

Synthesis and Characterization of Carboxyl-Substituted Polyanilines Doped with Halogenated Acids: Combining Conductivity with Solubility

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Copolímeros de anilina com ácido antranílico e seus ésteres metílico e etílico foram sintetizados utilizando uma variedade de ácidos dopantes e foram caracterizados por UV-Vis, espectroscopias no infravermelho com transformada de Fourier (FTIR) e Raman, e microscopia eletrônica de varredura. Os dados apóiam a existência de reações de acoplamento *para*- na construção da cadeia polimérica, embora a reação de acoplamento *orto*- seja competitiva e leve à formação de estruturas terminais do tipo fenazina. A condutividade elétrica e a solubilidade foram determinadas em uma diversidade de solventes e os resultados correlacionados com os dados espectrais. Observou-se que os copolímeros de anilina com ésteres antranílicos são mais solúveis do que as polianilinas correspondentes. Além disso, a condutividade do copolímero com antranilato de metila dopado com ácido trifluoroacético é da mesma ordem de magnitude que a observada para polianilinas comuns. Em geral, as condutividades mais elevadas foram obtidas para os polímeros e copolímeros dopados com os ácidos clorídrico e trifluoroacético.

Copolymers of aniline with anthranilic acid and two esters, ethyl and methyl anthranilate, were prepared through chemical synthesis using a variety of acids as the dopant. All polymers and copolymers were characterized by UV-Vis, Fourier transform infrared (FTIR) and Raman spectroscopies, as well as scanning electron microscopy. The data support the formation of variable amounts of phenazine-like structures due to *ortho*-coupling polymerization that competes with the *para*-coupling mode for the construction of the polymer backbone. The electrical conductivity and the solubility in a diversity of solvents were determined and correlated with the spectral data. The copolymers of aniline with anthranilic esters are more soluble than the corresponding polyanilines. In addition, the conductivity of the copolymer with methyl anthranilate doped with trifluoroacetic acid is of the same order of magnitude as that observed for the regular polyanilines. Overall, higher conductivities were obtained for all polymers and copolymers doped with hydrochloric acid and trifluoroacetic acid.

Keywords: anthranilic esters, polyaniline, copolymerization, conducting polymers, Raman spectroscopy

Introduction

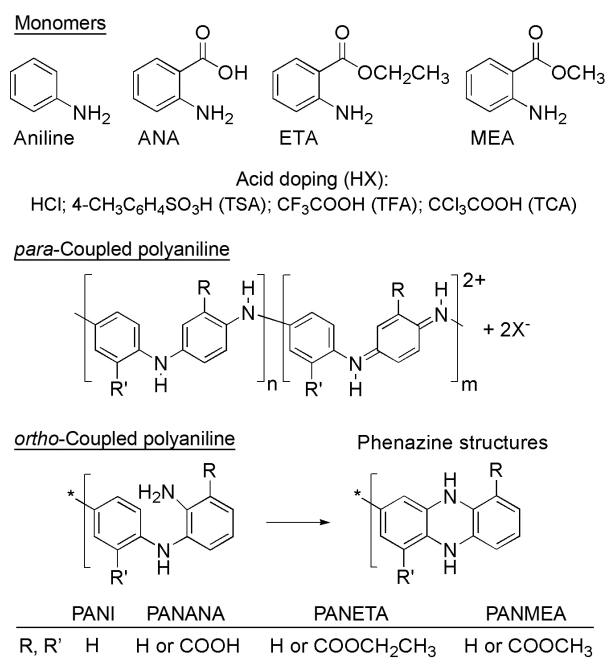
Polyaniline (PANI) is one of the most interesting conducting polymers due to its facile synthesis, controllable redox properties, high electrical conductivity, environmental

stability, and low cost.¹⁻⁴ However, broader exploitation of PANI for technological applications is severely restricted by its poor processability, which is related to the low solubility of the polymer in common solvents. Substituted PANIs with altered properties or enhanced performance have attracted a great deal of interest since they allow the processability limitation to be overcome. Several modifications have

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been investigated with a view to increasing the solubility of PANI, which include varying the acid used as the dopant, postmodification of PANI and copolymerization of aniline with substituted anilines.⁵⁻⁷ In the latter case, the incorporation of functional groups into the backbone of the copolymer can weaken the interchain interaction and increase the structural flexibility, enabling a more effective interaction with the solvent via the functional groups. However, an improvement in the solubility generally occurs concomitantly with a decrease in the electrical conductivity due to a reduction in the extended conjugation of π -orbitals along the main chain caused by the partial loss of planarity.^{8,9}

In this context, a copolymer of aniline and anthranilic acid (2-aminobenzoic acid; ANA) has been prepared by chemical polymerization to obtain better solubility and thermal stability compared with regular PANI¹⁰⁻¹⁴ (Scheme 1). In fact, the presence of the carboxyl group (COOH) confers greater solubility in polar solvents, such as dimethylsulfoxide (DMSO), dimethylformamide (DMF), tetrahydrofuran (THF), ethanol and acetone, but at the expense of a considerable reduction in the electrical conductivity, even in cases where the ANA:aniline ratio is low, thus disfavoring the incorporation of ANA monomers. Besides the perturbation of the coplanarity of the π -system exerted by the bulky COOH group in the copolymer chain, the observed decrease in conductivity has also been attributed to the possibility of self-doping by the carboxylic acid (due to the protonation of the amino groups in the polymer chain from the tethered carboxylic group), which is much less effective than a strong acid such as HCl.^{8,10,11,13,15}



Scheme 1. Aniline monomers, polymers and copolymers.

The replacement of the acidic H of the carboxylic function with a more hydrophobic group, such as the alkyl chain of an ester functional group, can not only prevent the inactivation of the copolymer by self-doping but also increase the solubility in apolar solvents.^{15,16} In this paper, we describe the chemical synthesis of copolymers of aniline with anthranilic acid (ANA) and aniline with one of two esters, ethyl anthranilate (ETA) and methyl anthranilate (MEA), and compared the samples obtained with neat PANI. In addition, we polymerized these combinations of monomers with four different dopants: trifluoroacetic acid (TFA), trichloroacetic acid (TCA), *para*-toluenesulfonic acid (TSA) and hydrochloric acid (HCl). These four sets of polyanilines (Scheme 1) were then compared in order to evaluate the conductivity and solubility and relate the bulk properties to the molecular structure.

Experimental

General information

The following materials were used to synthesize the polymers and copolymers: trifluoroacetic acid, trichloroacetic acid, *para*-toluenesulfonic acid, hydrochloric acid (12 mol L⁻¹), anthranilic acid, ethyl anthranilate, aniline, ammonium persulfate, ammonium hydroxide, distilled water, DMSO, DMF, THF, ethanol and chloroform. All chemicals were reagent grade and were used as received. Methyl anthranilate was prepared through the acid-catalyzed esterification of anthranilic acid with methanol according to conventional methods¹⁷ and was purified by column chromatography performed using silica gel (70-230 mesh) and hexane/ethyl acetate as the eluent.

The Fourier transform infrared (FTIR) spectra of the samples were recorded with a Bruker spectrophotometer in the 4000-600 cm⁻¹ range with 32 scans. The samples were prepared in KBr pellets. The Raman spectra were obtained using a Renishaw Raman image spectrophotometer, coupled to an optical microscope that focuses the incident radiation down to a spot of approximately 1 μ m. An Ar laser (emitting at 514.5 nm) was used, with an incidence intensity of < 1 mW over the 2000-100 cm⁻¹ region.

The UV-Vis spectra were obtained with Varian and Optizen UV-Vis spectrophotometers, using DMSO as the reference, in the 190-1000 nm range. All (co)polymers were previously deprotonated with 0.5 mol L⁻¹ of aqueous ammonium hydroxide solution under stirring for 48 h followed by filtration, washing and drying to give the corresponding emeraldine base. Field emission scanning electron microscopy (FEG-SEM) images were acquired with a JEOL JSM-6701F scanning electron microscope.

Transmission electron microscopy (TEM) was performed on a JEM-1011 TEM microscope. The resistivity of the samples was measured directly from powder pellets with the four-point probe technique using a JANDEL Universal probe. The distance between the points (tungsten carbide, 300 μm radii) was fixed at 1.0 mm.

The polymers (PANI-Acid) and copolymers with anthranilic acid (PANANA-Acid) and esters (PANETA-Acid and PANMEA-Acid) were prepared by the methods described below. The acronym for each polymer indicates the particular acid used for its synthesis (for example, the anthranilic acid copolymer PANANA-TFA was synthesized with TFA).

Synthesis of PANI polymers

PANI-HX (HX = Brønsted acid = HCl, TSA, TFA, TCA): To a magnetically stirred mixture of a Brønsted acid (26.7 mmol) in water (200 mL) at 0 °C (ice bath) was added aniline (53.4 mmol) followed by ethanol (20 mL). A solution of ammonium persulfate (20.0 mmol) in water (200 mL) was then added slowly over 10-15 min (pH of the reaction mixture ca. 2.5). After stirring at 0 °C for a further 3 h, the reaction mixture was allowed to settle and it was then kept in a refrigerator (5-10 °C) for 48 h. The solids formed were collected by filtration, thoroughly washed with water and then with a small amount of acetone and dried to give a dark greenish solid.

Synthesis of copolymers

PANANA-HX, PANETA-HX and PANMEA-HX (HX = HCl, TSA, TFA, TCA): To a magnetically stirred mixture of a Brønsted acid (26.7 mmol) in water (200 mL) at 0 °C (ice bath) was added aniline (40.0 mmol) followed by a solution of ANA, ETA or MEA (13.4 mmol) in ethanol (20 mL). A solution of ammonium persulfate (20.0 mmol) in water (200 mL) was then added slowly over 10-15 min (pH of the reaction mixture ca. 2.5). After stirring at 0 °C for a further 3 h, the reaction mixture was treated as above to give a dark greenish solid.

Results and Discussion

The polymers and copolymers produced with different dopants were prepared by conventional chemical synthesis with some adaptations involving the reaction conditions. The use of an organic co-solvent (ethanol¹² or DMF¹³) has been reported and it is in fact crucial to the success of the synthesis, otherwise the addition of neat ester (ETA or MEA) or acid (ANA) to the aqueous solution led to sluggish dispersions of

the substrate with consequent poor reactivity. After isolating the solid products formed by filtration, the final washing with acetone was performed to remove any trace of unreactive monomers and oligomers of low MW that have limited solubility in aqueous solutions, in particular when the more lipophilic esters ETA and MEA were employed.

All polymers and copolymers synthesized under the stated conditions presented regular PANI behavior, such as a reversible doping-dedoping process and the typical dark green color that was observed in the presence of acids. Besides the improvements in the desired properties such as solubility and conductivity, the copolymerization of aniline with small amounts of 2-substituted anilines can have a dual effect on the resulting material, which is related to the polymerization steps (the influence of the substituted monomer during the chain growth) and conformational assembling (the effect of the substituted group in the polymer chain). While the synthesis of the copolymers was carried out with a fixed ratio of 3:1 aniline:anthranilate, a random polymerization was expected due to the deactivating character of the carboxyl groups in the anthranilate monomers (ANA, ETA and MEA, see Scheme 1). The following discussion, focused on electronic and vibrational spectroscopy, elucidates the nature of each polymer and copolymer as well as its relation to the bulk properties of conductivity and solubility.

Spectroscopy analysis

The main absorption bands identified in the UV-Vis spectra for PANI and copolymers are illustrated in Figure 1. Each (co)polymer was previously treated with a basic solution of ammonium hydroxide to give the corresponding deprotonated (dedoped) material which showed two characteristic bands related to the emeraldine base form. The former signal, observed at around 330 nm, is assigned to the π - π^* transition that is related to the extent of conjugation between adjacent benzene rings in the polymer chain. The latter absorption peak falls at around 620 nm, which is typically attributed to the exciton transition from benzenoid to quinoid segments caused by interchain charge transfer.^{13,18} The UV-Vis spectra presented in Figure 1 were recorded from the basic treatment of TFA-doped PANI and copolymers, but the same behavior was observed for other dedoped (co)polymers prepared from HCl, TSA, and TCA. These results confirm that the polymers are in the emeraldine form, which can be further redoped to the conductive emeraldine salt through acid treatment.

Vibrational techniques (Raman and IR spectroscopy) were also employed to characterize PANI and copolymers (Figures 2 and 3). For the Raman spectra (Figure 2), a

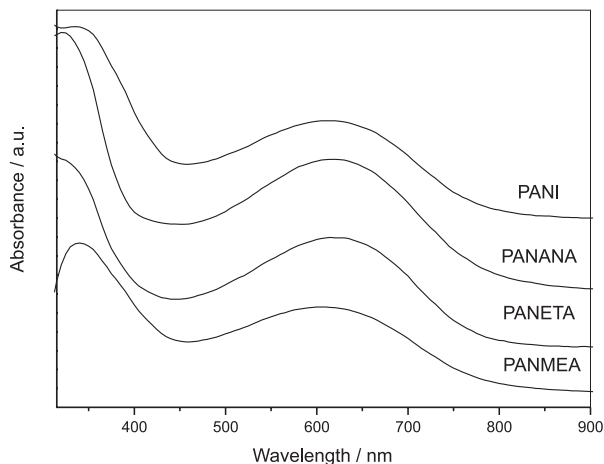


Figure 1. UV-Vis absorption spectra, in DMSO, for deprotonated PANI and copolymer samples obtained after basic treatment of TFA-doped (co)polymers.

514.5 nm excitation line was used to achieve spectral information with no bias, avoiding any resonant effect. The Raman spectrum of PANI-HCl shows the main bands expected for a typical PANI sample at 1179 cm^{-1}

(C–H bending), 1252 cm^{-1} (C–N stretching in benzene diamine units), 1336 cm^{-1} (C–N⁺ stretching of cation radicals), 1515 cm^{-1} (N–H deformation), 1599 cm^{-1} (C–C stretching in semiquinoid rings) and 1625 cm^{-1} (C–C stretching in benzenoid rings).^{19,20} The 1336 cm^{-1} mode extends over a shoulder at 1360 cm^{-1} . The frequency of this last band is highly sensitive to electron delocalization and it is blue-shifted for more localized polarons, as observed when doped polymers and oligomers of aniline are compared.²¹ The presence of multiple modes indicates the heterogeneous nature of the polymer, which is caused either by the copolymer composition or by the segments with different electron delocalization. The bands close to 1400 and 575 cm^{-1} can be assigned to the presence of phenazine structures formed by *ortho*-coupling (N–C2 coupling) of aniline monomers²² (Scheme 1), as will be discussed below.

In general, polyaniline chains follow a *para*-coupling (N–C4 coupling) polymerization to give 1,4-disubstituted anilines with head-to-tail regularity.²³ The set of Raman spectra (Figure 2) evidenced that both the substitution pattern of the monomer and the dopant acid exert an effect

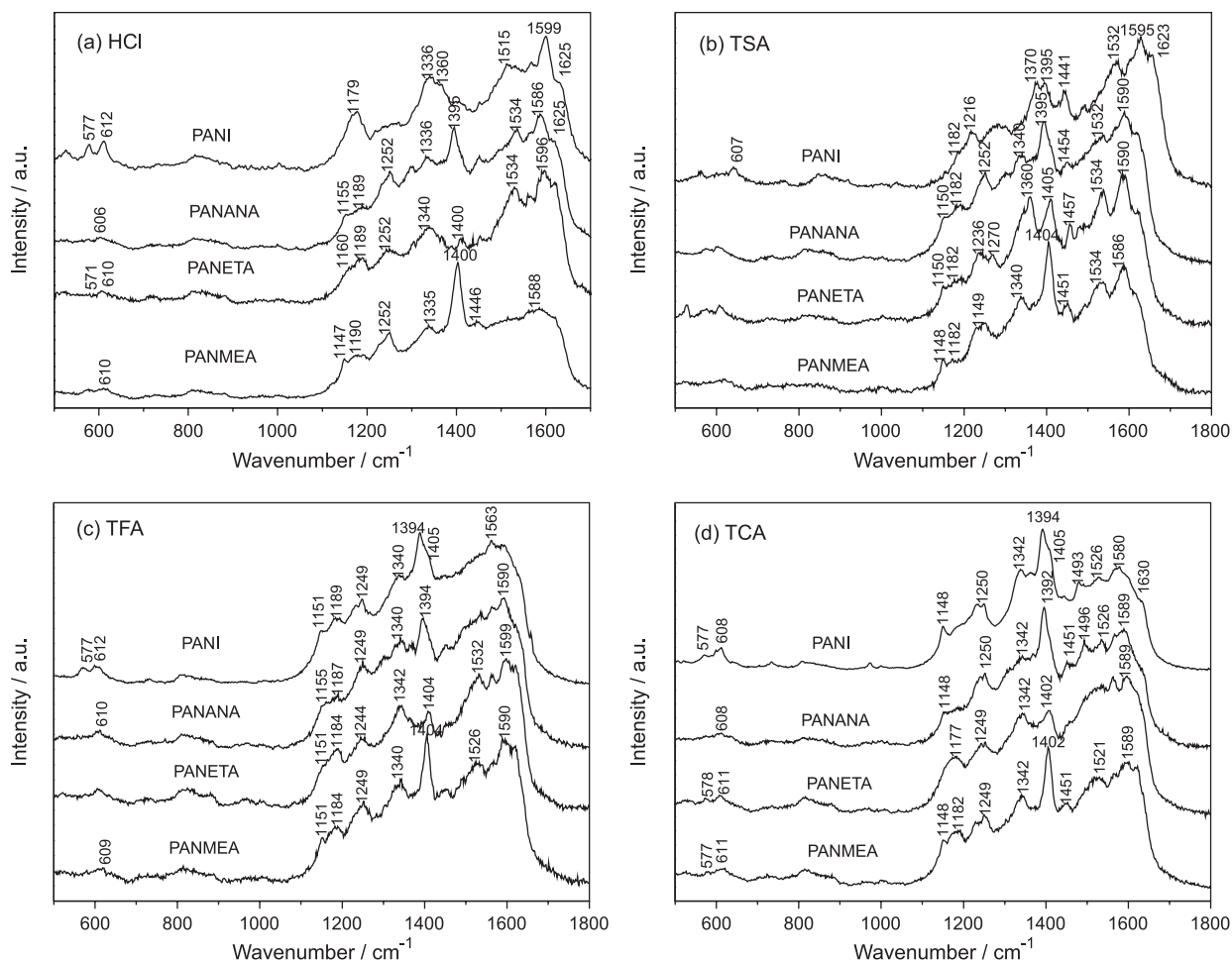


Figure 2. Raman spectra (514.5 nm) for PANI and copolymer samples polymerized in (a) HCl; (b) TSA; (c) TFA and (d) TCA.

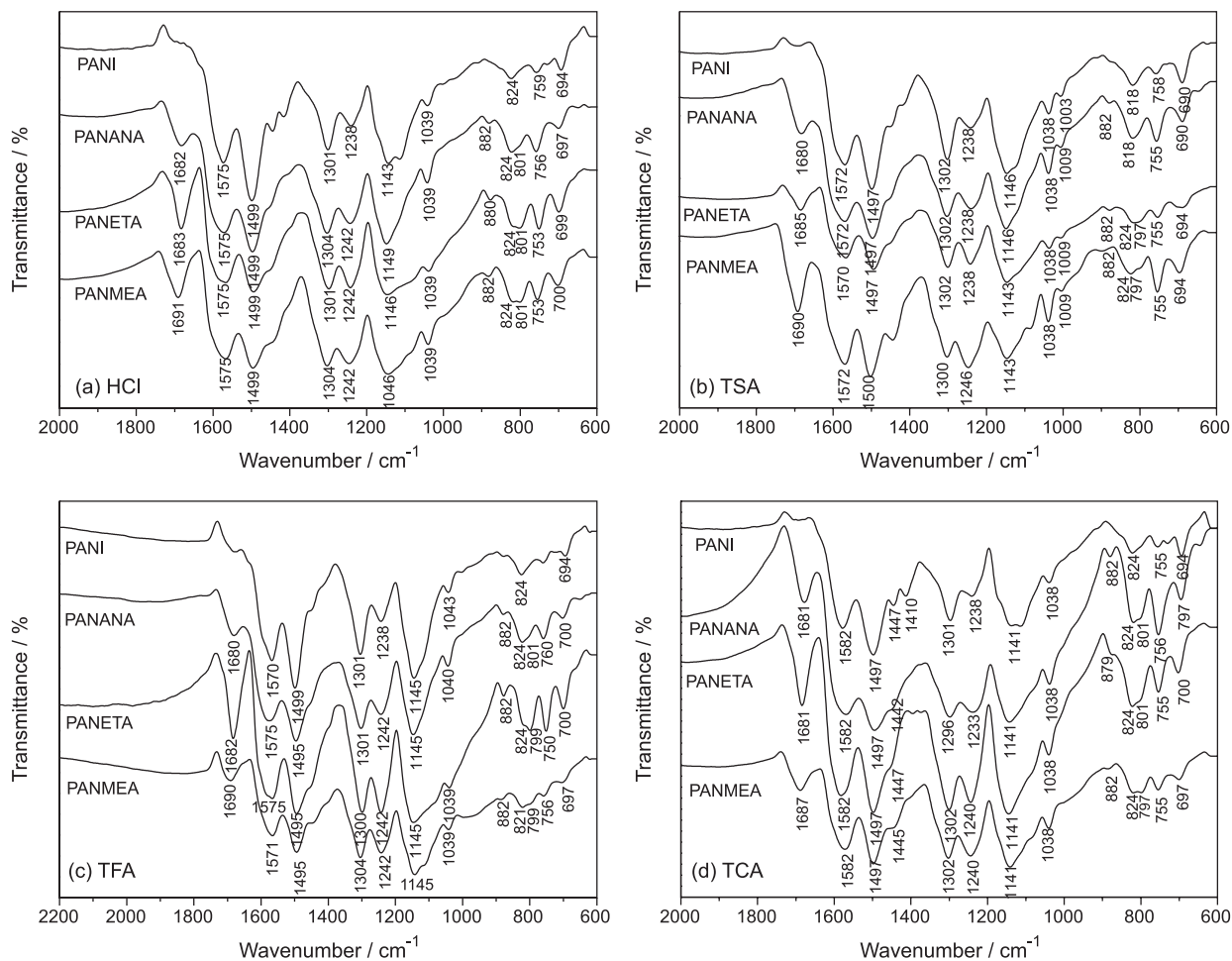


Figure 3. FTIR spectra for PANI and copolymer samples polymerized in (a) HCl; (b) TSA; (c) TFA and (d) TCA.

on the polymer, as seen in the spectra for the samples of PANI with different dopants (Figure 2a) and copolymerized with 2-substituted aniline monomers such as anthranilic acid (Figure 2b) and its ethyl (Figure 2c) and methyl esters (Figure 2d).

Despite the differences observed in the monomers, the effect of acidity during the synthesis cannot be neglected as it has a profound effect on the polymer structure²⁴ ($pK_a[\text{HCl}] < pK_a[\text{TSA}] < pK_a[\text{TFA}] < pK_a[\text{TCA}]$).²⁵ A synthetic medium with $\text{pH} > 3.5$ leads to the production of a less conductive polyaniline, as aniline monomers not only participate in *para*-coupling polymerization (1,4-disubstitution) but also in *ortho*-coupling (1,2-disubstitution), where the growth of chains occurs at low oxidation potential producing phenazine-like structures, which have typical spectral signatures.²³ Therefore, the *ortho*- or *para*-coupling mode of carboxyl-substituted aniline monomers must be considered to elucidate the chemical structure of the polymer (see Scheme 1).

Evidence for the formation of the 1,2,4-trisubstituted aniline moiety, assumed to be the product of *para*-coupling

from 2-substituted aniline monomers, can be found in the Raman spectra by observing the C–H bending mode. In Figure 2, a shoulder is observed at around 1150 cm⁻¹ for all substituted polyanilines (PANANA, PANETA and PANMEA). The band at around 1182 cm⁻¹ represents the typical frequency for the C–H bending (polaronic units) in unsubstituted polyaniline (regular 1,4-disubstituted aniline), while the band at 1150 cm⁻¹ can be attributed to the same mode in 1,2,4-substituted aniline.²⁶ The band observed at approximately 1400 cm⁻¹ can be attributed to phenazine-like structures formed due to *ortho*-coupling. This is confirmed by the appearance of two bands, a weak one located at 575 cm⁻¹ and a shoulder at around 1630 cm⁻¹.^{19,27,28} The intensity of these bands varies according to the experimental conditions.¹⁹ On comparing the intensity, PANETA seems to be more resistant to the formation of phenazine-like structures than PANMEA, in particular with stronger acids (HCl, TSA) as dopants. This observation might be related to higher steric hindrance of the ethyl group in PANETA compared with the methyl group in PANMEA. Overall, as observed from the Raman

spectra, the presence of the phenazine moiety can be found in all polymers, but with lower intensity in the case of PANI-HCl and PANI-TSA. It is also important to note that all spectra obtained for PANANA (a self-doped polymer) were similar, regardless of the acid, which should reflect in their conductive properties, as will be discussed later.

Analysis of the IR spectra (Figure 3) confirms the formation of phenazine structures, with the presence of shoulders at 1445 cm^{-1} , which are also present in the polyphenazine spectra.²⁹ The IR spectra of PANI also exhibited the bands related to the polymer chain as well as modes related to the doping process and the copolymerization. One of the main features is related to the bands located at approximately 1580 and 1500 cm^{-1} , which are assigned to C–C stretching in the quinoid and benzenoid rings, respectively.

The doping process is responsible for two other bands, located at around 1300 and 1240 cm^{-1} , which are associated with C–N stretching modes in doped polyaniline.³⁰ However, it should be pointed out that the vibrational stretching of the C–O bond related to the carboxyl group in the acid and ester copolymers is also present at *ca.* 1240 cm^{-1} , which causes an increase in the intensity of this band in the spectra for the copolymers.

The formation of *para*-coupling anilines from 2-substituted aniline monomers indicated in the Raman analysis is corroborated by the IR spectra (Figure 3), in which the signature of 1,2,4-trisubstitution can also be observed in C–H out-of-plane bending located at 882 and 800 cm^{-1} .²⁴ These two bands can be found only in the substituted polyaniline along with the band at approximately 820 cm^{-1} , assigned to this same mode but for regular 1,4-disubstituted aniline. The IR spectra at low frequencies ($< 1000\text{ cm}^{-1}$) show two bands located at approximately 760 and 690 cm^{-1} , which are attributed to C–H out-of-plane bending and ring out-of-plane deformation in monosubstituted rings.²⁴ Therefore, these bands can be used to evaluate the content of phenyl rings as terminal units in the chains and estimate the relative size of the polymer chains. For instance, the relatively higher intensity bands located at 760 cm^{-1} can be found in the spectrum of PANMEA doped with TSA and also in the spectra of PANANA doped with TSA, TFA and TCA. Two factors can contribute to this effect, the deactivation character of substituted anilines and the steric hindrance caused by the substituent group, which create a more difficult path for both the *ortho*- and *para*-coupling reactions. Also, the *ortho*-coupling of a substituted monomer at the end of a growing chain (with the formation of a phenazine-like structure as in Scheme 1) would prevent any other coupling due to steric hindrance (large R group), resulting in the termination of the chain growth leading to shorter polymer chains.

In the IR spectra for the copolymers (Figure 3), the stretching mode of the carboxyl group (O–C=O) is located at approximately 1680 cm^{-1} . This mode is not sensitive to the presence of the acid, as seen by its average frequency (PANANA 1680 - 1682 cm^{-1} ; PANETA 1681 - 1685 cm^{-1} ; PANMEA 1687 - 1691 cm^{-1}), indicating a weak interaction of the dopant with the carboxyl group, either acid (PANANA) or ester (PANETA or PANMEA). On the other hand, for the different dopants, a trend in the frequency is observed (in cm^{-1}): PANANA \leq PANETA $<$ PANMEA. It is worth mentioning that the frequency for these samples lies within the same range as that reported for the parent anthranilic ester monomers (ETA, MEA) and analogs,³¹ indicating that these monomers preserve their chemical and conformational structure after incorporation into the polymer chain.

Finally, no signature of TFA or TCA was observed in the IR spectra (Figure 3), possibly due to the coincidence with PANI modes.³² TSA can be identified through the band at around 1009 cm^{-1} (only present in the case of samples polymerized with TSA).³³

Morphological analysis

FEG-SEM micrographs were used to investigate the surface morphology of PANI and copolymer samples in order to evaluate the effect of the copolymerization. In Figure 4, representative images of the TFA-doped polymers and copolymers reveal a granular morphology with small clusters of irregular particles, some of which were in the nanoscale. The TEM images of the ester copolymers PANETA and PANMEA (results not shown) also presented irregular particles, in agreement with the FEG-SEM results. This granular morphology of copolymer esters is commonly observed in PANI powders prepared by precipitation polymerization under strongly acidic conditions.³⁴

Bulk properties: conductivity and solubility

The conductivity profiles of PANI and copolymer samples (Table 1) prepared by the method described herein indicated that this property is dependent both on the acid employed for the doping and on the polymer/copolymer substitution (“R” in Scheme 1). High conductivities (near 1 S cm^{-1}) were found when HCl was used as the dopant, but the use of TFA also improves the conductivity. In addition, PANMEA-HCl and PANI-HCl showed conductivity of similar magnitude. TCA and TSA, on the other hand, were not as effective as dopants and led to very low conductivities (up to 0.1 S cm^{-1}) regardless of the type of polymer/copolymer prepared.

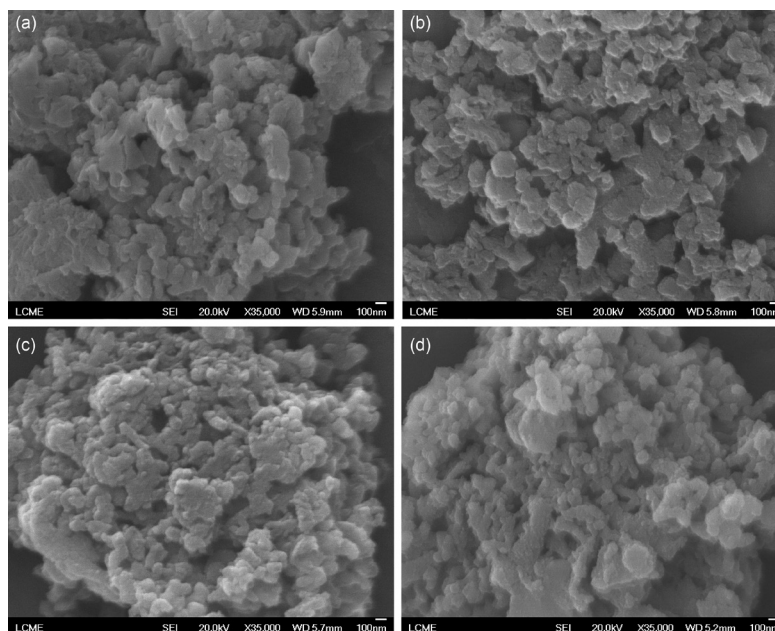


Figure 4. FEG-SEM micrographs for (a) PANI-TFA; (b) PANANA-TFA; (c) PANETA-TFA; and (d) PANMEA-TFA.

As expected based on the FTIR and Raman analysis discussed above, moderate-to-high conductivity values were found for PANI and PANMEA with slightly lower values being observed for PANETA. On the other hand, PANANA had a much lower conductivity. Indeed, the conductivity of PANANA was similar for all four acids showing no strong dependence on the dopant. This confirms the Raman spectroscopy results, which indicated that highly localized charge carriers are present in the PANANA samples, probably due to the self-doping process.

Table 2 shows the solubility of PANI and copolymer samples in a variety of solvents of different polarities. From

Table 1. Electrical conductivity (10^{-1} S cm^{-1}) of PANI and copolymer samples with different dopants

Dopant	PANI	PANANA	PANETA	PANMEA
HCl	9.1	0.13	3.9	9.7
TSA	0.59	0.05	1.1	0.30
TFA	0.11	0.29	3.4	3.9
TCA	0.92	0.52	0.26	0.40

the data compiled, ester polymers appear to be more soluble than PANI and, in particular, PANMEA was slightly better than PANETA and also compared well with PANANA,

Table 2. Solubility profile of PANI and copolymer samples with different dopants^a

(Co)polymer	DMSO	DMF	THF	EtOH	CHCl ₃	NH ₄ OH (0.1 mol L ⁻¹)
PANI-HCl	+++	+++	++	+	+	+
PANI-TSA	+++	+++	++	+	+	+
PANI-TFA	+++	+++	+	+	++	+
PANI-TCA	+++	++	++	+	+	+
PANANA-HCl	++++	+++	++	++	+	++
PANANA-TSA	++++	+++	++	++	+	++
PANANA-TFA	++++	+++	++	++	+	++
PANANA-TCA	++++	+++	++	++	+	++
PANETA-HCl	+++	++	+	++	++	+
PANETA-TSA	+++	+++	++	++	++	+
PANETA-TFA	+++	+++	++	++	++	+
PANETA-TCA	+++	+++	++	++	++	+
PANMEA-HCl	+++	+++	++	++	++	++
PANMEA-TSA	++++	++++	+++	+++	+++	++
PANMEA-TFA	++++	+++	++	++	++	++
PANMEA-TCA	+++	+++	++	++	++	++

^a++++: highly soluble (9-10 g L⁻¹); +++: soluble (6-8 g L⁻¹); ++: moderately soluble (3-5 g L⁻¹); +: sparingly soluble (1-2 g L⁻¹).

which is recognized as having good solubility in a variety of solvents.^{10,11} Although the observed conductivity of all polymers and copolymers doped with TSA was not high, their superior solubility in most solvents, in particular of PANMEA-TSA in DMF, is worth noting. In addition, compared with neat PANI, the PANMEA copolymer had similar conductivity but was much more soluble in both ethanol and chloroform (HCl as dopant), which are important features to be considered in relation to a novel material.

Conclusions

Copolymers of aniline with 2-substituted anilines bearing a variety of carboxyl groups were synthesized through oxidative polymerization employing four different acids as dopants. The copolymers were characterized by several techniques, including Raman spectroscopy, FTIR spectroscopy and microscopy, which confirmed the incorporation of the substituted monomer into the polymer chain. All spectroscopic evidence supported the formation of substituted phenazines in variable amounts through the competitive *ortho*-coupling polymerization. Nevertheless, the *para*-coupling mode for the 2-substituted monomer to give the 1,2,4-substitution pattern could be verified based on characteristic spectroscopic signatures. The results for the electrical conductivity correlate well with the spectral data, with higher conductivities being observed for the polymers and copolymers doped with HCl and TFA. This moderate-to-high solubility in a diverse set of solvents, allied with the good-to-excellent conductivity, indicates that PANMEA-TFA and PANMEA-HCl are promising candidates for further studies aimed at developing novel materials with potential technological application.

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