New Approach for the Controlled Cross-Linking of Polyaniline: Synthesis and Characterization

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ABSTRACT: A new strategy has been employed to control the cross-linking of polyaniline that allows the synthesis of high molecular weight, conducting copolymers. The new method utilizes aniline−formaldehyde condensates (AFC) to establish the upper limit of possible cross-link sites in an AFC−polyaniline copolymer. By changing the ratio of AFC to aniline during the polymerization reaction, it is possible to control the number of cross-linking sites, and in turn the bulk conductivity and molecular weight. The copolymer is obtained by oxidizing aniline in the presence of AFC, where the aniline is oxidized to form polyaniline through a cation radical mechanism. The AFC present in the mixture terminates the propagation of polyaniline chains while at the same time binding it to the AFC backbone. In essence, the AFC polymer molecules tether together polyaniline chains to form much larger molecular weight molecules. Varying the ratio of AFC to aniline monomer prior to chemical polymerization allows control over the conductivity, molecular weight, and solubility of the copolymer. Under appropriate conditions, high molecular weight copolymers (weight-average molecular weight of 10^6) with conductivities on the order of pure polyaniline ($k = 10\ \Omega^{-1}\ \mathrm{cm}^{-1}$) and similar redox behavior can be obtained. Adhesion measurements on glass demonstrate that of the copolymers have a significantly higher strength of adhesion compared to that observed for pure polyaniline.

Introduction

Conducting polymers continue to be the focus of active research in diverse fields, including electronics,[1] energy storage,[2] catalysis,[3] chemical sensing,[4] and biochemistry.[5] Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical, and optical properties, as well as good stability.[6] Polyaniline is typically synthesized by oxidizing aniline monomer either electrochemically[7,8] or chemically.[9−11] Electrochemically synthesized polyaniline is difficult to process due to its low solubility, while chemically synthesized polyaniline suffers from low molecular weight, which results in low mechanical strength.[11] In recent years, considerable effort has been devoted to developing new methods to synthesize polyaniline to achieve better mechanical properties while maintaining high conductivity. The most common strategy that has been implemented is to change the oxidizing agent employed in the chemical polymerization reaction.[11−13] For example, it has been shown that when $(NH_4)_2S_2O_8$ or $K_2Cr_2O_7$ is used, high molecular weights can be achieved by lowering the polymerization temperature to below 0 °C.[14] The highest weight-average molecular weights that have been reported using these approaches are on the order of 10^5.

In addition to low mechanical strength, adhesion of polyaniline on solid substrates is another important factor that has limited its utility in applications such as in antistatic coatings.[15,16] For example, although polyaniline films cast from *N*-methyl-2-pyrrolidone (NMP), dimethyl sulfoxide (DMSO), or dimethylformamide (DMF) solutions adhere strongly to glass in dry atmospheres, adhesion quickly fails when the films are immersed in water. Increasing the molecular weight of polyaniline is expected to increase the strength of adhesion as well as its mechanical strength.

The method described herein utilizes AFC to cross-link polyaniline. The copolymer can be synthesized by oxidizing AFC−aniline mixtures at room temperature. A wide range of molecular weights can be obtained by simply adjusting the ratio of AFC to aniline prior to polymerization. The conductivity and solubility of the copolymer is a function of the ratio of AFC to aniline and therefore can be varied systematically. The copolymers produced using this method show significantly better adhesion on glass in air and water as compared to pure polyaniline.

Experimental Section

Synthesis of AFC. AFC was synthesized by reacting formaldehyde with aniline as described in the literature.[17] In a 100 mL reaction vessel, 5 mL of 37% formaldehyde was added to a mixture of 9.3 g of aniline and 3 mL of 37% HCl. Condensation was carried at 100 °C for 2 h. The temperature was then decreased to 60 °C and the mixture was neutralized with 4 mL of 30% NaOH, resulting in an insoluble liquid resin. The resin was then washed with warm water three times and separated from the aqueous layer. The resin was kept at 80 °C under a reduced pressure of 10 kPa for 1 h to remove any unreacted aniline and/or formaldehyde.

Synthesis of Polyaniline and Cross-Linked Copolymer. The chemical polymerization of aniline was performed as described in the literature;[11−13] however, in this work, H_2O_2 was used as the oxidizing agent. In a 150 mL reaction vessel, AFC and aniline monomer were dissolved in 100 mL of 1 M HCl aqueous solution with varying ratios. A trace amount of $FeSO_4$ was added to the solution as a catalyst. Then 3 mL of 30% H_2O_2 was added dropwise to the solution with vigorous stirring. After polymerization for 6 h at 25 °C, a dark polymer powder was obtained. The powder was washed with 1 M HCl until the washing solution became clear. Lower molecular weight oligomers were removed by further washing with copious amounts of acetonitrile. The doped (or conducting) form of the polymers was obtained by acidification of the polymer with 1 M HCl. The base form of the polymers was obtained by treating the polymers with aqueous 1 M NH_3OH.

Instruments and Measurement Conditions. The ^1H NMR spectra were collected on a Brüker AMX 360 NMR spectrometer, DMSO-d_6 was used as solvent. The FTIR spectra were recorded using a Mattson Sirius-100 FTIR spectrometer, the samples were KBr pellets containing the corresponding polymers. The UV−vis spectra were obtained on a Shimadzu UV-2101PC UV−vis scanning spectrophotometer. Molecular weights of the polymers were determined on

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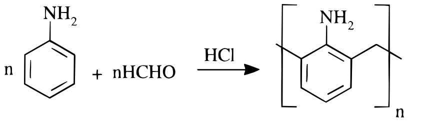
Scheme 1. Condensation Polymerization of Aniline and Formaldehyde



a Waters 150C gel permeation chromatograph (GPC) using a mobile phase of 50% NMP/50% THF (v/v) and polystyrene as a standard. The conductivities of acid (1 M HCl) doped polymer pressed pellets were determined using two Pt contacts and a multimeter in a well-defined geometry (cross sectional area of the polymer was 0.05 × 1 cm and the length was 2 cm). Cyclic voltammetry was performed on a BAS100 electrochemical analyzer, the working electrodes were polymer-coated Pt foils, the counter electrode was a Pt wire, and the reference electrode was a Ag/AgCl electrode. The relative strength of adhesion of the polymers on glass was determined by (i) observing the ability to remove thin films of polymer (~5 μm) with adhesive tape in a standard peel test and (ii) observing the time required for thin films to detach from glass slides while exposed to water. Because of the relatively low solubility of Pani5, films of this particular copolymer were cast from suspensions of the polymer in DMSO. All the experiments were carried out at 25 ± 2 °C.

Results and Discussions

Aniline–formaldehyde condensates can be synthesized as shown in Scheme 1, where the resulting polymer has alternating substituted aniline and methylene units. Although previous work[18] has demonstrated that 2,5-substituted anilines (i.e., 2,5-dialkylanilines) can be polymerized to form substituted polyaniline using both chemical and electrochemical methods, attempts in our laboratory to polymerize AFC by itself were not successful. The observed resistance to polymerization is attributed to the strong steric interactions associated with the substituted aniline units. In contrast, AFC can be oxidatively polymerized in the presence of aniline, resulting in copolymers that incorporate polyaniline and AFC. The fact that copolymerization occurs quite readily is attributed to the fact that the resulting structures allow AFC chains to be further apart, thereby reducing steric interactions.

Due to the highly conjugated nature of polyaniline, it possesses UV–vis absorbance spectra different from that of either the aniline monomer or AFC. Therefore, the amount of polyaniline formed during oxidative polymerization of aniline can be tracked as a function of time with UV–vis spectrophotometry. Figure 1 demonstrates that before the addition of H_2O_2, acidic aniline solutions do not show significant absorbance in the range 300–900 nm. However, upon addition of H_2O_2, polymerization occurs, resulting in two absorbance peaks at 340 and 700 nm. Similar UV–vis spectra were obtained for polymerization of AFC–aniline mixtures, where the absorbance peak positions are independent of the ratio of AFC to aniline in the reaction mixture. The fact that the absorbance maximum at 700 nm does not shift significantly allows tracking of the polymerization reaction for various AFC–aniline mixtures. Figure 2 shows results obtained for the polymerization of several AFC–aniline mixtures as a function of time (at 700 nm). Since the absorbance reflects the concentration of polyaniline formed in the reaction mixture, the slopes of the curves reflect the polymerization reaction rates under varying conditions.

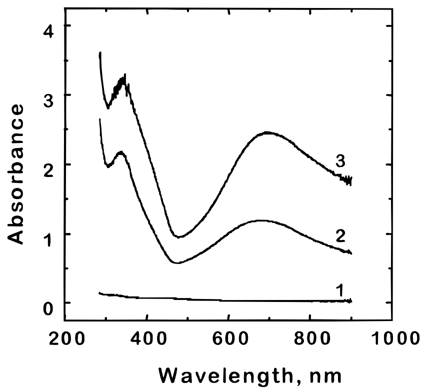


Figure 1. Uv–vis spectra of the a 30 g L^{-1} aniline in 1 M HCl solution after adding 20 g L^{-1} H_2O_2 obtained at (1) 0 min, (2) 2 min, and (5) 5 min.

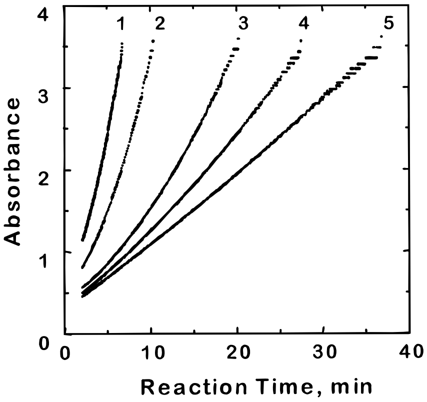
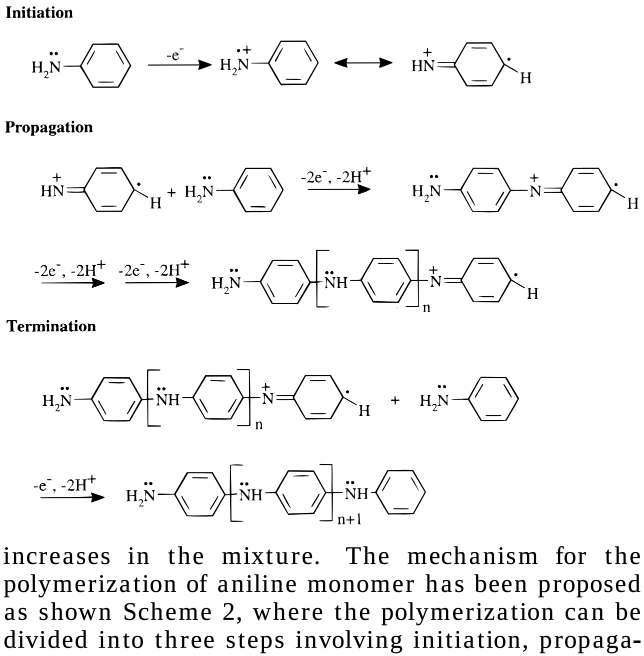


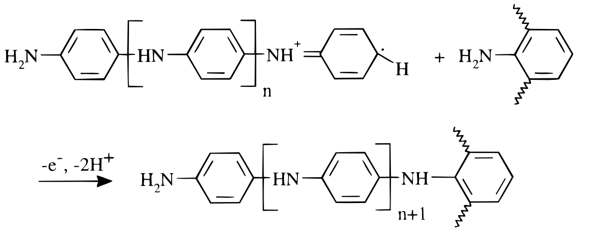
Figure 2. Absorbance at 700 nm of aniline–AFC mixtures with 20 g L^{-1} H_2O_2 as a function of reaction time: (1) 30 g L^{-1} aniline; (2) 30 g L^{-1} aniline + 1.5 g L^{-1} AFC; (3) 30 g L^{-1} aniline + 5 g L^{-1} AFC; (4) 30 g L^{-1} aniline + 10 g L^{-1} AFC; (5) 30 g L^{-1} aniline + 15 g L^{-1} AFC.

Scheme 2. Mechanism for Oxidative Polymerization of Aniline[17]



It is clear from the data shown in Figure 2 (constant concentrations of aniline and H_2O_2) that the rate of polymerization decreases as the concentration of AFC increases in the mixture. The mechanism for the polymerization of aniline monomer has been proposed as shown Scheme 2, where the polymerization can be divided into three steps involving initiation, propagation, and termination.[19] The role of AFC on the rate of polymerization can be determined by considering the influence of AFC on each step of polymerization. For example, AFC will not likely significantly influence the initiation or propagation steps due to the steric hindrance associated with AFC. However, AFC is expected

Scheme 3. Termination Step in the Polymerization of Aniline in the Presence of AFC



to act as an effective terminating agent since the steric effects of AFC will hinder further propagation. Therefore, it is expected that the most important role of AFC on the overall polymerization reaction will be in the termination step. A proposed mechanism in which AFC participates in a termination step is shown in Scheme 3.

The influence of AFC on the rate of the overall polymerization reaction can be summarized as follows:

Initiation $\mathrm{A} \xrightarrow{k_1} \mathrm{A}^{\bullet+} + \mathrm{e}^-$

Propagation $\mathrm{A}_n^{\bullet+} + \mathrm{A} \xrightarrow{k_2} \mathrm{A}_{n+1}^{\bullet+}$

Termination $\mathrm{A}_n^{\bullet+} + \mathrm{A} \xrightarrow{k_3} \mathrm{A}_{n+1} - \mathrm{e}^-$

$\mathrm{A}_n^{\bullet+} + \mathrm{AFC} \xrightarrow{k_4} \mathrm{A}_n(\mathrm{AFC}) - \mathrm{e}^-$

where A represents neutral aniline monomer; $\mathrm{A}^{\bullet+}$ represents the aniline cation radical, AFC represents the aniline–formaldehyde condensate, and k_1, k_2, k_3, and k_4 are corresponding reaction rate constants. The reaction rate for the above mechanism will then be a function of the rate of generation of $\mathrm{A}^{\bullet+}$ in the initiation step,

$$\mathrm{d}[\mathrm{A}^{\bullet+}]/\mathrm{d}t = k_1[\mathrm{A}] \qquad (1)$$

the rate of consumption of A in the propagation step through the reaction with monomer,

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_2[\mathrm{A}][\mathrm{A}_n^{\bullet+}] \qquad (2)$$

and the rate of consumption of $\mathrm{A}_n^{\bullet+}$ in the termination step

$$-\mathrm{d}[\mathrm{A}_n^{\bullet+}]/\mathrm{d}t = k_3[\mathrm{A}_n^{\bullet+}][\mathrm{A}] + k_4[\mathrm{A}_n^{\bullet+}][\mathrm{AFC}] \qquad (3)$$

Assuming that the rate for generation of $\mathrm{A}_n^{\bullet+}$ equals the rate for consumption of $\mathrm{A}_n^{\bullet+}$ (i.e., under steady-state conditions), eqs 1 and 3 will be equal, yielding

$$k_1[\mathrm{A}_n] = k_3[\mathrm{A}_n^{\bullet+}][\mathrm{A}_n] + k_4[\mathrm{A}_n^{\bullet+}][\mathrm{AFC}] \qquad (4)$$

or

$$[\mathrm{A}_n^{\bullet+}] = k_1[\mathrm{A}_n]\,/\{k_3[\mathrm{A}_n] + k_4[\mathrm{AFC}]\} \qquad (5)$$

If the rate of polymerization is taken to be the rate of disappearance of monomer, and the contribution of the initiation and termination steps to the disappearance of monomer is negligible, the rate of polymerization, R, will be equal to the rate of propagation (eq 2). Substituting eq 5 into eq 2 yields

$$R = k_2[\mathrm{A}][\mathrm{A}^{\bullet+}] = k_1k_2[\mathrm{A}]^2/\{k_3[\mathrm{A}] + k_4[\mathrm{AFC}]\} \qquad (6)$$

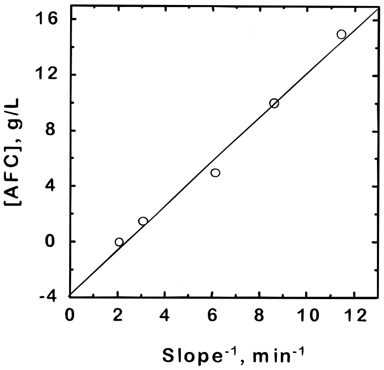
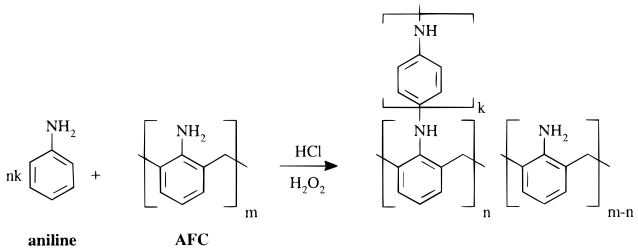


Figure 3. Plot of the concentration of AFC as a function of the corresponding reciprocal of slope obtained from Figure 2.

Scheme 4. Copolymerization of Aniline and AFC



Rearranging eq 6 yields

$$[\mathrm{AFC}] = (k_1k_2[\mathrm{A}]^2/k_4)R^{-1} - k_3[\mathrm{A}]/k_4 \qquad (7)$$

It is apparent from eq 7 that a plot of AFC concentration versus the reciprocal of the polymerization rate will yield a straight line with a negative intercept if the above assumptions are true.

If the slopes of the lines in Figure 2 are assumed to be proportional to the reaction rate at different concentrations of AFC, a plot of AFC concentration versus the reciprocal of the slope can be constructed as shown in Figure 3. The linear relationship observed supports the assertion that AFC acts as a terminating agent in the polymerization reaction. Further, as seen in eq 7, the y-intercept is proportional to k_3/k_4, which is the ratio of the rate constants for termination by monomer to termination by AFC. From Figure 3 a value of 1/8.5 was determined for k_3/k_4, indicating that AFC is 8.5 times more effective as a terminating agent compared to aniline monomer. These results suggest that the copolymer obtained from the polymerization of the AFC–aniline mixture has a structure similar to that represented in Scheme 4 where a single AFC polymer chain can bind many polyaniline chains.

Clearly, the ratio of AFC to aniline in the initial mixture will influence the degree of cross-linking and the spacing between polyaniline chains. These changes will in turn alter the molecular weight and the conductivity of the resulting copolymers. In order to investigate these relationships, copolymers were synthesized using different ratios of the starting materials. The polymerization yields for different copolymers are summarized in Table 1, where the weight ratio of aniline to AFC ranged from 2:1 (Pani2) to 100:0 (Pani100). The yields obtained using this method are higher than those reported for methods using $\mathrm{FeCl_3}$,[20] $\mathrm{(NH_4)S_2O_8}$[14], or $\mathrm{O_2}$[21] as oxidizing agents (typically reported to be less than 40%).

It is apparent that the yield of the polymerization reaction decreases with the increasing relative amounts

Table 1. Starting Materials and Yields for Different Copolymers

polymers	amt of AFC (g)	amt of aniline (g)	yield (%)
Pani100	0.00	3.0	62
Pani20	0.15	3.0	57
Pani5	0.50	2.5	47
Pani2	1.00	2.0	40

of AFC in the reaction mixture. There are two factors that are expected to influence the overall yield of the polymerization reaction. First, the substituted aniline units in AFC are not as reactive as aniline monomer due to strong steric effects, as discussed above. As a result, most of the AFC may remain unreacted after the polymerization. These unreacted AFC chains would then be removed in the washing process (AFC is soluble in 1 M HCl), thereby decreasing the overall yield. Under these conditions, the relative amount of AFC in the copolymer is expected to be lower than that in the starting materials. This assertion is supported by ^{1}H NMR and FTIR measurements. Figure 4 compares the ^{1}H NMR spectra of Pani100 and Pani20 (no spectra were obtained for Pani5 and Pani2 due to their relatively low solubility). As shown in Figure 4, Pani20 has a spectrum similar to that of pure polyaniline where the peak at 3.34 ppm corresponds to $-$NH$-$ and $-$NH$_2$ protons and the peaks around 7 ppm are assigned to protons on the benzene ring. The peak at 5.23 ppm is assigned to trace amounts of water. The spectrum of Pani20 shows a minor peak at 3.7 ppm, corresponding to the $-$CH$_2-$ group in the copolymer. The ratio of $-$CH$_2-$/$-$NH$-$ in the copolymer can be calculated from the area ratio of the 3.7 ppm peak to the 3.34 ppm peak. The value was determined to be approximately 1/150, suggesting that AFC chains in the copolymer account for less than 1% of the copolymer mass. In addition, all the polymers had nearly identical IR spectra with no identifiable peaks associated with methylene groups, further supporting the assertion that the copolymers have significantly less AFC than in the reaction mixtures.

The second factor likely to influence the overall yield of the polymerization is that the AFC is a stronger terminating agent than the aniline monomer, as described above. Since the rate of termination will increase as more AFC is added to the polymerization mixture (see Figure 2), it follows that the kinetic chain length of polyaniline (i.e., the average number of monomers that react with an active center from its formation until its termination), which is proportional to the reciprocal of the terminating rate of the polymerization,[22] will be shorter with increasing amounts of AFC. Since AFC and short chain aniline oligomers are more soluble in acidic aqueous conditions, it is expected that the percent yield will decrease, as observed in Table 1.

Although polyaniline is not soluble in conventional organic solvents in its acid-doped form, the base form (obtained upon exposure to 1 M NH$_3$OH) is soluble in NMP, DMSO, and DMF. The copolymers Pani100, Pani20, Pani5, and Pani2 exhibit significantly different solubilities in these same solvents. For example, both Pani100 and Pani20 dissolve in NMP or DMSO up to approximately 5% by weight while Pani5 and Pani2 are only partially soluble, with Pani2 being the least soluble. These changes in solubility can only be attributed to changes in molecular weight of the copolymers since both polyaniline and AFC are soluble in the above solvents on their own. Further, since AFC is soluble in the 1 M HCl used in the washing procedure, any unreacted AFC will be removed from the final products.

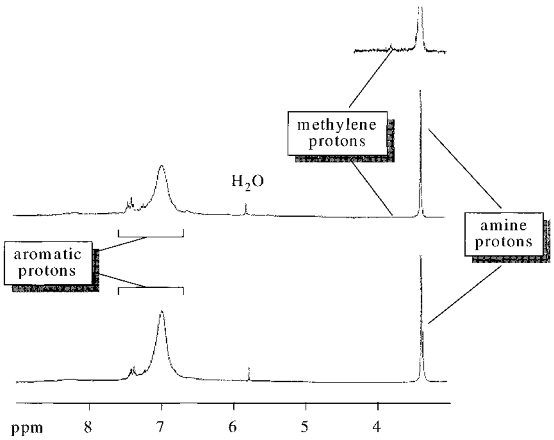


Figure 4. ^{1}H NMR spectra of different polymers in DMSO-d_6.

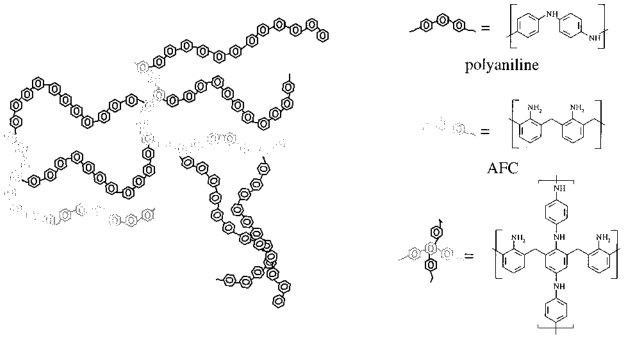


Figure 5. Schematic representation of AFC$-$polyaniline copolymer formed from the chemical oxidative polymerization of aniline in the presence of AFC.

The weight-average molecular weight of Pani100 and Pani20 were determined to be 8200 and 1.2 × 10^6 by GPC, respectively. The corresponding polydispersities were 1.39 and 6.75, respectively. Pani5 and Pani2, on the other hand, were not sufficiently soluble to characterize by this method. These results are consistent with the structure proposed above where AFC chains bind polyaniline chains to form larger molecular weight molecules, as illustrated in Scheme 4. This mechanism is expected to result in a complex network similar to that shown in Figure 5 where the ratio of AFC to polyaniline in the structure will depend on the ratio of AFC to aniline in the reaction mixture.

The influence of cross-linking on the conductivities of the acid-doped forms of the copolymers is shown in Figure 6. It is apparent that the conductivity of the copolymers decreases as the ratio of AFC$-$aniline increases. It should be noted that in all cases, the copolymers have higher conductivities than the $3.10 \times 10^{-6}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ reported for poly(2,5-dialkylanilines).[16] This behavior is expected since interchain electron hopping is the dominant charge transport mechanism in these materials,[23-25] and any factor that decreases the probability of electron hopping will decrease conductivity. It follows that the presence of AFC chains increases the interchain distance between polyaniline chains and therefore decreases conductivity. In addition, steric interactions associated with the AFC chains may also induce twisting of the polyaniline chains, further decreasing the conductivity of the copolymer.[26,27] There is, in turn, a tradeoff between molecular weight and conductivity, which can be controlled by varying the

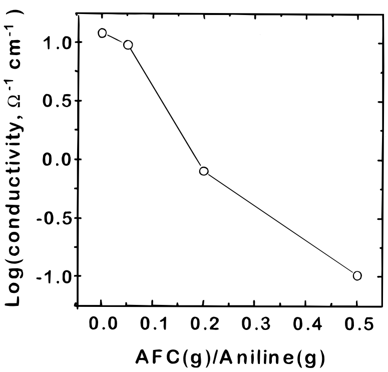


Figure 6. Plot of log(conductivity) as a function of AFC–aniline ratios used for the synthesis of the copolymers.

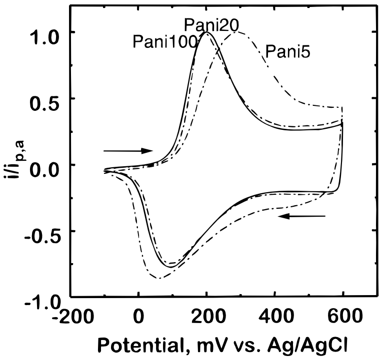


Figure 7. Cyclic voltammograms (normalized) of pure polyanilne (—) and copolymers (—•—) in 1 M H_2SO_4, scan rate = 100 mV·s^{-1}.

ratio of AFC to aniline. It is clear from the results obtained with Pani20 that in spite of this tradeoff, soluble copolymers with relatively high molecular weights (10^6) and high conductivities (10 Ω^{-1} cm^{-1}) can be produced using this method.

The redox properties of the copolymers were investigated with cyclic voltammetry. Figure 7 shows cyclic voltammograms of the polymer films on Pt in 1 M H_2SO_4. Pani20 has an anodic peak potential and peak separation similar to that of Pani100, indicating that the degree of cross-linking in Pani20 does not significantly influence its redox behavior.[28] On the other hand, the anodic peak potential of Pani5 shifts to positive potentials relative to Pani100, suggesting that there is a higher resistance to the movement of charge within Pani5. Previous work[29] has established that the voltammetric current in the potential window of positive of the anodic peak (between +0.4 and +0.6 V vs Ag/AgCl) is purely capacitive current associated with charging the conducting polymer film. As a result, the current response in this potential window is characteristic of the charging and discharging of an *RC* circuit, where *R* is the resistance of the polymer film and *C* is the capacitance of the polymer coated electrode. Under conditions where *R* is small, the circuit behaves like a pure capacitor, yielding a constant charging current as a function of potential with a fast rise time when the direction of the potential is reversed. As *R* becomes large, the time required to reach the charging current increases (i.e., longer rise times). As seen in the potential region between +0.6 and +0.5 V in Figure 7, the rise time increases noticeably as the degree of cross-linking increases. These results are consistent with the changes in conductivity observed in Figure 6.

Peal tests and water immersion tests were performed to estimate the strength of adhesion of the copolymers on glass. Polymer-coated glass slides were prepared by casting thin films (~5 μm thick) from DMSO solutions onto the slides followed by drying under vacuum for at least 12 h. Pani2 films could not be obtained due to its very low solubility. The dried polymer films were found to adhere well to glass. Although all the films survived peal tests with standard scotch tape, only the copolymers were able to survive peal tests using duct tape, which contains a stronger adhesive. The adhesion of the polymers on glass was also compared by immersing them in water and measuring the time required for polymer films to detach. As seen in Table 2, the polymers show significantly better adhesion to glass relative to pure polyaniline (Pani100). This enhanced performance is likely due to decreased permeability and increased mechanic strength resulting from cross-linking.

Table 2. Time Required for Polymer Films (~5 μm) To Detach from Glass in Contact with Water

polymer	Pani100	Pani20	Pani5	Pani2
time	5 min	> 2 weeks	>2 weeks	

Conclusions

Aniline–AFC copolymers can be synthesized by chemically oxidizing aniline–AFC mixtures. AFC acts as a terminating agent in the polymerization process, and by terminating many polyaniline chains, the resulting copolymers have a branchlike structure. By controlling the ratio of AFC to aniline prior to polymerization, one creates an upper limit on the number of possible cross-links. As a result, it is possible to vary the molecular weight, solubility, and conductivity of the cross-linked polymer. Under appropriate conditions, high molecular weight polymers, with conductivities and solubilities similar to pure polyaniline, can be obtained. The method introduced here describes a new strategy for controlling the molecular weight of polyaniline and in turn its physical properties. This approach may also be extended to the synthesis and modification of other polymers.

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