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Synthesis, Characterization, and Properties of Poly(*N*-alkylanilines)

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ABSTRACT: A series of soluble N-substituted poly(alkylanilines) have been chemically and electrochemically synthesized with alkyl groups ranging from methyl to *n*-dodecyl. The syntheses were made in 1.0 M perchloric acid using ammonium persulfate as oxidant or a constant-potential technique. The electrical and physical properties of the poly(*N*-alkylanilines) were investigated, and they were found to depend on the length of the substituents. These polymers also show multiple and reversible optical transitions that can be ascribed to the formation of polaron and bipolaron states.

Introduction

Conducting polymers with conjugated electronic structures have received considerable attention in recent years,[1,2] in particular aromatic polymers such as polypyrrole, polythiophene, polyaniline, etc. Among these polymers, polyaniline[3] has been intensively studied due to its good stability and its intriguing optical and electrochemical properties,[3] particularly in view of potential applications in light-weight batteries[4,5] and electrochromic devices.[6,7]

Polyaniline, which can be prepared either as thin films by electrochemical oxidation[8] or as powders by chemical means in aqueous acid[9] or organic solvents,[10] probably results from the preferential head-to-tail couplings between oxidized aniline species.[11] Chemically prepared polyaniline, which is built from the repeat unit ($-C_6H_4NHC_6H_4NHC_6H_4N{=}C_6H_4{=}N-$), can exist in various oxidation states characterized by the ratio of amine to imine nitrogen atoms.[12]

For useful applications, a conducting polymer must have, besides excellent electrochemical and mechanical properties, good stability and processability from solution or melt.[13] However, oxidized polyaniline, like many other conducting polymers, is not soluble in common organic solvents because of the stiffness of its backbone which results from its delocalized electronic structure. Recently several organic solvent soluble alkyl-[14-16] and alkoxy-[17] ring-substituted and alkyl-[18] and benzyl[19]-N-substituted polyanilines and even a water-soluble *N*-(propylsulfonyl)-substituted polyaniline,[20] all in the oxidized conducting form, have been prepared. The addition of side groups to polyaniline has enhanced its solubility and its processability and changed its properties.[14] However, only alkyl up to propyl-ring-substituted polyanilines can be prepared, and they are limited to low molecular mass (<10 000 g/mol).[14] The syntheses of poly(*N*-alkylanilines) by electropolymerization (molecular weights up to 20 000 for alkyl = butyl[18]) and of poly(*N*-benzylaniline) by both chemical and electrochemical polymerization (molecular weight higher than 100 000[19]) have been reported.

In this paper, we report on both chemical and electrochemical polymerization of *N*-alkylanilines (*N*-methyl, *N*-ethyl, *N*-propyl, *N*-butyl, *N*-pentyl, and *N*-dodecyl) in perchloric acid. The synthesized polymers are respectively termed as PMeA, PEtA, PPrA, PBuA, PPnA, and PDoA. They were characterized by visible, FTIR, and NMR spectroscopy, cyclic voltammetry, and steric exclusion chromatography. The electrochromic properties of the polymer thin films were determined by spectroelectrochemistry. The effect of the alkyl side chain on the polymerization yield, the average molecular weight, and the electrical and optical properties of the resulting polymers is presented.

Experimental Section

Materials. *N*-Alkylaniline derivatives were obtained from Aldrich Chemical Co., Inc., and TCI American Co. and were used without further purification. Reagent-grade ammonium persulfate, perchloric acid, ferric sulfate, and lithium perchlorate and HPLC-grade acetonitrile (ACN), tetrahydrofuran (THF), *N*-methylpyrrolidinone (NMP), chloroform, and dimethylformamide (DMF) were used as received.

Chemical Synthesis. Poly(*N*-alkylanilines) were synthesized by chemical oxidation of the monomers, using ammonium persulfate (30 mmol in 1.0 M $HClO_4$ aqueous solution) and ferric sulfate in a catalytic amount. The procedure consisted of the dropwise addition of the oxidant to the solution of the monomer (20 mmol in 1.0 M $HClO_4$) at room temperature and under an argon atmosphere. The mixture was vigorously stirred for several hours to continue the polymerization reaction. The polymer was then filtered, washed three times with 200-mL portions of 1.0 M

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Table I
Chemical Polymerization Yields and Electrical Conductivities of Chemically (ch) and Electrochemically (el) Prepared Poly(*N*-alkylanilines)

		conductivity ohm^{-1} cm^{-1}	
polymer	polymn yield, %	ch	el
PMeA	30	7×10^{-5}	2×10^{5}
PEtA	50	2×10^{-5}	1×10^{-6}
PPrA	50	9×10^{-7}	3×10^{-6}
PBuA	90	8×10^{-7}	2×10^{-7}
PPnA	90	6×10^{-6}	
PDoA	100	2×10^{-7}	

$HClO_4$ to remove excess monomer and oxidant, and finally dried under vacuum (48 h). The black powder obtained was in the oxidized form (doped with ClO_4^-).

Electrochemical Synthesis. Poly(*N*-alkylanilines) were deposited onto nickel foils by the electrochemical oxidation of solutions of monomers (0.05–0.10 M) in 1.0 M perchloric acid. For *N*-*n*-dodecylaniline, acetonitrile was used with 1.0 M $HClO_4$ in a 1:1 ratio to increase its solubility. The electropolymerization occurred at 1.0 V vs a Ag/AgCl reference electrode, and the auxiliary electrode was a platinum foil. The polymer powder collected onto the surface of the nickel electrode was washed with 1.0 M $HClO_4$ and dried under vacuum.

Physical Measurements. Cast films were prepared, using solutions containing 4–5 mg of oxidized polymer powder in 1 mL of acetonitrile for PMeA, PEtA, PPrA, PBuA, and PPnA or chloroform for PDoA, which evaporate easily, allowing the formation of a very thin polymer film (0.3–0.4 μm) onto an indium–tin oxide (ITO) glass electrode for electrochemical and spectroelectrochemical studies or onto a NaCl disk for FTIR spectroscopy. Elemental analyses were performed by Galbraith Co. on carefully dried samples. The conductivity of the polymers was determined by the van der Pauw technique,[21] using four equally spaced contacts on the periphery of a thin polymer pressed pellet (1 mm thick). Electrochemical studies were conducted using an EG&G PAR potentiostat (Model 362) and a BBC X-Y recorder (Model SE780). ^1H and ^{13}C NMR spectra of the polymers in deuterated chloroform were recorded with a Bruker WH-400 spectrometer. FTIR spectra of the polymers were recorded on a Bomem Michelson 100 spectrometer while a HP 8452A spectrophotometer was used for in-situ spectroelectrochemical studies. Solution and concentration studies (UV–visible–near-IR) of the polymers were conducted on a Philips PU8620 spectrophotometer. Solutions of polymers (3 mg/mL) in *N*-methylpyrrolidone (NMP) were used for molecular weight determination by steric exclusion chromatography (SEC). Molecular weight determinations were done at room temperature on a system including two Supelco trimethylsilyl-bonded phase columns (LC-1 and LC-301), a LKB pump (Model 2150), a ChemResearch absorbance detector (Model 2020) set at 280 nm, and a HP 3390A integrator. Monodisperse polystyrene standards from Supelco were used for the calibration of the system.[22]

Results

Synthesis, Solubility, and Conductivity. The polymerization yields of poly(*N*-alkylanilines) are presented in Table I. The yield increases markedly with the length of the alkyl group, from about 30% for PMeA up to 100% for PDoA. The doped polymers are very hygroscopic and can absorb a large amount of water in the air. The polymer obtained is powderlike in the cases of PMeA, PEtA, and PPrA; then it becomes more and more gumlike for polymers with longer N-alkyl substituents like *n*-butyl, *n*-pentyl, or *n*-dodecyl.

While the as-synthesized perchlorate-doped polyaniline is insoluble in most common solvents, doped poly(*N*-alkylanilines) synthesized by both chemical and electrochemical methods are soluble in numerous solvents as shown in Table II. This practical property of these polymers allowed us to proceed to their characterization using solution-cast films. One of the most useful solvents was acetonitrile in which we observed an increasing degree of solubility from PMeA to PPnA; all the polymers dissolved in NMP and DMF; they dissolved more or less in THF; finally, only PDoA was soluble in chloroform.

Table II
Solubility of Poly(*N*-alkylanilines)[a]

polymer	CH_3CN	$CHCl_3$	THF	NMP	DMF
PMeA	s	i	ss	s	s
PEtA	s	i	ss	s	s
PPrA	s	i	ss	s	s
PBuA	s	i	ss	s	s
PPnA	s	i	ss	s	s
PDoA	i	s	s	s	s

[a] s, soluble; ss, slightly soluble; i, insoluble.

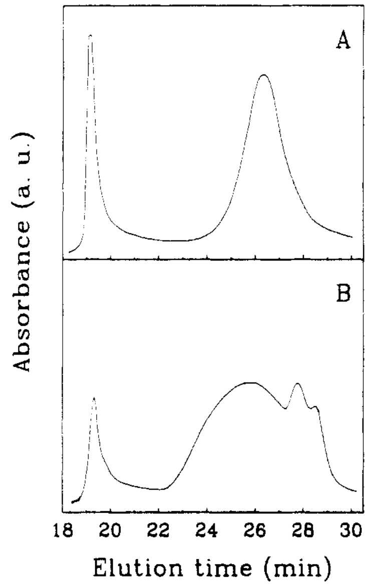


Figure 1. Steric exclusion chromatograms of chemically prepared PEtA (A) and electrochemically prepared PEtA (B).

Conductivity values obtained by the van der Pauw technique are presented in Table I. These values show that both chemically and electrochemically synthesized poly(*N*-alkylanilines) are semiconductor materials with conductivities ranging from 2×10^{-4} to 2×10^{-7} S/cm, much lower than that reported for polyaniline (5–10 S/cm).[14] Moreover, the polymer conductivity dropped with the alkyl chain length.

Steric Exclusion Chromatography. The steric exclusion chromatograms of chemically prepared PEtA (A) and electrochemically prepared PEtA (B) are shown in Figure 1. The elution pattern is quite the same from one polymer to another, regardless of the preparation method. One can see two distinct fractions, HP and LP, which correspond respectively to high molecular weight polymer (>10 000) and to oligomers (<2400) for chemically (Figure 1A) and electrochemically (Figure 1B) prepared PEtA. The main discrepancy appears in the low molecular weight fraction of electrochemically prepared PEtA, which is clearly trimodal. This is a general trend for electrochemically synthesized poly(*N*-alkylanilines).

The molecular weights of the HP fraction of chemically [MW(ch)] and electrochemically [MW(el)] synthesized poly(*N*-alkylanilines) dissolved in NMP are reported in Table III. These values range from 38 000 to 66 000, which confirm that the compounds are real polymers having high degrees of polymerization (D_p = 250–400).

UV–Visible and FTIR Spectroscopy. The UV-visible spectra of all the as-synthesized poly(*N*-alkylanilines) show essentially the same pattern as other N-substituted polyanilines[19,20,22,23] or unsubstituted poly-

Table III
Molecular Weights (MW) and Degree of Polymerization (D_p) of Electrochemically (el) and Chemically (ch) Polymerized Poly(*N*-alkylanilines)

polymer	MW (ch)	D_p(ch)	MW(el)	D_p(el)
PMeA	38 000	355	58 000	541
PEtA	43 000	355	44 000	363
PPrA	56 000	414	41 000	303
PBuA	52 000	348	44 000	295
PPnA	63 000	386		
PDoA	66 000	252		

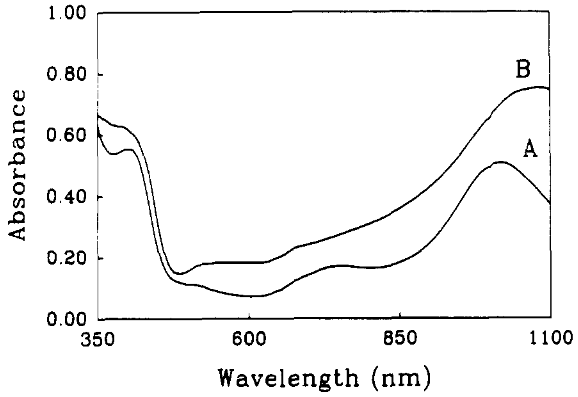


Figure 2. UV-visible–near-IR spectra of as-synthesized PPrA in acetonitrile: (A) chemically polymerized and (B) electrochemically polymerized.

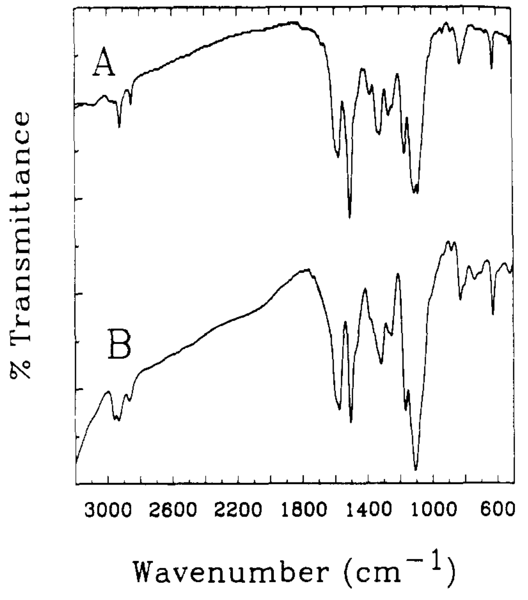


Figure 3. FTIR spectra (KBr pellets) of PEtA (A) and PPnA (B).

aniline. For the sake of clarity, only two spectra are shown in Figure 2: those of solutions of both chemically and electrochemically prepared PPrA in acetonitrile. These spectra are characteristic of moderately oxidized polymers. The onset of π–π^* absorption occurs at 350 nm, and the bands at 420 and 1000–1100 nm are related to polaron transition (benzenoid form) and the band at 730 nm to bipolaron transition (quinoid form), following the classical Scheme I. The qualitative differences between the spectra of chemically (Figure 2A) and electrochemically (Figure 2B) prepared polymers are small and appear to be mainly due to slight differences in the oxidation states (polaron or bipolaron) of the polymer.

Figure 3 shows the FTIR spectra of as-synthesized PEtA (Figure 3A) and PPnA (Figure 3B) in the 3200–500-cm^{-1} region. In fact, all poly(*N*-alkylanilines) present similar FTIR spectral patterns. The 3100–2800-cm^{-1} region is characteristic of C–H stretching vibrations; the aromatic C–H stretch, barely discernable due to the background absorption of charged species, is observed at 3080 cm^{-1} and the aliphatic C–H stretch of alkyl substituents at 3000–2800 cm^{-1}. The ring stretch of quinoid and benzenoid forms is observed at 1580 and 1500 cm^{-1},[22] respectively; the complex pattern of C–N stretch and C–H bend lies between 1400 and 1250 cm^{-1}; the vibrations due to the stretching modes of ClO_4^- counterions are at 1100 and 625 cm^{-1} and, finally, the presence of the band in the 810–830-cm^{-1} region is characteristic of the C–H out-of-plane bending vibrations of the para-substituted benzene ring. This latter observation confirms the expected head-to-tail coupling polymerization at the C-4 and N positions for poly(*N*-alkylanilines). In addition, the relative weakness of the band at 730–750 cm^{-1} (C–H out-of-plane bending vibrations of a monosubstituted terminal benzene ring) accounts for the high molecular weight of the polymers. Also, as stated by other workers,[24] the observed intensity ratio of the bands of the quinoid and benzenoid forms is characteristic of moderately oxidized polymers. This confirms the conclusion drawn from the UV-visible–near-IR spectra of Figure 2.

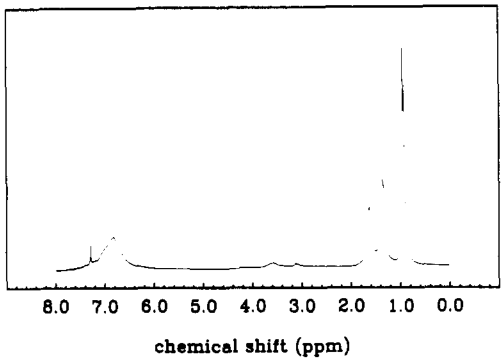
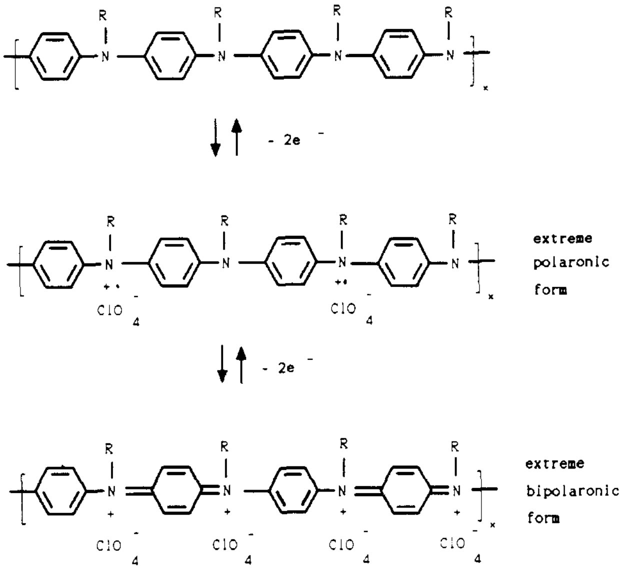


Figure 4. ^{1}H NMR spectrum ($CDCl_3$) of chemically reduced PBuA.

Scheme I



^{1}H and ^{13}C NMR Spectroscopy. Additional information about the polymer structures can be readily obtained from NMR spectroscopy. For example, the ^{1}H NMR spectrum of PBuA is shown in Figure 4. This polymer was chosen for its good solubility due to the relatively long alkyl chain. In addition, to avoid the presence of numerous peaks difficultly assigned due to charged species, the polymer was chemically reduced by hydrazine under an inert atmosphere. As seen in Figure

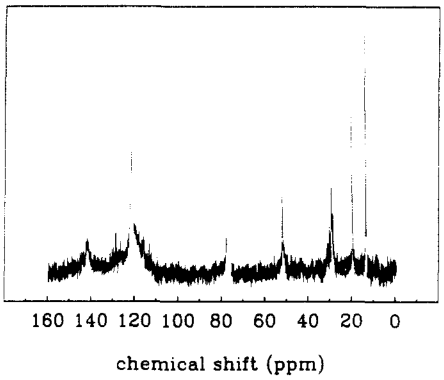


Figure 5. ^{13}C NMR spectrum ($CDCl_3$) of chemically reduced PBuA.

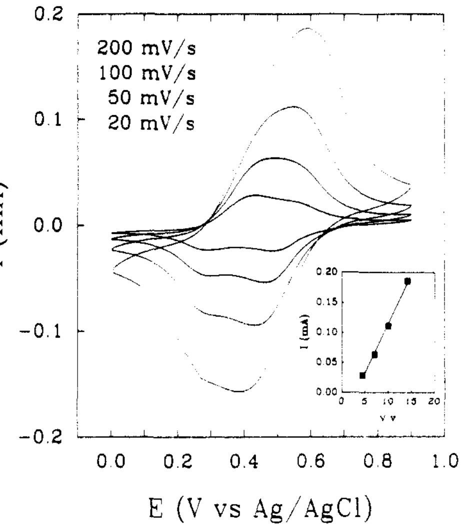


Figure 6. Cyclic voltammograms of PEtA in 1.0 M perchloric acid at different scanning rates.

4, the spectrum is quite simple: residual $CHCl_3$ in the deuterated solvent gives a peak (used as an internal reference) at 7.25 ppm, aromatic protons give a broad peak around 6.8 ppm, the protons of the methylene bonded to the nitrogen (C1) of the butyl group appear as a small peak at 3.07 ppm, and the protons of the other methylene groups (C2–C3) appear at 1.64 and 1.37 ppm and the terminal methyl group (C4) at 0.95 ppm. These assignments were made by comparison with the spectrum of the monomer *N*-butylaniline in $CDCl_3$ at 400 MHz which has the phenyl protons at 7.2–6.6 ppm (m, 5 H), the NH proton at 5.37 ppm (s, 1 H), the NCH_2 protons at 3.06 ppm (quad, 2 H), the CCH_2CH_2C protons at 1.63 ppm (quint, 2 H) and 1.47 ppm (hex, 2 H), and the terminal methyl protons at 1.02 ppm (t, 3 H). The absence of a peak near 5.4 ppm due to N-bonded protons in the polymer spectrum (Figure 4) also confirms the expected head-to-tail addition of the monomer during the polymerization.

Also, the ^{13}C NMR spectrum of chemically reduced PBuA was recorded, and it is shown in Figure 5. Once again, the spectrum is quite simple. There are two absorptions due to carbon atoms on the ring: according to some authors,[24-26] the benzenoid carbon atoms absorb at 121.5 ppm, while the quinoid ones absorb at 142.5 ppm. The carbon atoms of the butyl substituent absorb as observed for aliphatic alkylamines,[27] from the N-bonded carbon atom to the terminal methyl carbon, the absorptions occur at 52.5, 30, 20.5, and 14.5 ppm. The peak at 76 ppm is attributed to $CDCl_3$, and it is used as an internal reference.

Cyclic Voltammetry. Cyclic voltammetry curves of poly(*N*-alkylanilines) recorded at different scan rates between −0.1 and 1.0 V vs Ag/AgCl in 1.0 M perchloric acid show that they are electroactive polymers. No significant difference was observed between chemically and electrochemically synthesized polymers. A typical voltammogram is shown in Figure 6 for the electrochemically prepared PEtA polymerized on ITO glass. At a very low scan rate (20 mV/s), the polymer films show two oxidation peaks and two reduction peaks corresponding to the E_{pa} and E_{pc} values for the electrodeposited poly(*N*-alkylanilines) presented in Table IV. The inset of Figure 6 shows a linear relationship between the current and the square root of the scan rate, indicating that insertion/deinsertion of the perchlorate counterion into the polymer matrix is a diffusion-controlled process.[28,29]

Table IV
Cyclic Voltammetry Data (V) for Electrodeposited Poly(*N*-alkylanilines) in 1.0 M Perchloric Acid versus Ag/AgCl Reference Electrode at a Scan Rate of 20 mV/s

polymer	E_{pa1}	E_{pa2}	E_{pc1}	E_{pc2}
PMeA	0.32	0.55	0.25	0.49
PEtA	0.42	0.56	0.28	0.49
PPrA	0.45	0.56	0.40	0.50
PBuA	0.54	0.67	0.44	0.55
PPnA	0.50	0.58	0.45	0.50
PDoA	0.60	0.70	0.50	0.62

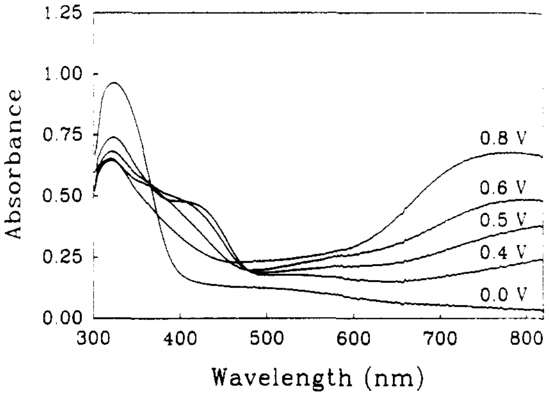


Figure 7. Absorption spectra of a PDoA film on ITO glass dipped in 1.0 M $LiClO_4$/acetonitrile at various applied potentials.

In correlation with the cyclic voltammetry, the polymer films exhibited electrochromic properties; i.e., they changed their colors with the applied potentials. The electrochromic effect is reversible, and it is much stronger for PMeA, PEtA, and PPrA than for PBuA, PPnA, and PDoA. For the first three polymers, the color varies from colorless (0.0 V) to yellow (0.3–0.4 V) to green (0.5 V), and to blue (0.7 V). For PBuA, PPnA, and PDoA, the variations go from yellow (0.2–0.3 V) to green (0.5 V), and to blue (0.7 V).

Spectroelectrochemistry. The optical properties of thin films of poly(*N*-alkylanilines) cast on ITO glass were studied in situ by spectroelectrochemistry in 1.0 M perchloric acid, except for PDoA which is not electroactive in this media. Its spectroelectrochemical properties were studied in acetonitrile using lithium perchlorate (1.0 M) as the supporting electrolyte, as seen in Figure 7. The spectroelectrochemical behavior is less pronounced than for other poly(*N*-alkylanilines), but it is still remarkable, taking into account that a very long alkyl chain is attached to the polymer backbone. The polymer film is pale yellow from 0.0 to 0.3–0.4 V; when the potential is increased at 0.3–0.4 V, an absorption band appears at 420–430 nm; at 0.5 V, the absorbance at 420–430 nm reaches its maximum. Meanwhile, a growing absorption band is observed in the 700–800-nm region, and the film turns to green; at higher potential (0.7–0.8 V), the polymer film becomes blue while a significant hypsochromic shift of this latter absorption band occurs in the 500–600-nm region. Also, one can see two main isosbestic points at 367 and 478 nm, indicating that probably a stoichiometric transformation of one species to another occurs when the applied potential is increased from 0 to 0.6 V. For the curve recorded at 0.8 V, the loss of the isosbestic point is expected since a new species begins to appear near 500 nm. There is no longer a simple transformation of one species to another one but the appearance of a large number of quinoid forms.[30] These observations are also valid for PBuA and PPnA; but in the case of PMeA, PEtA, and PPrA, in the reduced state, i.e., at 0.0 V, the polymer films are colorless; then they change to yellow at 0.3–0.4 V, to green at 0.5 V, and to blue at 0.7–0.8 V.

Discussion

It was recently shown that the polymerization yield of ring-substituted poly(alkylanilines) is strongly affected by the nature of the substituent.[14] Thus, the longer the substituent, the lower the polymerization yield. The results of Table I show exactly the opposite behavior for chemically prepared poly(*N*-alkylanilines); the polymerization yield increases markedly when the substituent becomes bulkier. This result seems to be very surprising, but it can be explained in terms of the solubility of the monomers in the polymerization media, viz. 1.0 M perchloric acid. The solubility of the *N*-alkylanilines decreases gradually when the length of the N-bonded side chain increases from methyl to *n*-dodecyl. In the latter case, a slight heating of the reaction mixture is needed to ensure complete dissolution. During the polymerization, such an hydrophobic behavior leads to the formation of micelles in which monomer is in high concentration. Consequently, higher yields are expected when the formation of micelles is favored since the high local concentration of monomer increases the overall probability of reaction.[31]

Chemically or electrochemically polymerized poly(*N*-alkylanilines) are insoluble in 1.0 M $HClO_4$, but they are soluble in most common solvents, as shown in Table II. This implies that the introduction of bulk alkyl groups into the polymer backbone is an efficient way of increasing its solubility. The enhanced solubility of poly(*N*-alkylanilines) allows us to prepare free-standing films, using solutions containing 14 mg of polymer in 1 mL of NMP. The solutions were deposited onto microscope slides (4 cm^2), and the evaporation of the solvent was performed at 45 °C during 48 h. The remaining polymer films were removed from the glass substrate by water dipping and then dried at room temperature and will be used for future investigations.

As previously observed for unsubstituted polyaniline,[32-35] well-separated bimodal molecular weight distributions are also obtained for either ring-substituted or N-substituted poly(alkylanilines) as seen in Figure 1. According to other workers,[34] such bimodal elution patterns can be explained by several possible causes: (1) the existence of an aggregation phenomenon, (2) cross-linking during the polymerization, (3) the presence of polymer chains having different oxidation states, and (4) the coexistence of different mechanisms of polymerization. The aggregation phenomenon can be ruled out since polymer solutions were found to be real ("true", i.e., following the Lambert–Beer law) solutions.[35] Also, the extent of any cross-linking reaction should be very low since linkage between repeat units appears to be mainly head-to-tail, as shown on the FTIR spectra of Figure 3. Actually, it is not yet possible to either confirm or discredit the two other possibilities. Differences in the oxidation state seem to modify the peak area ratio of high to low polymer fractions HP/LP for unsubstituted polyaniline,[35] a high oxidation state leading to a major increase of the LP fraction and vice versa. However, it remains impossible yet to check if polymer chains can bear different oxidation states from a single polymerization reaction. Moreover, from the available experimental data on the polymerization of aniline or its derivatives, there is no clear indication for the existence of more than one reaction mechanism.

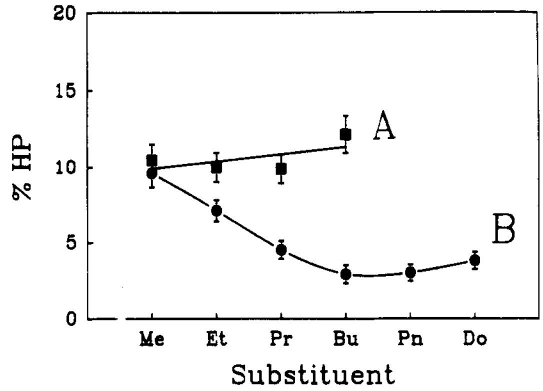


Figure 8. Variation of the percent of high polymer species, % HP, with the length of the substituent for electrochemically prepared polymers (A) and chemically prepared polymers (B).

SEC analyses have also shown that there is no clear relation between the degree of polymerization (D_p) of chemically prepared polymers and the nature of the substituent, as shown on Table III. PDoA has a slightly lower D_p value than the other polymers, but this is due to the far greater length of its side chain compared to other members of the series. The apparent rise of the molecular weight of the chemically prepared polymers from PMeA to PDoA is an artifact since the molecular weight of the repeating unit increases gradually from methyl- to *n*-dodecyl-substituted anilines. Nevertheless, a clear relationship between D_p and the length of the substituent can be seen for the electrochemically prepared polymers. The observed decrease of D_p from PMeA to PBuA can be attributed to a more difficult approach to the working electrode by the monomer units due to the higher steric hindrance of bulkier substituents.

Another striking feature obtained from SEC chromatograms of poly(*N*-alkylanilines) is shown on Figure 8. One can see the percent of high polymer (% HP) computed by integration of the corresponding peak as a function of the nature of the substituent. If there is no evidence of correlation for electropolymerized polymers (curve A), curve B shows a slight decrease of % HP followed by a plateau for the series of chemically prepared polymers. This behavior is explained by the decreasing solubility of the monomers in the polymerization media as mentioned earlier. The more gumlike the polymer, the more difficult the addition of new monomer units. From *n*-butyl to bulkier groups, the gumlike behavior is well established and no significant variations of % HP are noticed. These observations are corroborated by the FTIR spectra of Figure 3. The band of the monosubstituted terminal benzene rings at 730–750 cm^{-1} is more intense for PPnA than for PEtA, indicating that more oligomers are present.

Four-probe conductivity measurements (Table I) show two distinct behaviors: first a considerable decrease in conductivity occurs going from unsubstituted polyaniline to the first term of the series (PMeA) and then a regular but less accentuated decrease of conductivity occurs for the other members of the series when the alkyl side chain becomes longer. Other workers report the same behavior for PMeA, PEtA, PPrA, and PBuA.[22,23] To understand these variations, one can consider three distinct effects; a possible variation of the doping level with the alkyl chain length due to steric hindrance, the variation of the conjugation length, and the increase of the interchain distance.

First, the effect of the variation of the doping level with the length of the alkyl side chain can be ruled out. Since the electrochemically prepared polymers were synthesized at 1.0 V vs Ag/AgCl; i.e., after the second oxidation peak, the doping level should have reached its maximum value. As seen in Table I, conductivity values of electrochemically prepared polymers do not differ significantly from those of chemically prepared polymers. This indicates that the chemically synthesized polymers are almost fully oxidized and that the decrease of their conductivity values does not depend on their doping level.

Also, by comparing the values shown in Table IV, one can establish a clear relationship between the bulkiness of the alkyl substituents and the electrochemical properties of the polymers. The E_{pa} values show an almost regular increase from PMeA to PDoA. Such a phenomenon was already observed for poly(3-alkylthiophenes) by several workers.[36,37] The presence of increasingly bulky substituents induces additional deformations along the polymer backbone due to increasing steric hindrance. Consequently, the degree of conjugation decreases markedly from PMeA to PDoA and the oxidation potential increases.[38]

However, the great difference between the conductivities of unsubstituted polyaniline and those of N-substituted polymers cannot be explained only by the variations of the conjugation length. Therefore, it appears that another limiting factor in the achievement of high conductivities is the interchain conductivity. From polyaniline to PMeA, the presence of a more nonconductive material in PMeA, as well as the augmentation of the interchain distance due to the methyl group and the decrease of the conjugation length, explains the noticed decrease in conductivity. For the other members of the series, i.e., from PEtA to PDoA, the gradual decrease of the conjugation length accounts for the less rapid decrease of the conductivity.

As shown for electropolymerized PEtA in Figure 6, cyclic voltammograms of poly(*N*-alkylanilines) exhibit some qualitative similarities with those of unsubstituted polyaniline. One can see (at least at 20 mV/s) two distinct pairs of peaks, although they are closer together than for polyaniline. N-alkyl-substituted polymers are electrochromic since fully reversible color changes are observed when the potential is swept between 0.0 and 1.0 V vs Ag/AgCl. According to other workers,[22,23,39,40] the peaks are ascribed to polaronic and bipolaronic transitions for the first and second peaks respectively, as seen in Scheme I. For the sake of clarity, the transitions are depicted as extreme forms, the observed doping level always being lower than 100%. In fact, elemental analyses give a Cl to N ratio of 0.70 for combined protonated (-NHR-) and oxidized (=NR-) species. Finally, the changes observed in the UV-visible spectra of Figure 7 can be attributed to the transitions already described in Scheme I.

Conclusion

In this paper, we have investigated the effect of the length of the substituent of a series of chemically and electrochemically synthesized poly(*N*-alkylanilines) on their physical and electrical properties. These polymers are soluble in common organic solvents and they are therefore readily processable. Steric exclusion chromatography, as well as FTIR spectroscopy, shows that the polymers have a fraction with quite high molecular weights. Consequently, free-standing films can be easily prepared from solution in the proper solvent. In addition, FTIR and NMR spectroscopies show that polymer chains are consistent with the linear structure.

The poly(*N*-alkylanilines) are electroactive materials which show an interesting and fully reversible electrochromic behavior but somewhat low electrical conductivities in the doped form. The decrease of conductivity compared to that of unsubstituted polyaniline is attributed to simultaneous decreases of both intrachain and interchain contributions to the overall conductivity. Although the poly(*N*-alkylanilines) are easily processable, their electrical conductivities are too low for most potential applications.

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References and Notes

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Registry No. PMeA (homopolymer), 27082-18-4; PEtA (homopolymer), 88374-64-5; PPrA (homopolymer), 120743-26-2; PBuA (homopolymer), 120743-27-3; PPnA (homopolymer), 130463-78-4; PDoA (homopolymer), 133394-66-8; $HClO_4$, 7601-90-3; $[(HO)S(O)_2]_2O_2{\cdot}2NH_3$, 7727-54-0.