

Synthesis and properties of poly(aniline-co-azidoaniline)

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Abstract

Copolymers of polyaniline and *o*-azidoaniline were synthesized by chemical oxidative polymerization. The copolymers were characterized by powder X-ray diffraction (XRD) and UV/Vis and FT-IR spectroscopy. Thermal activation of the azido chromophore in the copolymer caused it to react and cross-link into adjacent polymer chains. The cross-linking of the copolymers was indicated by the depletion of the azido band in the FT-IR spectrum. The effects of the cross-linking were studied by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and four-probe conductivity. The TGA showed that the thermal stability of the copolymers is improved due to cross-linking. However, the increased thermal stability is accompanied by a decrease in electrical conductivity due to the loss of conjugation detected by UV/Vis spectroscopy and a loss of crystallinity due to the azido substituents, which was demonstrated by XRD.

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Keywords: Polyaniline; Cross-linking; *o*-Azidoaniline; Azides; Aryl azides; Nitrenes; Substituted polyaniline

1. Introduction

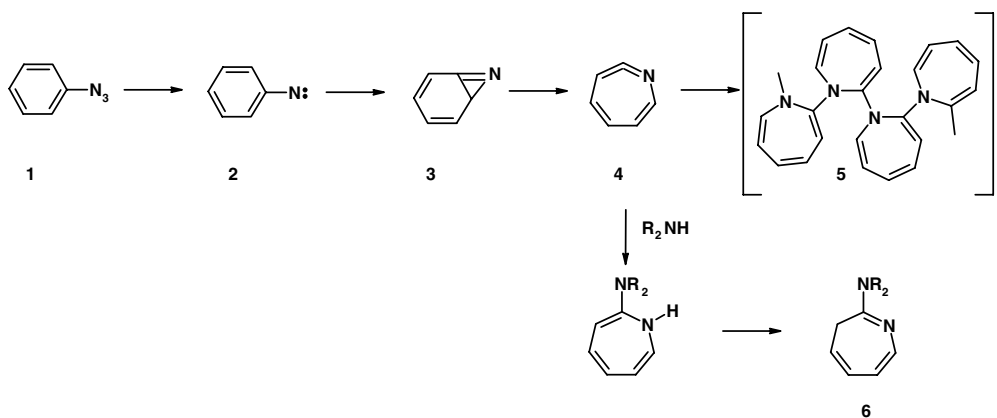
Polyaniline is currently the most promising conducting polymer for practical applications, because it can be synthesized and processed with ease [1–4]. Highly conductive emeraldine salts can be formed by simply protonating the emeraldine base form of polyaniline. Substituted polyanilines with altered properties can be made by adding functional groups to the backbone of the polymer. For example, polyanilines with sulfonic acid substituents are self-doped, highly conducting polymers that were synthesized using conventional chemical oxidative

polymerization [5–8]. Azobenzene functionalized polyanilines have improved conductivity [9], whereas alkyl and alkoxy-substituted polyanilines have increased solubility in water [10], and tert-butoxycarbonyl-substituted polyanilines are soluble in solvents such as tetrahydrofuran, dioxane, and chloroform [11]. Polyanilines with boronic acid substituents are used in sensors [12,13].

Thermal activation of phenyl azide **1** yields 1,2-azepine polymer **5**, which is moderately conductive upon oxidation [14]. Oxidation of **5** forms cations that delocalize over the backbone of the polymer and render it conductive. The thermal decomposition of phenyl azide takes place through the formation of a singlet phenyl nitrene **2**, which rearranges to form azacycloheptatetraene **4** via azirine **3** (Scheme 1) [15]. Compound **4** can polymerize to

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Scheme 1. Thermal activation of phenyl azide.

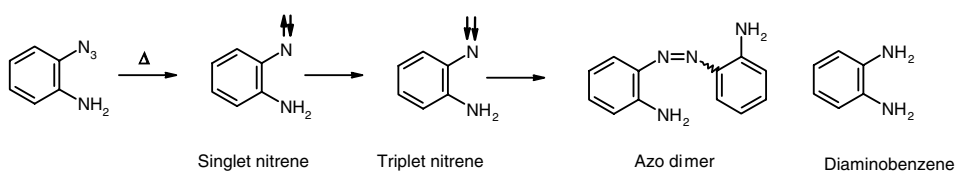
form **5**, but in the presence of nucleophiles such as amines it yields azepines **6**. Thus, by incorporating *o*-azidoaniline into polyaniline it is possible to cross-link the polymer, while maintaining the overall conjugation of the polyaniline.

However, depending on the substituents on the aryl azides [15–19] and the concentration [20,22], reaction solvent [18,21], and temperature [23], singlet aryl nitrene can (a) form azirines as described above, (b) undergo intersystem crossing to form triplet aryl nitrenes, or (c) insert into surrounding C–H and C–C bonds [15]. Singlet aryl nitrenes with electron-donating substituents such as amine or methoxy groups undergo efficient intersystem crossing to their triplet state and decay mainly by dimerization to form azobenzene dimers [15,19]. Thermal activation of *o*-azidoaniline in toluene mostly gives azo dimer along with 1,2-diaminobenzene, which is formed from the triplet nitrene abstracting a H atom from the solvent [24]. Thus, we expect that incorporation of *o*-azidoaniline into polyaniline will allow us to cross-link the polymer by the formation of azo dimers between adjacent azido moieties (see Scheme 2).

Polyaniline has been cross-linked by annealing the film at temperatures above 300 °C, which causes the quinoid bond to dimerize [25] and form three-

dimensional polymer networks. Cross-linked polyaniline has decreased solubility [26,27] and conductivity due to the shortening of its conjugation and inability to accommodate dopants.

We set out to synthesize polyaniline with azido substituents on the backbone of the polymer, with the idea of using the azido functional group to cross-link adjacent polymer strands. Forming a copolymer between *o*-azidoaniline and polyaniline makes it possible to cross-link the polymer after it has been processed and therefore circumvents the fact that cross-linked polyaniline is generally insoluble and difficult to process [26,27]. In this paper, we describe the oxidative copolymerization of aniline and *o*-azidoaniline and the characterization of the resulting copolymer by X-ray diffraction and IR and UV/Vis spectroscopy. We analyzed the thermal properties of the azido copolymers and found that they had improved thermal stability in comparison with plain polyaniline, thus verifying that the copolymers are cross-linked. However, films made from the copolymers doped with camphor sulfonic acid and cast from *m*-cresol were less conductive than similar films made from polyaniline, because the azido substituent disrupts the crystallinity and the conjugation length of the copolymer.

Scheme 2. Thermal reactivity of *o*-azidoaniline.

2. Experimental

2.1. Polyaniline-emeraldine base (PANi-EB) synthesis

Polyaniline was synthesized by chemical oxidative polymerization following the procedure of Adams et al. [28]. Aniline (9.313 g, 0.1 mol) was dissolved in aqueous HCl (100 g, 1.00 M) solution and the pH adjusted to 1.0 by further addition of HCl. Lithium chloride (LiCl: 23.03 g, 0.542 mol) was added to lower the freezing point of the solution, which was cooled to -20°C . A solution of ammonium peroxydisulfate ($[\text{NH}_4]_2\text{S}_2\text{O}_8$: 28.8 g, 0.125 mol) in distilled water (51.5 g) was added dropwise (8 mL/h) while the aniline solution was kept at -20°C . The emeraldine salt that precipitated out of solution was filtered and deprotonated with liquid ammonia over a period of 24 h, filtered, and washed with distilled water to obtain polyaniline-emeraldine base (8.2 g, 89% yield, PANi-EB) as a purple powder. This powder was washed thoroughly with distilled water and isopropyl alcohol before further use.

2.2. Synthesis of *o*-azidoaniline

o-Azidoaniline was prepared from *o*-nitroaniline following the procedure of Smith et al. [29] (Scheme 3).

2-Nitrophenylamine (14.1 g, 0.101 mol) was heated with phthalic anhydride (15 g, 0.101 mol) for 3 h to obtain 2-(2-nitro-phenyl)-isoindole-1,3-dione [30]. This resulting solid was re-crystallized from chloroform several times to obtain fine crystals of 2-(2-nitro-phenyl)-isoindole-1,3-dione (20 g, 0.074 mol, 74% yield).

IR (CHCl_3) ν_{max} : 3019, 1719, 1534 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.21 (2, 1H), 7.98 (m, 2H), 7.84 (m, 2H), 7.78 (d, 1H), 7.63 (t, 1H), 7.54 (d, 1H) ppm.

A mixture of 2-(2-nitrophenyl)isoindole-1,3-dione (15 g, 0.055 mol), acetic acid (100 mL), acetone (550 mL), water (100 mL), and iron (36 g, 0.644 mol) was refluxed for 5 h [30]. The solution was filtered

hot through silica using vacuum. The filtrate was extracted with ethyl acetate (3×200 mL) and dried over MgSO_4 , and the solvent was removed under vacuum to yield 2-(2-aminophenyl)isoindole-1,3-dione (10.2 g, 0.043 mol, 78% yield).

IR (CHCl_3) ν_{max} : 3472, 3396, 3019, 1719, 1624, 1534 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.94 (m, 2H), 7.79 (m, 2H), 7.25 (m, 1H), 7.11 (m, 1H), 6.89 (m, 2H), 3.48 (br, s, 2H) ppm.

To a suspension of 2-(2-aminophenyl)isoindole-1,3-dione (8.5 g, 0.0357 mol) in a mixture of THF (70 mL), water (120 mL), and HCl (15 mL, conc.) was added NaNO_2 (4.2 g, 60.8 mmol) over 20 min with constant stirring [31]. To this reaction mixture was added NaN_3 (5 g, 76 mmol) over 5 min while the reaction temperature was maintained at 0°C . Product formation was monitored by TLC. After completion, the reaction mixture was extracted with diethyl ether (3×200 mL); the extract was dried over MgSO_4 and the solvent removed under vacuum to give 2-(2-azidophenyl)isoindole-1,3-dione (4.5 g, 0.017 mol, 48% yield).

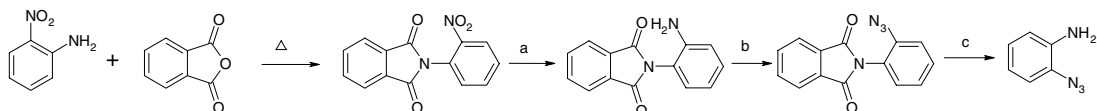
IR (CHCl_3) ν_{max} : 3020, 2130, 1719 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.98 (m, 1H), 7.96 (m, 2H), 7.83 (m, 1H), 7.79 (m, 2H), 7.51 (m, 1H), 7.28 (m, 1H) ppm.

A slurry of 2-(2-azidophenyl)isoindole-1,3-dione (4.5 g, 0.017 mol) and hydrazine hydrate (1 g, 0.019 mol) in ethanol (100 mL) was stirred for 1.5 h [29]. To this slurry was added 20 mL of aqueous NaOH (20 g NaOH, 100 mL water); the mixture was stirred for 5 min and filtered. Ice water (10 mL) was added to the filtered solution and the resulting crystals of 2-azidoaniline (1.2 g, 0.0089 mol, 52% yield) were filtered.

IR (CHCl_3) ν_{max} : 3470, 3379, 3020, 2130, 1719, 1621 cm^{-1} . $^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 8.14 (m, 1H), 7.33 (m, 1H), 6.75 (m, 1H), 6.07 (m, 1H) ppm.

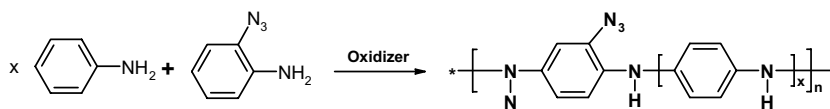
2.3. Synthesis of poly(*aniline-co-azidoaniline*) (PANAZ)

Ten percent by weight PANAZ was synthesized in the same way as PANi-EB, by chemical oxidative



(a) CH_3COOH , Iron. (b) NaNO_2 , NaN_3 , HCl. (c) NaOH, NH_2NH_2 .

Scheme 3. Synthesis of 2-azidoaniline.



Scheme 4. Synthesis of PANAZ.

polymerization. Aniline (4.2 g, 0.045 mol) and *o*-azidoaniline (0.42 g, 0.31 mmol) were mixed together, HCl (100 g, 1 M) solution was added, and the pH was adjusted to 1 by further addition of the HCl solution. LiCl was used as the antifreeze agent. A solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (14 g, 0.060 mol) in distilled water (30 mL) was added dropwise (5 mL/h) while the temperature of the reaction mixture was maintained at -20°C . This procedure yielded 3.5 g of 10% by weight poly(aniline-co-azidoaniline) or PANAZ10. Copolymers of aniline with 1% and 5% weight of *o*-azidoaniline (PANAZ1 and PANAZ5) were synthesized as described above (see Scheme 4).

2.4. Casting of films

The 1:1 mixture of PANi-EB or the PANAZ and camphor sulfonic acid was finely ground in a mortar and pestle to yield polyaniline camphor sulfonic acid salt (PANi-CSA) and poly(aniline-co-azidoaniline) camphor sulfonic acid salt (PANAZ-CSA). These powders were suspended in *m*-cresol and homogenized by use of a Powergen Model 700 homogenizer. The mixture was added gradually over 1 h to *m*-cresol to achieve a concentration of 2% by weight. The resulting solution was cast onto glass slides or silicon wafers, which were allowed to dry at 60°C for a period of 24 h to yield films with uniform thickness.

2.5. Thermal treatment of PANi-CSA and PANAZ-CSA films

Films of PANi-CSA and PANAZ-CSA cast from *m*-cresol were heated to 160°C and kept at this temperature for 3 h under normal atmosphere.

2.6. Characterization of PANi-EB and PANAZ

^1H NMR spectra were recorded on a 400 MHz NMR instrument using CDCl_3 as the solvent. IR spectra of PANi-EB and PANAZ in KBr pellets were obtained on a Perkin-Elmer 1600 spectrometer. UV/Vis spectra of PANi-EB and PANAZ in 1-methylpyrrolidinone were recorded with a Hewlett-Packard 8453 spectrophotometer.

The 2θ diffraction pattern of PANi-EB homopolymer and PANAZ copolymer powders were collected using a Philips X'pert X-ray diffractometer, using $\text{CuK}\alpha$ radiation at the rate of $2\theta = 5^\circ$ per minute.

The TGA and DSC studies of PANi-EB and PANAZ were carried out on a NETZSCH instrument under a nitrogen flow rate of 50 mL/min from 25°C up to 1000°C , with ramping rate of $10^\circ\text{C}/\text{min}$.

The thickness of the PANi-CSA and PANAZ-CSA films on the silica slides was measured using a Philips XL30 Environmental Scanning Electron Microscope (ESEM). The conductivities of the PANi-CSA and PANAZ-CSA films were obtained by measuring the resistances of the films using a four-point probe purchased from Jandell.

3. Results

3.1. IR and UV spectroscopy

FT-IR spectra of PANi-EB powder, PANAZ and the cross-linked PANAZ powders are shown in Fig. 1. The quinoid stretching is observed at 1583 cm^{-1} for PANi-EB and at 1577 cm^{-1} for PANAZ, and the benzenoid stretching is observed at 1490 cm^{-1} for PANi-EB and 1487 cm^{-1} for PANAZ. The IR spectra of PANi-EB and PANAZ are similar, except for the azide band at 2110 cm^{-1} . This band disappears when the copolymers are heated, indicating that the azide functional group has reacted to cross-link the polymer.

The UV/Vis spectra of PANi-EB homopolymer and PANAZ copolymers dissolved in 1-methylpyrrolidinone showed absorption bands with λ_{max} at 320 nm and approximately 600 nm (Fig. 2). The broad absorption at 634 nm for polyaniline has been assigned to quinoid formation in the backbone of the polymer, which indicates extended conjugation [32]. This absorption band shifted to lower wavelengths for the PANAZ copolymers. The maximum is at $\sim 607\text{ nm}$ for both the 1% and 5% copolymer but is shifted all the way to 567 nm for the 10% copolymer. The shift of the quinoid band to lower wavelengths in the copolymers implies that they are less conjugated than the PANi-EB homopolymer.

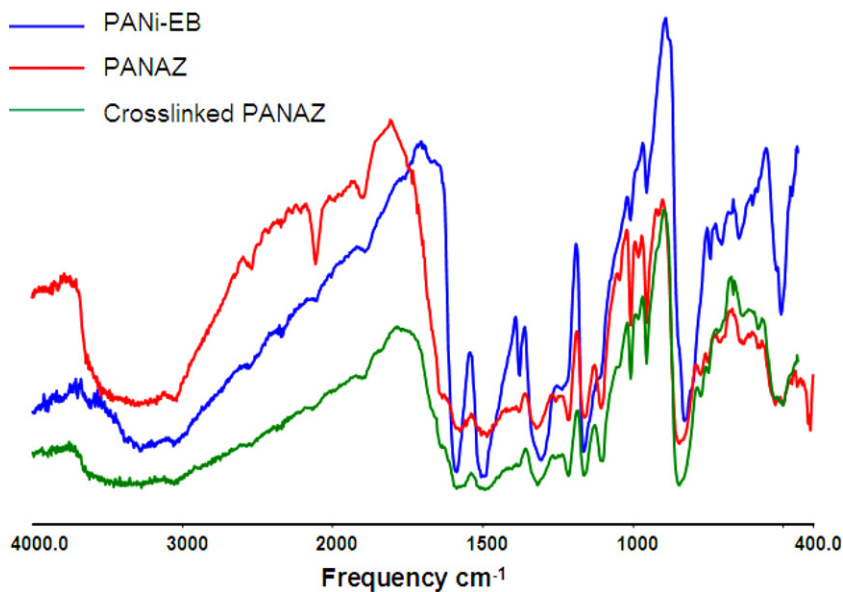


Fig. 1. Infrared spectra of PANi-EB and PANAZ.

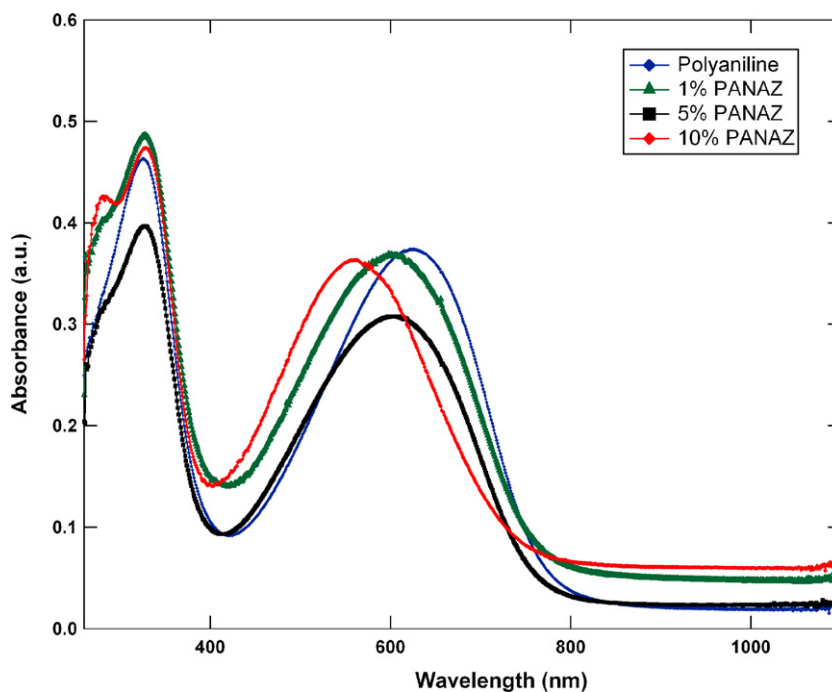


Fig. 2. UV-Vis spectra of PANi-EB and PANAZ.

3.2. XRD diffraction

Powder XRD of PANi-EB showed resolved diffraction peaks and it is therefore partially crystalline (Fig. 3). This is similar to what Jozefowicz et al. have shown previously [33]. In comparison, the diffraction patterns for PANAZ copolymers were broad, without any resolved peaks, indicating that they are amorphous.

3.3. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) studies

The TGA of PANi-EB and PANAZ showed weight loss between 50 and 100 °C (Fig. 4). The weight loss observed between 50 and 100 °C for TGA analysis of polyaniline has been previously assigned to vaporization of water from the sample

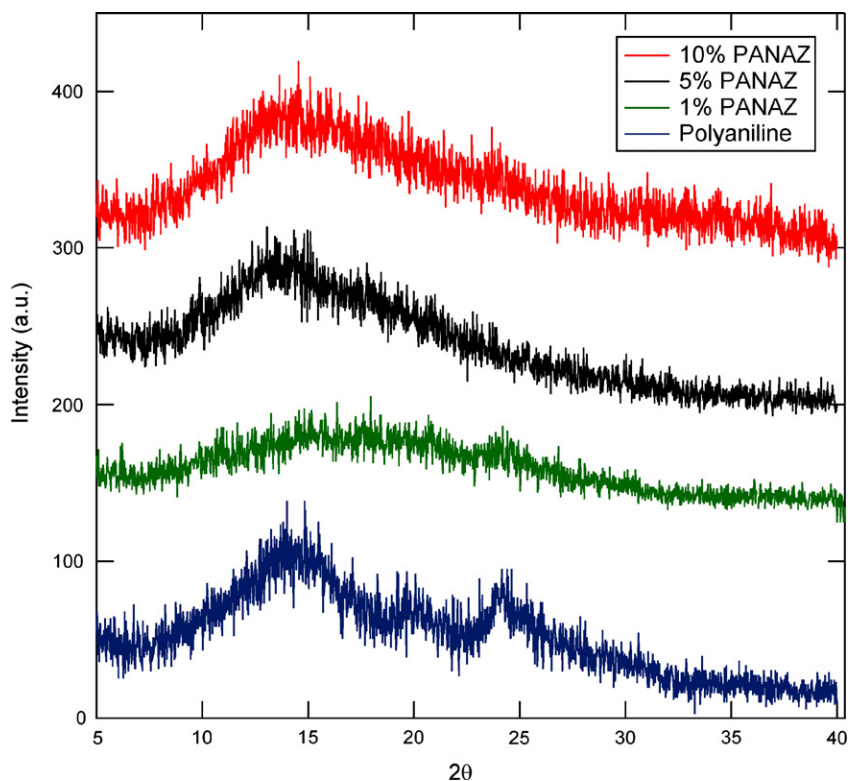


Fig. 3. XRD diffraction of PANi-EB and PANAZ samples.

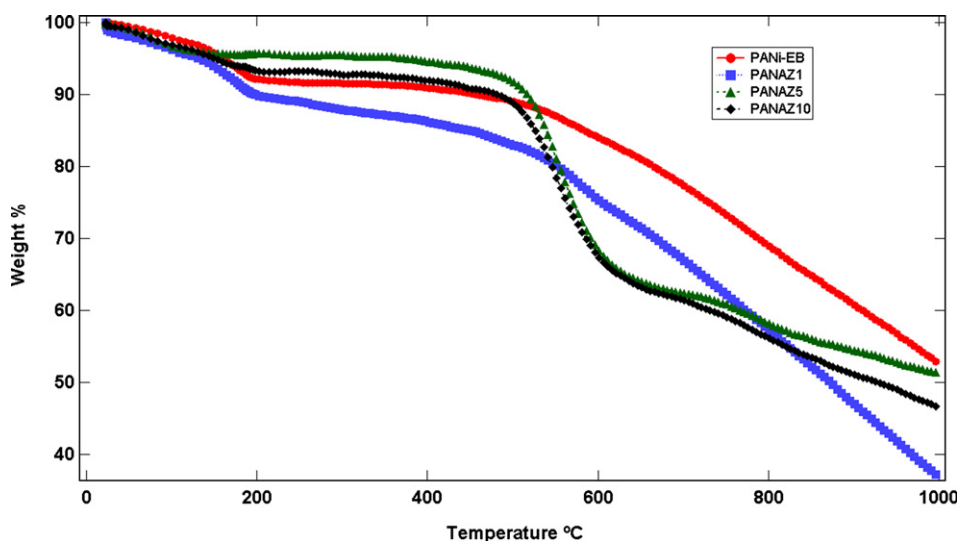
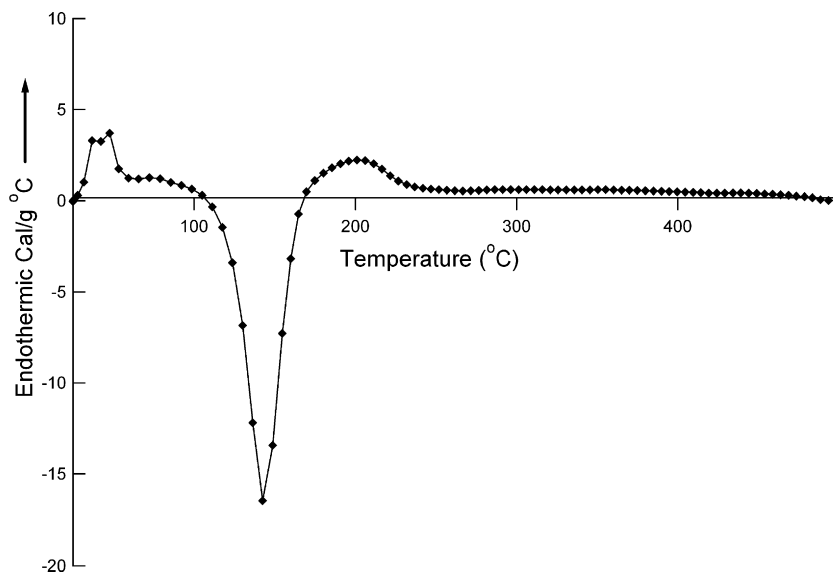
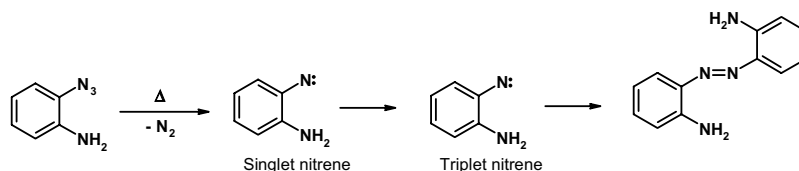


Fig. 4. TGA of PANi-EB and PANAZ.

[34]. The PANAZ5 and PANAZ10 copolymers show a higher degradation temperature in comparison to the PANi-EB and PANAZ1 samples [34]. We attributed this to a higher degree of cross-linking of these polymers. This is further verified by DSC analysis of these samples, as described below.

The DSC trace for *o*-azidoaniline showed a sharp exothermic transition centered on $\sim 150^\circ\text{C}$ (Fig. 5). *o*-Azidoanilines undergo thermal decomposition, resulting in a loss of nitrogen and presumably formation of the corresponding azodimer (Scheme 5). The decomposition temperature for *o*-azidoaniline

Fig. 5. DSC of *o*-azidoaniline.Scheme 5. Proposed thermal decomposition of *o*-azidoaniline.

is similar to what has been observed for some other *o*-azidoaniline derivatives [35].

Thermal analyses of PANi-EB powder demonstrate discernible moisture content [34], and the first endothermic peak has been assigned to the vaporization of water. This corresponded well with our TGA results. The endothermic transition for the activation of the azido group in PANAZ1 and PANAZ5 is observed at slightly lower temperature, $\sim 130^\circ\text{C}$, than for *o*-azidoaniline (Fig. 6). We speculate that the extended conjugation of the polymer backbone to the azide moiety decreases the bond dissociation energy for breaking the nitrogen–nitrogen bond in the azido group. In comparison, PANAZ10 has an exothermic transition $\sim 150^\circ\text{C}$. We hypothesize that the higher concentration of the azido functional group in PANAZ10 changes the thermal profile of the reaction, similar to what Schrock and Schuster observed for phenyl azides [20]. We speculate that some of the azido groups are trapped by nitrene intermediates before they release molecular nitrogen to form nitrenes in PANAZ10.

3.4. Conductivity measurements

The conductivity of PANi-CSA films cast from *m*-cresol, was approximately 177 S/cm, which corresponds well with the literature value of between 100 and 400 S/cm [36], whereas the conductivities of PANAZ-CSA films, before thermal treatment, were considerably lower (see Table 1). The conductivity decreased with increased azido substituents in PANAZ-CSA.

Thermal treatment of PANi-CSA and PANAZ-CSA films reduced their conductivities by 37% and between 21–56%, respectively. This agrees with the values of thermally aged PANi-CSA films in *m*-cresol [37].

4. Discussion

We were able to synthesize copolymers of aniline and *o*-azidoaniline, as demonstrated by IR spectroscopy. PANAZ-CSA films were significantly less conductive than PANi-CSA films, and their conductivity decreased with increased azido

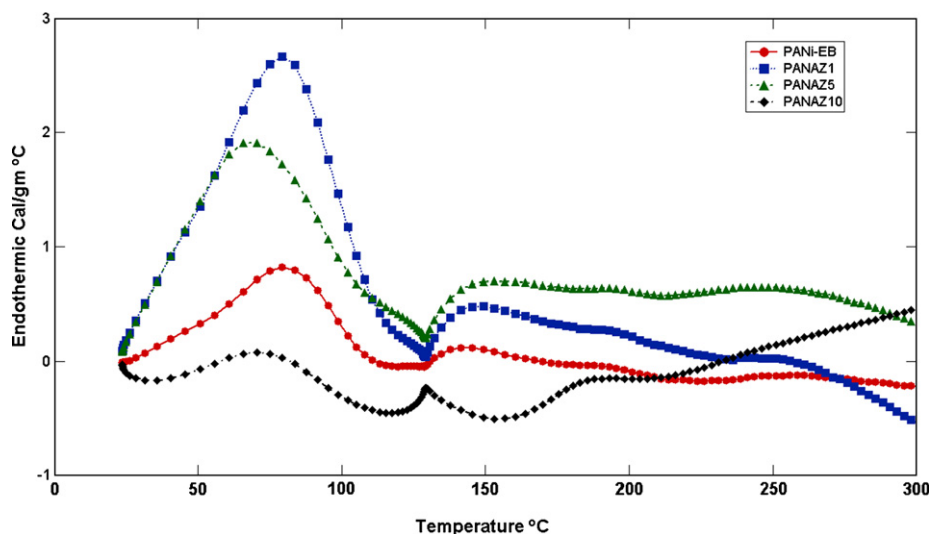


Fig. 6. DSC of PANi-EB and PANAZ.

Table 1
Conductivity of PANi-CSA and PANAZ-CSA films

	Non heated films (S/cm)	Heated films (S/cm)
PANi-CSA	177	111
PANAZ1-CSA	112	74
PANAZ5-CSA	56	44
PANAZ10-CSA	0.046	0.02

substitution. In agreement with this observation, the UV/Vis absorption spectra of the PANAZ showed less conjugation of the polymer backbone than for PANi-EB. Similarly, XRD spectra of PANAZ demonstrated that the copolymers are less crystalline than PANi-EB. Hence, we can conclude that the steric effect of the azido substituent reduces the conjugation length of the polymer by forcing the torsion angle between adjacent phenyl rings to become larger in order to ease the steric strain. Furthermore, the steric effect of the azido group also interferes with the ability of the copolymers to form crystalline regions. Similarly, steric affects in poly(*o*-methylaniline), poly(*o*-ethylaniline), and copolymers of polyaniline and poly(*o*-methylaniline) render them less conductive than polyaniline [39].

The PANi-CSA films showed conductivity of 177 S/cm. When these films were heated to 160 °C for 3 h, their conductivity decreased to 111 S/cm. Similar results were reported by Li and Wan [37]. Furthermore, thermal treatment of polyaniline films doped with HCl also decreases their conductivity

[38]. Annealing of the polyaniline films causes the residual solvent to evaporate, and the lack of this secondary doping from the solvent causes the polymer chain to be coiled rather than expanded and thus reduces the conductivity [38].

IR spectra of the annealed copolymer films reveal that the azido band has been depleted. Thermal treatment of the PANAZ copolymers causes the azido group to react and form triplet nitrenes that react with an adjacent nitrene or azido moiety to form a covalent nitrogen–nitrogen bond (Fig. 7). In competition with azo formation, the nitrene intermediates abstract a H atom to form amines, which does not result in cross-linking of the polymer. However, since TGA showed higher degradation temperatures for PANAZ5 and PANAZ10, their increased thermal stability can be credited to cross-linking of the polymers by azo dimer formation.

Furthermore, DSC of PANAZ also shows weight loss around 130 °C that can be attributed to release of nitrogen molecules from the azido groups, verifying that the azido groups have reacted.

The conductivity of PANAZ-CSA films decreased between 21% and 56% upon heating, which is slightly more than to what was observed for PANi-CSA films. Annealing the PANAZ-CSA films causes the azido group to react and cross-link adjacent polymer strands, but it also evaporates residual solvent and thus reduces their conductivity. Hence, we speculate that the decreased conductivity of the cross-linked films is mainly due to loss of the solvent

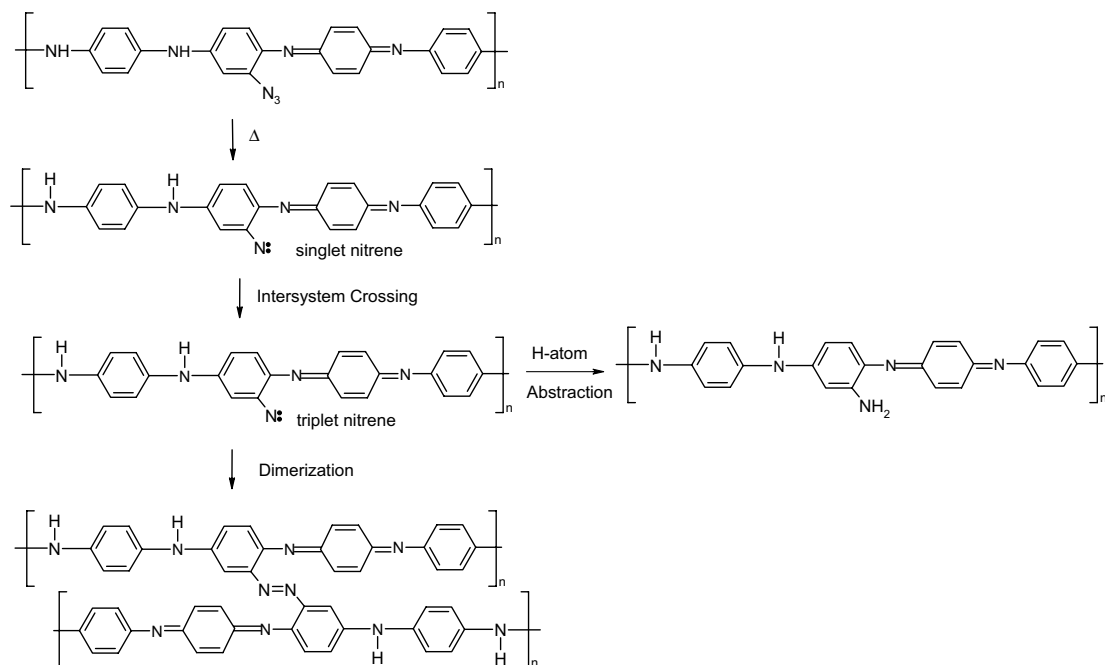


Fig. 7. Proposed cross-linking by annealing PANAZ.

plasticizer and is not due to the cross-linking. Furthermore, cross-linking of the polymer can be expected to reduce the conjugation length of the backbone, to accommodate for the new bond formation.

We are currently studying the tensile properties of PANAZ-CSA films to verify that cross-linking improves their mechanical properties.

5. Conclusion

We have prepared PANAZ copolymers by chemical oxidation of aniline and *o*-azidoaniline. PANAZ polymers showed no specific orientation and reduced conjugation in comparison with films made from pristine polyaniline. The conductivity of PANAZ-CSA films decreased with increased azido substitution. Azido substitution decreased both the crystallinity of the polymer and the conjugation of the polymer backbone. Thermal activation of the azido functional group in PANAZ causes it to react and form cross-links between adjacent polymer strands, as shown by the better thermal stability of PANAZ compared with PANi-EB. We propose that the evaporation of the residual solvent rather than the cross-linking of the polymer decreases the conductivity of the PANAZ-CSA films.

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