Copolymerization of aniline and *m*-chloroaniline. Chlorine addition and structure of the resulting material

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ABSTRACT

The copolymerization of aniline (Ani) and *m*-chloroaniline (mClA) in variable ratios was performed by chemical oxidation in HCl medium. The resulting copolymer composition was determined by elemental analysis and XPS. The results show the incorporation of additional Cl substituents in the polymer backbone when *m*-chloroaniline is present in the polymerization medium with a high mClA:Ani ratio. IR and NMR characterization confirms that finding. Conductivity measurements of the copolymers in salt form were also performed. UV–vis spectra for high mClA:Ani ratios show a main band centred *ca.* 380 nm. PM3-ZINDO/S spectra calculations suggest that the Cl substituents stabilize spinless semiquinone structures in the polymer chain which are responsible for the 380 nm band. Photoluminescence spectra are recorded and analyzed. The addition of chlorine is attributed to the lower reaction rate in high mClA:Ani ratio. Copolymers with high mClA:Ani ratio appear as materials very different from polyaniline, thus these differences should be considered regarding possible applications.

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1. Introduction

Aryl amine polymers such as poly(aniline) (PANI) and derivatives have received great attention since its rediscovery by Shirakawa et al. [1]. One of the main reasons is its wide range of potential applications, including presently fields such as actuators [2,3], electrochromic and photovoltaic devices [4–6], secondary batteries [7], fuel cells [8], supercapacitors [9,10], ionic sensors [11], biosensors [12–14], tissue engineering [15], electrocatalysts [16], nanomaterials [17,18], photocatalysts [19] and corrosion protection [20] among many other ones [21–23].

Despite the fact that PANI can be synthesized quite easily, there are difficulties in practical applications arising from its poor processability due, among other reasons, to the limited number of appropriate solvents available. To overcome that, polymers of derivatives such as *o*-methylaniline [24–27] or *o*-methoxyaniline [28–31] have been investigated, and also copolymers of aniline (Ani) and other suitable monomers [32–38] and references therein.

Among these copolymers, chloroanilines have been regarded as attractive candidates for copolymerization due to the enhanced solubility in common solvents. Athawale et al. [39] electropolymerized *m*-chloroaniline (mClA) and characterized the product, finding a more difficult and slower polymerization process due to the presence of the strongly electron withdrawing Cl atom in meta-

position. Sayyah et al. [40] prepared poly(*m*-chloroaniline) (PmClA) by chemical oxidation of the monomer with sodium dichromate in HCl medium; it was reported that the molecular weight, from viscosity measurements, increased with HCl and monomer concentration, but decreased with oxidant concentration. Diaz et al. [41] synthesized and characterized copolymers of aniline and dichloroanilines at several monomer ratios. The polymerization was carried out chemically in HCl medium with $K_2Cr_2O_7$ as oxidant. It was found that, by varying the aniline-comonomer ratio and doping level, the conductivity could be controlled from 10^{-9} to 10^{-2} S cm^{-1}. The UV–vis spectra were consistent with a decrease of the π conjugation in the polymer chain as the contents of dichloroanilines were increased. The actual product composition was computed from the determination of halogen contents in the copolymers and correlated with the composition of the synthesis medium. Li et al. [42] synthesized by chemical oxidation and characterized systematically copolymers of aniline with *o*- and *m*-chloroaniline. They found a slower polymerization as the ratio of chloroaniline to aniline increased, especially with the meta- moiety. In that case, also the average molecular weight decreased as the mClA proportion increased. These authors reported that, in their working conditions (ammonium persulphate:monomer ratio of 0.5:1), PmClA could not be obtained. The resulting polymers were characterized by IR and UV–vis spectra, XRD, thermogravimetric analysis, conductivity and air-separation performance in terms of the starting monomer composition (feed) in the synthesis medium. Waware and Umare [43] synthesized by chemical oxidation Ani-mClA copolymers in all the range, including PmClA homopolymer using

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an oxidant:monomer ratio of 1:1. They characterized the resulting polymers by IR and UV–vis spectra, magnetic susceptibility and solubility in common solvents. It was found that the solubility increased about one order of magnitude in going form PANI to PmClA, whereas the conductivity decreased by almost four orders. The properties studied were, as in Li et al. [42], related to the feed composition; in some cases the elemental composition was determined, but the authors reported discrepancies between the results and the expected values from the feed composition assuming equal reactivity of both monomers, and were attributed to presence of counter ions, protonation level, and reactivity.

In this work, the aim is to characterize the properties of Ani-PmClA homo- and copolymers in terms of their composition and structure. PANI and PmClA homopolymers and copolymers in different monomer ratios are chemically polymerized, its composition determined by elemental analysis and XPS measurements and characterized by conductivity measurements and IR, NMR, UV–vis and fluorescence spectra. These characterizations are discussed in terms of the polymer structure.

2. Materials and methods

2.1. Polymerization

PANI, PmClA and their copolymers were prepared by the usual procedure which consists of oxidation with ammonium persulphate [43]. AR grade chemicals and high purity water from a Milli-Q system were employed. Aniline was distilled under reduced pressure and reducing conditions shortly before use and *m*-chloroaniline (Fluka) was used shortly after receiving. All solutions used had a total monomer concentration of 0.4 M in HCl 1.0 M, but with different mole fractions in order to obtain copolymers of different composition.

The oxidant was a 0.4 M ammonium persulphate solution in 1.0 M HCl, so the molar ratio of monomer to oxidant was 1:1. All the solutions were previously cooled to 0 °C in an ice bath. Then, the oxidant was added slowly into the monomer solution with constant stirring at 0–4 °C. Each reaction mixture was kept for about 6 h at these conditions and afterwards at room temperature. In the case of monomer solutions with high mole fraction of aniline, within additional 12 h the green precipitated of emeraldine salt was observed. On the other hand, with solutions of high mole fraction of *m*-chloroaniline the reaction mixtures were kept 24 h at room temperature in order to obtain the brown solids. Then the precipitates were filtered and washed with a small volume of 1.0 M HCl. To obtain the base forms, the solids were suspended in a 1.0 M NH₃ solution for 24–48 h, filtered, washed and vacuum dried at 37 °C. The dark solids obtained were stored for their characterization.

2.2. Elemental analysis

Elemental analysis of the oxidized (co)polymers in the base form was carried out by a microanalytical technique using a Carlo Erba EA 1108 analyzer. Sulphanilamide was used as standard and BBOT and CEDFNI as control assays.

2.3. XPS measurements

X-ray photoelectron spectroscopy (XPS) measurements were performed using a Specs Sage 150 spectrometer equipped with a dual anode Mg/Al X-ray source and a hemispherical electron energy analyzer. Spectra were acquired using a monochromatic MgK$_\alpha$ (1253.6 eV) source with a 90° detection angle. Quoted binding energies (BEs) are referred to the adventitious C 1 s emission at 285 eV, in order to compensate for charging effects. Measurements were made by placing a thin layer of each solid (base form) on a circular metal surface by means of double sided conductive tape.

2.4. Conductivity measurements

The conductivity of the different copolymers as well as the corresponding homopolymers in salt form was measured on pressed pellets using a four-probe method.

2.5. NMR spectra

^{1}H NMR measurements were carried out using a Bruker Avance II 500 MHz multinuclear spectrometer. The sample was prepared dissolving 5 mg of the *m*-chloroaniline polymer in its oxidized base form in 0.6 ml of DMSO-d$_6$. The spectra were analyzed with the aid of simulations using two different simulators: the ACD/HNMR program (<www.acdlabs.com>) and the SPINUS-WEB free online service (<www2.ccc.uni-erlangen.de/services/spinus/>) for H atoms bond to C.

2.6. IR spectra

The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 8700 spectrometer, in the range 400–4000 cm^{-1}. The samples were pressed into pellets prepared dispersing 0.5 mg of each co(polymer) in base form in 150 mg of KBr. For each sample, 32 scans were accumulated.

2.7. UV–vis absorption spectra measurement and calculation

For the absorbance and fluorescence measurements the solids (in the untreated, as obtained, form) were dissolved in N-methylpyrrolidinone (NMP) and the UV–vis spectra were recorded in the range 300–700 nm. Then, hydroxylamine was added to reduce the (co)polymer and the absorption spectra were recorded again. All the UV–vis measurements were performed using a Shimadzu PC3101 spectrophotometer, under computer control.

Simulation of absorption spectra were conducted on oligomers of aniline, *m*-chloroaniline and dichloroanilines by first optimizing geometries using the PM3 method, then the spectra were calculated in the configuration interaction using the ZINDO/S method; for visualization, the resulting transition wavelengths were convoluted with gaussian shapes with a broadening of 20 nm taken arbitrarily. PM3 is a reparametrization of the Austin Method 1 (AM1) which has been found to be one of the most accurate semiempirical methods for calculation of geometries and heats of formation; the PM3 method has been more extensively tested and found especially adequate for organic molecules. The ZINDO/S method is specifically parameterized for calculation of electronic absorption spectra. This methodology has been found to produce good results for polyanilines [44]. Phenyl-capped tetramers and octamers were studied, as it has been shown that they are good models of the polymer [44,45]. In the CI calculations, 300–800 configurations were included, depending on the oligomer; however, the main spectra features were not strongly dependent on the number of configurations. Calculations were carried out using the HyperChem package version 7.03, which includes the appropriate ZINDO/S parameters for chlorine.

2.8. Photoluminescence spectra

Fluorescence emission spectra of the NMP solutions used for UV–vis measurements were recorded following usual procedures [46] in the range 330–600 nm; the excitation wavelength was fixed at 310 nm, which falls inside the π–π* absorption envelope of the

benzenoid units [47]. All the fluorimetric measurements were obtained using a PTI Quantamaster stationary spectrofluorometer.

3. Results and discussion

3.1. Polymer composition

From the XPS spectra (Fig. 1) the areas under the C 1s, N 1s and Cl 2p peaks were computed and, using appropriate instrumental factors, the ratios Cl/N ($r_{Cl/N}$) and C/N were obtained. In all the measurements, the ratio C/N was within 6.0 ± 0.3. Fig. 2 (closed circles) shows the $r_{Cl/N}$ values obtained as a function of the mClA mole fraction in the feed, f_{mClA}. Some products were also verified by elemental analysis, and these results are plotted as open circles, showing good agreement. It is found that the chlorine contents increases with f_{mClA} up to nearly 2 Cl atoms per monomer unit in PmClA, thus indicating an incorporation of this element during the polymerization. It should be noted that the presence of chloride ions coming from the polymerization solution can be discarded, as Cl^- appears at a different energy in XPS, and besides its absence was checked in the washing of the polymer base form. Thus, in the course of polymerization, additional Cl substituents are incorporated in the (co)polymer backbone when mClA is present, at least for large values of f_{mClA}.

3.2. Conductivity results

Fig. 3 shows the conductivity values for the salt forms obtained for the different copolymers as a function of f_{mClA}. Values reported by Li. et al [42] and Waware and Umare [43] are also plotted for comparison. All measurements show a strongly decreasing conductivity as the contents of mClA increases. However, there are differences in the shape of the curves. Li et al. [42] values present, in most of the range, the lowest conductivities; on the contrary, the values obtained in this work are the highest of Fig. 3 except for the high f_{mClA} range, but otherwise the curves show the same general shape. The values reported by Waware and Umare [43] present a non monotonical variation, showing a local minimum at around $f_{mClA} = 0.25$, then increasing up to $f_{mClA} = 0.5$ and afterwards decreasing again. The conductivity decrease for $f_{mClA} > 0.5$ is, as discussed below, attributable to the Cl substituents, decreasing conjugation by preventing the formation of quinone imine structures. It should be noted that the conductivities of aniline–dichloroaniline copolymers reported by Diaz et al. [41] show the same
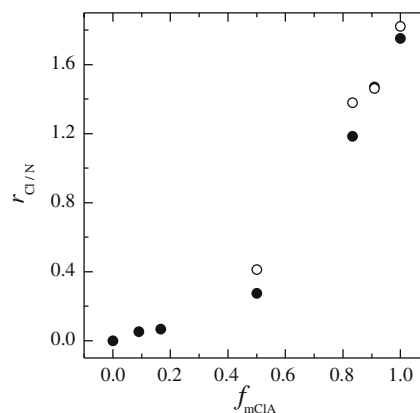

Fig. 2. Cl/N ratio ($r_{Cl/N}$) as a function of m-chloroaniline mole fraction in the polymerization solution (feed), f_{mClA}, obtained by XPS (closed circles) and elemental analysis (open circles).
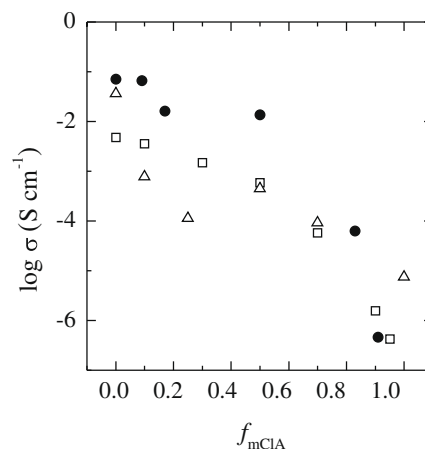

Fig. 3. Conductivity (in logarithmic form) of copolymers in salt form as a function of m-chloroaniline mole fraction in the polymerization solution (feed), f_{mClA}. (●) this work; (□) Li at al. [42]; (△) Waware and Umare [43].

general behaviour, but with lower values in all the range. The differences between the values reported here and those of Refs. [42,43] may by attributed to somewhat different polymerization
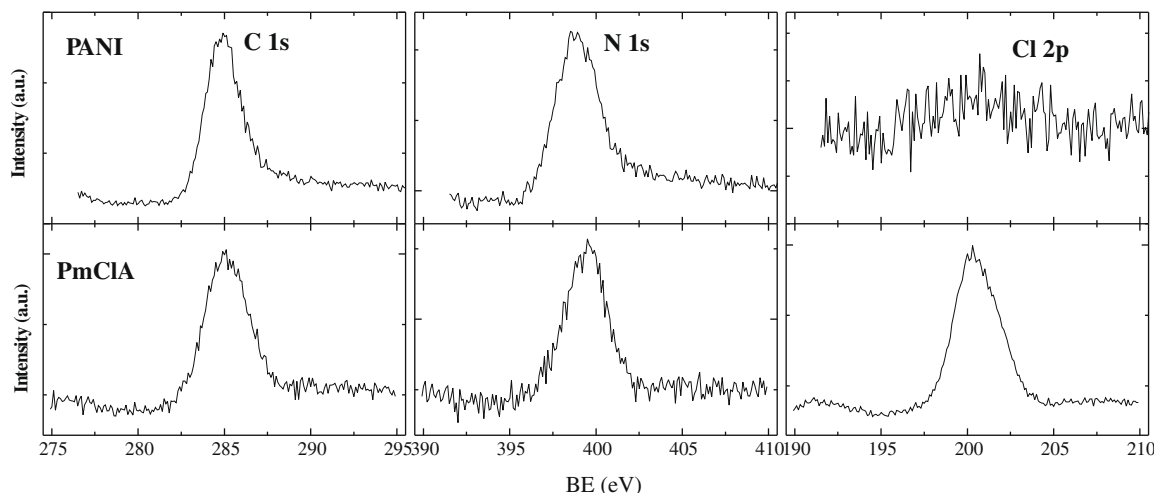

Fig. 1. The C 1s, N 1s and Cl 2p XPS spectra of poly(aniline) (PANI) and poly(m-chloroaniline) (PmClA).
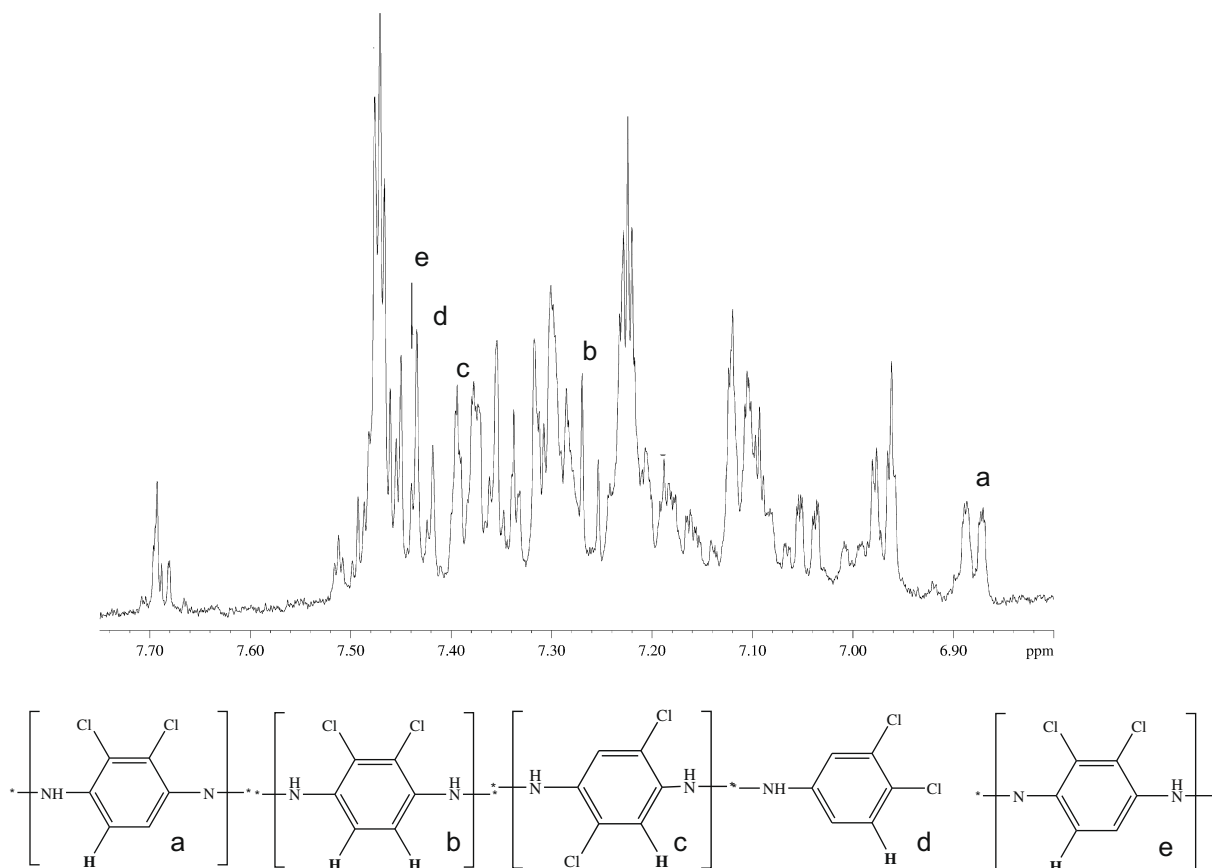
Fig. 4. (Top) ^{1}H NMR spectrum of PmClA in the aromatic region; (bottom) groups assigned to the corresponding peaks marked in the spectrum.

procedures: Li et al. [42] used a different monomer:oxidant ratio; the method of Waware and Umare [43] is very similar to that employed here, the only difference being the drying procedure, at 70–80 °C in [43] and in vacuum at 37 °C here. These facts suggest that the polymerization procedure has a quite strong influence on the properties of the resulting copolymers.

3.3. ^{1}H NMR spectra

Fig. 4 (top) shows the ^{1}H NMR spectrum of PmClA in the aromatic H (5.8–7.5 ppm) region. As it has been reported, this region corresponds mainly to benzenoid H atoms in aryl amine polymers, whereas quinoid protons show up at about 7.9–9 ppm [36,37]. In this last region (not shown), only very few peaks appear in the PmClA spectrum, thus indicating the nearly absence of quinoid structures. In Fig. 4, it is observed a high number of peaks, which can be due either to different structures present in the polymer composition and/or different discrete conformational states of the polymer chain. The complexity of the spectrum makes peak assignation difficult, especially when several peaks appear together, likely due to splitting. The assignations which emerge as more conclusive from the simulations are those presented at the bottom of Fig. 4 (a–e), which correspond with the peaks marked in the spectrum. The important fact is the presence of several dichloroaniline structures, as observed in the figure; besides the original Cl substituent in metha position, the added Cl atoms lie in positions ortho and para relative to the amino group, which strongly suggests chlorination of the mClA monomer, as the amino directs substitution to such positions. Copolymers synthesized with high f_{mClA} showed similar spectra. Thus, the NMR measurements confirm Cl addition in the product and show that this addi-

tion proceeds in several locations in the aromatic ring: either position 2, 4 or 6 can carry the second Cl substituent. It should be noted that a Cl atom in para will render the monomer unable to be incorporated to the growing polymer chain, which is consistent with the lower yield and lower molecular weight observed by Li et al. [42]. In our synthesis a lower yield for reaction mixtures with high f_{mClA} was also qualitatively observed.

3.4. IR spectra

Fig. 5 shows IR spectra for PANI (a), PmClA (d) and copolymers with f_{mClA} = 0.5 (b) and 0.8 (c). The general features are in agreement with literature reports for this type of polymers [26,48,49] and with previous reports on PmClA [42,43]. A broad band increasing towards the high wavenumber region is observed, due to the delocalized charge carriers of the conducting form of PANI [48]. The intensity of this band decreases as the contents of mClA increases, in agreement with the lower conductivity found for these copolymers. In the 3000–3500 cm^{-1} region, the usual bands are observed [50,51]: the NH$^+$/NH$_2^+$ stretching band at about 3200 cm^{-1}, broadened due to hydrogen bonding; the NH stretching band, at about 3400 cm^{-1}, and the CH stretching around 3000 cm^{-1}, both overlapped by the NH$^+$ band. In PmClA, this last is less broadened indicating a lesser extent in the formation of hydrogen bond; this can be related to steric hindrance by the bulky Cl atoms preventing the polymer chains to approach each other enough as to form H bonds.

Fig. 6 shows the 1800–400 cm^{-1} part of the same spectra, revealing a number of differences as the contents of mClA increases. The inset shows an expanded view of the 2000–1700 cm^{-1} region in the PmClA spectrum. We begin by briefly

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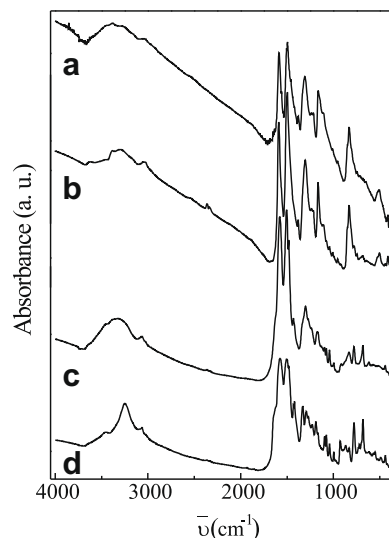
Fig. 5. IR spectra of PANI (a), PmClA (d) and copolymers with f_{mClA} of 0.5 (b) and 0.8 (c). Polymers are in the base form without further treatment.

reviewing the PANI IR spectrum assignments (Fig. 6a). In the 1600–1450 cm^{-1} region, two main bands are observed at about 1600 and 1500 cm^{-1}, assigned to C=C ring stretching and the first one also to quinoid C=N stretching, unresolved [26]. Other intense bands are the C–N stretching at 1300 cm^{-1}, the C–H rocking at about 1160 and the 830 cm^{-1} one due to out of plane C–H deformation of two adjacent H atoms. As it is known [50] the frequency of these vibrations shifts to lower values as the number of adjacent H atoms in the aromatic ring increases. In PANI, which has only pairs of H atoms, only this band is observed [26].
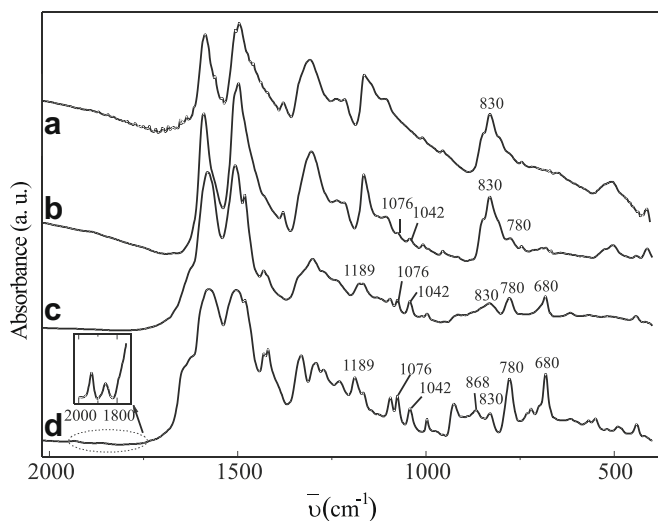
Turning now to the PmClA spectrum (Fig. 6d) its more complex nature is immediately apparent. The ring stretching bands of PANI are also present, albeit broadened and/or split; it should be noted that actually up to four bands can be found in this region [50], so the change observed (comparing with PANI) can be attributed to the presence of the Cl substituents. The C–N stretching band is also present, with a somewhat lower intensity. In the lower part of the spectrum, where out of plane C–H vibrations appear, it is observed the 830 cm^{-1} band as in PANI, but with much lower intensity. A

Fig. 6. Expanded view of the IR spectra from Fig. 5: PANI (a), PmClA (d) and copolymers with f_{mClA} of 0.5 (b) and 0.8 (c). Inset: further expanded view of the 1700–2000 cm^{-1} region of (d), baseline removed.

band at 868 cm^{-1}, consistent with single aromatic H between two substituents is also found. Two new bands at 780 and 680 cm^{-1}, relatively strong, are observed. Both fall in the range of C–Cl stretching vibrations [50,51]; however that at 680 cm^{-1}, sometimes attributed to C–Cl is observed in chlorobenzene and fluorobenzene, and other substituted aromatics as well. We thus assign the 780 cm^{-1} band to C–Cl stretching vibrations, and the other one to skeletal vibrations. In view of the presence of additional Cl substituents, the observations so far are consistent with either unchanged PmClA (1,2,4 substitution, 1 isolated and 2 adjacent H), o-dichloro monomers (1,2,3,4 substitution, only 2 adjacent H) and m- or p-dichloro (1,3,4,5 and 1,3,4,6 substitution, only 1 isolated H) [51]. Additionally there are bands at 1042 cm^{-1} corresponding to an o-dichloro substitution and at 1076 cm^{-1} compatible with a m-dichloro one [51]. However, this last case is true mainly if there are no other substituents in between the Cl atoms. Additionally, the band observed at 1189 cm^{-1} is frequently observed in o-dichlorobenzenes. More information can be found in the 1600–2000 cm^{-1} region, where a group of combination bands with a pattern characteristic of the type of substitution is often found [50,51]. In the PmClA spectrum (inset) two bands are observed, albeit part of the region is overlapped by the strong 1600 cm^{-1} ring band. The pattern observed (one stronger band near 1900 cm^{-1} and one weaker at about 1850) is consistent with 1,2,3,4 substitution; other tetra substituted rings produce patterns which are incompatible with the bands observed [51], but the presence of the 1600 cm^{-1} band does not allow to completely discard them. Other compatible pattern is that of 1,2,4: one weaker band between two stronger ones, the lower lying at about, 1700 cm^{-1}, which in the PmClA spectrum would be overlapped by the strong aromatic ring band; this pattern is consistent with rings with Cl atoms in position metha only. Thus, the IR spectra are consistent with the findings discussed above: the polymer presents Cl atoms substituting the aniline aromatic rings in positions 2 and 6, that is, ortho relative to the amine group. The spectra corresponding to copolymers of intermediate composition (Fig. 6b and c) show intermediate features, confirming the copolymer formation and indicating a similar structure.
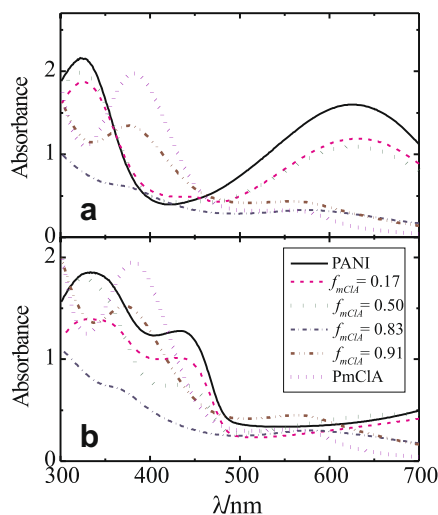
3.5. UV–vis spectra

Fig. 7a shows the absorbance spectra of different (co)polymers in their native (oxidized) form, whereas Fig. 7b shows the corresponding spectra after treatment with a reducing agent. It is observed in Fig. 7a that copolymers with predominant aniline ($f_{mClA} \leqslant 0.5$) present very similar spectra; these show the features already reported for PANI, presenting a relatively broad band centred at about 620 nm, attributed to the quinone imine moieties, along with the π–π^* band at 320 nm [52,53]. However, those with high mClA content show a new band at 380 nm which increases with f_{mClA}, with the band at 320 nm shifting to lower wavelengths and that at 620 nm nearly disappears. Moreover, upon applying the reducing treatment the spectra of (co)polymers with high Ani contents show the expected behaviour [52]: the 620 nm band is absent and a new band ca. 450 nm is observed. On the other hand, the spectra for (co)polymers with $f_{mClA} > 0.5$ do not show changes, indicating that the oxidation state of these products do not change appreciably, even with excess hydroxylamine added. Li et al. [42] presented similar spectra for copolymers with high mClA:Ani ratio. Diaz et al. [41] copolymerized aniline with dichloroanilines and their UV–vis spectra reported for aniline-co-2,3-dichloroaniline show similar features to those presented here, showing an incipient band at about 380 nm.

To analyze the spectral features of copolymers with high mClA contents, and taking into account the above results, theoretical estimations of the electronic absorption bands where conducted

Fig. 7. UV–vis spectra of PANI, PmClA and copolymers in the (oxidized) base form obtained from the synthesis (a) and after hydroxylamine treatment (b).

on phenyl-capped tetramers and octamers of aniline and metha and di-Cl substituted anilines. All were geometry optimized using the PM3 method, afterwards the absorption spectra were calculated with ZINDO/S in the single excited configuration interaction method. Several structures were studied, as exemplified in Scheme 1. Here, phenyl-capped dichloroaniline octamers (diClAni-8) are shown, where one Cl atom is in metha position whereas the second one may be in any of the ortho positions relative to the N atom. The results reported below correspond to a mix of 2,3 and 2,5 dichloro monomer units; oligomers with all identical units gave similar results. Equivalent oligomers constituted by mClA without further chlorination (mClAni-8), and by aniline alone (Ani-8) were studied. The corresponding phenyl-capped tetramers (dClAni-4, mClAni-4 and Ani-4) were also used in the calculations. These simulations

were done for the oxidized (emeraldine) state. A number of different structures have been proposed in the literature for emeraldine, including quinone imine units, radical cation semiquinones (polaron, doublets and triplets), spinless semiquinones (spinless defects, singlet) [54–58] and references therein. After preliminary calculations, the following oligomer structures were examined in detail. As shown in Scheme 1, for each octamer the oxidized state was assumed in one of the following forms: Q form, a quinone imine moiety as usually considered; SQ1 form, a semiquinone where two "semiquinoidic" N atoms are separated by two rings (and so by a normal aminic N); SQ2 and SQ3, where the semiquinoidic N atoms are separated by 2 and 3 aminic N atoms, respectively. Phenylcapped tetramers with configurations Q, SQ1 and SQ2 were also studied. The simulated electronic spectra for aniline and dichloroaniline octamers are shown in Fig. 8 (normalized for comparison purposes), and the calculated heats of formation are presented in Table 1. The simulated spectra for the tetramers are similar (not shown). As it is observed in Fig. 8, the spectra for Q structures qualitatively resemble the features of the experimental PANI spectrum, in agreement with experimental and theoretical literature results for aniline oligomers [44,45,59–61]: two bands are observed, at *ca.* 340 and 500 nm, respectively. The SQ1 structures show different spectra, not coincident with the experimental ones for PANI and PmClA. The SQ2 and SQ3 forms, on the other hand, do present a band centred near 380 nm, whereas the band in the red region is absent, in agreement with the experimental observations. Either Ani-8, mClAni-8 and dClAni-8 show the same features in the SQ2 and SQ3 variants, and similarly for the tetramers. Thus, these simulations predict that the Cl substituents do not affect substantially the spectra, only the polymer backbone configuration does. It should be remarked that these spectra are only predicted from singlet (spinless) structures; calculations with doublet and triplet oligomers did not show the 380 nm band, and mostly showed a band in the red half of the spectrum (about 500–550 nm). Considering now the heats of formation in Table 1, it is noticed that in aniline oligomers the Q structure is the most stable, whereas in Cl
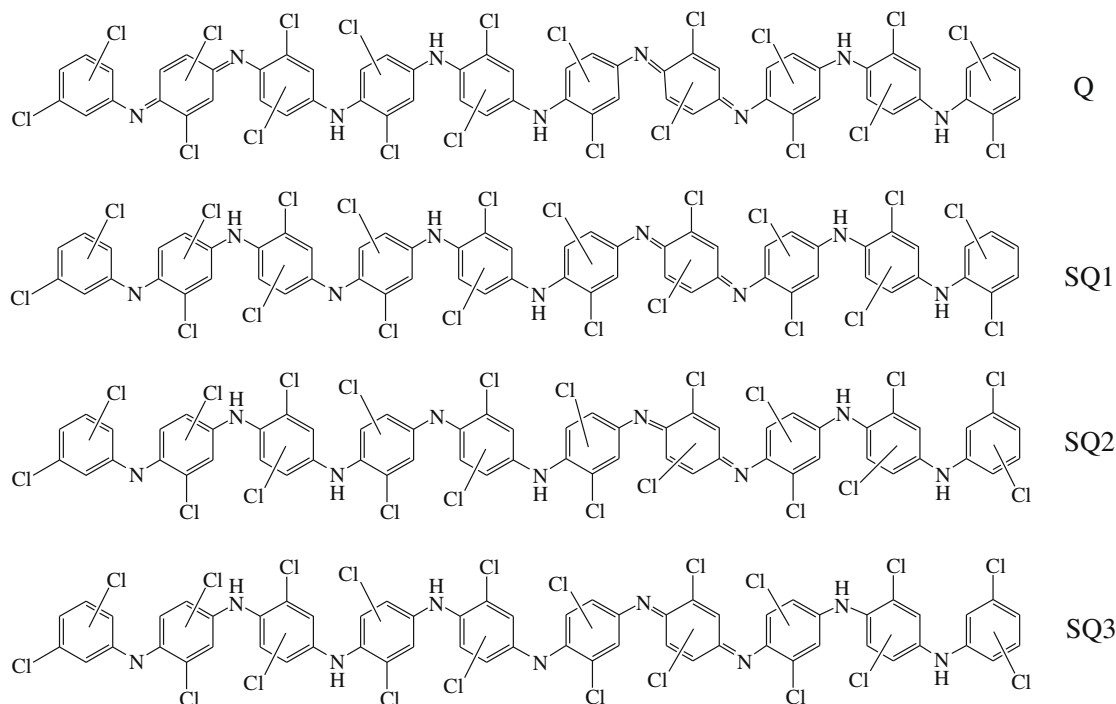
Scheme 1. Phenyl capped octamer structures of poly(m-chloroaniline) with added Cl substituents in several positions studied by PM3-ZINDO/S calculations. Q, normal emeraldine form; SQ1, semiquinone units separated by a single aminic N atom; SQ2, the same separated by two aminic N atoms; SQ3, separated by three aminic N. See text for details.
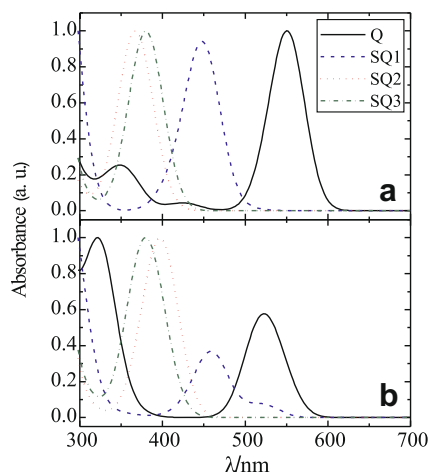
Fig. 8. Simulated UV–vis spectra of (a) PANI and (b) PmClA in several structures; Q: normal emeraldine quinone imine; SQ1: singlet semiquinone groups with two rings (one amine group) in between; SQ2: singlet semiquinone groups with two amine groups in between; SQ3: idem with three amine groups (four rings) in between.

Fig. 9. Fluorescence spectra of PANI, PmClA and copolymers in the (oxidized) base form obtained from the synthesis (a) and after hydroxylamine treatment (b).

Table 1
PM3 predicted heats of formation of aniline and chloroaniline oligomers (kJ mol^{-1}).

Structure	Q	SQ1	SQ2	SQ3
Ani-4	703	715	771	–
mClAni-4	564	603	561	–
diClAni-4	495	508	489	–
Ani-8	1170	1176	1178	1172
mClAni-8	1079	1100	957	943
diClAni-8	812	920	750	751

See text for details.

substituted oligomers, especially those disubstituted, the SQ2 and SQ3 forms appear as the most stable. These results predict that the presence of chlorine substituents stabilizes the spinless semiquinone groups, which is in agreement with the experimental observation that the 380 nm band arises for high mClA:Ani ratios. In our knowledge, spinless semiquinone moieties were only predicted previously for particular states of the emeraldine salt form [58]. On the basis of our calculations, the spectra for f_{mClA} = 0.83, 0.91 and 1.0 of Fig. 7a can be explained by an increased proportion of polymer segments containing dichloro substituted rings, such proportion being related to the intensity of the absorption band at *ca.* 380 nm. Moreover, the lower heats of formation of the SQ2/3 structures strongly suggest a higher stability, which would explain that the treatment with hydroxylamine did not reduce the products with high mClA:Ani ratios. These results are consistent with the fact that Cl substituents in ortho relative to the amine group participate in the resonant structure and thus would stabilize the semiquinone moieties.

3.6. Photoluminescence spectra

Fig. 9 shows the photoluminescence spectra for PANI, PmClA and copolymers in the oxidized (as obtained from the synthesis) form (a) and after reducing treatment (b); the spectra have been normalized for comparison purposes. The general features of PANI fluorescent emission are in agreement with literature reports [62–65]. The reduced form shows a maximum emission around 450 nm (2.8 eV), which is 1.2 eV below the main absorption band at 4 eV. The oxidized form shows emission centred *ca.* 390 nm (3.2 eV), with a blue shift of 0.4 eV compared with the reduced polymer.
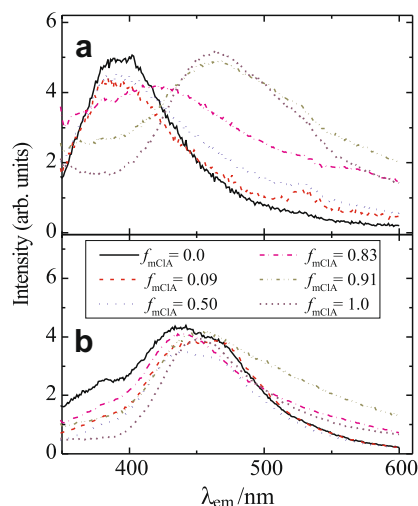
This shift can be attributed to a new energy band arising from the presence of quinone imine units. Copolymers with high Ani contents show the same behaviour; however, as f_{mClA} increases the fluorescence spectra in Fig. 9a show a gradual red shift, with PmClA having an emission band centred at 460 nm, almost coincident with the hydroxylamine treated form in Fig. 9b. Moreover, all the "reduced" (co)polymers in Fig. 9b show fairly coincident spectra. These results are consistent with the absence of quinone imine units in (co)polymers with high f_{mClA} which do not show evidence of changes when treated with a reducing agent.

3.7. General discussion

We attribute the extra chlorination to the slower polymerization kinetics observed for mClA, as was already reported by Li et al. [42], and observed qualitatively in our experiments. In the case of PANI, Morales et al. [66] studied the chemical polymerization in high HCl concentrations, finding a lower rate and the incorporation of Cl in the polymer up to about 8% w/w. Adams et al. [67] polymerized aniline in HCl medium at temperatures down to −35 °C, also finding Cl in the product at the lower temperatures. These results suggest that Cl is slowly incorporated in the monomer; this process will be favoured by a slow polymerization, due to both the slow monomer consumption and the oxidant accumulation, which in turn will favour the oxidation of Cl$^-$ to Cl$_2$ [66]. We discard incorporation of Cl in the polymer because in our experiments PANI polymerizes fast and Cl is not found in the polymer, even when the product remains in the synthesis bath in the presence of excess oxidant for several hours. Thus, the competence between the addition of a monomer to a growing chain and the addition of chlorine to the monomer determines the composition, as schematically depicted in Scheme 2. As it is generally accepted [68–71], these polymers grow through electrophilic attack of an oxidized chain to a monomer molecule (Scheme 2a). In the case of mClA, the similar addition would be a slower reaction (Scheme 2b). That would allow the chlorination of mClA; assuming that it proceeds through an electrophilic substitution by Cl$_2$ [66], the amino group should orient to ortho and para positions, even with the Cl in meta-, as shown in Scheme 2c. The two first cases would result in a dichloro substituted monomer which would then be incorporated in the polymer chain, in agreement with NMR assignments (structures a, b, c, and e of Fig. 4). On the other hand, the addition in para yields a monomer unable to polymerize (it is in principle
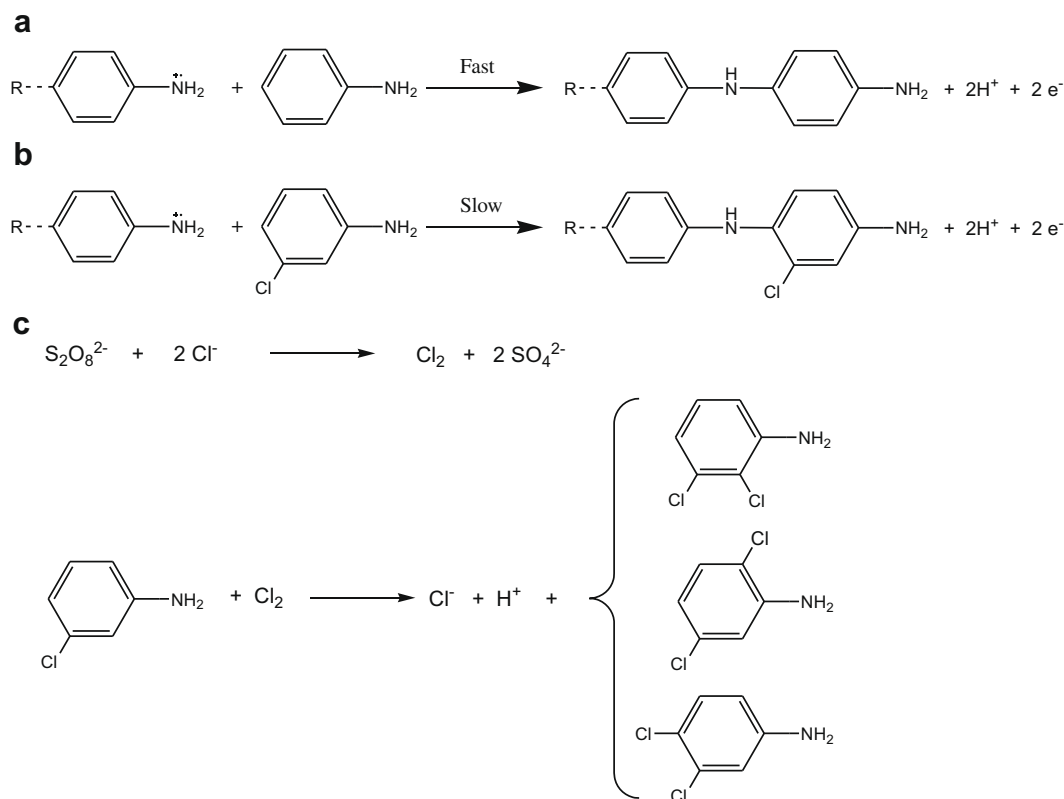
Scheme 2. Basic reactions leading to dichloro substitution during (co)polymerization of mClA. (a) Aniline polymerization fast propagation step; (b) mClA slow propagation step; (c) addition of a second Cl substituent due to oxidant accumulation in the presence of mClA monomers.

still possible to polymerize at the ortho- position, but this should have important steric restrictions). Li et al. [42] found with high f_{mClA} a lower molecular weight and a much lower yield; both facts are consistent with our interpretation. Also, Sayyah et al. [40] found a decreased average molecular weight with increased oxidant concentration, which is consistent with (partial) monomer chlorination in the para- position. It should be noted that increased Cl contents was also found by these authors, attributed to retained chloride ions in the polymer, even when it was treated with NH_3 to stop the polymerization.

Diaz et al. [41] synthesized aniline–dichloroaniline copolymers in conditions of low yield attained through a low oxidant:monomer ratio. Comparing the spectra in [41] with those presented here, it is observed that the spectra for aniline-*co*-2,3-dichloroaniline are similar to those of Fig. 7a with f_{mClA} = 0.83. Other dichloroanilines did not produce in their copolymers similar spectra. This fact suggests, along with the NMR and IR results, that PmClA and the copolymers with high f_{mClA} have preferently units with 2,3 dichloro substitution. Also, they reported increased reactivities for 2,3- and 2,5-dichloroanilines, a fact consistent with the high $r_{Cl/N}$ value found, close to 2: having higher reactivity, dichlorinated monomers will be incorporated to the growing polymer preferentially over mClA.

As reported above, a strong decrease (about 5 orders of magnitude) in the electrical conductivity of the doped forms of these polymers is found in going from PANI to PmClA, also observed in Refs. [41–43]. This decrease has been attributed to several facts [42]: i) the bulky Cl substituents will cause main-chain twisting, which results in a barrier to the intrachain transfer and interchain jumping of the electrons, shortening the conjugation length; ii) the Cl substituent electron withdrawing effect might influence the energy band and distribution of the electrons along the polymer chains; and iii) bulky Cl substituents will prevent acid doping of the polymers due

to static repulsion and steric hindrance. Decreased conjugation was also considered the cause of the differences found with increasing f_{mClA} in Refs. [41,43]. From our results this explanation arises in more detail, which do not excludes the points i–iii above: the stabilization of isolated semiquinone structures instead of quinone imines would prevent conjugation through the chain thus strongly reducing the electrical conductivity.

In agreement with Refs. [41–43], the characterization results show the effective formation of copolymers at the molecular level, with conductivity (among other properties) being a function of f_{mClA}. However, our spectroscopic results suggest that copolymers with high f_{mClA} would not show redox switching, at least in the same conditions as PANI.

As expected, copolymers of aniline and *m*-chloroaniline show increased solubility in a number of solvents [41–43], which improves processability. However, the properties and behaviour of aniline-*co*-*m*-chloroaniline with a mClA:Ani ratio higher than 1:1 appear to be quite different from those of PANI, so that its properties should be considered regarding possible applications.

4. Conclusions

The following conclusions stem from this work:

1. Chemical polymerization of *m*-chloroaniline and copolymerization of aniline-m-chloroaniline in HCl medium lead to the addition of chlorine in the polymer chain, consistent with the slower polymerization rate of mClA.
2. The presence of Cl substituents in the polyaniline chain stabilizes semiquinone singlet moieties, which become more stable than the quinone imine structure; those moieties are not reduced by common reducing agents.

3. The copolymers with a high mClA:Ani ratio appear to be materials quite different from PANI, thus their properties should be considered regarding possible applications.

Acknowledgments

References

[1] H. Shirakawa, E. Louis, A.G. MacDiarmid, C.K. Chiang, A.J. Heeger, J. Chem. Soc. Chem. Commun. 16 (1977) 578.
[2] G. Vozzi, F. Carpi, A. Mazzoldi, Smart Mater. Struct. 15 (2006) 279.
[3] C.O. Baker, B. Shedd, P.C. Innis, P.G. Whitten, G.M. Spinks, G.G. Wallace, R.B. Kaner, Adv. Mater. 20 (2008) 155.
[4] C.-H. Yang, Y.-K. Chih, W.-C. Wu, C.-H. Chen, Electrochem. Solid-State Lett. 9 (2006) C5.
[5] E. Kim, S. Jung, Chem. Mater. 17 (2006) 6381.
[6] R.J. Mortimer, Chem. Soc. Rev. 26 (1997) 147.
[7] S.C. Canobre, R.A. Davoglio, S.R. Biaggio, R.C. Rocha-Filho, N. Bocchi, J. Power Sourc. 154 (2006) 281.
[8] H. Gharibi, M. Zhiani, R.A. Mirzaie, M. Kheirmand, A.A. Entezami, K. Kakaei, M. Javaheri, J. Power Sourc. 157 (2006) 703.
[9] V. Gupta, N. Miura, Mater. Lett. 60 (2006) 1466.
[10] T.C. Girija, M.V. Sangaranarayanan, Synth. Metals 156 (2006) 244.
[11] T. Lindfors, L. Harju, A. Ivaska, Anal. Chem. 78 (2006) 3019.
[12] V. Bracircnzoi, L. Pilan, Mol. Crys. Liq. Crys. 484 (2008) 303.
[13] X. Yin, J. Ding, S. Zhang, J. Kong, Biosens. Bioelectr. 21 (2006) 2184.
[14] N. Prabhakar, G. Sumana, K. Arora, H. Singh, B.D. Malhotra, Electrochim. Acta 53 (2008) 4344.
[15] L. Huang, X. Zhuang, J. Hu, L. Lang, P. Zhang, Y. Wang, X. Chen, Y. Wei, X. Jing, Biomacromolecules 9 (2008) 850.
[16] Z.-A. Hu, X.-L. Shang, Y.-Y. Yang, C. Kong, H.-Y. Wu, Electrochim. Acta 51 (2006) 3351.
[17] O. vandenBerg, M. Schroeter, J.R. Capadona, C. Weder, J. Mater. Chem. 17 (2007) 2746.
[18] R. Gloukhovski, Y. Oren, C. Linder, V. Freger, J. Appl. Electrochem. 38 (2008) 759.
[19] H. Zhang, R. Zong, Jincai Zhao, Yongfa Zhu, Environ. Sci. Technol. 42 (2008) 3803.
[20] S. Chaudhari, P.P. Patil, J. Appl. Polym. Sci. 109 (2008) 2546.
[21] P.G. Pickup, in: R.E. White et al. (Eds.), Modern Aspects of Electrochemistry, vol. 33, Kluwer Academic- Plenum Publishers, New York, 1999, p. 549.
[22] R.H. Baughman, L.W. Shacklette, L. Welsenbaumer, E. Plichta, C. Becht, in: J.L. Bredas, R.R. Chance (Eds.), Conjugated Polymeric Materials. Opportunities in Electronics, Optoelectronics and Molecular Electronics, Kluwer, Deventer, The Netherlands, 1990, pp. 559–582.
[23] P. Chandrasekhar, Conducting Polymers and Applications, Kluwer Academic Publishers, Boston, MA, 1999 (Chapter 21).
[24] A.A. Khan, A. Khan, Inamuddin, Talanta 72 (2007) 699.
[25] K. Mallick, M.J. Witcomb, M.S. Scurrell, Eur. Polym. J. 42 (2006) 670.
[26] E.M. Andrade, F.V. Molina, M.I. Florit, D. Posadas, J. Electroanal. Chem. 419 (1996) 15.
[27] G.B.V.S. Lakshmia, V. Alia, P. Kulriyab, A.M. Siddiquia, M. Husaina, M. Zulfequar, Physica B 392 (2007) 259.
[28] S.M. Ahmed, J. Solut. Chem. 27 (2008) 919.
[29] D. Patil, Y.-K. Seo, Y.K. Hwang, J.-S. Chang, P. Patil, Sens. Act. B 128 (2008) 374.
[30] L. Valentini, V. Bavastrello, E. Stura, I. Armentano, C. Nicolini, J.M. Kenny, Chem. Phys. Lett. 383 (2004) 617.
[31] F.A. Viva, E.M. Andrade, M.I. Florit, F.V. Molina, Phys. Chem. Chem. Phys. 4 (2002) 2293.
[32] S. Mu, J. Phys. Chem. B 112 (2008) 6344.
[33] M.M. Ayad, N.A. Salahuddin, A.K. Abou-Seif, M.O. Alghaysh, Eur. Polym. J. 44 (2007) 426.
[34] A.T. Özyılmaz, G. Ozyilmaz, N. Çolak, Surf. Coat. Technol. 201 (2006) 2484.
[35] K. Buga, R. Pokrop, A. Majkowska, M. Zagorska, J. Planes, F. Genoud, A. Pron, J. Mater. Chem. 16 (2006) 2150.
[36] X.-G. Li, M.-R. Huang, W. Duan, Y.-L. Yang, Chem. Rev. 102 (2002) 2925.
[37] M.-R. Huang, X.-G. Li, Y.-L. Yang, X.-S. Wang, D. Yan, J. Appl. Polym. Sci. 81 (2001) 1838.
[38] Q.-F. Lü, M.-R. Huang, X.-G. Li, Chem. Eur. J. 13 (2007) 6009.
[39] A.A. Athawale, S.F. Patil, B. Deore, R.C. Patil, K. Vijayamohasnan, Polym. J. 29 (1997) 787.
[40] S.M. Sayyah, A.A. Abd El-Khalek, A.A. Bahgat, H.M. Abd El-Salam, Polym. Int. 50 (2000) 197.
[41] F.R. Diaz, C.O. Sanchez, M.A. del Valle, J.L. Torres, L.H. Tagle, Synth. Metals 118 (2001) 25.
[42] X.-G. Li, M.-R. Huang, Y.-Q. Lu, M.-F. Zhu, J. Mater. Chem. 15 (2005) 1343.
[43] U.S. Waware, S.S. Umare, React. Funct. Polym. 65 (2005) 343.
[44] Z.T. de Oliveira, M.C. dos Santos, Chem. Phys. 260 (2000) 95.
[45] J.P. Sadighi, R.A. Singer, S.L. Buchwald, J. Am. Chem. Soc. 120 (1998) 4960.
[46] G.G. Guilbault, in: G.G. Guilbault (Ed.), Practical Fluorescence, second ed., Marcel Dekker, New York, 1990, pp. 1–40 (Chapter 1).
[47] M.K. Ram, E. Maccioni, C. Nicolini, Thin Solid Films 303 (1997) 27.
[48] N.S. Sariciftci, H. Kuzmany, H. Neugebauer, A. Neckel, J. Chem. Phys. 92 (1990) 4530.
[49] R. Baddour-Hadjean, F. Fillaux, P. Colomban, A. Gruger, A. Regis, S. Parker, T. Yu, Synth. Metals 81 (1996) 211.
[50] L.J. Bellamy, The infrared spectra of complex molecules, Wiley, London, 1968.
[51] E. Pretsch, T. Clerc, J. Seibl, W. Simon, Tables of Data for Structure Determination of Organic Compounds, third ed., Springer-Verlag, New York, 1990.
[52] D.E. Stilwell, S.-M. Park, J. Electrochem. Soc. 136 (1989) 427.
[53] Y. Fu, R.L. Elsenbaumer, Chem. Mater. 6 (1994) 671.
[54] M.E. Josefowicz, R. Laversanne, H.H.S. Javadi, A.J. Epstein, J.P. Pouget, X. Tang, A.G. MacDiarmid, Phys. Rev. B 39 (1989) 12958.
[55] A.P. Monkman, G.C. Stevens, D. Bloor, J. Phys. D Appl. Phys. 24 (1991) 738.
[56] F. Genoud, J. Kruszka, M. Nechtschein, C. Santier, S. Davied, Y. Nicolau, Synth. Metals 43 (1991) 2887.
[57] M.M. Wienk, R.A.J. Janssen, J. Am. Chem. Soc. 118 (1996) 10626.
[58] A. Varela-Alvarez, J.A. Sordo, J. Chem. Phys. 128 (2008) 174706.
[59] Z.T. de Oliveira, M.C. dos Santos, Solid State Commun. 114 (2000) 49.
[60] Z.C. Zun, X.B. Jing, X.H. Wang, J. Li, F.S. Wang, Synth. Metals 119 (2001) 313.
[61] L. Chen, Y. Yu, H. Mao, X. Lu, W. Zhang, Y. Wei, Synth. Metals 149 (2005) 129.
[62] Y. Son, H.H. Patterson, C.M. Carlin, Chem. Phys. Lett. 162 (1989) 461.
[63] J.Y. Shimano, A.G. MacDiarmid, Synth. Met. 123 (2001) 251.
[64] P.S. Antonel, E.M. Andrade, F.V. Molina, Electrochim. Acta 49 (2004) 3687.
[65] P.S. Antonel, F.V. Molina, E.M. Andrade, J. Electroanal. Chem. 599 (2007) 52.
[66] G.M. Morales, M. Llusa, M.C. Miras, C. Barbero, Polymer 38 (1997) 5247.
[67] P.N. Adams, P.J. Laughlin, A.P. Monkman, Synth. Metals 76 (1996) 157.
[68] D.E. Stilwell, S.-M. Park, J. Electrochem. Soc. 135 (1988) 2254.
[69] Y. Wei, G.-W. Jaag, C.-C. Chan, K.F. Hsueh, R. Hariharan, S.A. Patel, C.K. Whitecar, J. Phys. Chem. 94 (1990) 7716.
[70] H. Yang, A.J. Bard, J. Electroanal Chem. 339 (1992) 423.
[71] A. Petr, L. Dunsch, J. Electroanal Chem. 419 (1992) 55.