Electrical and Physical Properties of New Electrically Conducting Quasi Composites. Poly(aniline-*co*-*N*-butylaniline) Copolymers

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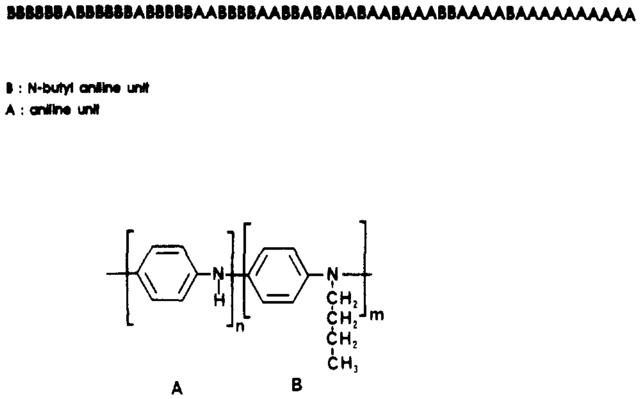
ABSTRACT: A series of poly(aniline-*co*-*N*-butylaniline) copolymers has been chemically synthesized in 0.1 M perchloric acid with ammonium persulfate as oxidant. The composition of the resulting copolymers has been determined by ^{1}H NMR analysis. The electrical and physical properties of the copolymers were also investigated, and they were found to depend strongly on the actual composition. The poly(aniline-*co*-*N*-butylaniline) copolymers show a percolation transition in the conductivity for aniline contents higher than 15%. They are probably the first known example of a "quasi composite" where both conducting and insulating segments are located within the same macromolecule.

Introduction

In the past few years, aromatic conducting polymers such as polypyrrole, polythiophene, or polyaniline have received considerable attention owing to their good electrical, optical, and electrochemical properties.[1,2] Among these polymers, a great deal of work was devoted to polyaniline which can be readily used in applications such as light-weight batteries[3,4] and electrochromic devices.[5,6] However, due to the stiffness of its backbone, polyaniline is almost insoluble in common organic solvents.[7] Consequently, its postsynthesis processability is quite difficult. In most cases, the solubilization of a polymer can be achieved through functionalization of the starting material with a suitable side chain prior to polymerization. On the one hand, alkyl-ring-substituted polyanilines show good conductivities (>0.1 S/cm), but they are mainly limited to low molecular weight species.[8,9] On the other hand, poly(*N*-alkylanilines) are soluble high molecular weight polymers, but their conductivities remain low (10^{-3}–10^{-7} S/cm).[10–14] Considering these data, of great interest should be the synthesis of a material combining the conductivity of polyaniline and the solubility of poly(*N*-alkylanilines). Therefore, the copolymerization of aniline with a suitable solubilizing comonomer should lead, upon proper adjustment of the copolymer composition, to a soluble *and* conducting material.

Until recently, this strategy was used only by a few workers for the synthesis of new aromatic conducting polymers. Pure pyrrole and thiophene monomers were copolymerized respectively with *N*-alkylpyrroles[15] and 3-alkylthiophenes[16–18] while the copolymerization of a mixed system of aniline and thiophene comonomer precursors was also attempted.[19] The synthesis of copolymers having a polyaniline backbone was performed with halogen- or alkyl-ring-substituted aniline comonomers[20,21] or with *N*-methylaniline comonomers,[22–24] but very little was known about the tractability/conductivity behavior of these materials. In this paper, we report on the chemical synthesis of a series of poly(aniline-*co*-*N*-butylaniline) copolymers PABA (Scheme I). The resulting copolymers have been characterized by various experimental techniques. The copolymers have been found to exhibit a unique behavior in the variation of their electrical conductivities. Estimates of composition and computation of the reactivity ratios of the comonomer pair were also performed. Results are discussed on the basis of electron-withdrawing and steric effects of the alkyl side chain and of the percolation transition theory.

Scheme I



Experimental Section

Materials. The monomers, aniline (ACS reagent, Anachemia) and *N*-*n*-butylaniline (American Tokyo Kasei, Inc.), were used without further purification. Reagent-grade ammonium persulfate, iron(II) sulfate, perchloric acid, and ammonium hydroxide and HPLC-grade acetonitrile, dimethylformamide, and *N*-methylpyrrolidinone were also used as received. Deuterated dimethyl sulfoxide, used for ^{1}H NMR measurements, was purchased from Aldrich Chemical Co., Inc.

Chemical Synthesis. The perchlorate salts of both poly(aniline-*co*-*N*-butylaniline) copolymers and the corresponding polyaniline and poly(*N*-butylaniline) homopolymers were synthesized in a 1.0 M aqueous solution of perchloric acid by chemical oxidation with ammonium persulfate in the presence of a catalytic amount of iron(II) sulfate according to a published procedure.[8] Various molar fractions of aniline (component 1) in the feed ranging from 0.50 to 0.95 produced copolymers which are referred to by the following terms: 50-PABA, 63-PABA, 69-PABA, 75-PABA, 85-PABA, and 95-PABA. Also, the monomer/oxidant ratio was kept constant at a value of 1.5. A typical copolymerization reaction can be detailed as follows. First, a comonomer solution (f_1 = 0.75) of 2.82 g (30.2 mmol) of aniline and 1.50 g (10.0 mmol) of *N*-butylaniline in 200 mL of 1.0 M perchloric acid was prepared, and a few crystals of iron(II) sulfate were added as a catalyst. A solution of 13.69 g (60.0 mmol) of ammonium persulfate in 50 mL of 1.0 M perchloric acid was then added dropwise to the comonomer solution within 15 min with vigorous stirring at room temperature and under an argon atmosphere. The reaction mixture was further stirred for 23 h and then filtered through a Buchner funnel. The resulting finely powdered copolymer was washed with 1.0 M perchloric acid until the filtrate became colorless. Finally, the copolymer was stirred with five

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Table I
Comonomer Feed Composition f_1, Composition of the Copolymers F_1, and Solubility (in Acetonitrile) of the Synthesized Polymers[a]

f_1	F_1	solubility	f_1	F_1	solubility
0.00	0.00	100	0.75	0.36	11
0.50	0.12	100	0.85	0.56	3
0.63	0.20	100	0.95	0.84	<1
0.69	0.24	100	1.00	1.00	<1

[a] Aniline and *N*-butyl aniline are respectively components 1 and 2.

successive 200-mL portions of 1.0 M perchloric acid, filtered, and dried under vacuum for several days. To obtain the base form of the copolymer, 1.25 g of the finely ground perchlorate salt were stirred 3 h in 250 mL of a 0.1 M aqueous solution of ammonium hydroxide. The resulting deep blue powder was then filtered and dried under vacuum for 48 h.

Physical Measurements. Solutions of the base form of the copolymers (0.5 mg/mL) in dimethylformamide were used for molecular weight determination by steric exclusion chromatography (SEC). Molecular weight determinations were conducted at 45 °C on a system including LC-1 and LC-301 Supelco trimethylsilyl-bonded phase columns, a LKB pump (Model 2150), a ChemResearch absorbance detector (Model 2020) set at 280 nm, a HP 3390A integrator, and a Shimadzu column oven (Model CTO-6A). The system was calibrated with monodispersed polystyrene standards from Supelco. ^{1}H NMR spectra of the polymers were recorded at room temperature from 1% (w/v) solutions in dimethyl-d_6 sulfoxide on a Bruker WZH-400 spectrometer operating at 400 MHz. The residual proton signal of dimethyl sulfoxide at 2.50 ppm was used as an internal standard. FTIR spectra of the polymers (pressed KBr pellets) were recorded on a Bomem Michelson 100 spectrometer. The conductivity of the polymers was determined by a four-probe in-line method using a Keithley 197 digital multimeter and a Keithley 616 digital electrometer. The measurements of the oxidation potentials of the monomers were conducted in 1.0 M perchloric acid using 10^{-3} M solutions of the monomers. The analyses were done with an EG&G PAR scanning potentiostat (Model 362) and a BBC X-Y recorder (Model SE780), using a Ag/Ag$^+$ reference electrode and platinum wires as a counterelectrode and a working electrode. Spectroelectrochemical measurements were conducted in situ on polymer thin films cast onto indium–tin oxide (ITO) glass elctrodes from solutions of the perchlorate salts of the polymers in *N*-methylpyrrolidinone (3 mg/mL) dipped in 1.0 M perchloric acid with a HP 8452A diode array spectrophotometer, a platinum wire as the counterelectrode, and a Ag/Ag$^+$ reference electrode. Prior to the film casting, ITO glass electrodes were coated with a thin layer of platinum using a Hummer X sputter coater in order to enhance film adherence.

Results and Discussion

Synthesis. Several poly(aniline-*co*-*N*-butylaniline) copolymers and their corresponding homopolymers were chemically synthesized, giving in all cases a dark blue–green granulous precipitate in high yields (above 90%). The various comonomer feed compositions f_1 (in mole fractions of component 1, aniline) are shown in Table I. The resulting materials are more and more finely powdered as the mole fraction of aniline in the feed increases. The copolymer compositions F_1 (in mole fractions of aniline units) were calculated from the ^{1}H NMR data. The copolymers give resonance peaks of variable intensity at around 7–8 ppm for the aromatic protons of both $-C_6H_4-NH-$ and $-C_6H_4NCH_2CH_2CH_2CH_3-$ units, at 2.9 ppm for the two protons of the C1 methylene group bonded to the nitrogen, at 1.50 and 1.31 ppm for the four protons of the C2 and C3 methylene groups, and at 0.87 ppm for the three protons of the methyl group (Scheme I) as shown in Figure 1 for the 50-PABA copolymer. The strong resonance at 3.4 ppm is due to adsorbed water in both solvent and copolymer. The integration of the peaks of both aromatic and methyl protons gives the proportion of components 1 (aniline units) and 2 (*N*-butylaniline units) in the copolymer chain. These results are listed in Table I, and the relation between the comonomer feed composition f_1 and the copolymer composition F_1 can be seen in Figure 2. The observed behavior indicates that the aniline comonomer is far less reactive than the *N*-butylaniline comonomer and that any copolymer will be enriched in *N*-butylaniline compared to the comonomer feed composition.

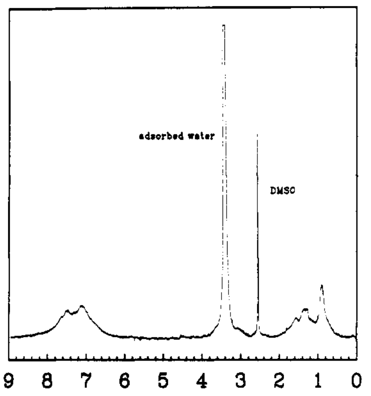

Figure 1. ^{1}H NMR spectrum of copolymer 50-PABA in deuterated DMSO.

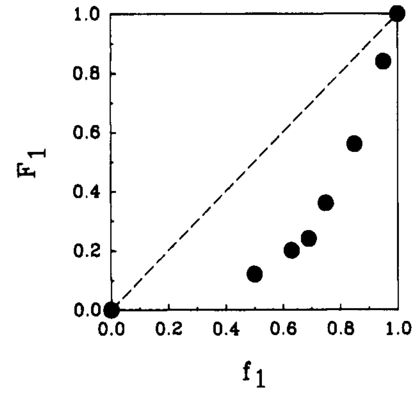

Figure 2. Variation of the copolymer composition F_1 (mole fraction of aniline units in the copolymer) with the comonomer feed composition f_1 (mole fraction of aniline in the feed).

From the data listed in Table I, one can evaluate the reactivity ratios r_1 and r_2 for the system aniline/*N*-butylaniline using the following Mayo–Lewis equation.[25]

$$r_2 = \left[\frac{1-F_1}{F_1}\right]\left[\frac{f_1}{1-f_1}\right]^2 r_1 + \left[\frac{f_1}{1-f_1}\right]\left\{\left[\frac{1-F_1}{F_1}\right] - 1\right\}$$

Knowing both f_1 and F_1 for each separate copolymerization of the series, it is possible to compute for each one a straight-line equation of r_2 as a function of r_1. As shown in Figure 3, the best approximation of the coordinates of the intersection of these straight lines on a graph of r_2 versus r_1 gives the reactivity ratios for the comonomer system. Taking into account experimental error, values of 0.4 and 8.9 are obtained for r_1 and r_2, respectively. Although the Mayo–Lewis equation is believed to give results having limited accuracy at high conversion or when r_1 and r_2 differ widely,[26,27] a recent work on the electrochemical copolymerization of pyrrole and bithiophene[28] shows that reactivity ratios computed using the Mayo–Lewis equation are quite similar to those computed by the very accurate nonlinear error-in-variables method proposed by O'Driscoll and co-workers.[26,27] As for the co-

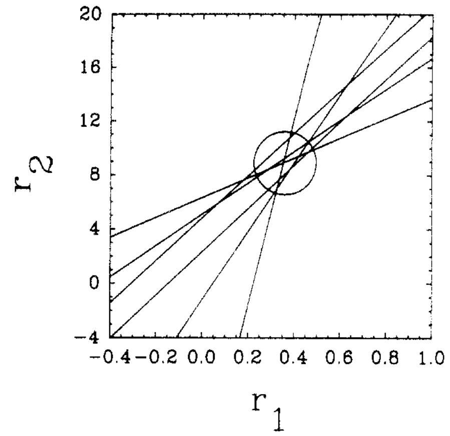

Figure 3. Determination of reactivity ratios r_1 and r_2 by the slope intersection method (Mayo–Lewis equation). The circle represents the most probable area for r_1 and r_2 values.

polymerization of pyrrole and N-substituted pyrrole,[15] the reactivities of the comonomers are strongly controlled by their oxidation potentials E_{pa}. By a cyclic voltammetry study of dilute solutions of the monomers in 1.0 M perchloric acid, we found the E_{pa} to be respectively 1.01 and 0.78 V versus Ag/Ag$^+$ for aniline and *N*-butylaniline. The inductive effect of the butyl substituent, which efficiently stabilizes the radical cations formed on the nitrogen atom, accounts for the lower E_{pa} value of this comonomer compared to aniline. These observations are consistent with the far greater reactivity ratio computed for *N*-butylaniline than for unsubstituted aniline.

Owing to these reactivity ratios, the problem of the monomer compositional drift in the reaction mixture must be considered. The monomer which is consumed faster, i.e., *N*-butylaniline, will be depleted from the polymerizing mixture, and the composition of the remaining comonomers will shift. Consequently, the composition of the copolymer being produced at the moment will shift too. At an early step of the reaction, mostly relatively long *N*-butylaniline sequences should be formed with only a few intercalations of aniline units. As the *N*-butylaniline comonomer is depleted, the length of its sequences is lowered and the length of the aniline sequences increases regularly, while at a later step of the reaction, mostly long sequences of aniline units should grow. Computation of the average sequence length m_1 of aniline units gives values ranging from 1.4 (50-PABA) to 7.8 (95-PABA). However, such a computation does not take into account the depletion of the *N*-butylaniline content in the reaction vessel, so the m_1 values for the last terms of the series (copolymers 75-, 85-, and 95-PABA) are probably greatly underestimated. Consequently, for identical reaction times, typical copolymer chains should have a nearly block structure and be formed of two almost homogenous terminal aniline or *N*-butylaniline segments of variable length separated by a more heterogenous interval of shorter sequences of both comonomers as depicted in Scheme I.

Finally, the PABA copolymers are soluble in solvents such as *N*-methylpyrrolidinone or dimethylformamide, their solubility in acetonitrile was also checked, and the results are shown in Table I. The measured solubilities are excellent up to an aniline unit content F_1 of 0.24 (copolymer 69-PABA). The polyaniline and poly(*N*-butylaniline) homopolymers show respectively low and high solubilities in the same organic solvent. Free-standing films of the copolymers (5 cm^2) can be easily obtained by evaporation at 120 °C of 1% (w/v) solutions in *N*-methylpyrrolidinone. The films are hard and brittle since they are made of doped material.

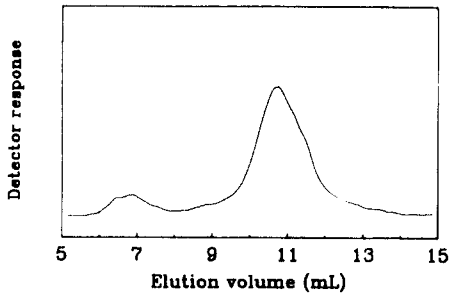

Figure 4. Exclusion chromatogram of the copolymer 95-PABA.

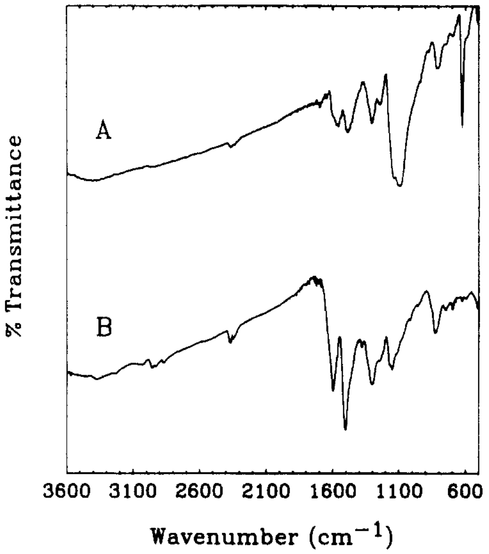

Figure 5. Transmission FTIR spectra of (A) the doped form and (B) the base form of the copolymer 69-PABA.

Table II
Molecular Weights (MW) of the Base Form of the Chemically Synthesized PABA Copolymers and Related Homopolymers[a]

polymer	MW HP	MW LP	polymer	MW HP	MW LP
poly(*N*-butylaniline)	75 000	3000	75-PABA	620 000	4000
50-PABA	525 000	3000	85-PABA	525 000	6000
63-PABA	540 000	4000	95-PABA	525 000	6000
69-PABA	650 000	6000	polyaniline	620 000	6000

[a] First entry: high MW fraction HP. Second entry: low MW fraction LP.

Steric Exclusion Chromatography (SEC). Figure 4 shows a typical exclusion chromatogram of a copolymer (95-PABA) which is sparingly soluble in acetonitrile but completely soluble in dimethylformamide. Two well-defined elution peaks can be seen. The less intense peak is ascribed to a very high molecular weight fraction HP (525 000 and 15% area) and the other to a somewhat lower molecular weight fraction LP (6000 and 85% area). This bimodal distribution is observed for all of the copolymers as well as for the homopolymers. The molecular weights of both high and low molecular weight fractions of the synthesized polymers are given in Table II. These values are believed to be overestimated since conducting polymer chains, which are known to have a rigid-rod conformation in solution,[7] have a higher hydrodynamic volume than the more flexible polystyrene chains used for the calibration.

FTIR Spectroscopy. Figure 5 shows transmission FTIR spectra of both the doped form (Figure 5A) and the base form (Figure 5B) of a typical poly(aniline-*co*-*N*-butylaniline) copolymer (69-PABA). They exhibit numerous characteristic bands common to polyaniline-like homopolymer spectra.[10,29,30] First, the C–H out-of-plane

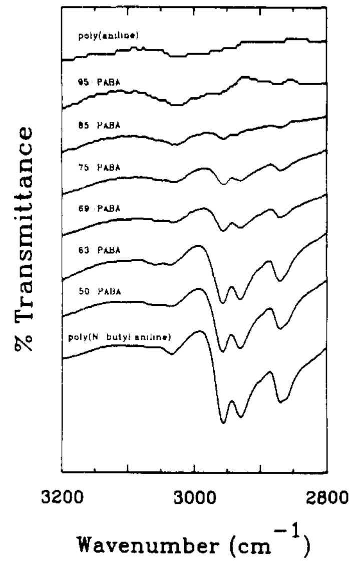

Figure 6. Transmission FTIR spectra of the C–H and C–N stretching bands of the base form of the PABA copolymers and of the related homopolymers.

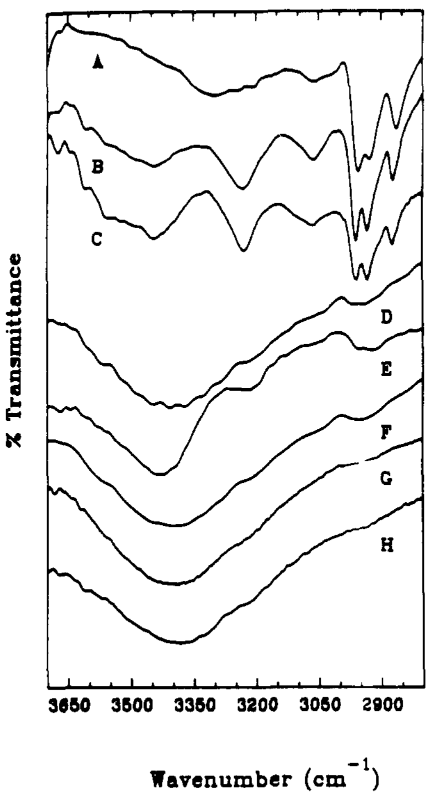

Figure 7. Transmission FTIR spectra of the N–H and C–H stretching bands of the doped PABA copolymers and of the related homopolymers: (A) poly(*N*-butylaniline), (B) 50-PABA, (C) 63-PABA, (D) 69-PABA, (E) 75-PABA, (F) 85-PABA, (G) 95-PABA, (H) polyaniline.

Table III
Electrical Conductivities of the PABA Copolymers

polymer	conductivity, S/cm	polymer	conductivity, S/cm
poly(*N*-butylaniline)	8×10^{-7}	75-PABA	0.4
50-PABA	6×10^{-7}	85-PABA	0.3
63-PABA	2×10^{-5}	95-PABA	0.2
69-PABA	0.2	polyaniline	0.3

bending band located near 812 cm^{-1} in both spectra is ascribed to a para-substitution pattern, indicating that a head-to-tail coupling occurs during the polymerization. No bands due to other substitution patterns (meta, ortho, or mono) are clearly observed. This means that the copolymers are relatively free of chain defects and that the degree of polymerization is quite large, as shown by SEC analyses. On the other hand, the main differences between these spectra occur in the 1100- and 625-cm^{-1} regions (perchlorate counterion stretching bands) and between 3600 and 2800 cm^{-1} (N–H and C–H stretching bands). The treatment with 0.1 M ammonium hydroxide accounts for the observed decrease of the perchlorate bands in the spectrum of Figure 5B.

In the 3600–2800-cm^{-1} region of the spectrum of doped 69-PABA, the intense absorption background is attributed to the presence of charged species (amine salts) which give numerous and broad absorption bands between 3000 and 2200 cm^{-1}. This background adsorption disappears in the spectrum of Figure 5B due to the alkali treatment. In the spectra of the base form of PABA copolymers shown in Figure 6, one can see the aliphatic C–H and C–N stretching bands at 2955, 2928, and 2868 cm^{-1} whose intensities vary with the copolymer composition F_1, while the aromatic C–H stretching band at 3060 cm^{-1} remains practically unchanged. The absorption of the aliphatic bands decreases markedly as the effective aniline unit content F_1 is raised from poly(*N*-butylaniline) ($F_1 = 0$) to polyaniline ($F_1 = 1$).

Finally, the variation of the N–H stretching band pattern of the doped PABA copolymers (in the 3600–2800-cm^{-1} region) with their composition F_1 is shown in Figure 7. A strong qualitative pattern change occurs for the polymers having a higher aniline unit content than 63-PABA. For pure poly(*N*-butylaniline), 50-PABA, and 63-PABA copolymers, the spectra of parts A–C of Figure 7 show nearly the same aspect. In addition to C–H and C–N stretching bands, one can see the band of secondary unassociated ("free") N–H stretching at 3450 cm^{-1} [31] and a band arising from H-bonded NH groups near 3250 cm^{-1}.[30,31] The spectrum of pure poly(*N*-butylaniline) (Figure 7A) shows no free NH group band, since only tertiary amines are present, and a vanishing H-bonded band near 3273 cm^{-1} is probably due to protonated amine salts. For the spectra of copolymers 69-PABA to 95-PABA (Figure 7D–G) and of polyaniline (Figure 7H), the bands become broader and more intense, and this can be ascribed to the appearance of strong intermolecular hydrogen bonding and to the formation of H-bond networks.[22-24,30] As one can see, the other stretching bands are completely overlapped by the very broad hydrogen-bond band.

Conductivity Measurements. Several requirements have to be met to avoid any dependence of the electrical conductivity of the PABA copolymers on the postsynthesis treatment. Consequently, the washing procedure, the drying time, and the particle size of the polymer powders were verified to be identical. The conductivities of both copolymers and homopolymers are listed in Table III. One can see very sharp variations of up to 6 orders of magnitude when the comonomer feed composition varies. However, according to other workers,[32] it is more rigorous to consider the variation of the logarithm of the conductivity with the copolymer composition F_1 as shown in Figure 8. The measured electrical conductivities remain low (10^{-7} S/cm) until the aniline unit content F_1 exceeds approximately 0.15 S/cm, and then the conductivities rise abruptly to up to 0.3 S/cm. Similar relationships between conductivity and composition, ascribed to a percolation transition, were also reported for blends of polypyrrole or polyaniline conducting polymers in an insulating matrix of poly(vinyl chloride).[33,34] At low percentages of conducting polymer, the conductivity is quite insensitive to

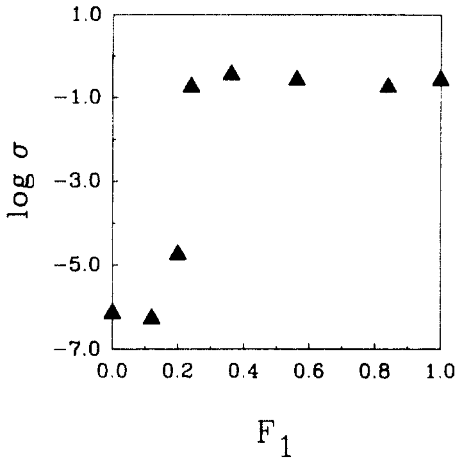

Figure 8. Variation of the conductivity with the copolymer composition F_1 (mole fraction of aniline units in the copolymer).

loading, although it increases sharply when the percolation threshold is reached.

Since conducting polyaniline blocks of various length are believed to be part of the structure of the poly(aniline-*co*-*N*-butylaniline) copolymers, we suggest that the observed sharp conductivity rise results from a percolation mechanism between these conducting sequences, the *N*-butylaniline segments being the insulating phase. Since both conducting and insulating phases are located on the same molecule and since properties of each phase are very different, these copolymers are termed as "quasi composites" rather than "internal blends" or "interpenetrating networks". For the PABA copolymers, the percolation threshold seems to occur when about 15% of aniline units are present in the polymer chain. This is in good agreement with theoretical computations that give values between 10 and 16% for three-dimensional lattices.[33,35]

As reported in recent papers,[22,24,32,36] the conductivity of polyaniline is ascribed to the formation of a polaron lattice[37-40] which is strongly and efficiently stabilized by a two- or three-dimensional interchain hydrogen-bonding system. Owing to the presence of this interchain hydrogen bonding, the increase of conductivity at the microscopic level is attributed to the lowering of the intermolecular barrier, which is very significant for charge-transport properties. For the PABA copolymers, as shown in Figures 7 and 8, the rise of conductivity at the percolation threshold can be correlated with a dramatic increase of the strength of the N–H stretching due to hydrogen bonding. In summary, the formation of an hydrogen-bonding lattice through the polyaniline sequences seems to occur simultaneously with the percolation transition in conductivity. The formation of the polaron lattice is believed to be responsible of the high conductivity of the copolymers 69-PABA to 95-PABA and of the polyaniline homopolymer. The macroscopic conductivity of copolymers 50-PABA and 63-PABA and of poly(*N*-butylaniline) homopolymer is strongly limited by a weak interchain hopping due to the disruption of the hydrogen-bonding lattice by the butyl substituents. From another point of view, the fact that copolymer 69-PABA (F_1 = 0.24) is fully soluble in acetonitrile *and* shows a high conductivity is a strong proof that real copolymers were synthesized rather than a mixture of two pure homopolymers. In a control experiment, it was found that, for a blend having the same composition, i.e., 24% polyaniline and 76% poly(*N*-butylaniline), the conductivity is nearly the same (0.1 S/cm), but the polyaniline fraction of the blend is totally insoluble in acetonitrile.

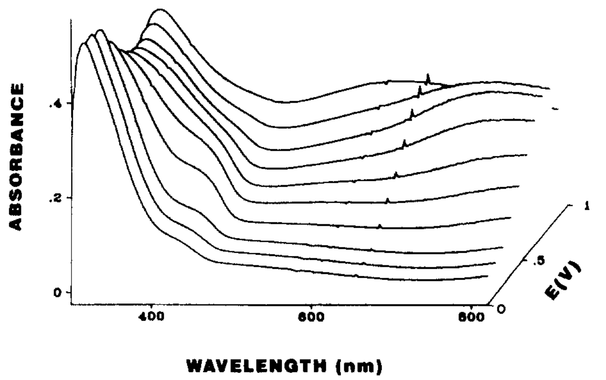

Figure 9. Absorption spectra of a thin 69-PABA film on ITO glass dipped in 1.0 M perchloric acid at various applied potentials.

Spectroelectrochemistry. The UV–visible absorption provides an insight into the electronic defect structures which are created upon oxidation of the PABA copolymers. They are electroactive materials which show various and reversible color changes depending on the applied potential. For example, the UV–visible spectra of a 69-PABA film (cast onto platinum-sputtered ITO glass) at applied potential values ranging from +0.1 to +1.0 V versus Ag/Ag^+ are shown in Figure 9. These spectra are interpreted as representing the extensively studied redox mechanism involving polaron and bipolaron states within a polyaniline structure.[32,36,40] The presence of up to 36% (since F_1 = 0.36 for copolymer 75-PABA) of *N*-butylaniline units in the copolymer chain (as more or less long sequences) does not appreciably modify the spectroelectrochemical behavior.

At low applied potential (+0.1 V), the copolymer is pale yellow and the spectrum shows only one peak near 320 nm (3.9 eV) which is ascribed to a transition from a benzene molecular orbital to a quinoid molecular orbital. Upon oxidation from +0.2 to +0.4 V, the color changes to green and two new absorptions appear near 420 nm (3.0 eV) and 800 nm (1.5 eV), while the band at 320 nm becomes less intense. These bands correspond to transitions to a half-filled polaron band. Finally, at applied potentials higher than +0.4 V, the polarons gradually recombine into bipolarons and the peak near 420 nm decreases gradually while the peak at 800 nm shifts slowly toward 610 nm (2.0 eV). Simultaneously, the copolymer film becomes dark blue. This latter band is attributed to molecular excitons corresponding to a transition from a benzene molecular orbital to a mixed benzene–quinoid state.

Conclusion

In this paper, we have examined the effect of the actual composition (in mole fractions of aniline units F_1) of chemically synthesized poly(aniline-*co*-*N*-butylaniline) copolymers on their electrical and physical properties. The reactivity ratios to chemical oxidation of the comonomer pair were found to be strongly controlled by their oxidation potentials E_{pa}. The aniline comonomer has a lower reactivity than the *N*-butylaniline comonomer, their reactivity ratios r_1 and r_2 being respectively 0.4 and 8.9. Consequently, we find a very large discrepancy between feed composition f_1 and copolymer composition F_1, and we suggest that PABA copolymers have a quasi-block structure with well-defined pure polyaniline and poly(*N*-butylaniline) sequences.

Steric exclusion chromatography, as well as FTIR spectroscopy, shows that the PABA copolymers have bimodal distributions of about 85% of oligomers and 15% of high molecular weight species. These materials are fully soluble in dimethylformamide and *N*-methylpyrrolidinone; therefore, free-standing films can be easily cast. The copolymers having less than 36% of aniline units in their backbone are fully soluble in acetonitrile, indicating that true copolymers were synthesized and not a mixture of homopolymers. The conductivity of the copolymers was also found to be controlled by their actual composition. The dramatic rise of conductivity for copolymers having more than 15% of aniline units in the backbone was ascribed to a percolation transition which occurred between the polyaniline sequences. Such an increase in conductivity is attributed to the formation and stabilization of a polaron lattice by an interchain hydrogen-bonding system formed between the polyaniline sequences. The synthesis of various poly(aniline-*co*-*N*-alkylanilines) from other aniline/N-substituted aniline comonomer pairs will allow a family of copolymers to be obtained over a wide range of conductivities and solubilities.

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Registry No. PABA (copolymer), 131826-07-8; $[(HO)S(O)_2]_2O_2 \cdot 2NH_3$, 7727-54-0.