Synthesis and Characterization of Poly(alkylanilines)

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ABSTRACT: Aniline and alkyl ring-substituted anilines have been polymerized by chemical and electrochemical methods. The resulting polymers have been studied by cyclic voltammetry and spectroelectrochemistry. The presence of alkyl substituents affects not only the polymerization reaction but also the electrochemical properties of the polymers. These polyaniline derivatives show multiple optical transitions (yellow–green–blue–violet) in correlation with proton and electron exchanges. However, these oxidation reactions occur in a smaller potential range than that observed for the unsubstituted polyaniline. Similar electrochemical and optical properties were obtained for every pair of ortho- and meta-substituted polyanilines, but the ortho isomers always give better polymerization yields and more regular head-to-tail structures.

Introduction

Since the discovery that polyacetylene can be doped by oxidizing or reducing agents to the metallic regime,[1] many studies have been devoted to the electrical properties of polymers.[2,3] Other conjugated molecules were investigated, and several aromatic polymers (e.g., poly(*p*-phenylene),[4] polypyrrole,[5] polythiophene,[6] polyaniline,[7] etc.) have also shown an increase of their electrical conductivities upon chemical or electrochemical doping.

Among these conducting polymers, polyaniline has recently received great attention owing to its good stability in the presence of oxygen and water and its interesting electrochemical properties for the development of lightweight batteries[8,9] and electrochromic display devices.[10,11] It has been found that polyaniline exhibits insulator-to-metal transitions and multiple color changes (pale yellow–green–blue–violet) depending on both oxidation state and pH.[12–14] Polyaniline, which can be prepared either as thin films by electrochemical oxidation[7] or as powders by chemical means,[14] results probably from the preferential head-to-tail couplings between oxidized aniline species.[15] Chemically prepared polyaniline, which is built from repeat units ($-C_6H_4-NH-C_6H_4-NH-C_6H_4-N{=}C_6H_4{=}N-$), can exist in various oxidation states characterized by the ratio of amine to imine nitrogen atoms.[12–14] However, this polymer, like many other conducting polymers, is not soluble in common organic solvents because of its chain stiffness. This limitation creates some problems for large-scale applications.

The incorporation of long and flexible substituents in the polymer backbone is a common technique for preparing soluble polymers, and this concept was successfully applied to thiophenes.[16–18] Soluble, conducting polythiophenes were obtained by the incorporation of alkyl groups in positions 3 and 4 of the thiophene ring. These polythiophene derivatives are soluble in their neutral and doped states, and in addition they are quite stable in the presence of oxygen. On the other hand, as shown for substituted polyacetylenes[19] and N-substituted polypyrroles,[20] steric interactions between the substituents may lead to nonplanar conformations, which decrease the electrical conductivities of these polymers.

The purpose of this work is to prepare alkyl ring-substituted polyanilines by chemical and electrochemical oxidation, to study the influence of the alkyl groups at the ortho and meta positions on the polymerization processes and on the properties of the resulting polymers. More specifically, polymerization of 2-methylaniline, 3-methylaniline, 2-ethylaniline, 3-ethylaniline, and 2-propylaniline was investigated.

Experimental Section

Materials. Aniline derivatives were obtained from Aldrich Co. and used without further purification. Reagent grade ammonium persulfate, hydrochloric acid, and sulfuric acid (Fisher Scientific Co.) were also used as received.

Chemical Synthesis. Polyanilines were synthesized by chemical oxidation with ammonium persulfate ($(NH_4)_2S_2O_8$) according to a procedure similar to that of Focke et al.[14] In a 500-mL three-neck flask, 0.020 mol of monomer were dissolved in 200 mL of 1 M HCl, and the solution was cooled to below 5 °C by using an ice bath. A few drops of a saturated $FeSO_4$ solution were also added as a catalyst. A prechilled solution of 0.030 mol of ammonium persulfate in 80 mL of 1 M HCl was added dropwise under vigorous stirring. During these manipulations, the mixtures was always kept under argon atmosphere. The resulting solution was left in the ice bath for 2 h. After this period of time, the precipitate was collected on a Büchner funnel and washed with 1 M HCl until the filtrate became colorless. The polymers were finally dried under vacuum for 48 h.

Electrochemical Synthesis. Electrochemical polymerization was done in a one-compartment cell equipped with 1-cm^2 platinum electrodes as working and auxiliary electrodes and a saturated calomel electrode (SCE) as reference. Oxidative deposition of polymer films on platinum plates was carried out by cycling the potential between 0.0 and 0.9 V vs SCE at a scan rate of 100 mV/s. All monomers exhibited an oxidation peak near 0.9 V. The electrolyte was an aqueous solution of 0.5 M monomer in 1 M H_2SO_4 that was degassed for at least 15 min and then kept under argon during the experiments. The electropolymerization was stopped at 0.2 V, and the thin polymer films were then washed with 1 M H_2SO_4 to remove the oligomers and the excess of monomer.

Physical Measurements. Elemental analyses of the chemically prepared polymers were done by the Galbraith Co. The polymers were previously dried under vacuum for 48 h at room temperature. The polymerization yields were calculated after having subtracted the hydrochloric acid content. Upon treatment with a 0.5 M NH_4OH solution, substituted polyanilines become completely soluble in tetrahydrofuran (THF) or chloroform ($CHCl_3$), and it was then possible to determine their molecular weight by gel permeation chromatography (GPC). A similar procedure was recently used by Watanabe et al.[21] for the molecular weight determination of electropolymerized polyaniline. Molecular weight measurements were performed in THF at 40 °C with a Waters GPC apparatus (Model 502), Styragel columns, and polystyrene standards. Cyclic voltammograms were obtained with a potentiostat/galvanostat (EG&G Model 362) and an *X*–*Y* recorder (BBC, Model SE-780). Voltammograms of the chemically prepared polymers were obtained by casting thin polymer films on platinum electrodes. The oxidation potential of the monomers was determined by cyclic voltammetry in 1 M H_2SO_4. Low monomer concentrations (0.01 M) and high scan rates (100 mV/s) were used to prevent polymerization. Visible absorption spectra were measured in situ in a quartz cell with 0.1 M H_2SO_4 solution by a LKB spectrophotometer (Ultrospec 4050). For spectroe-

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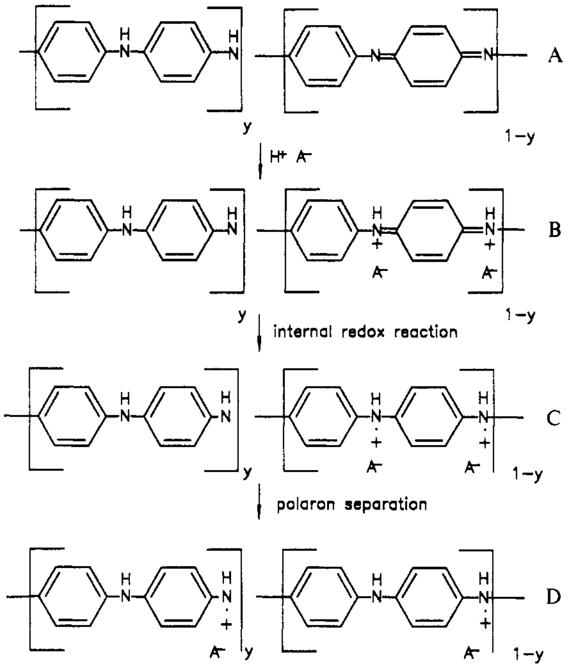
Table I
Chemical Polymerization Yields, Acid Doping Levels, and Electrical Conductivities of Polyanilines

monomer	polym yield, %	Cl/N	conductivity, Ω^{-1} cm^{-1}
aniline	82	0.44	5
2-methylaniline	80	0.65	0.3
3-methylaniline	29	0.70	0.3
2-ethylaniline	16	0.68	1
3-ethylaniline	1[a]		
2-propylaniline	2[b]		

[a] Completely soluble in methanol. [b] Completely soluble in methanol, no electroactivity.

Scheme I



lectrochemical measurements, an indium tin oxide (ITO) coated glass plate (Applied Films, 20–50 Ω/□) and a platinum wire were used as anode and cathode. Before each measurement, the potential was kept at the desired value for 5 min. Four-probe conductivity measurements were carried out on pressed pellets by using a 616 Keithley electrometer and a 197 Keithley multimeter.

Results

Synthesis. The chemical synthesis of alkylmonosubstituted anilines (e.g., 2-methylaniline, 3-methylaniline, 2-ethylaniline, 3-ethylaniline, and 2-propylaniline) was performed in 1 M HCl aqueous solutions with ammonium persulfate and iron sulfate as catalysts. For comparison, polyaniline was also prepared in the same conditions. In all cases, a dark green precipitate was obtained besides a large amount of blue–green oligomers dissolved in the solution. Table I shows the polymerization yields of the chemical syntheses. These polyaniline derivatives were also prepared by electropolymerization except 2-propylaniline and 3-ethylaniline, which did not give any polymer product.

MacDiarmid et al.[22] have reported a "protonic acid doping" of polyaniline that involves the protonation of the nitrogen atoms (Scheme I). Since one Cl^- accompanies each H^+ that reacts with a nitrogen atom, the molar ratio of Cl to N gives the protonation percentage. Doping levels ranging from 65 to 70% were then calculated for these substituted polyanilines (Table I). Similar protonation levels were recently reported for some poly(dimethylanilines) in 1 M HCl solution.[23] As shown in Table I, this

Table II
Molecular Weights of Some Chemically and Electrochemically Prepared Polyanilines

polymer	mol wt chem	mol wt electrochem
polyaniline	80000[a]	9000[b]
poly(2-methylaniline)	7000	4300
poly(3-methylaniline)		4000
poly(2-ethylaniline)	5000	

[a] From ref 42. [b] From ref 19.

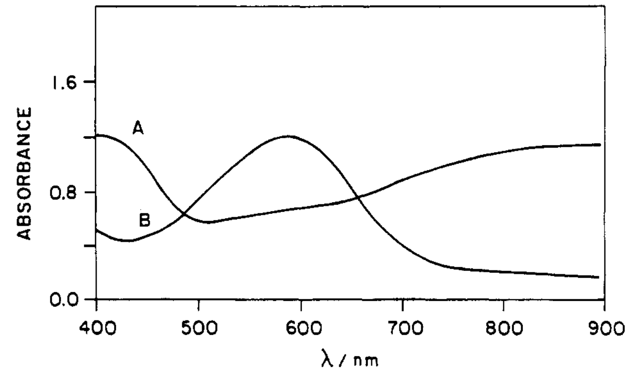


Figure 1. Optical absorption spectra of chemically prepared poly(2-ethylaniline): (a) as-synthesized polymer; (b) base-treated polymer.

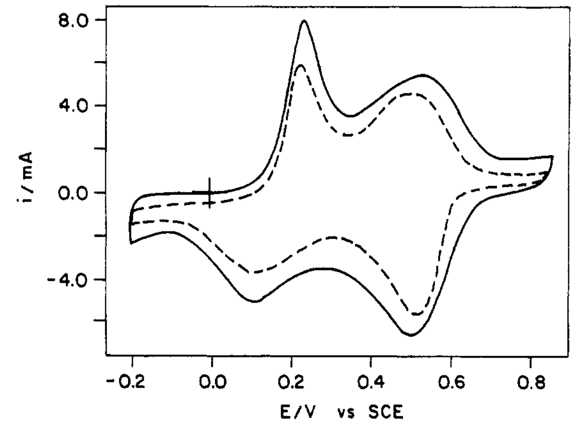


Figure 2. Voltammograms of chemically prepared poly(2-methylaniline) (—) and poly(3-methylaniline) (---) in 1 M H_2SO_4. Potential scan rate: 100 mV/s.

acid doping leads to good conductivity levels (0.3–5 Ω^{-1} cm^{-1}), while insulator behaviors (conductivities lower than 10^{-9} Ω^{-1} cm^{-1}) were found for the base-treated polymers. These electrical conductivities are in good agreement with those reported for poly(3-methylaniline) and polyaniline.[24]

As-synthesized polyaniline derivatives are insoluble in common organic solvents but become completely soluble in chloroform or tetrahydrofuran after deprotonation in 0.5 M NH_4OH. It was then possible to determine the molecular weight of the base-treated polyaniline derivatives by gel permeation chromatography, and these results are shown in Table II. This treatment also induces a color transition for all polymers from dark green to violet (Figure 1). Redoping the base-treated polymers makes them insoluble and conducting again. However, due to their relatively low molecular weight, cast polyaniline films are brittle and do not exhibit a good mechanical resistance.

Cyclic Voltammetry. Figure 2 shows the cyclic voltammograms of chemically prepared poly(2-methylaniline) and poly(3-methylaniline). An oxidation peak is found at 0.22 V, and a large anodic wave near 0.5 V. This large peak is the sum of two oxidation reactions that occur at 0.45 and

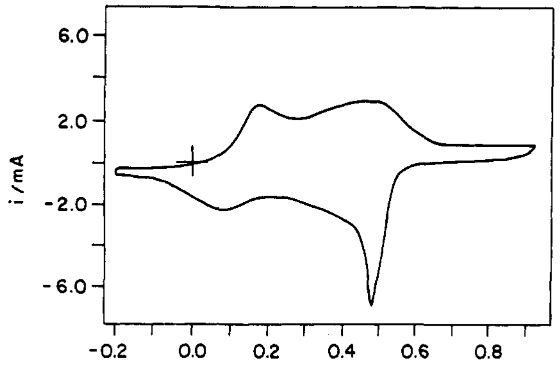


Figure 3. Voltammogram of electrochemically prepared poly(3-methylaniline) in 1 M H_2SO_4. Potential scan rate: 100 mV/s.

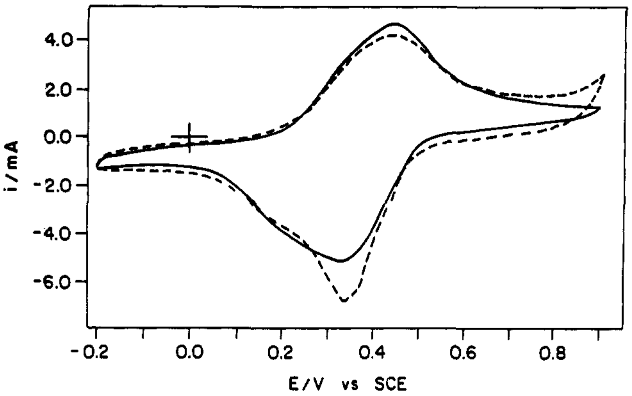


Figure 4. Voltammograms of chemically prepared poly(2-ethylaniline) (—) and poly(3-ethylaniline) (---) in 1 M H_2SO_4. Potential scan rate: 100 mV/s.

Table III
Cyclic Voltammetric Data for Anilines and Polyanilines in 1 M H_2SO_4 versus SCE with a Sweep Rate of 100 mV/s

compound	monomer	polymer[a]	
	E_{pa}, V	E_{pa}, V	E_{pa}, V
aniline	1.02	0.17[b]	0.75[b]
2-methylaniline	0.86	0.22	0.55
3-methylaniline	0.90	0.21	0.53
2-ethylaniline	0.81	0.32	0.45
3-ethylaniline	0.84	0.32	0.45

[a] The midpotential redox peak related to degradation products and irregular couplings have been neglected. [b] From ref 23.

0.55 V, respectively. Similar voltammograms have been observed with electrosynthesized poly(methylanilines)[25] but with a higher contribution of the 0.45 V peak (Figure 3).

An anodic peak was also observed at 0.45 V in polyaniline voltammograms and was related to degradation products (formation of benzoquinone)[26] and irregular couplings (cross-linkings and ortho couplings).[27,28] Figure 4 shows the voltammograms of poly(2-ethylaniline) and poly(3-ethylaniline) obtained by chemical polymerization. Two anodic peaks are observed at 0.32 and 0.45 V. As found with poly(methylanilines), the last oxidation peak might involve two oxidation reactions. The voltammogram of electropolymerized poly(2-ethylaniline) also shows a large anodic wave near 0.4 V, but in this case the 0.32- and 0.45-V peaks are indistinguishable (Figure 5). Table III summarizes the cyclic voltammetric data of the different polyanilines.

Spectroelectrochemistry. In correlation with these anodic processes, poly(methylanilines) and poly(ethylanilines) show multiple and reversible color changes. Visible absorption spectra of these polymers on ITO electrodes are reported in Figures 6 and 7. Poly(2-methylaniline) changes color from yellow to green to blue-violet as the potential is swept between −0.2 and 0.6 V vs SCE (Figure 6). After an increase of the potential from −0.2 to 0.2 V, two new absorption peaks appear at 420 and 830 nm. Above this potential, the absorbances at 420 and 830 nm decrease with the appearance of a new absorption band at 570 nm. Similar optical properties were found for either chemically or electrochemically prepared polymers. Moreover, as previously observed with electrosynthesized poly(methylanilines),[25] chemically prepared poly(2-methylaniline) and poly(3-methylaniline) show essentially the same color transitions at the same potentials.

Poly(ethylanilines) also exhibit an electrochromic behavior (Figure 7). In the reduced state, these polymers are pale yellow and become green at 0.3 V vs SCE. This transition is related to the appearance of two new absorption bands at 430 and 810 nm. Increasing the potential above 0.3 V, the 810-nm peak is shifted to a shorter

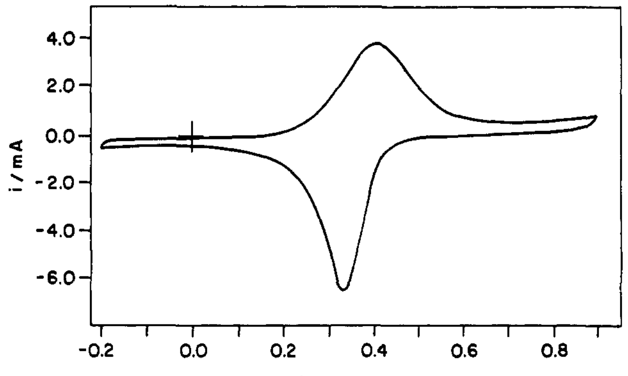


Figure 5. Voltammogram of electrochemically prepared poly(2-ethylaniline) in 1 M H_2SO_4. Potential scan rate: 100 mV/s.

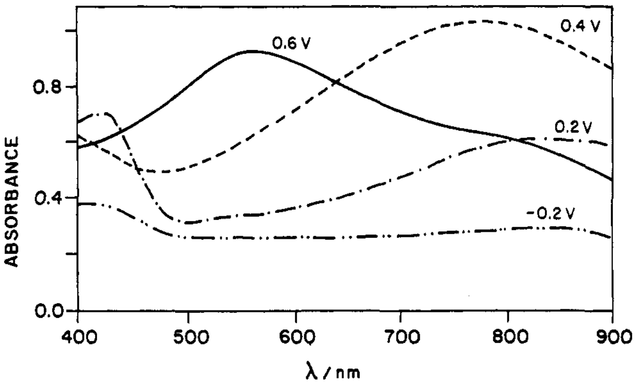


Figure 6. Optical absorption spectra of poly(2-methylaniline) in 0.1 M H_2SO_4 at various potentials vs SCE.

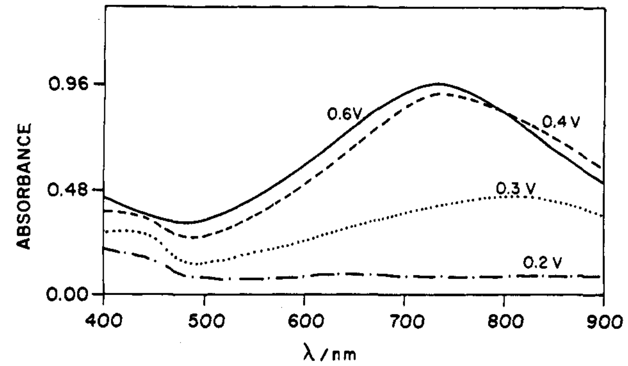


Figure 7. Optical absorption spectra of poly(2-ethylaniline) in 0.1 M H_2SO_4 at various potentials vs SCE.

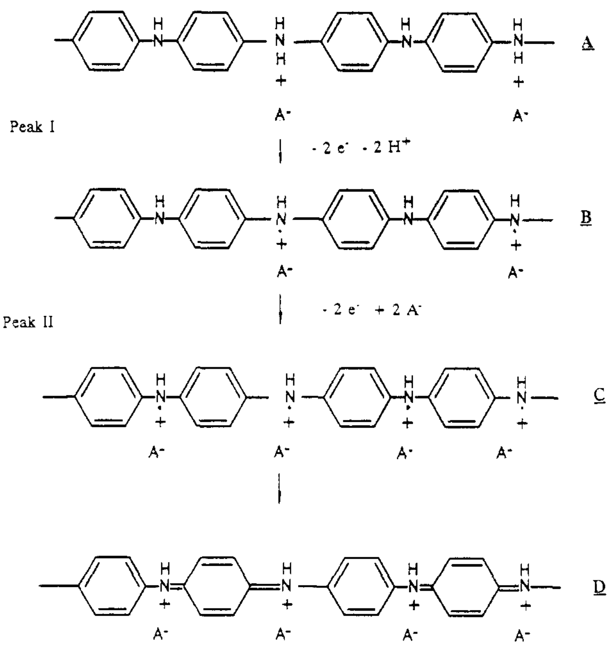
wavelength (730 nm), but the blue shift is smaller than that observed for the methyl derivatives and, therefore, highly oxidized poly(ethylanilines) are blue-green instead of blue-violet. Finally, as found with poly(methylanilines), similar optical properties were observed with the different poly(ethylanilines).

Discussion

The results of Table I clearly show that the polymerization yields are strongly affected by the bulkiness and the position of the substituent. For a pair of ortho- and meta-substituted isomers, the ortho-substituted aniline always gives a higher polymerization yield. Since one ortho position is blocked in 2-substituted anilines, a lower content of ortho couplings can be expected, leading to a more regular head-to-tail polymer structure and, thereby, to higher polymerization yields. Moreover, as shown in Table II, higher molecular weights are obtained by chemical synthesis than by electrochemical polymerization. In that regard, it has been shown that potentials higher than 0.6 V vs SCE induce some degradation in the polyaniline.[26] Therefore, since the electropolymerization of anilines involves high oxidation potentials (up to 0.9 V vs SCE) while chemically prepared polyanilines have a potential of only 0.36 V,[22] the higher molecular weights in chemically prepared polymers can be related to a lower degradation content. Base-treated poly(alkylanilines) are completely soluble in common organic solvents (e.g., THF, chloroform). On the other hand, no electroactive polymer was synthesized with a substituent having more than two carbon atoms (ethyl group). This can be explained by the presence of bulky substituents which hinder the formation of head-to-tail couplings. In agreement with this assumption, recent theoretical calculations on unsubstituted polyaniline[29-31] have shown a strong steric interaction between the hydrogen atoms of neighboring rings. Therefore, substitution of the hydrogen atoms by alkyl chains necessarily leads to an increase of the steric hindrance that seems to limit the polymerization processes.

As previously observed with the unsubstituted polyaniline,[14,25,32,33] the cyclic voltammograms of the alkyl-substituted polyanilines in 1 M H_2SO_4 exhibit two oxidation peaks in addition to an anodic peak at 0.45 V. The 0.45-V peak was related to degradation products,[26-28] while the two other anodic peaks have been explained, for the first peak (Scheme II, peak I), by the oxidation of the amine nitrogen atoms to the radial cation B and, for the second peak at higher potential, by the oxidation of B to the dication C which relaxed to D (Scheme II, peak II).[33,34] These oxidation potentials are however dependent upon the nature of the substituents (Table III). With the introduction of electron-donating substituents, the monomers are more easily oxidized, and a similar behavior can be expected for the polymers. In contrast to this assumption, a positive shift is observed for the first oxidation reaction of the substituted polyanilines, while the last oxidation peak is shifted to a lower potential. The electronic effects of the substituents cannot explain the positive shift of the first oxidation potential, and, consequently, the steric effects as well as the electronic effects of the substituents have to be taken into account. In fact, it has been shown that the presence of bulky substituents can induce some nonplanar conformations that decrease the conjugation along the polymer backbone and thus giving higher oxidation potentials.[35,36] Therefore, on the basis of a positive shift of the first oxidation peak, higher torsion angles are expected in reduced polyaniline derivatives than in the unsubstituted polyaniline. On the other hand, similar conformations are assumed in 50% oxidized polyanilines, and, therefore, the contribution of the electron-donating effect of the alkyl substituents becomes more important, which leads to the negative shift of the last oxidation peak.

Scheme II



MacDiarmid et al.[22] have recently shown that chemical polymerization of aniline gives almost as 50:50 copolymer of diamine and diimine (Scheme IA, $y = 0.5$) repeat units. In 1 M HCl, protonation of the imine groups occurs, and this leads to the formation of radical cations (Scheme IC) by an internal redox reaction.[13,37] This phase transition is related to the known instability of diamine and diprotonated diimine toward disproportionation and formation of two semiquinone radical cations.[37,38] This protonic doping also involves the insertion of anions to preserve the electrical neutrality in the polymer, and since only the imine nitrogen atoms of polyaniline are protonated in 1 M HCl (Scheme IB), the maximum molar ratio of chlorine to nitrogen found in polyaniline was 50%.[22] However, higher doping levels (65–70%) have been obtained in substituted polyanilines (Table I). These high doping levels might be explained by a higher oxidation state of the polymer (Scheme I, $1 - y > 0.5$, i.e., a higher imine content) and by the protonation of these imine groups. Protonation of some amine groups might also explain these results since the presence of electron-donating substituents increases the basicity of the nitrogen atoms. Similar assumptions were proposed by Huang et al.[32] for polyaniline in concentrated HCl solutions (between 1 and 6 M HCl).

As expected, protonated polyanilines show good conductivity levels, while base-treated polymers are electrical insulators. Surprisingly, however, poly(2-ethylaniline) exhibits a higher electrical conductivity than poly(methylanilines) (Table III). It has been shown that the electrical conductivity of polyaniline is dependent on pH, oxidation state, and water content.[14,39] Therefore, to give an accurate description of the electrical behavior of these polymers, more complete measurements are presently being carried out.

Protonation of the imine groups in polyanilines also involves some optical changes (Figure 1). Chemically prepared polyanilines treated with base exhibit only one absorption band in the visible range (590 nm), which has been interpreted as an excitonic absorption of the quinonic

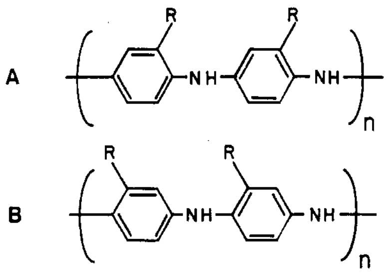


Figure 8. Repeat unit of reduced (A) ortho-substituted polyaniline and (B) meta-substituted polyaniline.

rings.[40] On the other hand, protonated polyanilines show two absorption bands near 820 and 420 nm. These peaks have been related to the formation of radical cations in polyaniline.[41]

Optical changes can also be induced by electrochemical doping. As shown in Figures 6 and 7, the polymer films exhibit multiple color changes (pale yellow–green–blue) as the potential is swept from −0.2 to 0.6 V vs SCE. These spectral changes correspond to the different electronic structures that appear upon oxidation (Scheme II). The yellow-to-green color transition is attributable to the deprotonation and oxidation of aromatic amine nitrogen atoms of A to stable radical cations B while the second oxidation to dications C induces a green-to-blue color transition.[33,34]

Another interesting point to consider is the remarkable similarity between the electrochemical and optical properties of poly(2-alkylanilines) and poly(3-alkylanilines) (Table III). From these results, polymerization of 2-methylaniline and 3-methylaniline seems to give almost the same polymer structure. As shown in Figure 8, it must be the same, since, neglecting the chain ends and degradation, these two structures are equivalent. This equivalence is also true for poly(2-ethylaniline) and poly(3-ethylaniline) and for every pair of ortho- and meta-substituted anilines.

Conclusion

Methyl- and ethyl-monosubstituted polyanilines have been synthesized in acidic media by chemical and electrochemical polymerizations. These polyaniline derivatives exhibit multiple and reversible color changes (pale yellow–green–blue–violet) depending on both oxidation state and pH. As reported for polyaniline, these optical transitions were related to the formation of radical cations and diimine species, but these anodic reactions occur at a smaller potential range for substituted polyanilines than for polyaniline. It has also been observed that the position and the bulkiness of the substituent have a strong effect on the polymerization yields, while equivalent polymer structures are obtained from either 2-substituted or 3-substituted aniline. Therefore, since the 2-substituted anilines always give better polymerization yields and more regular structures, this isomer must be favored in the synthesis of new ring-substituted polyanilines.

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Registry No. Poly(2-methylaniline), 97917-08-3; poly(3-methylaniline), 104318-58-3; poly(2-ethylaniline), 116267-92-6; poly(3-ethylaniline), 117021-78-0; poly(2-propylaniline), 117021-79-1.

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