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Thermal Properties of Polyaniline and Poly(aniline-*co*-*o*-ethylaniline)

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ABSTRACT: Block copolymers of aniline ($r_1 < 1$) and ethylaniline ($r_2 > 1$) can readily be formed by acid-catalyzed oxidation. These copolymers have enhanced solubility in common solvents, compared to polyaniline. For example, while a 47 mol % *o*-ethylaniline copolymer is 2–7 times more soluble in ethanol, methanol, and acetone than polyaniline, the solubility of the copolymer in tetrahydrofuran increases by more than 20 times. Thermal effects on the properties of polyaniline and poly(aniline-*co*-*o*-ethylaniline) in their emeraldine base forms have been studied by means of thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), electron paramagnetic resonance (EPR), four-probe conductivity, UV–vis, and FT-IR spectroscopies. Upon heating, the number of free electrons in the polymer, as determined by EPR, increases by up to 10 times. An irreversible exothermic transition was observed by DSC, which is believed to be an indication of cross-linking. The electron-donating character of the ethyl group appears to help stabilize the intermediates during the cross-linking reaction. Complete characterization of the copolymer is given.

Introduction

Conducting organic polymers have shown great potential for many applications including rechargeable batteries, light-emitting diodes, molecular sensors, and gas separation membranes.[1–6] To be useful in these applications, the polymers must be highly processable and chemically stable for long periods of time. Polyaniline has been among the most widely studied of the conducting polymers because of its chemical and oxidative stability. However, as is common with other conjugated polymers, polyaniline is limited by poor thermal processability and solvent solubility.

Improved solubility can be achieved by introducing bulky alkyl substituents on the polyaniline backbone.[7–14] Ordinarily, polyaniline is cast into films from the emeraldine base, or undoped, nonconducting form (Figure 1, top), from a dispersion of the powder in *N*-methyl-2-pyrrolidinone (NMP). The emeraldine acid, or doped, conducting form (Figure 1, bottom), of this polymer is insoluble in organic solvents. Intensive grinding is often used to disperse the polyaniline powder in order to prepare free-standing films. By substituting an alkyl group on the polymer backbone, improved solubility can be achieved, but limitations are then imposed on the conductivity of the polymer produced. For example, poly(*o*-toluidine), synthesized from methyl-substituted aniline, dissolves readily in tetrahydrofuran and chloroform, in contrast to insoluble unsubstituted polyaniline. However, the conductivity of acid-doped poly(*o*-toluidine) is only 0.01–0.1 S·cm^{-1}, whereas the conductivity of doped polyaniline ranges from 1 to 100 S·cm^{-1}.[15,16]

Combining the conductivity of polyaniline with the solubility of substituted polyanilines is important and can be achieved through copolymerization. For example, copolymers of aniline with *o*- or *m*-toluidine and *N*-butylaniline have been reported.[15–24] These copolymers of aniline with substituted anilines show improved solvent solubility, while maintaining high electrical conductivity. In addition, the conductivities of these copolymers can be readily tailored by varying the composition of the copolymer.[15]

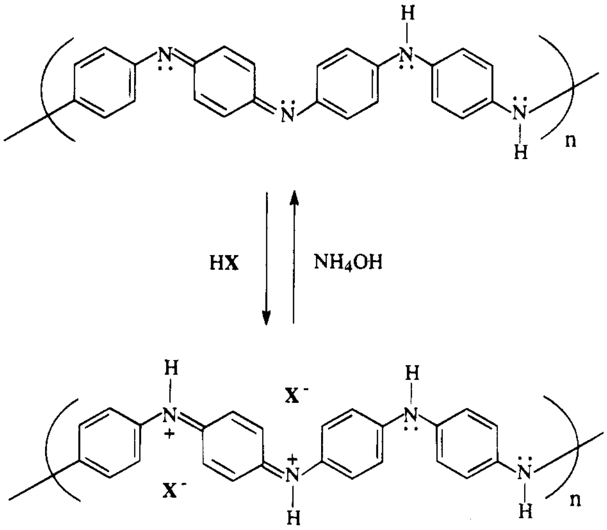

Figure 1. Repeat unit of polyaniline in the undoped, emeraldine base form (top) and the fully acid doped, emeraldine salt form (bottom).

Another important feature for film formation and processability of polyaniline is the thermal stability of the polymer in its base powder form over long periods of time. While polyaniline is a highly stable conducting polymer, a gradual decrease in polymer solubility in NMP with time is observed. For example, when polyaniline powder is stored in air at room temperature for several weeks, it loses solubility in NMP and becomes exceedingly difficult to process into coherent films. Since solvent solubility is crucial for processing polyaniline, it is useful to understand the origins of thermal aging in polyaniline base powder.

The causes of thermal deterioration for either acid-doped or base-undoped polyaniline are still unclear. The mechanisms of thermal degradation for acid-doped polyaniline proposed by several research groups include changes in morphology, loss of dopants, cross-linking, and decomposition of the polymer backbone.[25–28] The acid-doped polymer has been studied for thermal degradation by TGA, DSC, X-ray photoelectron spectros-

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copy (XPS), and mass spectrometry. However, there have been few studies on the thermal stability of the emeraldine base form of polyaniline reported in the literature.[29] Emeraldine base is the most useful form of polyaniline for processing powders into films because of the low solubility of other forms of polyaniline in most solvents. Therefore, it is important to explore the thermal properties which influence the solubility of the emeraldine base form. The base form also provides a simple system to investigate thermal behavior without the added complexity caused by counteranions.

The chemical copolymerization of aniline and *o*-ethylaniline and the thermal properties of the emeraldine base form of the copolymer and homopolymers are reported herein. The resulting copolymer powders readily dissolve in many organic solvents to produce high-quality free-standing films. The conductivities of the acid-doped films vary with copolymer composition. The compositions of the copolymers were determined by proton nuclear magnetic resonance measurements (^{1}H-NMR). Further characterization of polyaniline and its copolymers includes EPR, UV–vis, FT-IR, TGA, and DSC to study the induced thermal changes to the polymers in the emeraldine base form. An understanding of the mechanisms behind thermal aging in emeraldine base polyaniline should better enable polyaniline to be protected from degradation, while improving solution processability and maintaining conductivity.

Experimental Section

Polyaniline and copolymers of aniline and *o*-ethylaniline were synthesized by chemical oxidation in an acidic medium following a common procedure for polyaniline synthesis.[30] Aniline (Aldrich, 99.5%), *o*-ethylaniline (Aldrich, 98%), and ammonium peroxydisulfate (Fisher, reagent grade) were used without further purification. Both the homopolymers and the copolymers were synthesized using similar conditions. For example, a typical copolymer synthesis consisted of aniline and *o*-ethylaniline mixtures having a total volume of 100 mL, dissolved in 1.5 L of a 1.0 M HCl(aq) solution. Ammonium peroxydisulfate (58 g) dissolved in 1 L of 1.0 M HCl served as the oxidizing solution. After both solutions were cooled to approximately 1 °C in an ice–ethylene glycol bath, the ammonium peroxydisulfate solution was added dropwise to the monomer mixture over a period of 1 h. The monomer solution was allowed to stir overnight, followed by filtration with a Büchner funnel. The resulting green precipitate was ground into a powder and continuously washed with 1.0 M HCl solution until the filtrate became colorless. The polymer powder was then repeatedly washed with 0.1 M NH_4OH and 1 M HCl solution until the filtrate turned colorless again. The powders were washed once more with acid and dried in air for 1 day. This produced copolymers in the acid form. Typical yields of the copolymerization were 16–20%. Similar yields were observed for the homopolymers.

The compositions of the repeat units were determined by integrated ^{1}H-NMR peak areas. The copolymers were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and filtered through quartz wool to remove any remaining solids. ^{1}H-NMR spectra were recorded on a Bruker AM200 spectrometer. DSC measurements (DuPont, 910 differential scanning calorimeter) were carried out on dried samples under a nitrogen flow rate of approximately 50 mL/min at 10 °C/min ramping rate, up to 300 °C. Thermogravimetric analyses (DuPont, 951 thermogravimetric analyzer) were performed in a nitrogen atmosphere at a ramping rate of 10 °C/min up to 500 °C.

The solubilities of polyaniline, poly(aniline-*co*-*o*-ethylaniline), and poly(*o*-ethylaniline) in acetone, methanol, ethanol, tetrahydrofuran (THF), dimethyl sulfoxide DMSO), and NMP were obtained using the following procedure. The base form of each powder was ground with a mortar and pestle and put through an 80-mesh sieve before solubility testing. Approximately 0.25 g of powder was added to 10 mL of each solvent and magnetically stirred for 1 h before filtering through Whatman filter paper no. 1 with particle size retention >11 μm. The filtering flasks were preweighed, and the filtrate was allowed to evaporate at room temperature (for acetone, methanol, ethanol, and THF) or at 110 °C (for DMSO and NMP) before weighing the flasks again. The increased weight of each flask after complete evaporation was used to determine the amount of powder which dissolved in the solvents.

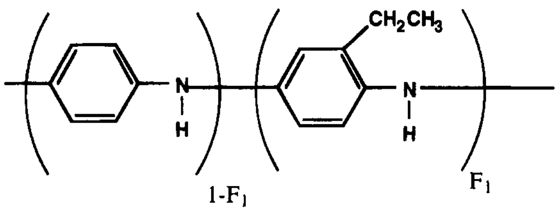

Figure 2. Repeat unit of the block copolymer poly(aniline-*co*-*o*-ethylaniline), where F_1 = mole fraction of *o*-ethylaniline in the copolymer and, therefore, $1 - F_1$ is the mole fraction of aniline.

The free base form of the polymers was used to prepare free-standing films. To convert an acid-doped polymer into the base form, the polymer powder was stirred in 0.1 M NH_4OH for 4 h, then filtered, and dried in air for 1 day. This brown powder was dissolved in NMP (25% w/v). The viscous polymer solution was spread out uniformly onto a glass plate. Evaporation of the NMP solvent in a 110 °C oven for 3 h resulted in a strong free-standing film. Conductivities were measured on free-standing acid-doped films using a standard four-probe technique. The copolymer thin film samples were cast from THF solutions onto NaCl or KBr windows for infrared measurements. The FT-IR experiments were carried out with a Perkin-Elmer 1600 spectrometer.

The thermal properties of polyaniline were investigated by placing 50 mg of pure polyaniline emeraldine base powder in a sealed Pyrex glass tube under vacuum to prevent any reaction between oxygen and the polymer. The tubes were then heated in a furnace to the desired temperature, either 150 °C (for solubility studies) or 200 °C (for EPR experiments). For a given temperature, each tube was heated for a different period of time. To measure the solubility of the heated polyaniline, approximately 10 mg of the polyaniline powder was dissolved in 100 mL of NMP, stirred for 110 min, and then filtered. The relative solubility of these resulting filtrates were calculated from the UV–vis maximum absorption peak centered at approximately 600 nm. The free radical concentrations of heated polyaniline powders were measured at ambient temperature by an electron paramagnetic resonance spectrometer (IBM 200D, X-band).

Results and Discussion

Ethylaniline Copolymers. Copolymers of aniline and *o*-ethylaniline at varying ratios were chemically synthesized to form poly(aniline-*co*-*o*-ethylaniline). Figure 2 shows the general structure of the copolymers formed. The composition of the repeat unit (where F_1 is the mole fraction of *o*-ethylaniline actually in the copolymer) was calculated from the ratio of integrated ^{1}H-NMR peak areas of methyl protons (δ = 1.1) to aromatic protons (δ = 6.8). The calculation, which is based on an assumption of infinite chain length, reportedly gives a slightly lower F_1 value than the compositional value actually in the copolymer.[31] For each of the copolymers made, the molar composition of *o*-ethylaniline in the copolymer (F_1), obtained from NMR experiments, was plotted against that of *o*-ethylaniline in the monomer feed mixture (f_1), as shown in Figure 3. The diagonal line represents identical reactivity of the two monomers, which would yield a copolymer with a composition equivalent to the feed mixture. All the

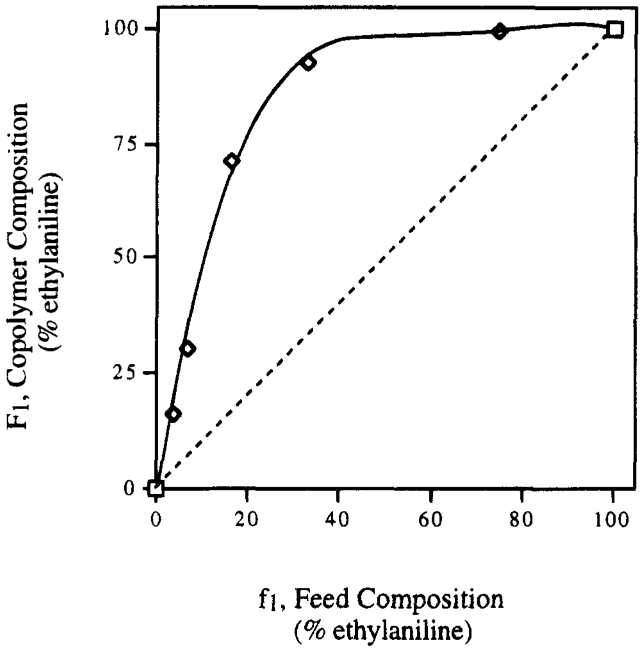

Figure 3. Molar composition of *o*-ethylaniline, F_1, in the copolymer relative to the feed mixture composition of the *o*-ethylaniline monomer, f_1. The solid line is drawn using the following polynomial fit: $y = -0.000010x^4 + 0.0015x^3 - 0.15x^2 + 6.4x - 3.0$.

data points are well above this diagonal line, indicating that *o*-ethylaniline has a higher reactivity ratio than aniline. The reactivity ratios, r_1 and r_2, can be calculated from the copolymer composition equation:[30]

$$\frac{(1 - 2F_1)f_1}{(1 - f_1)F_1} = r_2 + r_1\frac{f_1^2(F_1 - 1)}{(1 - f_1)^2F_1} \qquad (1)$$

The reactivity ratios are related to the ability of a monomer to react in copolymerization, and they are dependent on steric factors, resonance stabilization, and polarity of the monomers.[32] The r_1 and r_2 values, which are determined from the slope and intercept of the straight line produced by (1), are 11.7 for *o*-ethylaniline and 0.128 for aniline, respectively. When r_1–r_2 is greater than 1, radicals of a given kind are more likely to react with a like unit than with an unlike unit.[33] The value of the product of r_1 and r_2 for copolymerization of aniline and *o*-ethylaniline is 1.5. This strongly suggests that the faster propagation rate of *o*-ethylaniline during polymerization compared to that of aniline will lead to a block copolymer with long blocks of *o*-ethylaniline and short blocks of aniline. Analogous block copolymers result when aniline is copolymerized with *o*-toluidine, *m*-toluidine, and *N*-butylaniline in HCl solutions.[15,19] In these cases, aniline also showed lower reactivity when compared to the substituted anilines. The higher reactivities of all the substituted anilines can be mainly attributed to the electron-donating alkyl substituents which stabilize the cation free radical intermediates during the course of polymerization. For copolymers of aniline and ethylaniline, steric factors should play a minor role since they affect r_1 and r_2 in a similar fashion.

Infrared spectra of various copolymer thin films cast on NaCl or KBr plates showed strong sp^3 C–H stretching bands at approximately 2872, 2930, and 2963 cm^{-1}. In addition, several other bands in the region 600–900 cm^{-1} can be attributed to vibrations involving out-of-plane C–H bending. Benzene rings with 1, 2, and 4 substituents, as in poly(*o*-ethylaniline), showed characteristic infrared absorption bands in the regions between 805–825 and 870–885 cm^{-1}, whereas benzene rings with 1 and 4 substituents, as in polyaniline, show only a single absorption band between 790 and 840 cm^{-1}. The infrared spectrum of each copolymer gave a superposition of these absorptions with intensities dependent on composition. Therefore, qualitatively, FT-IR data support the quantitative ^{1}H-NMR compositional results by showing the presence of both monomer units in the copolymers formed.

Improved solubility of the copolymers was observed by comparing the copolymers directly in various organic solvents. Equal amounts of the copolymers (0.25 g) were added to 10 mL of each of the following solvents: acetone, methanol, ethanol, THF, DMSO, and NMP. Table 1 shows the solubility of the parent polymers and copolymers in these solvents. The improved solubility of these copolymers over polyaniline appears to be related to the introduction of the functional groups on the polymer backbones. The more soluble fractions in THF, DMSO, and NMP formed films on evaporation.

Solubility was also used to prove that the products were indeed copolymers by following a method similar to that outlined by Bergeron *et al.*[19] A copolymer composed of 36% aniline and 64% *o*-ethylaniline, and the homopolymers in the same ratios, were dissolved separately in NMP (0.5 g/100 mL) to distinguish the copolymer from a composite mixture of the two homopolymers. The copolymer dissolved completely, while considerable amounts of undissolved particles were observed in the mixed homopolymer solution. This result indicates that true copolymers have been synthesized from the two monomers rather than a simple mixture of two homopolymers.

Thermal Studies. Thermogravimetric analysis has shown that polyaniline in its emeraldine base form is stable up to ~420 °C, above which temperature the polymer begins to decompose. The decomposition temperature (defined as ≥10% weight loss) of the *o*-ethylaniline/aniline copolymers decreases with increasing *o*-ethylaniline content (Table 2). The decomposition temperature for polyaniline, found here to be 486 °C, is difficult to determine accurately due to residual water. Emeraldine polyaniline powder begins to lose moisture at ~50 °C. The amount of water which evaporates from a powder sample varies from 2 to 10%, depending on its exposure to humidity, and was not considered part of the 10% weight loss for determining weight loss decomposition temperatures.

A DSC trace of polyaniline powder indicates an endothermic transition starting at approximately 50 °C and centered at approximately 120 °C (Figure 4e). This result, again, agrees with the evaporation of water molecules, which are trapped inside the polymer or bound to the polymer backbone. This endothermic peak is less distinguishable in poly(*o*-ethylaniline), and the copolymers (Figure 4a–d). The endotherm completely disappears at higher ethylaniline contents, as is apparent in Figure 4. This result can be attributed to the hydrophobic character of the ethyl substituents on the benzene rings. The temperature of the exotherm in the DSC patterns also shows a linear decrease with increasing ethylaniline content.

The glass transition temperature for polyaniline is a difficult thermal event to observe by DSC, although a complete study using differential mechanical analysis was performed by Wei *et al.*[34] Generally, the T_g is not

Table 1. Solubility (in g/10 mL) of Polyaniline, Poly(aniline-*co*-*o*-ethylaniline), and Poly(*o*-ethylaniline) in Acetone, Methanol, Ethanol, THF, DMSO, and NMP[a]

polymer (mol % ethylaniline)	acetone	methanol	ethanol	THF	DMSO	NMP
0.0	0.0015	0.0026	0.0020	0.0020	0.0551	0.2255
25.4	0.0029	0.0065	0.0034	0.0035	0.0759	0.2227
46.8	0.0112	0.0063	0.0046	0.0478	0.0657	~complete
84.1	0.0412	0.0222	0.0204	~complete	~complete	~complete
100.0	0.0508	0.0262	0.0289	~complete	~complete	~complete

[a] Complete solubility is defined as the solution becoming so viscous that filtration is not possible.

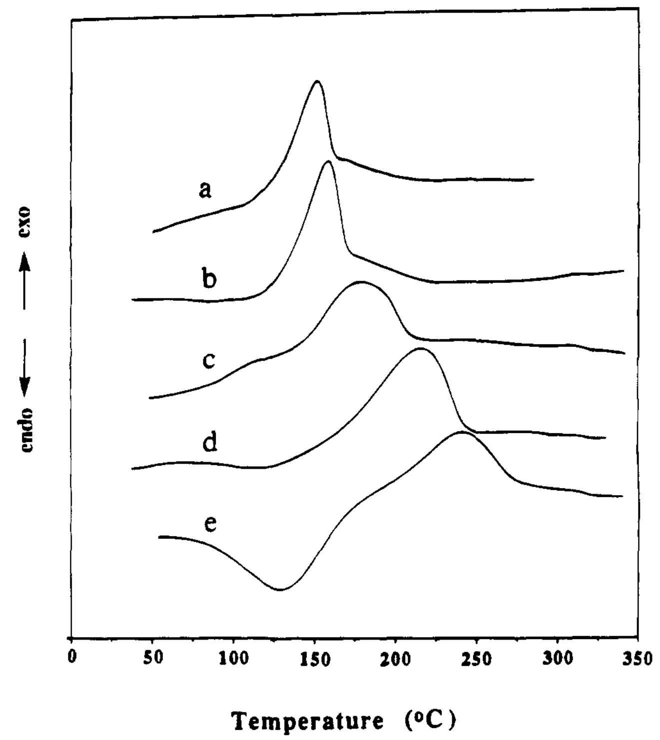

Figure 4. Transition temperatures determined by differential scanning calorimetry (DSC). The mole fraction of *o*-ethylaniline relative to aniline in each copolymer is (a) 100%, (b) 82%, (c) 71%, (d) 30%, (e) 0%.

Table 2. Onset Temperature of Weight Loss in the Copolymers Using TGA

copolymer composition (% ethylaniline)	temp (°C)	copolymer composition (% ethylaniline)	temp (°C)
100	420	66	450
87	420	49	461
79	419	0	486

evident in the thermographs of this polyaniline powder. The exothermic transition observed at ~240 °C is not believed to be a glass transition temperature based mainly on the fact that it does not exhibit hysteresis. When the polymer powder is heated above 240 °C, cooled, and reheated, no exotherm is observed upon reheating. If the transition were a T_g, it should be observed repeatedly upon heating and cooling. Cross-linking in this polymer is an irreversible chemical reaction and therefore would be observed only upon heating the polymer to 240 °C for the first time. This exotherm observed in the DSC trace can be attributed to a series of chemical reactions. These likely involve bond scissioning, followed immediately by new chemical bond formation. Bond cleavage is usually endothermic and bond formation exothermic, with the overall reaction being an exothermic process. Bond cleavage shortens the conjugation length, resulting in an increase in the free radical concentration and a decrease in the conductivity of the doped polymer, as described below.

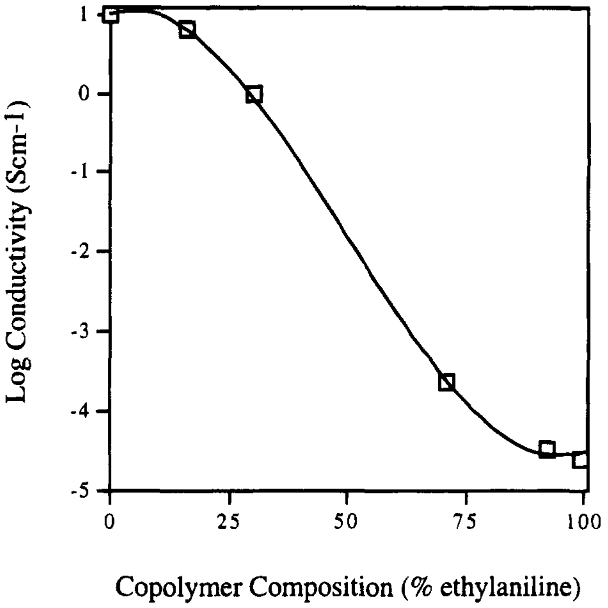

Figure 5. Electrical conductivity vs mole fraction of *o*-ethylaniline in the doped HCl copolymer. The solid line is drawn using the following polynomial fit: $y = 0.000020x^3 - 0.0023x^2 + 0.020x + 1.0$.

Cross-linking and new bond formation between polymer chains account for the decreasing solubility of the polymers in NMP. This whole process slowly proceeds even at room temperature. As a result, the solubility of emeraldine polyaniline in NMP decreases after being stored at room temperature for several weeks.

To investigate the exothermic transition in more detail, including the free radicals formed in the polymers, emeraldine polyaniline powder samples were heated at 200 °C in sealed tubes under vacuum. This procedure prevented the likely reaction between polyaniline and oxygen. The concentration of free radicals in the polyaniline powder before heating, as well as in the heated polyaniline powders, was examined by EPR spectroscopy. These experiments were carried out by double integration of a single differential peak centered at a *g* value of 2.002, which is characteristic of free electrons in organic polymers.[35] Since the total number of free radicals is proportional to the integrated areas of the EPR signal, the relative concentration of free radicals can be easily calculated by dividing the integrated area by the weight of the sample. The concentration of free radicals for polyaniline heated 2 h at 200 °C increased approximately 4 times compared to that of comparable as-synthesized polyaniline samples. Continuous heating keeps increasing the number of free radicals. After heating for 24 h, the polyaniline powder possessed 10 times the free radical concentration compared to the original, unheated polyaniline sample. The increasing number of unpaired electrons after heat treatment suggests that the polyaniline framework

Table 3. Wavelength of Maximum Absorbance of Polyaniline in NMP after Heating at 150 °C

heating time (min)	λ_{max} (nm)	heating time (min)	λ_{max} (nm)
59	628	468	594
130	624	727	596
240	620	1291	538
348	612		

undergoes bond cleavage which can produce two free radicals for each bond broken, consistent with the results found by DSC.

Conductivity. As-cast emeraldine free-base polyaniline is an electrical insulator. When reacted with protonic acids, polyaniline exhibits increased electrical conductivity. The reported conductivities of polyaniline in the acid form varies from approximately 1 to 100 S·cm^{-1}.[16] This range may be due to the different sample preparation methods, molecular weight distributions, counterions, and difficulty in obtaining uniform film thicknesses. Generally, conducting polymers with substituents on their frameworks show lower conductivities compared to those of the original polymers. For example, the room temperature conductivity of acid-doped poly(*o*-ethylaniline) found by the four-probe technique is 2×10^{-5} S·cm^{-1}, which is at least 5 orders of magnitude lower than that of doped polyaniline. The conductivity of HCl-doped poly(aniline-*co*-*o*-ethylaniline) decreases as the mole fraction of *o*-ethylaniline increases, as illustrated in Figure 5. However, even with 30% *o*-ethylaniline content, conductivity is still on the order of 1 S·cm^{-1}.

Heating polyaniline films at 200 °C under vacuum results in the loss of solvent (NMP), which can be identified by the disappearance of the characteristic carbonyl stretch (centered at ~1688 cm^{-1}) for NMP in the infrared absorption spectrum.[36] NMP acts as a plasticizing agent, and hence the film becomes somewhat brittle after NMP is removed.

The conductivity of the heated polyaniline films after doping with hydrochloric acid is 5 orders of magnitude less than unheated polyaniline films doped under the same conditions ($\sigma \approx 10$ S·cm^{-1}). Similar results have been shown for heating already doped polyaniline. Upon heating, the hydrochloric acid doped polyaniline loses counterions and its conductivity drops.[27-37] Redoping the heated polyaniline does not restore the doping level or original conductivity. Boyle *et al.* have also observed thermally induced chain oxidation for perchloric acid and sulfuric acid doped polyanilines.[24] A reasonable explanation for the decrease in conductivity and loss of counterions is that both thermal approaches trigger or accelerate some chemical reactions which irreversibly yield a shorter conjugation length along the polymer backbone. In the case of heating doped polyaniline, shortening the conjugation length decreases the capability of accommodating all the dopants associated with the polyaniline, resulting in dopant loss. This shortened conjugation length, coupled with the decrease in doping capability after heating, indicates that chain scission occurs at imine nitrogens, making them chain ends that are now in the amine form, and no longer able to be doped. On the other hand, decreasing the conjugation length of pristine polyaniline makes the doping experiments more difficult and lowers the doping levels achievable.

Solubility. The solubility of heated polyaniline powder in NMP was determined by UV–vis absorption. Emeraldine polyaniline dissolved in NMP showed an intense blue color with UV–vis light absorption bands at ~330 and 630 nm.[23] A blue shift is observed for thermally treated polyaniline with different heating periods. The absorption shifts are summarized in Table 3. The maximum absorbance shifted from 630 nm for pristine polyaniline to 540 nm after heating ~21 h at 150 °C. The blue shift of the absorption band, along with conductivity loss, again suggests shortened conjugation lengths for heated polyaniline. After being heated at 200 °C for 30 min, polyaniline completely loses its solubility in NMP. Lowering the heating temperature reduces the rate of thermal degradation. Storage of polyaniline powder at low temperatures, for example 0 °C, can be used to slow the rate of thermal degradation.

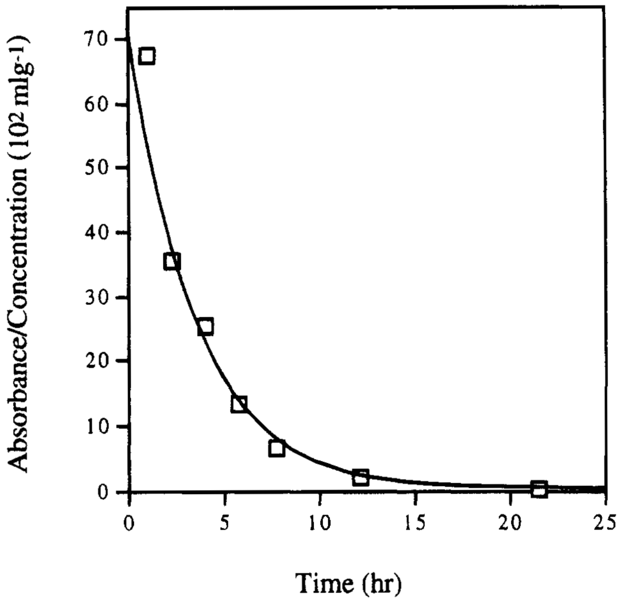

Figure 6. Normalized UV–vis absorbance at 600 nm for polyaniline heated at 150 °C for 1–23 h.

Figure 6 shows the normalized absorbance of emeraldine polyaniline powders after heating at 150 °C for different periods of time. The absorbance of a heated polyaniline solution represents the concentration of polyaniline powder dissolved in NMP solution. For a given amount of heated polyaniline powder in 100 mL of NMP, the relative solubility of each individual sample can be determined by the intensity of the UV–vis absorption. The solubility of polyaniline obtained from the maximum absorption band at ~600 nm decreases exponentially with increasing heating periods. Polyaniline did not dissolve in NMP after being heated at 150 °C for 21 h. This phenomenon can be attributed to the cross-linking of the polyaniline backbone, which forms larger molecular segments. As the molecular segments increase in size, their solubility would tend to decrease. Polyaniline powders heated at 110 °C for 2 h maintain high solubility in NMP. This is very important to ensure that the polyaniline does not deteriorate at the temperature at which polyaniline films are normally cured.

Genies *et al.* have studied electrochemical redox reactions of polyaniline using cyclic voltammetry and have proposed cross-linked products.[38] After these cross-linking reactions, polyaniline evolves toward a two-dimensional polymer with phenazine type rings. The possibility of phenazine rings in cross-linked polyaniline was also suggested by Rodrigue *et al.*[27] and Thyssen *et al.*[39] These products are likely formed in our heat-treated samples as a result of thermally cross-linking the emeraldine base powders.

Conclusions

Copolymerizing aniline and its ethylated derivative, *o*-ethylaniline, has produced powders with improved solubility compared to parent polyaniline, that easily form films from NMP. The solubility of the polymers in organic solvents has been found to dramatically increase with increasing ethylated monomer repeat units. The physical properties of this copolymer depend heavily on the ratio of monomers as well. The thermal properties of these copolymers, and the parent homopolymer, polyaniline, were investigated to determine solubility and cross-linking. Polyaniline, in the emeraldine base form, irreversibly cross-links at ~250 °C and completely loses solubility in NMP. The copolymers cross-link at lower temperatures, depending on their composition. Combining the results from these studies leads to a better understanding of how to protect polyaniline from degradation and improve solubility to allow for the formation of high-quality free-standing films. Future investigations concerning the copolymers' utility as membranes for both gas and liquid separations are now in progress.

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