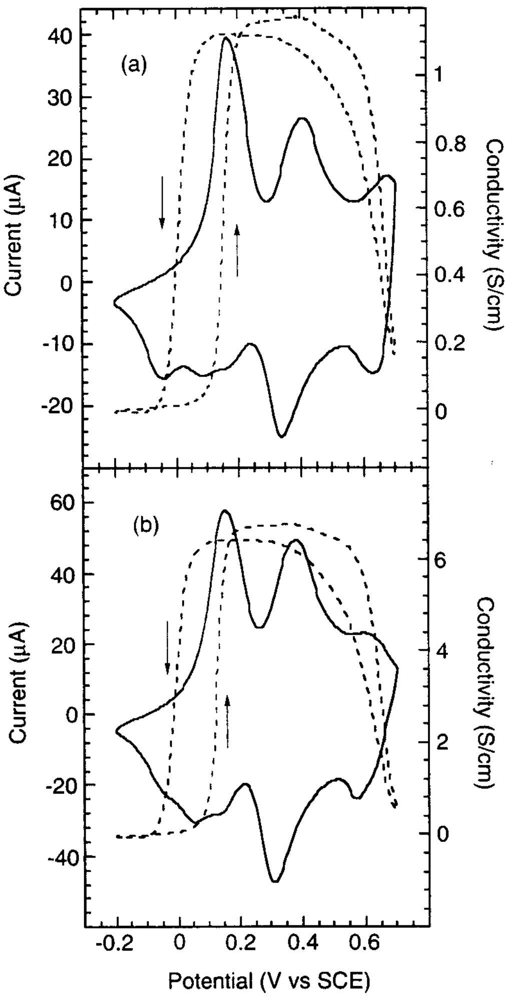


Figure 5. Cyclic voltammetric and in situ conductivity measurements (dotted line) of films of random copolymers (a) poly(**7**) and (b) poly(**8**). Poly(**7**) was electropolymerized from a solution containing equimolar aniline and *o*-anisidine, and poly(**8**) was electropolymerized from a 2:1 molar amount of aniline/*o*-anisidine. Conditions: same as described in Figure 4 caption.

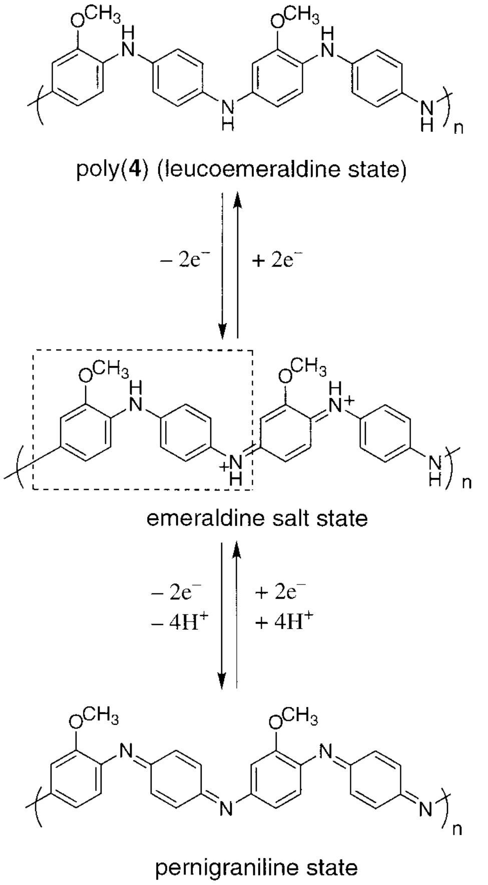


Figure 6. Different oxidation states of regiospecifically substituted poly(**4**). Dotted lines highlight unit of poly(**4**) represented by the crystal structure of **3**.

by Baughman and co-workers[12] and for the methoxy derivatized dimeric compound **3** (Figure 1). The tetrameric oligomer displayed a dihedral angle of 30° between the planes of the aniline rings. For **3**, a larger dihedral angle of 41.8(1)° is observed which can be attributed to steric effects between the methoxy group and hydrogen on the adjacent nitrogen atom.

Poly(**4**), which has a methoxy group on every other aniline unit, and poly(**6**), which has a methoxy per every three aniline units, exhibit a first major oxidation event at nearly the same potential (0.18−0.19 V). This peak can be ascribed to the two-electron per tetrameter oxidation of the neutral leucoemeraldine state of the polymer to the emeraldine form (Figure 6).[11] The potentials for this first oxidation process for poly(**4**) and poly(**6**) are greater than that for poly(*o*-anisidine) because of the lesser degree of methoxy substitution (electronic effect) but lower than that for polyaniline. In the corresponding most negative reduction wave, a 50 mV cathodic shift is observed for poly(**4**) (−0.03 V) in comparison to poly(**6**) (0.02 V). For poly(*o*-anisidine) this reduction process occurs at yet a lower potential of −0.06 V, which is closer to the value observed with poly(**4**) than with that of poly(**6**). The origin of the increased electrochemical irreversibility of this lowest reduction wave may be structural or kinetic. It is possible that the methoxy groups promote a structural change which stabilizes the doped polymer and thereby makes more difficult to undope. Alternatively, the methoxy groups could be interacting with ions and restricting the ion diffusion necessary to return to the emeraldine state. For random copolymers poly(**7**) and poly(**8**), two cathodic waves correspond to one anodic wave for the first redox process (Table 1). This is due to the compositional heterogeneity of the random copolymer which leads to nonspecific redox potentials.

The second major oxidation process, attributed to a further two-electron oxidation to the pernigraniline state per tetrameter (Figure 6),[11] for poly(**4**) appears at 0.49 V for poly(**4**) and at 0.46 V for poly(**6**). The corresponding reduction processes are found at 0.43 and 0.40 V for poly(**4**) and poly(**6**), respectively. For random copolymers poly(**7**) and poly(**8**), the oxidation potentials are in the range of 0.37−0.41 V and reduction processes at 0.32−0.34 V. The oxidation potentials of both major processes of the random copolymers poly(**7**) and poly(**8**) are lower than that of their regiospecific counterparts. In this instance, electronic effects are likely dominating due to the probability of a larger degree of anisidine incorporation into the polymer when polymerizing from a solution of mixed monomers. Both regiospecific polymers have higher conductivities, which supports a more planar structure (i.e., less methoxy substitution).

Regiospecific poly(**4**) and poly(**6**) exhibit weak oxidation processes at 0.34−0.35 V with corresponding reduction processes at 0.31 V. These have been seen in methoxy substituted polyanilines, such as poly(*o*-anisidine), and were attributed to structural defects.[1c,13] These same redox processes, although not clearly evident in the CV's of poly(**7**) and poly(**8**), may be hidden due to the broadness of the redox waves. The broadness of the CV features for random copolyanilines poly(**7**) and poly(**8**) again may be the result of the irregular substitution of methoxy groups in the backbone, as previously mentioned, leading to a distribution of potentials. The sharp CV features for poly(**4**) and poly(**6**), in particular the first major redox process, appear to be the result of the regiospecificity of methoxy substitution leading to specific redox potentials.

Potential-dependent in situ conductivity traces for poly(**4**) and poly(**7**) are centered at approximately 0.02 and 0.04 V, respectively, with a hysteresis of approximately 0.15 V for each. Regiospecific poly(**4**) exhibits a slightly higher conductivity maxima ($\sigma_{\max}$) of 3.2 S/cm compared to 1.1 S/cm for poly(**7**) just beyond (anodic side) the first major redox wave. At this point the polyaniline backbone is oxidized 0.5 e^- per aniline unit, the point at which it is expected to exhibit its highest conductivity.[14] The conductivity trace drops after the second major redox event (emeraldine → pernigraniline state), at which point the polyaniline backbone becomes oxidized to the extent of 1 e^- per aniline unit. This same behavior is observed as expected for poly(**6**) and poly(**8**). At the first major redox wave a hysteresis of 0.15 V centered at 0.03 V for poly(**8**) is seen and for poly(**6**) a hysteresis of 0.10 V at a higher potential of 0.08 V. Poly(**6**) exhibits a higher conductivity of 9.1 S/cm than that measured for poly(**8**), 6.8 S/cm. Hence, poly(**4**) and poly(**6**) exhibit higher conductivities than their random copolymer counterparts. This is to be expected since a more regular structure should lead to enhanced packing of the polymer chains, resulting in a higher degree of crystallinity of the films which in turn would explain the conductivity trends. This same behavior has been demonstrated in other conjugated polymer systems. For example, it has been shown that regioregular head-to-tail coupled poly(3-alkylthiophenes) exhibit a much larger degree of crystallinity, extended conjugation lengths, and resulting higher electrical conductivities than their irregularly substituted counterparts.[15] Detrimental head-to-head couplings lead to steric interactions between alkyl groups on adjacent thiophene units which results in the polythiophene backbone to conformationally distort.

Structural effects must also dominate the conductivity differences for regiospecific poly(**4**) and poly(**6**). Poly(**6**) displays a conductivity of nearly 3 times that of poly(**4**), which can be attributed to a more planar structure from less methoxy substitution.

Another facet of the in situ conductivity traces is that a slightly higher conductivity is reached when scanning anodically vs cathodically. This has been explained by Wrighton and co-workers as a Coulombic repulsion driven reorganization of the polymer backbone to configurations which stabilize localized charges, thereby lowering the conductivity of the polymer.[14b]

In conclusion, this work has shown that new families of regiospecifically substituted polyanilines are possible using Pd-catalyzed aryl amination chemistry. By varying the substituents and location and frequency at which they appear on the polyaniline backbone, the electrochemical properties may be controlled. This may lead to polyanilines which can be tuned depending on the application desired.

Acknowledgment. We are grateful to the Office of Naval Research for funding of this project. This work made use of MRSEC Shared Facilities supported by the National Science Foundation under Award DMR-9400334. We thank Dr. William M. Davis for single crystal X-ray measurements. We are particularly grateful to Professor Stephen L. Buchwald, Dr. Robert A. Singer, Dr. Joseph P. Sadighi, and Dr. Xiao-Xang Zhang for helpful discussions.

Supporting Information Available: Full tables of crystallographic data, atomic coordinates, bond lengths and angles, isotropic and anisotropic thermal parameters, and structure factors. This material is available free of charge via the Internet at http://pubs.acs.org.

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