# Electrochemical Polymerization of Aniline Investigated Using On-Line Electrochemistry/ Electrospray Mass Spectrometry

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A thin-layer electrochemical flow cell coupled on-line with electrospray mass spectrometry (EC/ES-MS) was used to investigate the soluble products from the controlledpotential anodic polymerization of aniline in H<sub>2</sub>O and H<sub>2</sub>O/CH<sub>3</sub>OH (1/1 v/v) with ammonium acetate and acetic acid or ammonium hydroxide as electrolytes (pH 4, 6.5, or 9). At a working electrode (glassy carbon) potential of 1.0 V versus Ag/AgCl, singly protonated aniline oligomers containing as many as 10 aniline units (10-mer) were observed in the ES mass spectra when the polymerization in H<sub>2</sub>O/CH<sub>3</sub>OH at pH 4 was carried out. The abundance of the higher *n*-mers decreased at higher solution pH and in 100% H<sub>2</sub>O at pH 4. Most of the oligomers were observed in more than one redox state ranging from fully oxidized (all imine nitrogens) to fully reduced (all amine nitrogens). The number of different redox states observed for the *n*-mers increased with increasing *n*. The structures of the reduced (m/z 185) and oxidized (m/z 183) aniline dimer ions (head-to-tail, tail-to-tail, or head-to-head) produced from the polymerization of aniline at pH 4, 6.5, and 9 in H<sub>2</sub>O/CH<sub>3</sub>OH were revealed to vary as a function of pH by comparison of their tandem mass spectrometry product ion spectra with the product ion spectra of the dimer standards. EC/ES-MS potential scan experiments, in which the working electrode current and major *n*-mer ions for n = 2, 3, and 4 were monitored as a function of electrode potential, were used to probe the growth mechanism to higher aniline oligomers. Under the conditions used, the controlled-current electrolytic process inherent to the operation of the ES ion source did not significantly influence the formation or nature of the oligomers observed. Beyond the current application, the results presented here serve to demonstrate the utility of EC/ES-MS as a tool in identifying the initial products of electropolymerization and in studying the products of electrode reactions in general.

Conducting polymers are of considerable interest given their possible application in numerous areas including electronics, energy storage, and medicine.<sup>1–4</sup> Among such polymers, poly-

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aniline<sup>5</sup> has been studied extensively and has found use in batteries, ion exchange, and corrosion control among other areas. This polymer is readily prepared electrolytically from aqueous solution (anodic polymerization onto the electrode surface), is insoluble in H<sub>2</sub>O, has a high conductivity and redox reversibility, and is air stable. The base (i.e., neutral) polyaniline is thought to be of the general structure and formula **1** 



which consists of alternating reduced (amine nitrogen) and oxidized (imine nitrogen) head-to-tail linked aniline dimeric subunits.<sup>5</sup> The value of *Y* in each individual unit *X* may be *Y* = 1, the fully reduced form (leucoemeraldine base), *Y* = 0.5, the form that is half-oxidized (emeraldine base), and *Y* = 0, the fully oxidized form (pernigraniline base).<sup>6–8</sup> The net oxidation state of a given polymer has been described as arising from a mixture of various amounts of these three different base forms.<sup>9–11</sup> The value of *X* may be as small as that value which renders the polymer H<sub>2</sub>O insoluble up to a value of ~1000. For example, approximate molecular weights of polyaniline fractions soluble in *N*-methylpyrrolidinone have been found using gel permeation chromatography to range from about 4800 (light fraction) to 200 000–350 000 (heavy fraction).<sup>2</sup>

The electrochemical polymerization mechanisms leading to the insoluble polymeric state of aniline, particularly early in the polymerization process, have been widely debated and extensively studied over the last three decades using a variety of electro-

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Scheme 1



chemical and spectroscopic techniques.<sup>8,12–21</sup> The majority of these studies have focused on the insoluble product deposited on the electrode, although a few have looked at the soluble dimer species formed.<sup>16,17,20</sup> For illustration, Scheme 1 shows a proposal for the reactions that take place in the early stages of the electrochemical polymerization, which is based largely upon the mechanistic work of Mohilner et al.<sup>8</sup> and Yang and Bard.<sup>18</sup>

In this scheme, it is presumed that all of the aniline oligomers (*n*-mers) are formed via a series of oxidation/addition reactions starting with the oxidation of aniline to the radical cation followed by radical—radical coupling to form the head-to-tail (**4**, *N*-phenyl-1,4-phenyldiamine), tail-to-tail (**5**, benzidine or (1,1'-biphenyl)-4,4'-diamine), and/or the head-to-head (**6**, hydrazobenzene) dimer (2-mer). The dimers in turn are oxidized (**4a**, *N*-phenyl-1,4-phenyldiimine, **5a**, (1,1'-biphenyl)-4,4'-diimine, and **6a**, azobenzene, respectively) and grow to larger *n*-mers via addition of aniline to

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In reference to Scheme 1, it is apparent that direct information regarding the mass, redox state, and structure of the soluble products formed at the early stage of aniline polymerization would provide corroboration of this or other polymer formation mechanisms. The combination of electrochemistry on-line with mass spectrometry<sup>22</sup> provides one means to acquire such information. In fact, electrochemistry coupled with thermospray mass spectrometry<sup>23</sup> (EC/TS-MS) has already been applied by Stassen and Hambitzer<sup>24,25</sup> to the analysis of aniline oxidation in H<sub>2</sub>O containing 0.1 M sulfuric acid. Upon oxidation of aniline they observed in the mass spectrum, as the singly charged protonated molecules,

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the reduced form of the dimer (m/z 185) and, at a factor of 10 lower abundance, the reduced form of the trimer (m/z 276). No oxidized oligomers, nor oligomers beyond the trimer, were observed. It was concluded that the higher *n*-mers, when formed, were deposited onto the electrode because of their insolubility in H<sub>2</sub>O and, therefore, were not observed in the mass spectra. Deuterium-exchange experiments indicated that the reduced dimer ions observed in their experiments were exclusively the head-to-tail structure **4**. This latter finding is in fact inconsistent with electrochemical studies, which have found that both the headto-tail and tail-to-tail dimers are formed under these same electropolymerization conditions.<sup>11</sup> Furthermore, their observation of only the reduced dimer and trimer is intriguing as it has been demonstrated that the aniline dimers and higher polyaniline *n*-mers are significantly easier to oxidize than aniline.<sup>8,11</sup>

One anticipates that it might be of advantage to reexamine the aniline anodic polymerization process using electrochemistry on-line with electrospray mass spectrometry (EC/ES-MS). A particular attribute of ES-MS<sup>26</sup> is the ability to readily produce abundant gas-phase ions from high-molecular-weight, nonvolatile and polar analytes, including polymers, that are dissolved in solution. Although 100% H<sub>2</sub>O can be sprayed at flow rates of 30-50  $\mu$ L/min (the flow rates necessary for direct on-line coupling of our EC cell) with pneumatic or heat-assisted ES, signals are generally much better if a large fraction of the solvent system (~50% (v/v) or more) is organic (e.g.,  $CH_3OH$ ).<sup>27</sup> Use of an organic solvent in the oxidation of aniline might provide additional solubility for the higher *n*-mers allowing for their detection. Therefore, ES-MS, particularly with a mixed H<sub>2</sub>O/CH<sub>3</sub>OH solvent, should have advantage in the detection of higher molecular weight polyaniline *n*-mers. One caveat, however, is the fact that the ES ion source is by nature a controlled-current electrolytic (CCE) flow cell.<sup>28</sup> Therefore, care must be taken to ensure that the CCE processes that take place in the ES emitter do not also produce aniline oligomers or otherwise influence the nature of the aniline oligomers generated in the upstream controlled-potential cell.

In this article, we report on the investigation of the soluble products generated during the electrochemical polymerization of aniline in H<sub>2</sub>O and H<sub>2</sub>O/CH<sub>3</sub>OH (1/1 v/v), at different solution pH, using a thin-layer electrochemical flow cell coupled on-line with ES-MS. Soluble polyaniline *n*-mers up to n = 10 were produced and detected and most of these oligomers were observed in more than one redox state, ranging from fully oxidized to fully reduced. We show that, under the operational parameters used in this study, the CCE process in the ES emitter has little or no influence on the aniline oligomers observed. In addition, changes in the relative fraction of the electrochemically generated aniline dimer ions of a given structure, as a function of solution pH, are revealed by tandem mass spectrometry.<sup>29</sup> Also discussed are potential scanning experiments used to investigate the growth mechanism of the polymer beyond the dimer.

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The experimental setup used in this study has been described in detail elsewhere.<sup>30,31</sup> Briefly, a three-electrode, thin-layer electrochemical cell combining commercially available and inhouse-built parts was coupled on-line with a PE Sciex API165 single-quadrupole or API365 triple-quadrupole instrument (Concord, ON, Canada) using a "Turbo ion spray" ES ion source. The three electrodes of the cell were a model RE-4 Ag/AgCl reference electrode (Bioanalytical Systems, Inc. (BAS), West Lafayette, IN), an offset, 6.0-mm-diameter glassy carbon (GC) disk in a PEEK block (BAS), and a Pt foil counter electrode centered in a PEEK block. A 16-µm-thick Teflon spacing gasket (BAS) between the working and counter electrode blocks provided a cell volume of  $\sim$ 1.0  $\mu$ L. The reference electrode was mounted in the counter electrode block and contacted the solution between the working and counter electrodes through a small bore-through to the center of the cell. A microprocessor-controlled gas displacement pump pressurized with N<sub>2</sub> was used to pump a carrier/electrolyte solution through a six-port, two-position PEEK injection valve (1.0 mL loop) controlled by the same unit (Microneb 2000, Cetac, Omaha, NE), through the cell, and on to the ES ion source. The ES current at the curtain gas plate of the mass spectrometer was measured by grounding this plate (normally held at 1.0 kV) through a Keithley model 610C electrometer (Cleveland, OH). The potential of the ES capillary was lowered by 1.0 kV to maintain the same potential drop between these electrodes as in the normal experiments (i.e., 3.2 kV), and the capillary was moved laterally to a position at which none of the ES plume could travel through the curtain plate. A PAR model 173 potentiostat with a PAR model 175 universal programmer (Princeton Applied Research Corp., Princeton, NJ) was used to step (20 V/s) or scan among the various potentials applied to the working electrode during the course of an experiment. Potential and current readouts from the potentiostat were directed to the mass spectrometer computer system, and stored there, by means of a dual-channel PE Nelson model 970A A/D interface (Perkin-Elmer, San Jose, CA) and the PE Sciex sample control software (Version 1.463). This synchronized in time the acquisition of potential, current, and mass spectral data. The time taken for the products generated in the cell to reach the mass spectrometer and be detected (i.e., the response time) was 5.1 s.

All samples were prepared in deionized  $H_2O$  (Milli-RO 12 Plus, Millipore, Bedford, MA) or 1/1 (v/v)  $H_2O/CH_3OH$  (HPLC grade, J. T. Baker, Phillipsburg, NJ) containing 5.0 mM ammonium acetate (NH<sub>4</sub>OAc, 99.999%, Aldrich, Milwaukee, WI, pH 6.5). To these solutions were added 0.75% (v/v) acetic acid (HOAc, PPB/ Teflon grade, Aldrich, pH 4) or a sufficient quantity of ammonium hydroxide (NH<sub>3</sub> content 28.0–30.0%, Aldrich) to achieve pH 9. Solution pH was estimated using ColorpHast indicator strips (EM Science, Gibbstown, NJ). Samples were always injected into a flowing stream of 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH containing 5.0 mM NH<sub>4</sub><sup>-</sup> OAc and 0.75% (v/v) HOAc (pH 4). Aniline (**2**, 99%, ChemService, West Chester, PA) was vacuum distilled prior to use. *N*-Phenyl-1,4-phenyldiamine (**4**, 98%, Aldrich), benzidine (**5**, ~95%, Sigma, St. Louis, MO), and hydrazobenzene (**6**, contains varying amounts of **6a**, Aldrich) were used as received. Solutions of each were

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**Figure 1.** Full-scan EC/ES-MS mass spectrum of aniline obtained at a working electrode potential of 1.0 V. The spectrum shown is the sum of six scans from which was subtracted the six scan summed spectrum obtained at 0.6 V (0.1 *m/z* step size and 10-ms dwell time per step for each spectrum). At this latter potential, little or no oxidation of the aniline was observed and the subtraction therefore removes from the spectrum ions of unreacted aniline and background ions unrelated to aniline. Multiplication factors applied to reach near 100% on the relative abundance scale for the higher *n*-mers are shown in the spectra. Solvent/electrolyte: 100  $\mu$ M aniline, 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH/5.0 mM NH<sub>4</sub>OAc/0.75% HOAc, pH 4. Flow rate, 30  $\mu$ L/min.

prepared immediately prior to analysis to avoid oxidation caused by exposure of the sample to oxygen and light. **Caution: 2, 4, 5, and 6, and their respective oxidation products are highly toxic and care should be taken in the handling, analysis, and disposal of these substances.** 

Cyclic voltammetry experiments were controlled with a CH Instruments model 660 electrochemical workstation (Cordova, TN) and a C-2 cell stand (BAS). Experiments were carried out with a freshly polished 3.0-mm GC disk working electrode (BAS) in a 10-mL batch cell using a Pt wire counter electrode (BAS) and Ag/AgCl reference electrode (model RE-5B, BAS). Cyclic voltammograms (CVs) were recorded for 80–100  $\mu$ M solutions of **2**, **4**, **5**, and **6** in 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH containing 5.0 mM NH<sub>4</sub>OAc and 0.75% (v/v) HOAc at a variety of scan rates.

Correction for isotopic overlaps within the individual *n*-mer ion clusters in the mass spectrum of electropolymerized aniline was carried out by first calculating the theoretical isotope pattern (using the Sheffield ChemPuter<sup>32</sup>) for each *n*-mer ion in a cluster. It was assumed that all ions observed were protonated molecules and the different *n*-mer species in a cluster differed in mass by 2 Da (e.g., m/z 183 and 185 for the dimer, m/z 363 and 365 for the tetramer, etc.). Starting with the lowest m/z ion in each *n*-mer cluster, its contribution to the abundance of each of the other peaks in the cluster was calculated and subtracted from the abundance value for those respective peaks in the original data. These corrected intensities were then used for the calculation of the contribution of the *n*-mer species 2 m/z units higher in the cluster, to the abundance of the remaining peaks in the cluster, in the cluster of the remaining peaks in the cluster, in the cluster of the remaining peaks in the cluster, in the cluster, species 2 m/z units higher in the cluster, to the abundance of the remaining peaks in the cluster, in the cluster, in the cluster, in the cluster, in the cluster of the remaining peaks in the cluster, in the cluster, in the cluster, in the cluster, in the cluster of the remaining peaks in the cluster, in the cluster, in the cluster, in the cluster, in the cluster of the remaining peaks in the cluster, in the cluster to the abundance of the remaining peaks in the cluster, in the

and so on. The corrected abundance values were then normalized to the largest peak in each cluster.

### **RESULTS AND DISCUSSION**

Soluble Oligomers from Anodic Polymerization of Aniline. Off-line cyclic voltammetry (data not shown) and on-line EC/ ES-MS potential sweep experiments (see below) showed that both aniline oxidation and the observation of polymerization products in the ES mass spectrum began at a working electrode potential of  $\sim$ 0.7 V. A representative mass spectrum obtained from the online EC/ES-MS oxidation/polymerization of aniline in 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH at pH 4, at a constant working electrode potential of 1.0 V, is shown in Figure 1. Multiplication factors have been applied to various portions of the spectrum to make visible all the major oxidation products. The major peaks may be assigned to a series of aniline oligomers or *n*-mers, where *n* is 2-10 aniline molecules, which are observed as the respective singly charged protonated molecules  $((n-mer + H)^+, see 1 and Scheme 1 for$ the assumed basic structure of the oligomers). The base peak in the spectrum is due to the trimer (m/z 274) with the next most abundant ions those of the dimer (m/z 183). Successively lower abundances of the tetramer and higher *n*-mers are noted. This is the first on-line EC/MS experiment in which discrete soluble polyaniline *n*-mers larger than the 3-mer have been detected.

Two of the more minor peaks in the top panel of this spectrum correspond to the sodiated trimer (m/z 296) and the sodiated pentamer (m/z 476). Ions at m/z 166 (not shown) and at m/z 257 are fragment ions (i.e., NH<sub>3</sub> loss), formed by collision-induced dissociation (CID) of the dimer and trimer ions, respectively, in the atmospheric sampling interface. Two other minor ion clusters of significance are observed at m/z 227.5 and 318. On the basis

<sup>(32)</sup> Winter, M. Sheffield ChemPuter. An isotope pattern calculation algorithm accessible on the Internet at www.shef.ac.uk/chemistry/chemputer/, 1998.



**Figure 2.** Replotted EC/ES-MS data from Figure 1 showing the abundances for each cluster of aniline *n*-mer ions corrected for isotopic overlaps and renormalized to the most abundant peak within each of the respective *n*-mer clusters. The numbers in parentheses indicate the calculated redox state of the *n*-mer (see text for details). Each tick mark on the *x*-axis represents 1 *m/z* unit.

of these m/z values and the fact that the isotopic peak clusters were not fully resolved, these ions can be assigned to the doublycharged pentamer,  $(5\text{-mer} + 2\text{H})^{2+}$ , and heptamer,  $(7\text{-mer} + 2\text{H})^{2+}$ , respectively. No other multiply charged *n*-mers are readily apparent in this spectrum. However, multiply charged *n*-mers from the even-numbered *n*-mers, if they occur, fall at m/z values that overlap the more abundant singly charged *n*-mer ions. Therefore, their presence at abundance levels below that which might distort the singly charged isotopic clusters (an indication of their presence) cannot be ruled out.

Assuming a growth mechanism as in Scheme 1 and the presence of mainly the singly charged protonated molecules of each *n*-mer, the cluster of peaks for each *n*-mer and their m/zvalues reveals that many of the *n*-mers exist in several redox states. These redox states are defined<sup>5</sup> as the ratio of the number of amine nitrogens to total (amine plus imine) nitrogens present in the oligomer (see structure 1) and thus range in value from 1.0 for a fully reduced *n*-mer (all amine nitrogen) to 0.0 for a fully oxidized n-mer (all imine nitrogen). To obtain a more accurate picture of the distribution of redox states it was necessary to correct the relative abundances of the peaks within each n-mer cluster for isotopic overlaps (see Experimental Section). The corrected data are presented in Figure 2 with the redox state for the respective major ions at each *n*-mer listed in parentheses above the peaks. One notices differences in redox states among the evenand odd-numbered n-mers and among the lower n-mers and higher *n*-mers. Except for the dimer, which shows a 30% relative abundance of m/z 185, a significant abundance of the fully reduced n-mer is not observed for any of the n-mers. The low abundance

of the fully reduced n-mers is consistent with the results of previous electrochemical experiments that have found that each *n*-mer is generally easier to oxidize than aniline or the preceding n-mer.<sup>8,11</sup> A significant abundance of the fully oxidized n-mer is observed only for the even-numbered n-mers. The fully oxidized species is the base peak within the dimer and tetramer clusters, and is observed at about 46 and 28% relative abundance in the 6and 8-mer cluster, respectively. The fully oxidized species was not observed for the 9- or 10-mer. In reference to the general formula 1 ascribed to polyaniline above, this observation is consistent with the capacity to draw a stable, fully conjugated structure for the fully oxidized species of the even-numbered n-mers. In addition, the number of different redox states observed for the *n*-mers is seen to increase with increasing *n*. To our knowledge, this is the first discrete measurement of individual electrochemically generated polyaniline oligomers in multiple redox states.

When the polymerization was attempted in 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH at pH 6.5 and pH 9, or in 100% H<sub>2</sub>O at pH 4 (data not shown), there was an overall reduction in the abundance of the higher *n*-mers with the 7-mer being the largest *n*-mer observed. At pH 9 in 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH, the dimer, rather than the trimer, was the base peak in the spectrum. However, abundances of the individual redox states for those *n*-mers for which we did observe ions were similar to that shown in Figure 2.

Several reasons may be put forward to account for the lesser abundance of the higher *n*-mers under these conditions. First, at neutral or basic pH, there is some indication in the literature that the extent to which aniline polymerizes to higher *n*-mers is less than at acidic pH.<sup>12</sup> Second, at these higher pH values the solubility of the high *n*-mers, if formed, might be less because of their lower degree of protonation in solution.<sup>33</sup> Reduced solubility of the higher *n*-mers in 100% H<sub>2</sub>O versus the organic-containing solvent could also account for the lesser abundance of the higher *n*-mers in 100% H<sub>2</sub>O. Finally, the use of a solvent with neutral or basic pH, or 100% H<sub>2</sub>O as the solvent at any pH, may adversely affect ion formation in ES-MS. This relates both to the general need in ES-MS for preformed ions in solution (promoted for amine/imines at acidic pH) and to the generally lower ion signals achieved when using 100% H<sub>2</sub>O versus mixed H<sub>2</sub>O/organic solvents in ES-MS.<sup>27</sup>

It is very important to note that the nature of the electrochemically generated polyaniline spectra we observe here does not appear to be influenced substantially by oxidative processes in the metal ES capillary. The operational characteristics of the ES ion source are known to be analogous to that of a CCE flow cell.<sup>28</sup> Therefore, it is possible under some conditions for analytes to be involved in electrolytic reactions in the ES capillary (the working electrode of this system), which in positive ion mode, would be oxidation reactions. The use of a low ES capillary voltage (3.2-kV voltage drop), which minimizes the ES current ( $\sim 0.6 \mu$ A), a stainless steel spray capillary, which is easily corroded and can, therefore, provide some or all of the Faradaic current the system requires, and the combination of a relatively high flow rate (30  $\mu$ L/min) and high concentration of aniline (100  $\mu$ M) tend to minimize the electrolysis efficiency for analyte species in the solution. A Faraday's law calculation indicates that a maximum of  $\sim$ 5% of the aniline present (assuming a total of 2e<sup>-</sup> transferred, the occurrence of no other reactions, and the availability of all the analyte for reaction at the metal/solution interface within the capillary) could be involved in the electrolysis and go on to form the reduced dimer. (Note also that this small magnitude of Faradaic current would little effect solution pH if oxidation of water was the electrolytic reaction, because of both the high flow rate and the buffering effect of the NH<sub>4</sub>OH/HOAc electrolyte.<sup>34</sup>) The efficiency for the multielectron reactions required to produce the oxidized dimer and the higher n-mers would be expected to be even less. Examination of the ES mass spectrum of freshly distilled aniline acquired under the same flow conditions as those used to acquire the data in Figure 1, without the cell on-line, found that ions corresponding to the fully oxidized dimer and trimer were present. However, their absolute abundances were at least 30 times less than those abundances recorded for the same ions (m/z)183 and 274, respectively) in the spectrum in Figure 1. No higher n-mers were observed. To increase the abundance of these dimer and trimer ions by just a factor of 2 required that the flow rate be dropped to 10  $\mu$ L/min. Further proof that the ES electrolytic process did not substantially affect the nature of the ions observed is illustrated by the fact that standards of 4, 5, and 6, when sprayed without the EC cell on-line, were not oxidized to any significant extent. However, near-quantitative conversion of 4, 5, and 6 to oxidation products was observed with the EC cell online at a working electrode potential of 1.0 V (see Figure 3 and related discussion below).







**Figure 3.** ES-MS mass spectra showing the molecular ion region of the three dimer standards (a) **4**, (d) **5**, and (g) **6**, which were obtained without the EC cell on-line and the spectra of these same standards obtained with the EC cell on-line at a working electrode potential of 1.0 V, viz., (b), (e), and (h), respectively. Solvent/ electrolyte: 100  $\mu$ M **4**, **5**, or **6**, 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH/5.0 mM NH<sub>4</sub>-OAc/0.75% HOAc, pH 4. Flow rate, 30  $\mu$ L/min. Spectra are the sum of 10 scans obtained over the shown *m*/*z* range using a 0.1 *m*/*z* step size and 10-ms dwell time per step. CVs shown are those of (c) **4**, (f) **5**, and (i) **6**, obtained in an off-line experiment in the same solvent system. Arrows indicate the original scan direction. Scan rate, 10 mV/s.

**Structure of Dimers.** The electrochemically generated polyaniline dimer ions were observed in two redox states, viz., fully reduced at m/z 185 and fully oxidized at m/z 183 (Figure 2). Using our EC/MS setup and tandem mass spectrometry (MS/MS)<sup>29</sup> it was possible to qualitatively determine whether different dimer structures were formed from the anodic polymerization of aniline at pH 4.0, 6.5, and 9.0 in 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH. For this determination, we needed standards of all the possible reduced and oxidized dimers. We assumed that the dimer ions observed in the spectrum in Figure 1 at m/z 185 were the protonated molecules of **4**, **5**, and/or **6** and that the dimer ions at m/z 183 were the protonated molecules of **4a**, **5a**, and/or **6a**. Standards of **4a**, **5a** and **6a** were prepared by on-line electrochemical oxidation of **4**, **5**, and **6**, respectively.

Panels a, d, and g of Figure 3 show the ES mass spectrum of standards **4**, **5**, and **6**, respectively, recorded *without* the thinlayer EC cell on-line. Under these conditions, the most abundant ions observed correspond to  $(\mathbf{4} + \mathrm{H})^+$ ,  $(\mathbf{5} + \mathrm{H})^+$ , and  $(\mathbf{6} + \mathrm{H})^+$  each appearing at m/z 185. Only in the case of **6** was a substantial signal owing to the oxidized form of the standard dimer observed

(i.e., **6a** at m/z 183, ~35% relative abundance). As the CVs in Figure 3 indicate, 6 is also the easiest to oxidize of the three reduced dimers (Figure 3i,  $E_0 = 0.12$  V). The source of **6** contains an unspecified amount of 6a, and when "aged" on the bench for even short periods (a few hours), the ES mass spectrum of the standard solution of 6 shows an increased abundance of 6a, which is formed by exposure of the sample to oxygen and light. We believe, therefore, that most of the signal owing to  $(6a + H)^+$  in Figure 3g arises from **6a** in the original solution. The amount of 6a formed via oxidation in the ES capillary must be small for the same reasons as already discussed above. The ES mass spectra in Figure 3b and h show that with the EC cell on-line, at a working electrode potential of 1.0 V, it was possible to anodically generate **4a** nearly quantitatively from **4** (m/z 183, Figure 3b;  $E_{\rm p} = 0.31$  V, Figure 3c) and to generate **6a** quantitatively from **6** (m/z 183,Figure 3h;  $E_p = 0.12$  V, Figure 3i). Surprisingly, generating a significant amount of the ion at m/z 183 corresponding to (5a + H)<sup>+</sup> via oxidation of **5** at 1.0 V proved much more difficult. Rather, the major oxidation product was m/z 184, presumably the radical cation  $(5)^{+}$ . A dimer of 5 (nominally a protonated aniline tetramer) at m/z 365 was also observed at a much lower abundance (Figure 3e and inset;  $E_p = 0.57$  V, Figure 3f). Nonetheless, enough  $(5a + H)^+$  was produced to obtain an MS/ MS spectrum.

Figure 4 presents the EC/ES-MS/MS product ion spectra of the ions at m/z 183, corresponding to the oxidized dimeric species generated from the anodic polymerization of aniline at pH 4.0, 6.5, and 9.0, and the product ion spectra of the standard dimer ions  $(4a + H)^+$ ,  $(5a + H)^+$ , and  $(6a + H)^+$ , produced by on-line oxidation of the respective reduced standards. Inspection of the product ion spectra of each of the oxidized standards (Figure 4df) reveals each to be distinct, and this fact can be used to qualitatively determine whether particular dimeric species are present in the polyaniline spectra. Simple visual inspection reveals that the MS/MS spectrum of the ions at m/z 183 from aniline oxidation at pH 4.0 is almost an exact match for the MS/MS spectrum of  $(4a + H)^+$ . Thus, the structure of these oxidized dimer species is concluded to be exclusively the oxidized headto-tail dimer 4a. At pH 6.5 and pH 9, the appearance of ions at m/z 77 and 95 in the product ion spectra indicates that ions corresponding to the head-to-head dimeric structure are present. Because the peak at m/z 156 (a feature characteristic of (5a + H)<sup>+</sup>, Figure 4e) shows no increase in abundance as pH is raised (Figure 4b and c), one can conclude that little if any of the tailto-tail oxidized dimer 5a is present. This is not unexpected. As already discussed, 5 proved difficult to anodically oxidize to 5a, preferring to form the radical cation (m/z 184) and to dimerize (m/z 365). Thus, at pH 6.5 and 9, the oxidized dimer ions are a mixture  $(6a + H)^+$  and  $(4a + H)^+$ .

Figure 5 presents the EC/ES-MS/MS product ion spectra of m/z 185 ions corresponding to the reduced dimeric species generated from the anodic polymerization of aniline at pH 4.0, 6.5, and 9.0, and the product ion spectra of the dimer ions (**4** + H)<sup>+</sup>, (**5** + H)<sup>+</sup>, and (**6** + H)<sup>+</sup>. In this case, the product ion spectra of each of the reduced dimer standards (Figure 5d–f) are not as distinctive. The product ion spectra of (**5** + H)<sup>+</sup> and (**6** + H)<sup>+</sup> are quite similar, making it difficult to determine whether one or both of these dimers might be present in the polyaniline spectrum.



**Figure 4.** Product ion tandem mass spectra of *m*/*z* 183 formed during the electrochemical polymerization of aniline (**2**) at pH (a) 4, (b) 6.5, and (c) 9, and the product ion tandem mass spectra of *m*/*z* 183 from (d) the protonated molecule of *N*-phenyl-1,4-phenylenediimine ((**4**a + H)<sup>+</sup>), (e) the protonated molecule of (1,1'-biphenyl)-4,4'diimine) ((**5**a + H)<sup>+</sup>, and (f) the protonated molecule of azobenzene ((**6**a + H)<sup>+</sup>, Solvent/electrolyte: 100  $\mu$ M **2**, **4**, **5**, or **6**, 1/1 (v/v) H<sub>2</sub>O/ CH<sub>3</sub>OH/5.0 mM NH<sub>4</sub>OAc. HOAc added for pH 4, NH<sub>4</sub>OH added for pH 9; see Experimental Section. Flow rate, 30  $\mu$ L/min. Center-ofmass collision energy,  $E_{CM} = 3.3$  eV with a N<sub>2</sub> collision gas thickness of ~1.8 × 10<sup>15</sup> cm<sup>-2</sup>. Oxidation of aniline and standard dimers **4**, **5**, and **6** to **4a**, **5a**, and **6a**, respectively, performed on-line at 1.0 V. Spectra are the sum of 10 scans obtained over the shown *m*/*z* range using a 0.1 *m*/*z* step size and 10-ms dwell time per step.

Furthermore, inspection of the product ion spectrum of the ions at m/z 185 from aniline oxidation at pH 4.0 reveals, in contrast to the dimeric species at m/z 183, that a mixture of dimer structures is present at m/z 185. A simple addition of the normalized product ion spectra of  $(\mathbf{4} + H)^+$  and  $(\mathbf{5} + H)^+$  and/or  $(\mathbf{6} + H)^+$  would generate much the same spectrum as that in Figure 5a. The prominence of the minor ions at m/z 141, 151, and 158 (which are a feature characteristic of  $(5 + H)^+$ , Figure 5e), however, leads one to believe that the dimer ions at pH 4 are in fact a mixture of  $(4 + H)^+$  and  $(5 + H)^+$ . A significant presence of the reduced dimer structure 5 would be consistent with the fact that it is the most difficult of the dimers to oxidize (Figure 3f). As the pH was increased, there was an increase in the abundance of the ion at m/z 93 in the reduced dimer product ion spectra (Figure 5b and c). Both that trend and the diminishing abundance of the minor ions at m/z 141, 151, and 158, are consistent with an increase in the relative abundance of  $(6 + H)^+$  and a decrease in the abundance of  $(5 + H)^+$ . Thus, we believe that at pH 9, the reduced dimer ions observed in the polyaniline spectrum are a mixture of  $(4 + H)^+$  and  $(6 + H)^+$ .



**Figure 5.** Product ion tandem mass spectra of *m*/*z* 185 formed during the electrochemical polymerization of aniline (**2**) at pH (a) 4, (b) 6.5, and (c) 9, and the product ion tandem mass spectra of *m*/*z* 185 from (d) the protonated molecule of *N*-phenyl-1,4-phenylenediamine ((**4** + H)<sup>+</sup>, (e) the protonated molecule of benzidine ((**5** + H)<sup>+</sup>, and (f) the protonated molecule of hydrazobenzene ((**6** + H)<sup>+</sup>. Solvent/electrolyte: 100  $\mu$ M **2**, **4**, **5** or **6**, 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH/5.0 mM NH<sub>4</sub>OAc. HOAc added for pH 4, NH<sub>4</sub>OH added for pH 9; see Experimental Section. Flow rate, 30  $\mu$ L/min. Center-of-mass collision energy,  $E_{\rm CM} = 3.3$  eV with a N<sub>2</sub> collision gas thickness of ~1.8 × 10<sup>15</sup> cm<sup>-2</sup>. Oxidation of aniline performed on-line at 1.0 V. Spectra are the sum of 10 scans obtained over the shown *m*/*z* range using a 0.1 *m*/*z* step size and 10-ms dwell time per step.

 Table 1. Distribution of Dimer Structures Produced by

 Aniline Polymerization

		$\mathrm{pH}^{a}$	
	dimer	4	9
m/z 183 (~75% of total dimers)	4a	+	+
	5a	-	_
	6a	_	+
m/z 185 (~25% of total dimers)	4	+	+
	5	+	_
	6	-	+
<sup><i>a</i></sup> +, detected; -, not detected.			

The structures of the electrochemically generated aniline dimers formed at pH 4 and 9 are summarized in Table 1. Determining the exact amount of each dimer present in all these cases is difficult with the current analytical scenario. Combining an on-line separation of the electrochemically generated dimers with the ES-MS/MS analysis for structure determination would provide a more definitive measurement of the distribution of structures.<sup>22</sup>

**Polymer Growth Mechanism beyond the Dimer.** Two EC/ ES-MS experiments were carried out in which the working



**Figure 6.** Time-synchronized working electrode anodic current and selected ion current profiles for the protonated molecules of aniline ((2 + H)<sup>+</sup>, m/z 94) and the dimer (2-mer, m/z 183 and 185), trimer (3-mer, m/z 274), tetramer (4-mer, m/z 363 and 365), and pentamer (5-mer, m/z 454 and 456) species formed during the EC/ES-MS experiment as a function of applied potential. Each ion current profile normalized relative to maximum intensity of that respective ion. Freshly polished electrode. Potential scan rate, 2.0 mV/s. Solvent/ electrolyte: 100  $\mu$ M aniline, 1/1 (v/v) H<sub>2</sub>O/CH<sub>3</sub>OH/5.0 mM NH<sub>4</sub>OAc/ 0.75% HOAc, pH 4. Flow rate, 30  $\mu$ L/min. Multiple ion monitoring mode, dwell time, 5.0 ms per m/z.

electrode potential was scanned at 2 mV/s from 0.6 to 1.2 V and back again while the working electrode current and the ions corresponding to protonated aniline (m/z 94), the major dimer (m/z 183, 185), trimer (m/z 274), tetramer (m/z 363 and 365), and pentamer (m/z 454 and 456) species were monitored. The first of these experiments, the data from which are displayed in Figure 6, was carried out with freshly polished and conditioned electrodes.<sup>30</sup> The anodic current was observed to increase above background levels at 0.7 V and reached a maximum at 1.2 V, the turnaround point in the potential scan. Note that the current profile in the return potential sweep was not symmetric with the initial potential sweep, indicating a change in the electrode surface as expected for the deposition of polyaniline. For the most part, however, the ion current profiles were symmetric. In the initial potential sweep to 1.2 V, the increase in current measured at the working electrode above baseline was mirrored by the appearance in the ES mass spectrum of the oxidized dimer, reduced dimer, mixed redox state trimer, reduced tetramer, and reduced pentamer. Only the oxidized tetramer and oxidized pentamer were first observed at higher potentials. Thus, one can conclude that the higher order oxidized species follow formation of the higher

order reduced species. Though these data are not definitive proof of the polymer growth mechanism, they are consistent with the reaction mechanism in Scheme 1. Because each *n*-mer is easier to oxidize than aniline,<sup>8,11</sup> one would expect to observe the dimer and higher *n*-mers at or very near the same potential at which the polymerization is initiated by aniline oxidation (i.e., ~0.7 V).

Curious is the fact that, except for the trimer (m/z 274) and reduced pentamer (m/z 456), *n*-mer ion intensities level off beyond ~0.85 V and then decrease as the potential is swept back to less positive values. The intensities of m/z 274 and 456 begin to decrease beyond 0.85 V and then start to increase as the potential is swept to less positive values, again maximizing at ~0.85 V and continuing to decrease with potential. This behavior may indicate that these two species are consumed in further reactions to form higher oligomers at potentials more positive than 0.85 V. On the other hand, this decrease also coincides with the depletion of aniline. Assuming these odd-numbered *n*-mers are formed from the preceding oxidized even-numbered *n*-mer by aniline addition (e.g., formation of **7** and **7a** in Scheme 1), significant depletion of aniline would reduce the amount of these species formed.

Another potential sweep experiment (data not shown) was carried out 2 h and several additional potential scanning experiments after the data in Figure 6 were acquired. Thus, it could be assumed that polyaniline deposits covered at least some of the working electrode surface. In this case, the working electrode current and ion current profiles were much different from the data in Figure 6. Rather than reaching a steady-state level or bimodal maximum, the ion current profiles all showed a shallow increase to a maximum at 1.2 V and a return to baseline level of the same shape with the return scan to 0.6 V. The reduction in aniline intensity again mirrored the working electrode current, but both were significantly less than before. While the appearance of the dimer and trimer ions still began at  $\sim$ 0.7 V, the occurrence of the pentamer ions in particular was shunted to significantly higher potentials (~0.85 V). It was apparent from these data that initial formation of the lower n-mers was best studied using a "fresh" electrode surface. The change in the electrode surface reaction due to the deposition of polyaniline, as well as the contribution to solution of *n*-mers already deposited onto the electrode, are just two factors that complicated interpretation of the data obtained with a polyaniline coated electrode.

#### CONCLUSIONS

The use of a thin-layer electrochemical flow cell on-line with electrospray mass spectrometry provided important information regarding the soluble products from the electrochemical polymerization of aniline. In contrast to the electrochemical or optical spectroscopic approaches that have been applied to this issue, the EC/ES-MS approach provided directly, for the first time, both the molecular weight and redox state of not only the soluble dimeric species formed but also aniline oligomers ranging up to n = 10. Distinct differences in the redox-state distribution of the smaller *n*-mers were apparent between even- and odd-numbered n-mers. The number of different redox states observed for the various *n*-mers increased with increasing *n*. Structural evaluation of the aniline *n*-mers observed, using tandem mass spectrometry, was limited to the dimers in this study. One could probe the structure of the higher *n*-mers by a similar approach, and such an EC/ES-MS/MS investigation is underway. The results of that study are expected to provide further insight into the growth mechanism of the aniline *n*-mers beyond the dimer stage.

The current study revealed the structure of the dimeric ions produced from the polymerization of aniline at pH 4 and 9 as summarized in Table 1. In the ES mass spectrum of oxidized aniline, at all pH values,  $\sim$ 75% of the total dimer ion current was from the oxidized dimers and the remaining 25% of the ion current that of reduced dimers. At pH 4, the oxidized species present were found to be exclusively structure 4a, the head-to-tail dimer, while the reduced species were mixture of structures 4 and 5 (tail-totail dimer). At pH 9, we found that the oxidized dimers were a mixture of 4a and the head-to-head structure 6a while the reduced dimers were a mixture of structures 4 and 6. Classical electrochemical studies have previously shown that the distribution of different dimeric species generated from aniline oxidation changes with pH.11,13 Specifically, in acidic solution, down to pH 4, formation of 4 and 4a is favored. Below pH 4, formation of 5 and 5a increases at the expense of 4 and 4a. Under basic conditions, formation of the head-to-head dimers 6 and 6a occurs at the expense of 4 and 4a.<sup>16</sup> The EC/ES-MS/MS results presented here are consistent with those earlier studies, with one possible exception. No significant amount of  $(5a + H)^+$  was found under any conditions. However, this latter result was consistent with our findings that **5** was preferentially oxidized to form **5**<sup>+</sup> rather than 5a.

The fact that the head-to-tail, tail-to-tail, and head-to-head aniline dimers were shown to be present in the ES mass spectrum resulting from aniline oxidation indicates that the higher polyaniline *n*-mers (depending on solution pH and assuming their possible growth from all dimers) may be a mixture of linkage sequences, not just the head-to-tail sequence shown in structure **1** and Scheme 1. These conclusions are in line with the data of Bacon and Adams<sup>11</sup> and the reaction sequence proposed by Yang and Bard.<sup>18</sup> One must be aware, however, that *the distribution of dimer structures we detected may reflect both their relative rates of production from aniline and their consumption leading to the growth of larger n*-mers. That is, the distribution we observe may be skewed toward the species less likely to continue polymer growth. The actual contribution of the individual dimers to the larger *n*-mers is currently under study.

At this point it should be noted that the EC/ES-MS spectrum in Figure 1 is distinctly different from the EC/TS-MS spectrum obtained by Hambitzer and Stassen.<sup>24,25</sup> Hambitzer and Stassen<sup>24,25</sup> observed only the protonated molecules of the fully reduced dimer (m/z 185) and trimer (m/z 276) of aniline whereas we observed aniline oligomers up to the 10-mer and a distribution of oligomer redox states. Several explanations for our observation of larger n-mers are possible, but a major factor is probably the use of ES-MS. ES-MS usually provides excellent signals for high molecular weight, polar analytes, which probably benefits the detection of the higher aniline *n*-mers.<sup>27</sup> The work of Hambitzer and Stassen<sup>24,25</sup> was carried out using H<sub>2</sub>O/0.1 M sulfuric acid while our spectrum was obtained in a mixed H<sub>2</sub>O/CH<sub>3</sub>OH solvent (1/1 v/v) under less acidic conditions (5.0 mM NH<sub>4</sub>OAc/0.75% (v/v) HOAc, pH 4). The higher *n*-mers would be expected to be more soluble in the organic solvent system, and thus, it is possible that higher *n*-mers produced at the electrode in our experiment remain in solution rather than deposit at the electrode. However, we

obtained a spectrum very similar to that shown in Figure 1 using the same electrolyte and 100% H<sub>2</sub>O. The major difference in 100% H<sub>2</sub>O was an overall reduction in the abundance of the higher *n*-mers with the 7-mer the largest *n*-mer observed. Flow dynamics and the electrolytic characteristics of the electrochemical cell, (e.g., electrolysis efficiency and response time) might also influence which oligomers are formed and remain in solution. For example, the linear velocity in our thin-layer cell may be considerable because of the narrow spacing of electrodes (16  $\mu$ m, ~1  $\mu$ L volume) and high flow rate (30  $\mu$ L/min), which may develop enough shear force at the electrode surface to somewhat inhibit oligomer deposition. Flow dynamics and the electrolytic characteristics of the electrochemical cell would also certainly affect the redox state of the different oligomers. As has been shown, our observation of polyaniline *n*-mers up to n = 10 and the distribution of *n*-mer redox states was not caused or influenced by electrolytic processes in the ES ion source.

In any event, the results from the EC/ES-MS study presented here, in addition to providing new information on anodic aniline polymerization, are consistent with previous electrochemical studies of anodic aniline polymerization.<sup>8,11,18</sup> These results also

demonstrate that EC/ES-MS and EC/ES-MS/MS should prove generally to be a highly informative tool in the study of the initial stages of electropolymerization processes and in the study of the products of any number of other electrode reactions.

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