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Synthesis and characterization of poly(diarylamines): a new class of electrochromic conducting polymers

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Synthesis and Characterization of Poly(diarylamines). A New Class of Electrochromic Conducting Polymers

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ABSTRACT: The electropolymerization of diphenylamine and *N*-phenyl-1-naphthylamine leads to the formation of poly(diphenylamine) (poly(DPA)) and poly(*N*-phenyl-1-naphthylamine) (poly(PNA)), respectively, with the incorporation of the aryl groups into the polymer backbone. The polymer films were characterized by cyclic voltammetry, spectroelectrochemistry, FTIR, and XPS. Poly(DPA) shows two reversible, stable electrochemical processes in its voltammogram, while poly(PNA) displays only one set of redox peaks. These two polymers exhibit very interesting optical properties; poly(DPA) films reversibly change color from pale yellow to yellow to green to blue when the potential (vs Ag/AgCl) is swept from 0.0 to 1.2 V, and poly-(PNA) films change from pale yellow to red to blue between 0.0 and 0.8 V vs Ag/AgCl. XPS, spectroelectrochemistry, and FTIR measurements indicated the presence of polarons and bipolarons. Electrical conductivities of 2 Ω^{-1} cm^{-1} and doping levels as high as 53% were obtained for poly(DPA). Poly(PNA) shows a lower conductivity (10^{-3} Ω^{-1} cm^{-1}) and a lower doping level (30%).

Introduction

Recently, poly(aniline) has become of great interest owing to its good electrical conductivity and environmental stability.[1] This polymer can be obtained by electrochemical or chemical oxidation of aniline[2] in aqueous acidic[3] or organic media[4] and results from a head-to-tail coupling between oxidized species.[5] Poly(anilines) with alkyl[2,6] and aryl[7] substituents on the aromatic ring and alkyl,[8,9] benzyl,[10,11] and aryl[12–14] substituents on the nitrogen have also been successfully prepared. Because of the preferential

head-to-tail polymerization mechanism, only anilines with an aryl substituent on the para position (e.g., 4-amino-biphenyl) can be polymerized, and the resulting polymer has a structure intermediate between that of poly-(aniline) and poly(*p*-phenylene).[7] A similar structure was also reported for poly(diphenylamine), which was obtained by the electrochemical polymerization of diphenylamine via a 4,4' C–C phenyl–phenyl coupling mechanism.[15,16]

In this paper, we report the synthesis and characterization of two electrochromic conducting polymers, poly(*N*-phenylaniline) (poly(DPA)) and poly(*N*-naphthylaniline) (poly(PNA)), obtained by electro-

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chemical oxidation of diphenylamine and *N*-phenyl-1-naphthylamine, respectively. These polymers represent a new class of conducting polymers intermediate between poly(aniline) and poly(*p*-phenylene).

Experimental Section

Materials. Diphenylamine and *N*-phenyl-1-naphthylamine were obtained from Aldrich Chemical Co. and used without further purification. Reagent grade lithium perchlorate (Aldrich) and HPLC grade acetonitrile (Caledon) were also used as received.

Electrochemical Polymerization. Electropolymerization was performed in a two-compartment cell equipped with 1-cm² platinum electrodes as working and auxiliary electrodes and a Ag/AgCl 3.8 M KCl reference electrode. Oxidative deposition of polymer films was obtained from solutions containing 0.1 M monomer and 1.0 M lithium perchlorate. Uniform polymer films on Pt electrodes were obtained by applying a constant potential of 0.80 V for diphenylamine and 0.65 V for *N*-phenyl-1-naphthylamine. Electropolymerization of both polymers on indium tin oxide (ITO) coated glass plate (Applied films, 20–30 Ω/cm²) was performed at 0.80 V. The polymer films were then washed with acetonitrile in an ultrasonic bath to remove the oligomers and the excess of monomer. For elemental analysis, conductivity measurements, and FTIR data, a constant potential of 1.0 V was used for both monomers. The polymers were removed from the electrode and then placed in an Erlenmeyer flask. The products were stirred in 500 mL of acetonitrile for 30 min and, after this period, the powder was collected on a Büchner funnel. This last procedure was repeated twice to remove the excess salt and oligomers. The polymers were finally dried under vacuum for 24 h. In all cases, the isolated polymers are doped with perchlorate.

Physical Measurements. Elemental analysis of the polymers was performed by Galbraith Laboratories, Inc. Cyclic voltammograms were obtained with a BAS potentiostat (Model CV-27) and an XY recorder (HP-7045A). The oxidation peak potentials of the polymers and monomers were determined by cyclic voltammetry in a 1.0 M LiClO₄/CH₃CN solution. For the monomer potential determination, a low concentration (10^{-3} M) and a high scan rate (100 mV/s) were used to prevent polymerization. UV–visible absorption spectra were measured in situ in a quartz cell with a diode array spectrophotometer (HP 8452A). For spectroelectrochemical measurements, an ITO glass plate and a platinum wire were used as anode and cathode. The infrared absorption spectra were recorded on a Bomem FTIR spectrophotometer (Michelson 100). Spectra were taken at room temperature under a nitrogen atmosphere from pressed KBr disks in which the sample was dispersed. X-ray photoelectron spectroscopy (XPS) analyses of the polymer films were performed by means of a VG Escalab spectrometer. The incident radiation was Mg Kα, and the analyzer energy was set to 20 eV to enhance the resolution in the spectra. Poly(DPA) and poly(PNA) films on Pt electrodes were obtained by four successive electrodepositions of 3 min each at 0.80 and 0.65 V (vs Ag/AgCl) in order to get pinhole-free films. They were rinsed with acetonitrile between each deposition. Then they were placed in an electrolyte free of monomer, held at a fixed potential to obtain the desired redox state, and finally washed with acetonitrile and dried under vacuum for 24 h. The thicknesses of the polymer films deposited on platinum electrodes were determined by scanning electron microscopy (SEM). Four-probe conductivity measurements were carried out with a Keithley Model 616 electrometer and a Keithley Model 197 multimeter on pressed pellets of carefully washed polymer samples. This procedure is important since we observed higher conductivity (almost one order of magnitude higher) for washed samples compared to the as-synthesized material. This difference may be due to the presence of oligomers in the samples.

Results

Cyclic Voltammetry. Figures 1 and 2 show the cyclic voltammograms in 1.0 M LiClO₄/CH₃CN solution, at different scan rates, between 0.0 and 1.2 V for poly-(DPA) and between 0.0 and 1.0 V for poly(PNA),
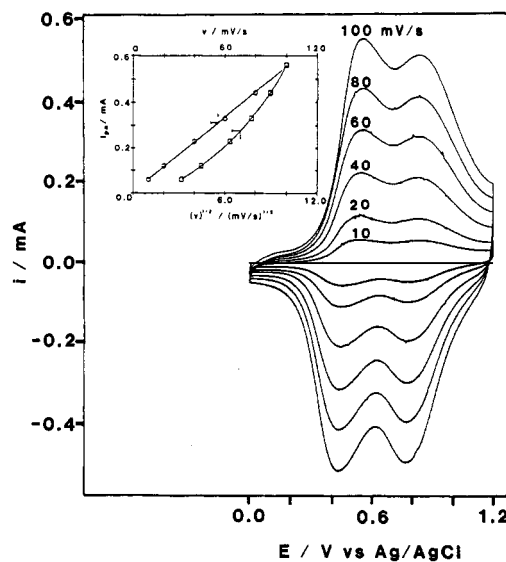

Figure 1. Cyclic voltammograms of a poly(diphenylamine) film on Pt in 1 M LiClO₄/CH₃CN at different scanning rates.
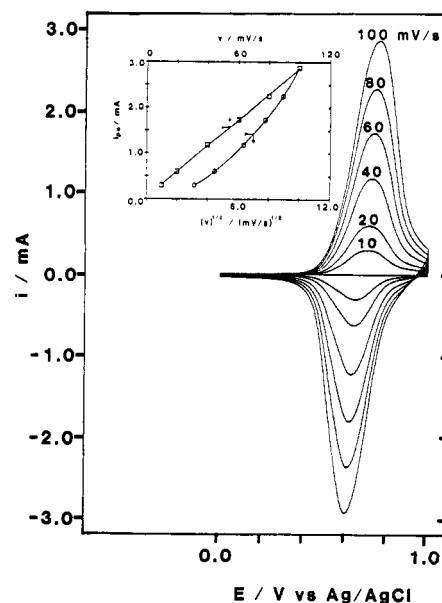

Figure 2. Cyclic voltammograms of a poly(*N*-phenyl-1-naphthylamine) film on Pt in 1 M LiClO₄/CH₃CN at different scanning rates.

respectively. The thickness of the films on Pt electrodes has been evaluated as 1 μm for both polymers. For poly-(DPA) (Figure 1), the voltammogram shows two, poorly resolved electrochemical processes, which are stable within the potential range shown, in contrast to polyaniline, which gradually loses its electroactivity when the second oxidation peak is reached.[17,18] These peaks correspond to the oxidation of the amine groups in the polymer. Surprisingly, cyclic voltammetry of poly(PNA) (Figure 2) reveals only one pair of redox peaks. Moreover, the poly(PNA) anodic and cathodic peaks, which correspond to the oxidation and reduction of amine groups, are almost symmetrical at about the E_p value. This comportment is unusual for conducting polymers and is more characteristic of nonconjugated redox polymer film systems such as poly(2-isopropenyl-naphthalene),[19] poly(4-vinylpyridine),[20] and the well-known poly(vinylferrocene).[21]

As expected for the reaction of a material localized on the electrode surface, the i_{pa} values scale linearly with the sweep rate between 10 and 100 mV/s for both polymers (inset of Figures 1 and 2). The same behavior has been
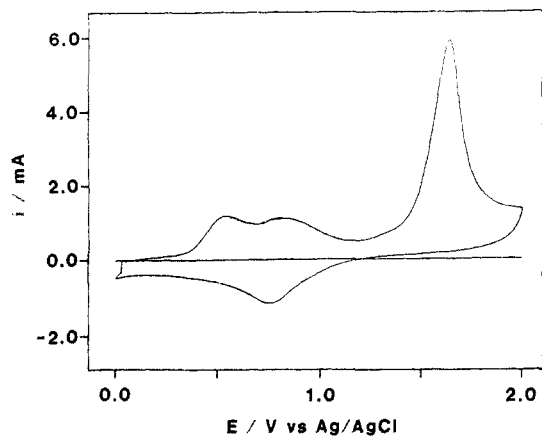
Figure 3. Cyclic voltammogram of a poly(diphenylamine) film on Pt in 1 M LiClO$_4$/CH$_3$CN with extended anodic potential limit.
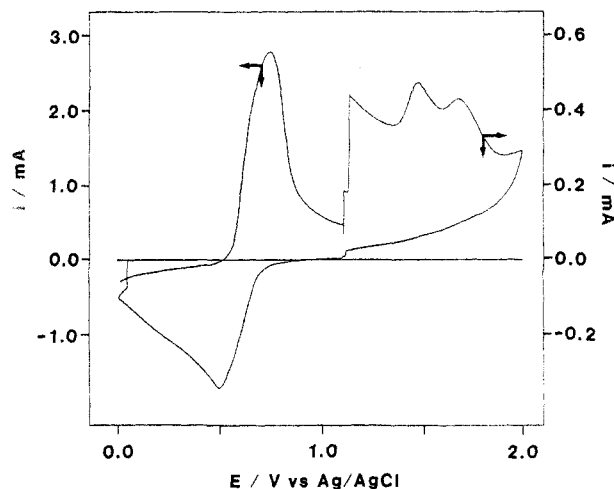

Figure 4. Cyclic voltammogram of a poly(N-phenyl-1-naphthylamine) film on Pt in 1 M LiClO$_4$/CH$_3$CN with extended anodic potential limit.

Table I
Oxidation Potentials of Polymer Films in LiClO$_4$/CH$_3$CN[a]

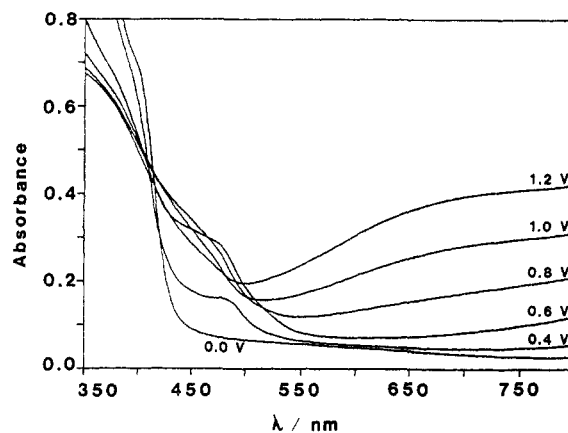| polymer	E_{pa}(NH), V	E_{pa}(aromatic), V
poly(DPA)	0.54, 0.83	1.66
poly(PNA)	0.73	1.48, 1.68
poly(1,4-naphthylene)		1.47

[a] Reference electrode: Ag/AgCl.

Figure 5. Absorption spectra of a poly(diphenylamine) film on ITO in 1 M LiClO$_4$/CH$_3$CN at various applied potentials (Ag/AgCl reference electrode).
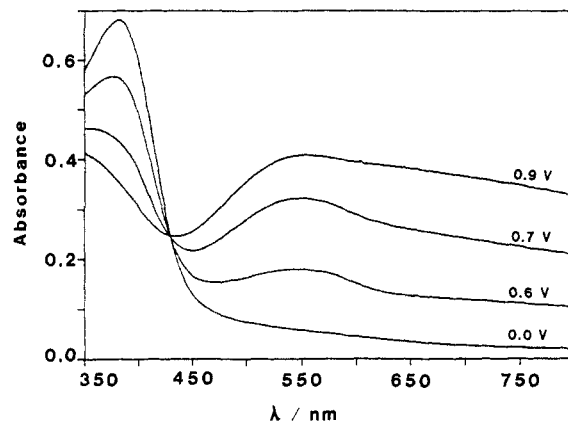
Figure 6. Absorption spectra of a poly(N-phenyl-1-naphthylamine) film on ITO in 1 M LiClO$_4$/CH$_3$CN at various applied potentials (Ag/AgCl reference electrode).

observed for polyaniline films.[22,23] They also have widths at half-height >90 mV, a value that is to be expected for a surface reaction involving single-electron transfer with a Nernstian behavior.[24]

Figures 3 and 4 respectively show the cyclic voltammograms of poly(DPA) and poly(PNA) films on Pt electrodes in 1.0 M LiClO$_4$/CH$_3$CN solution at a scanning rate of 50 mV/s, with the positive potential limit extended to 2.0 V vs Ag/AgCl. When cycled to this limit, poly(DPA) reveals an oxidation peak at 1.66 V, which probably corresponds to the oxidation of the aromatic moieties (Figure 3). However, on the reverse scan, only one reduction peak is observed (compared to the two seen previously (Figure 1)). Then the film became inactive. On the other hand, poly(PNA) shows two additional irreversible oxidation peaks at 1.48 and 1.68 V when the potential range is extended to 2.0 V (Figure 4). These peaks are probably also due to the oxidations of aromatic moieties. On the reverse scan, the cathodic peak has been modified (compared to Figure 2) but the film retains most of its electroactivity upon further cycling. The peak potential values of poly(DPA) and poly(PNA) that correspond to the oxidation of the amine groups and aromatic rings are listed in Table I together with that of poly(naphthylene) obtained in an acetonitrile solution (vs Ag/AgCl).[25]

Spectroelectrochemistry. In correlation with these anodic and cathodic processes, poly(DPA) and poly(PNA) show multiple and reversible color changes. In situ

UV–visible absorption spectra of these polymers on ITO electrodes dipped in 1 M LiClO$_4$/CH$_3$CN are reported in Figures 5 and 6. At 0.0 V, a single, large absorption band around 350 nm is seen for poly(DPA) (Figure 5). When the potential is swept from 0.0 to 0.6 V, a new absorption band appears at 484 nm and at the same time an increase in the absorbance at longer wavelengths is observed. Above this potential, a concurrent decrease of the absorbance at 484 nm and an increase in the absorbance at 700 nm are observed. Together with these modifications, the band around 350 nm diminishes and shifts to lower wavelength. If the potential is then returned to 0.0 V, the original, reduced form is restored. These changes in the visible portion of the spectrum correspond to the modifications in the color of the poly(DPA) thin film. The color of the polymer films at different applied potentials is reported in Table II.

Figure 7 shows the variation of the absorbance at 484 and 700 nm of poly(DPA) as a function of the applied potential. It must be noted that the absorbance of the reduced form has been subtracted and the absorbance at 484 nm has been corrected for the background absorption caused by the evolution of the band at higher wavelength.

Table II
Electrochromism of Poly(diarylamines)

$E_{applied}$, V	coloration	
	poly(DPA)	poly(PNA)
0.0	colorless	pale yellow
0.6	yellow	red
0.8	yellow-green	blue
1.0	green	blue
1.2	blue	blue

Figure 7. Absorption difference (ΔA) of a poly(diphenylamine) film on ITO in 1 M $LiClO_4/CH_3CN$ at various applied potentials (Ag/AgCl reference electrode): (A) at 484 nm; (B) at 700 nm.
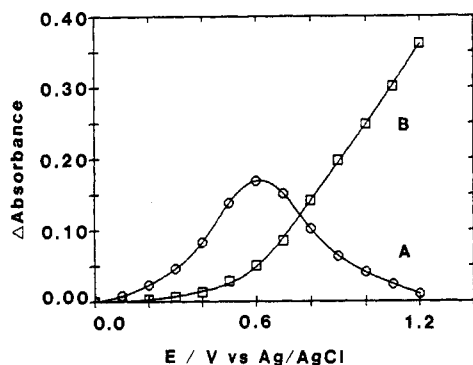
As shown in Figure 7A, the absorbance at 484 nm increases smoothly to a maximum at around 0.60 V and then decreases to nearly zero at 1.2 V. At the same time, the absorbance at 700 nm slowly changes between 0.0 and 0.6 V and then increases rapidly with the applied potential (Figure 7B).

The spectrum of poly(PNA) (Figure 6) is also modified when the applied potential is raised from 0.0 to 1.0 V. In the reduced state (0.0 V), one absorption band is present at 382 nm. When the potential is increased to 0.6 V, a band appears at 542 nm together with a broad absorption between 600 and 800 nm. With the increase of the applied potential, the two absorption bands continue to grow to cover almost the entire visible portion of the spectrum. At the same time a decrease in the absorption intensity and a blue shift of the band at 382 nm are observed. The original, reduced form of the spectrum is recovered when the applied potential returns to 0.0 V. The electrochromic behavior of poly(PNA) is also summarized in Table II.

Infrared Spectra. Figure 8 shows the FTIR spectra of poly(DPA) and poly(PNA) from 2000 to 400 cm^{-1}. In both cases, an absorption band appears around 3400 cm^{-1} (not shown) corresponding to the N–H stretching vibration. In Figure 8A, the bands at 1594 and 1484 cm^{-1} are caused by the ring-stretching mode of the phenyl groups in poly(DPA).[26,27] These bands were also observed in the infrared spectra of poly(aniline) and received the same assignment.[28,29] The absorption band at 1515 cm^{-1} corresponds to the N–H bending vibration (scissoring) of secondary aromatic amine in poly(DPA).[26] The doped state of poly(DPA) and poly(PNA) is characterized by a band at 1555 cm^{-1} (N–H bending of amine salts).[26] In the case of poly(PNA) (Figure 8B), the assignment of the absorption bands between 1630 and 1450 cm^{-1} is more difficult, since this region contains many unresolved bands. The presence of naphthyl and phenyl groups in the polymer certainly explains the complexity of this region. For both polymers, the absorption bands in the region 1240–1350 cm^{-1} are due to the C–N stretching vibration of the aromatic amine,[26] and bands observed between 1040
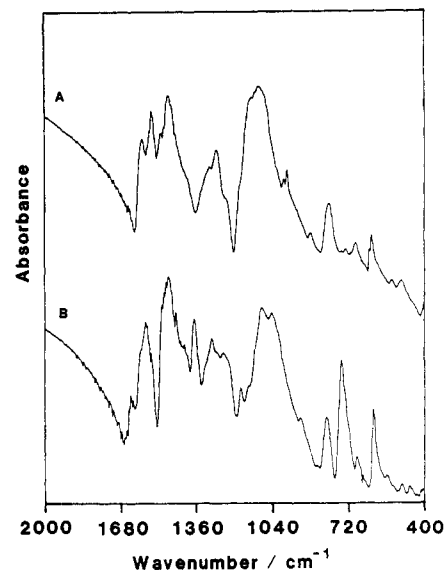

Figure 8. FTIR absorption spectra of pressed KBr disks of (A) poly(diphenylamine) and (B) poly(*N*-phenyl-1-naphthylamine).

and 1140 cm^{-1} and also around 625 cm^{-1} [30] are characteristic vibrations of ClO_4^- ions. In the infrared spectrum of poly(DPA) (Figure 8A), the bands at 808 and 694 cm^{-1} are respectively assigned to the C–H out-of-plane bending vibrations of para-disubstituted and monosubstituted benzene rings.[26,28] The latter vibration is found at 689 cm^{-1} in the spectrum of poly(PNA) (Figure 8B). The presence of a monosubstituted band in the spectrum of both polymers is attributed to their chain ends. Poly(PNA) also displays bands at 820 and 755 cm^{-1} caused respectively by the C–H out-of-plane bending vibrations of 1,2,3,4-substituted and ortho-disubstituted benzene rings.[26] These two bands are also found in the infrared spectrum of poly(1,4-naphthylene)[31] and are produced by the naphthyl group, which can be considered as a benzene ring substituted in the ortho and 1,2,3,4 positions. Note that the ortho-disubstituted frequency of *N*-phenyl-1-naphthylamine and naphthalene[32] monomers is found at 770 cm^{-1}.

XPS Measurements. Parts A and B of Figure 9 show respectively the N 1s peaks of neutral (0.0 V) and partially oxidized (0.65 V) poly(DPA) films, while the N 1s peak of oxidized (1.0 V) poly(PNA) is shown in Figure 9C. For each sample the C/N ratio, ranging from 12 to 14 for poly(DPA) and from 15 to 17 for poly(PNA), agrees with the theoretical values of 12 and 16, respectively. The reduced form of poly(DPA) (Figure 9A) shows a single N 1s peak. It is still seen in the oxidized form (Figure 9B), but with an additional shoulder caused by the presence of two more peaks in the spectrum. These modifications are related to the formation of charged nitrogen due to the oxidation of the polymer. The poly(PNA) spectrum (Figure 9C), which also shows a component in the neutral form, exhibits a similar shape, indicating that two other types of charged nitrogen are created when the polymer is oxidized. In parts B and C of Figure 9, a shake-up satellite peak is also observed around 406 eV. Complete analysis of the XPS measurements and additional experiments on these polymers are in progress, and the results will be published in due course.

Conductivity, Doping Level, and Degree of Polymerization. Table III shows the degree of polymerization (DP), the ratio of Cl atoms (from ClO_4^-) to N atoms (which gives the doping level), and the electrical conductivity (σ), at 25 °C, of poly(DPA) and poly(PNA).
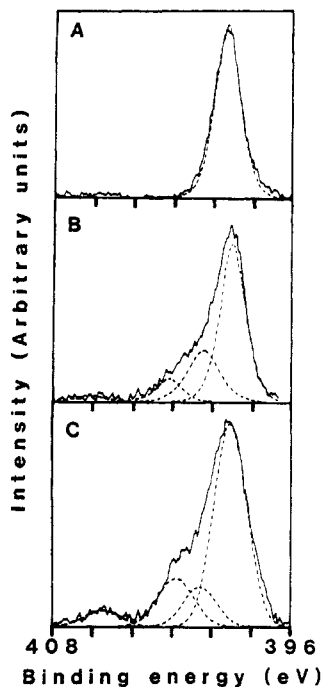
Figure 9. XPS N 1s spectra of (A) neutral poly(diphenylamine), (B) oxidized poly(diphenylamine), and (C) oxidized poly(N-phenyl-1-naphthylamine). Dashed lines are the results of deconvolution.
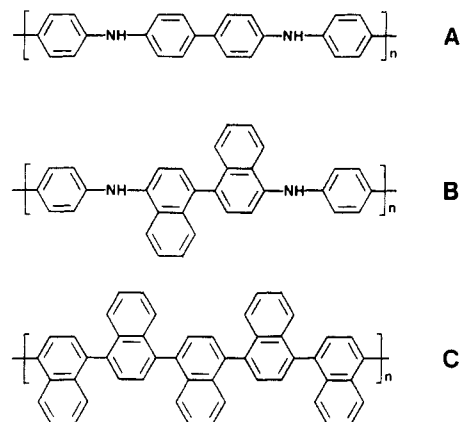

Figure 10. Repeat unit of reduced (A) poly(diphenylamine), (B) poly(N-phenyl-1-naphthylamine), and (C) poly(naphthylene).

(PNA), respectively (Table III). Variable electrical conductivities of 10,[12] 0.5, and 10^{-6}–10^{-2} Ω^{-1} cm^{-1} [34] have been reported for poly(DPA), while a value of 10^{-3} Ω^{-1} cm^{-1} has been observed for poly(naphthylene).[35]

Discussion

We have already shown that poly(DPA) is formed by a 4,4- C–C phenyl–phenyl coupling mechanism[16] to yield a polymer with a structure intermediate between poly(aniline) and poly(p-phenylene) (Figure 10A). However, poly(PNA) is a new conducting polymer and its structure has not yet been elucidated.

Assuming that like diphenylamine, N-phenyl-1-naphthylamine will polymerize only via a C–C aryl–aryl coupling mechanism, three types of coupling are possible: (1) phenyl–naphthyl, (2) phenyl–phenyl, which also implies naphthyl–naphthyl, and, finally, (3) a mixture of (1) and (2). Based on cyclic voltammetry and FTIR spectroscopy data, the following structure for poly(PNA) is proposed (Figure 10B). From Table I, one can see that poly(PNA) has two oxidation processes (1.48 and 1.68 V) which correspond to the oxidation process in poly(1,4-naphthylene) (1.48 V) and poly(DPA) (1.66 V). This means that poly(PNA) must include units of poly(1,4-naphthylene) and poly(DPA) in its backbone. This result also indicates that a coupling of the type (2) is preferred. This finding also corroborates the results obtained by FTIR spectroscopy, which showed that poly(PNA) has some characteristic vibration bands of poly(1,4-naphthylene) (vide infra). Moreover, the type of coupling proposed here is in agreement with the results of Lapkowski et al.[36] They showed that 1-naphthylamine cannot form a polymer and observed that the oxidation of the monomer led to the formation of 1-naphthidine, which is the result of naphthyl groups coupling at the 1 position.[36] The structures of poly(PNA) and poly(1,4-naphthylene) are shown in Figures 10B and 10C, respectively.

The doping process in conducting polymers leads to strong modifications of their electronic structures, which can be observed by UV–visible spectroscopy. For poly(DPA) (Figure 5), an increase of the potential applied to the electrode causes two new absorption bands to appear, one at 484 nm and the other at a wavelength higher than 800 nm (the limitation of the spectrophotometer does not allow the determination of its exact position, but the increase in absorbance on the high-wavelength side testifies to its existence). The band around 350 nm, which can be related to the $\pi \rightarrow \pi^*$ transition, is shifted to lower wavelength. A $\pi \rightarrow \pi^*$ transition has also been assigned for poly(aniline) at around 320 nm[37] and for poly(p-phenylene) at around 360 nm.[38]

Table III
Properties of Poly(diarylamines)

polymer	DP[a]	Cl/N[b]	σ, Ω^{-1} cm^{-1}
poly(DPA)	16	0.53	2
poly(PNA)	15	0.30	10^{-3}

[a] From IR. [b] From elemental analysis.

The value of DP has been evaluated from the FTIR spectra of N,N-diphenylbenzidine (dimer of diphenylamine), N-phenyl-1-naphthylamine, and their corresponding polymers (Figure 8a,b). Since the ratio of para-disubstituted to monosubstituted phenyl "groups" is exactly known for N,N-diphenylbenzidine (2 para-disubstituted and 2 monosubstituted phenyl groups; therefore the ratio is equal to 1), the intensity ratio of the characteristic out-of-plane bending vibration "bands" of para- and monosubstituted benzene rings in N,N-diphenylbenzidine can be used as a reference unit to compare with the intensity ratio of the same characteristic "bands" observed in poly(DPA). The result of the ratio of the intensity ratios of poly(DPA) and N,N-diphenylbenzidine permits one to evaluate the degree of polymerization of poly(DPA). In the case of poly(PNA), the ratio of the out-of-plane bending vibration bands of ortho-disubstituted and monosubstituted phenyl rings in the polymer and monomer has been used, since the ratio of ortho to mono groups is exactly known for the monomer (equal to 1). The degrees of polymerization obtained for poly(DPA) and poly(PNA) are listed in Table III. The infrared technique has been used to evaluate the DP of poly(phenylene) and has been found to be as good as other chemical techniques.[33] The ratio of chlorine atoms to nitrogen atoms, determined by elemental analysis, was used to calculate the doping level (Table III). Doping levels of 0.53 and 0.30 were obtained for poly(DPA) and poly(PNA), respectively (Table III). Lower doping levels of 0.25[12] and 0.40[16] have been reported for poly(DPA), but under different polymerization conditions and with a different analytical technique. Electrical conductivities of 2 and 10^{-3} Ω^{-1} cm^{-1} were obtained from pressed pellets of poly(DPA) and poly-

The band at 484 nm has been used to follow the evolution of polarons in poly(DPA). Figure 7A shows the absorbance difference (ΔA) at this wavelength versus the potential applied to the electrode. The curve obtained shows a bell-like form, with a maximum around 0.63 V, which means that polarons are formed from 0.0 to 0.63 V and then almost completely vanish when the potential reaches 1.20 V. Using the band at 420 nm in the spectrum of poly(aniline), Cushman et al.[39] obtained a similar curve. On the basis of an in situ ESR study which showed an increase and a decrease of the ESR signal versus the applied potential,[40] they explained this behavior by the formation of polarons followed by their transformation into bipolarons.[39] In correlation with the anodic processes observed from the cyclic voltammetry of poly(DPA) (Figure 1), the potential at which ΔA is at a maximum corresponds to the end of the first anodic peak. Moreover, the potential value at which ΔA returns to almost zero corresponds to the end of the second redox process observed in Figure 1.

The formation of bipolarons in poly(aniline) shifts the second polaronic transition, located at 800 nm,[39,41,42] toward the lower wavelength region, and the displacement, proportional to the ratio of imine groups to amine groups,[43] leads to a new band at 580 nm, which has been used to follow the evolution of bipolarons.[39] This band probably results from the formation of a localized molecular exciton with the electron on the quinoid moiety and the hole on the two conjugated benzenoid moieties.[44] Since the shift of the second polaronic transition in poly(DPA) is also observed (Figure 6), the absorption difference (ΔA) at 700 nm versus the applied potential has been used to follow bipolaron evolution (Figure 7B). The ΔA at 700 nm shows only a small increase until the applied potential reaches ca. 0.60 V and then it increases sharply for higher applied potentials. Similar behavior has been observed for poly-(aniline) using the absorbance at 580 nm.[39] In correlation with the anodic process obtained from the cyclic voltammetry of poly(DPA) (Figure 1), the potential value at which ΔA at 700 nm increases rapidly corresponds to the end of the first redox peak and the beginning of the second redox process of the polymer. From the results of Figure 7, it can be deduced that the oxidation of poly(DPA) leads to the formation of polarons which are subsequently transformed into bipolarons.

The existence of these charge carriers is also confirmed by the XPS results. The spectrum of oxidized poly-(DPA) (0.65 V vs Ag/AgCl) (Figure 9B) shows two additional N 1s peaks, when compared to the neutral form (Figure 9A), which can be related to the presence of polarons (400.5 eV) and bipolarons (402.2 eV) in poly-(DPA). These results are similar to those found by Nakajima et al., who have recently studied the XPS N 1s spectra of poly(aniline) and showed that radical cation and positively charged nitrogen induced two new peaks at 400.8 and 402.4 eV, respectively, while the neutral nitrogen gave a peak at 399.1 eV.[45]

The electronic structure of poly(PNA) also undergoes strong modifications when the potential applied to the electrode is changed (Figure 6). In the neutral form (0.0 V), only one absorption band at 382 nm is observed, which can be assigned to the $\pi \rightarrow \pi^*$ transition. Upon oxidation, the poly(PNA) visible spectrum (Figure 6) shows a band at 542 nm together with a large background absorption that almost overwhelms the first band when the potential reaches 0.90 V. Due to the poor resolution of these bands, we have not been able to follow their evolution as for poly-(DPA). Nevertheless, the band at 542 nm is believed to

Scheme I
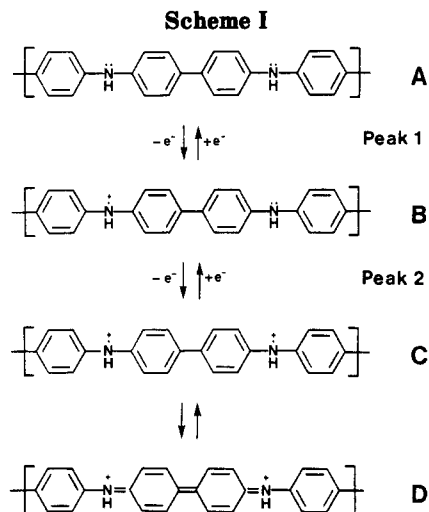
originate from the formation of polarons while the increase in the absorbance around 650 nm is probably caused by the presence of bipolarons. These hypotheses are confirmed by the N 1s spectrum of oxidized poly(PNA) (Figure 9C), which shows three peaks (399.0, 400.5, and 402.0 eV) that we assign to the neutral amine, polarons, and bipolarons, respectively.

On the basis of the results obtained with FTIR, visible spectroscopy, and XPS measurements, the mechanism of oxidation and reduction, corresponding to the peaks observed in the cyclic voltammetry for poly(DPA) and poly-(PNA), can be proposed. The redox mechanism proposed for poly(DPA) is shown in Scheme I. The first peak (Scheme I, peak 1) corresponds to the oxidation of amine nitrogen which leads to the formation of polarons (form B) and the second peak to the oxidation of another amine group (form C) which will give bipolarons (form D) via a disproportionation mechanism. A similar mechanism has been proposed for poly(aniline).[5,18] Unlike poly(aniline), however, the form D of poly(DPA) does not undergo a deprotonation reaction to form imine bases. The first proof that such a reaction does not take place is in the FTIR spectra of poly(DPA), which show a strong absorption band, ranging from 1800 to 4000 cm^{-1}, which can be attributed to the stretching vibration of amine salts.[26] The second argument is that a fully oxidized and deprotonated form of poly(DPA) must lead to an electrically insulating material like poly(aniline) when it is completely oxidized.[39,46] But conductivities around 1 Ω^{-1} cm^{-1} have been obtained for poly(DPA) samples fully oxidized between 1.0 and 1.4 V. The stabilities of positive charges on two adjacent nitrogen atoms appear to be greater in poly(DPA) than in poly(aniline), perhaps because these charges are submitted to lesser repulsive forces since the distance between them is twice as great in poly(DPA) than in poly(aniline).

The mechanism proposed for poly(PNA) (Scheme II) is quite different from that proposed for poly(DPA) since all the oxidation steps occur in the single peak observed in its cyclic voltammetry (Figure 2). On the basis of UV-visible spectra (Figure 6) and cyclic voltammetry (Figure 2), probably poly(PNA) A was successively oxidized to B (polarons) and C in a narrow potential range, the two peaks overlapping to form only one peak. Polaron and bipolaron states in C, the latter occurring after the second oxidation step which relaxed via a disportionation mechanism, were confirmed by XPS measurements (Figure 9C). Here again, no deprotonation reaction should occur since the FTIR spectrum of fully oxidized poly(PNA) shows absorption between 1800 and 4000 cm^{-1} which is due to

Scheme II
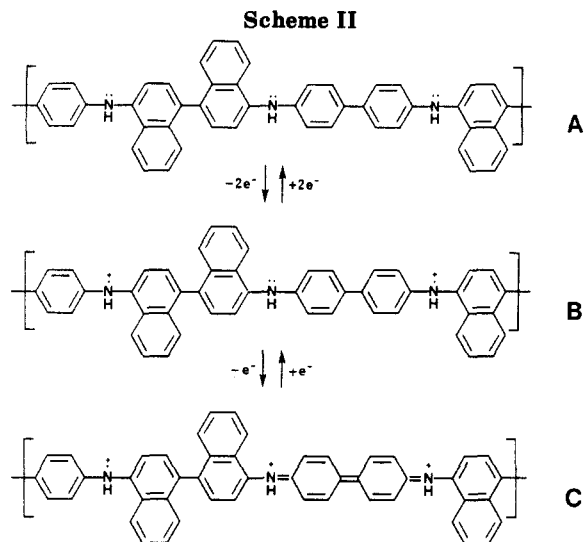
amine salt stretching vibrations.[26] However, we believe that bipolarons will be formed mostly through p-phenylene units. Indeed, the presence of bipolarons also implies the existence of quinoid forms which force a dihedral twist angle of around 0° between two adjacent phenyl groups as observed in poly(p-phenylene).[38] This angle is certainly difficult to achieve between two adjacent naphthyl groups in the polymer since the steric hindrance due to the hydrogen atoms at the 2 and 8 positions of the 1,1'-binaphthyl unit gives a dihedral twist angle of nearly 90° between the two naphthyl groups.[47]

The electrical conductivity obtained for poly(DPA) (Table III) is similar to those obtained by Dodd et al. (10 Ω^{-1} cm^{-1})[12] and Zotti et al. (0.5 Ω^{-1} cm^{-1})[15] but relatively higher than those reported by Pater et al. (10^{-6}–10^{-2} Ω^{-1} cm^{-1}),[34] who used a mixture of methanol and aqueous HClO$_4$ to polymerize diphenylamine instead of a pure organic medium. In addition, the electrical conductivity value of poly(DPA) is similar to those published for poly(aniline) (0.5–10 Ω^{-1} cm^{-1})[48,49] and poly(p-phenylene) (100 to 10^{-4} Ω^{-1} cm^{-1}),[50-52] reflecting the similarities in their structures. On the other hand, the conductivity value obtained for poly(PNA) (Table III) is relatively low compared to the above-mentioned polymers. The difference in electrical conductivity is probably due to naphthyl groups, which introduce a nonplanar conformation in the polymer, leading therefore to poor interchain contacts by keeping the chains away from one another and thereby reducing the probability of charge carrier hopping.[53] The conductivity of poly(PNA) is comparable to that of poly(naphthylene) (10^{-3} Ω^{-1} cm^{-1}), for which steric hindrance has also been invoked to explain this low value.[35] The degree of polymerization may also influence the electrical conductivity since values of 0.5 and 10^{-2} Ω^{-1} cm^{-1} for samples of poly(DPA) having DP values of around 11 and 3, respectively, have been reported.[15] In this study, degrees of polymerization of 15 and 16 for poly(PNA) and poly(DPA) have been found. It is important to note that the value of the DP for poly(DPA) can be considered a lower limit since the presence of quinoid forms in the oxidized polymer decreases the para/mono infrared ratio used to evaluate the DP. The value obtained for poly(DPA) is similar to the values, also evaluated by the infrared technique, reported for poly(p-phenylene), which are respectively 9 and 20 for the electrochemically[54] and chemically[20] prepared polymers, but rather lower than the value of 100 found for the electrochemically prepared poly(aniline).[55] The DP value of 15 obtained for poly(PNA) is, however, higher than the value of 6 reported for electrochemically prepared poly(1,4-naphthylene)[25] but lower than the value of 38 for the chemically synthesized polymer.[30]

From elemental analysis, the doping levels of poly(PNA) and poly(DPA) have been calculated as 0.30 and 0.53, respectively (Table III). The value obtained for poly(PNA) is typical of polymers such as poly(thiophene) and poly(pyrrole), which present doping levels ranging from 0.10 to 0.33.[56] A value of 0.25 has already been reported for poly(DPA)[12] but the polymerization conditions were very different from ours (the polymerization potential was around 2.0 V and Et$_4$NBF$_4$ in acetonitrile was used as the electrolyte). We believe that these conditions are responsible for the different values of doping level since a study on poly(pyrrole) shows that the doping charges decrease when the potential of polymerization used is too high and also that the type of counterion present in the solution has an effect.[57] The doping level of poly(DPA) is one of the highest for the conducting polymers. A high doping level has also been reported for poly(aniline), around 0.42–0.50 with chlorhydric acid as dopant,[58] and for poly(carbazole), 0.50.[59]

Conclusion

Poly(diphenylamine) and poly(phenylnaphthylamine) have been prepared in organic media by electrochemical polymerization. These poly(diarylamine) polymers are electroactive and exhibit multiple and reversible color changes depending on the oxidation state. The existence of polaron and bipolaron charge carriers is confirmed by spectroelectrochemistry and XPS. Poly(DPA) has a very high doping level and an electrical conductivity similar to those of poly(aniline) and poly(p-phenylene). Poly(PNA) presents a lower doping level and electrical conductivity, probably due to a nonplanar conformation and poor interchain contacts created by naphthyl groups. Contrary to poly(anilines), which were obtained by a head-to-tail C–N coupling mechanism, poly(diarylamines) are the result of a C–C aryl–aryl coupling mechanism with the incorporation of the aryl groups in the polymer backbone. In the case where the aryl is a phenyl group, a new class of conducting polymers (Figure 10B), intermediate between poly(aniline) and poly(p-phenylene), was obtained. The synthesis and characterization of new alkyl ring-substituted and N-substituted poly(diphenylamines) prepared by electrochemical and chemical polymerization are in progress in order to study the changes in the electronic state and the solubility of the conducting polymers induced by the introduction of alkyl groups on the polymer backbone.[60]

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