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A Journey into the Determination of Polyaniline Molecular Weight

Claudia L. Bianchi[1,2], Ridha Djellabi[1], Ermelinda Falletta[1,2,3]*

1. Department of Chemistry, University of Milan, via C. Golgi 19, 20133, Milan (Italy)
2. Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), via Giusti 9, 50121 Florence (Italy)
3. ISTM-CNR, via Golgi 19, 20133 Milano (Italy)

***Corresponding author: Ermelinda Falletta, Email:** ermelinda.falletta@unimi.it.

Abstract

Over the last decades, the construction and design of conducting polymer-based materials have received a huge attention due to their special physico-chemical characteristics making them very useful and alternative materials in various fields. Among intrinsically conducting polymers, polyaniline (PANI) has been widely used and a pool of scientific research has been done to improve its properties and/or to combine it with other materials to get multifunction materials with enhanced efficiency. However, the scarce information is available to date on its molecular weight (Mw) limits obtaining structural information. In fact, owing to the poor solubility of the material the most part of the results concerns dimeric and oligomeric species, whereas a complete characterization of the longest chains is still far away.

Since the synthetic strategies used to produce PANI critically affect its properties and chemical-physical characteristics, included Mw, the present work summarizes the most common methods applied for PANI synthesis and the different analytical approaches used to determine the Mw of the polymer and of its oligomers, in order to stimulate further investigation that can contribute to widen the information on this unique polymer.

Keywords

Polyaniline; Molecular weight; Structural information; Analytical techniques; Oligomers

1. INTRODUCTION

From their discovery to date, intrinsically conducting polymers (ICPs) have gradually captured the attention of the scientific community and the industrial world thanks to their outstanding properties that make them interesting for many applications in different sectors, such as supercapacitors [1, 2], sensors [3-6], environmental remediation [7-10] and so on.

Among them, polyaniline (PANI) occupies a special place due to its unique ease doping/dedoping process that allows to switch quickly from the insulating form to the conducting one and *viceversa*. Numerous synthetic approaches have been developed in order to improve the performances of the material depending on the desired application. However, a few information is generally obtained by their structural investigations because of the poor tractability of the polymer.

One of the main problems related to PANI characterization is the determination of its molecular weight (Mw). In this regard, numerous techniques have been applied ranging from dynamic and static light scattering (DLS, SLS) [11, 12], to mass spectrometry (MS) [13-21] and gel permeation chromatography (GPC) [12, 22], passing from nuclear magnetic resonance (NMR) [22] and so on.

Even though each of these techniques represents an important tool that contributes to increase the information on PANI structure, some of them suffer from some shortcomings, such as lack of proper reference standards.

If compared to the other analytical approaches, mass spectrometry can be considered as a powerful technique that offers many advantages such as large number of ionization methods, possibility to connect the mass spectrometer with a chromatograph for the separation of mixtures, possibility to work in the absence of reference standards, *etc.*

From the late 1980s to early 2000s all the technological progresses carried out on MS were exploited to deepen knowledge in the field of Mw of PANI.

However, owing to the poor solubility of the longer polymeric chains of this material, only information on its oligomers and degradation products have been obtained by this technique.

Although knowing the real Mw would open the way to innovative synthetic approaches for PANI preparation and would allow to tune its features finely, more recently this kind of studies have been shelved. Here, we retrace the main attempts made in about thirty years to characterize PANI in terms of its Mw.

2. POLYANILINE

Polyaniline (PANI) is one of the most representative and oldest exponents of ICPs. Thanks to the diverse structural forms that can assume, high environmental stability and fast and reversible doping/dedoping process, this polymer is continuously the centre of attention of the scientific community.

PANI consists of numerous aniline repeat units that can have different oxidation degree alternating -NH- aromatic groups to –N = benzenoid components. In fact, rather than a polymer it would be more correct to refer to PANI as a family of polymers. Although many forms of PANI have been isolated and characterized, the three most common ones are leucoemeraldine (the totally reduced form), emeraldine (the half-oxidized form) and pernigraniline (the totally oxidized form) (Figure 1).

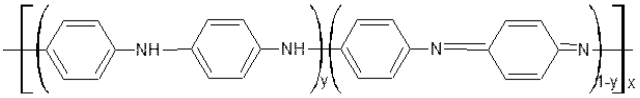


Figure 1: Polyaniline structure. y = 1, leucoemeraldine, y = 0.5 emeraldine, y = 0 pernigraniline.

The structure plays a crucial role in the electroconductive properties of the material. In fact, even though leucoemeraldine could find application in several fields, such as electrochromic devices and Li–PANI batteries [23], the most interesting form of PANI is the half-oxidized half-protonated one, called emeraldine salt, because it is the unique type of PANI that shows electroconductive ability [24]. Owing to its low stability pernigranile does not find practical applications, quickly leading to the corresponding emeraldine form by spontaneous reduction. However, due to its low solubility in common organic solvents, chemically and electrochemically synthesized conducting PANIs have not been widely transferred to industrial applications. In addition, it is almost impossible to overcome such an issue when the structural information is not well-identified. At the same time, regardless of its low solubility, the lack of complete data on PANI does not allow to find solutions for improving and tuning its properties.

3. THE IMPORTANCE OF THE MOLECULAR WEIGHT

The Mw of PANI, as well as the length of its polymeric chains, is an important parameter that directly affects the polymer properties, in particular its conductivity.

From the theoretical point of view, long chains should guarantee higher values of conductivity than oligomers. However, this is not always true, because during the oxidative polymerization reaction, side reactions and other phenomena, such as over-oxidation, local high level of saturation/unsaturation, branching, *etc.*, can cause the interruption of the conjugation which negatively affects the charges localization along the polymeric chains and, as a consequence, reducing the conductivity of the material [25-27]. However, the conduction mechanism does not take place if a minimum value of Mw is not reached. In fact, many researchers correlated the Mw of the polymer to its conductivity by two types of conduction mechanisms: intra- and inter-chains approaches.

On the basis of the theory of De Gennes [28], the conductivity of this kind of materials is related to two main parameters: τc (the mean lifetime of each charge carrier on the chain) and τi (the time that each charge carrier employs to explore the chain). If on the one hand τc has a direct effect on the *inter*-chain conduction mechanism, on the other hand τi is mainly responsible of the *intra*-chain conduction phenomena. The two equations reported below (Eq. 1 and Eq. 2) take in consideration the contribute of the two parameters (τc and τi) along with others to the PANI conductivity, where L is the length of the chain that is strictly correlated to the Mw of the polymer, a is the persistence length of the chain, n is the density charge, e is the charge per carrier and D is the diffusion coefficient for the charge carrier along the chains.

$$\sigma \propto \frac{ne^2}{kT} \bullet \frac{aL}{\tau c} \qquad \text{Eq. 1}$$

$$\sigma \propto \frac{ne^2}{kT} \bullet a\sqrt{(Di \bullet \tau c^{-1}} \qquad \text{Eq. 2}$$

4. A GLANCE TO THE MAIN SYNTHETIC APPROACHES

It has been demonstrated that the Mw of PANI is critically depending on several factors, most of which is related to the reaction conditions applied for the synthesis [29]. For this reason, below the main synthetic procedures for PANI synthesis are reported and discussed in terms of Mw.

4.1 Chemical method

Large scale PANI production is still based on chemical oxidative polymerization reaction [30]. Although this method doesn’t guarantee a fine control of the final features of the polymer, it is still the most applied approach even in the most advanced applications [31].

Generally, the reaction is carried out in acidic aqueous solution in the presence of different oxidizing agents (typically ammonium persulfate [30, 32] or metals in high oxidation states [33]) that dramatically affect the chemical-physical characteristics of the polymer (morphology, conductivity, processability, *etc.*). In fact, the reaction parameters have a dramatic effect on the formation of branched structures and on the molecular weight of the polymer. For example, it was demonstrated that passing from 18°C to -25°C the molecular weight of the polymer gradually decreases [34].

4.2 Co-polymerization

One of the first strategies proposed to increase the PANI solubility was the copolymerization of aniline monomer with other different monomers or substituted anilines. As demonstrated by Yue *et al.*, the copolymer has lower Mw than traditional PANI, as confirmed by the values of conductivity [35]. However, for specific applications, the possibility to extend and finely tune the properties of the final material exceeds any other possible consideration and, as a consequence, to date aniline co-polymerization is widely applied for the preparation of sensors, electrodes and so on [36, 37].

4.3 Electrochemical methods

Besides chemical oxidation, electrochemical polymerization is another old traditional way widely used for PANI synthesis. It is not recommended for the production of PANI in large amount. However, it permits a fine control of the morphology and the conductivity of the polymer [38] with evident advantage in the field of films, electrodes, *etc.* [39, 40]. As for chemical oxidation, also for the electropolymerization process the reaction parameters strongly affect the chemical-physical characteristic of the polymer. In general, the Mw of electrosynthesized PANI is much lower than that obtained by chemical polymerization, ranging from 1000 to 50000 gmol-1 depending on the electropolymerization conditions [41]. Mattoso *et al*. demonstrated that a significant increase of Mw is obtained when the reaction is carried out in the presence of neutral salts, in particular LiCl. In this case, owing to charge screening effects, values of Mw from about 91000 to about 106000 were obtained depending on the used salts [42].

4.4 Enzymatic methods

As for the other cited methods, also in the case of enzymatic polymerization the reaction conditions have an effect on the properties of the polymer, even though the scientific literature lacks information about this aspect. In the case of PANI, one of the major drawbacks consists in the formation of highly branched not conductive low MW polymer. However, enzymatic polymerization represents an alternative and important environmentally friendly approach that can be easily used for the production of PANI nanoparticles [43, 44], colloid-microparticles [45], films [46], *etc.*

5. ANALYTICAL METHODS FOR MW DETERMINATION OF PANI

Despite Mw of different materials can be determined by numerous techniques, because its low solubility and processability, in the case of PANI the number of analytical methods is much less. Below the main analytical approaches applied for the determination of the PANI’s MW are reported and discussed.

5.1 Molecular weight by Light Scattering (LS) technique

Stejskal *et al*. were pioneers in the application of LS to PANI characterization [11].

LS is an optical technique that allows to measure the scattered light produced by randomly oriented objects dispersed in a solvent when a monochromatic laser light interacts with them. The intensity of scattered light is proportional to size and Mw of the objects, but also to the difference between the refractive index (n) of the objects (scattering centres) and the solvent. As a consequence, only for values of Δn other than zero LS can be applied.

If on the one hand static light scattering (SLS) allows to determine sample properties like M_w and second virial coefficient (A_2) from the light scattered at different concentrations of the sample, in contrast dynamic light scattering (DLS) allows to calculate other properties, such as hydrodynamic radius (R_h), from the recording of the fluctuations in scattering intensity over time.

In order to overcome the limitation due to the poor solubility of the polymer, the aniline oxidative polymerization was carried out in presence of the steric stabilizer poly(vinyl alcohol) (PVA) allowing the production of submicrometer-sized spherical dispersion particles. DLS was applied for the determination of the R_h of the polymer obtaining an average value of 116 nm. Even though this result seems to be in contrast with the geometrical radius measured by Scanning Electron Microscopy (SEM) (ca. 75 nm), it is important to highlight that DLS method takes into consideration also the presence of the stabilizer around the PANI particles. Moreover, the technique allowed the evaluation of the polydispersity of the particles on the basis of the M_{wD}/M_{wn} ratio (2.3), where M_{wD} is the weight average molecular weight, while M_{wn} is the number average molecular weight. The mass average particle molar mass was determined by SLS and resulted to be $5.2x10^8$ g/mol. About in the same period, other researchers applied LS for the Mw determination of sodium salt of sulfonic acid ring-substituted polyaniline (SPAN) [47]. The average M_w of hydrazine-reduced SPAN was 11,000 g/mol and the number of ring-nitrogen units per polymer chain resulted to be 39. Kolla *et al*. deepened these studies, measuring the absolute Mw of PANI in the three main oxidation states (leucoemeraldine, emeradine and pernigraniline) comparing the results obtained by LS with those resulted by refractive index (IR) both connected to GPC technique [12]. Table 1 summarizes the number of aniline repeat units and the Mw obtained both by LS and GPC for the materials in base form synthesized by potential-time profiling the chemical oxidative polymerization of aniline at 0°C.

Table 1: Number of aniline repeat units (N) and average molecular weight (Mw) for PANI base in different oxidation states by light scattering (LS) and gel permeation chromatography (GPC).

Kind of PANI	Mw (LS)	Mw (GPC)	N (LS)	N (GPC)	ΔN (GPC-LS)
Leucoemeraldine	55950	67252	267	321	54
Emeraldine	68580	82296	316	378	62
Pernigraniline	52478	64092	265	323	58

As it is possible to observe, for emeraldine the value of N obtained by GPC is 17% greater than that calculated by LS. This discrepancy can be reasonably ascribed to the different hydrodynamic radii of emeraldine if compared to polystyrene standards used for GPC analyses. In addition, the authors observed that the N overestimation by GPG is Mw dependent. The analysis carried out on pernigraniline, isolated at the maximum of the time-profile, demonstrated that for this PANI structure N = 265, 51 fewer aniline units than emeraldine, obtained by spontaneous pernigraniline reduction at the end of the reaction. These results confirm the two-step reaction mechanism previously proposed by Manohar *et al.* [48]. According to this mechanism, during the oxidative polymerization of aniline about 84% of emeraldine base originates from the reduction of the intermediated pernigraniline by the excess of aniline. The remaining ca. 16% of emeraldine is due to the polymerization of other aniline units. This second polymerization can take place independently of pernigraniline, leading to a mixture of $\text{emeraldine}_{\text{pernigraniline}}$ and $\text{emeraldine}_{\text{aniline}}$, or on pernigraline causing the formation of 84% $\text{emeraldine}_{\text{pernigraniline}}$ -16% $\text{emeraldine}_{\text{aniline}}$ copolymer.

Thanks to these extraordinary results, some aspects of the reaction mechanism of aniline polymerization were definitely clarified, demonstrating the enormous importance of the study of Mw for a deeper knowledge of these materials, although these investigations took in consideration only the soluble fractions of the polymers.

5.2 Molecular weight by ^{15}N NMR

Even though ^{15}NMR is a spectroscopic technique that is not able to give direct information on Mw, it can indirectly contribute to the polymers characterization, as reported by Adams *et al*. [22]. Richter and co-workers [49], via the use of ^{15}NMR solid state and solution state NMR, proposed emeraldine base structure alternating copolymers of reduced and oxidized units containing only secondary (2°) amines but not primary (1°) ones. Inspired by these results the authors wanted to deeper explore this latter aspect, taking into consideration that PANI should be the result of head-to-tail aniline polymerization at the 1,4- position.

First of all, using poly(vinyl pyridine) instead of polystyrene as the reference standard, the authors demonstrated the presence of 1° amines and calculated the 2°/1° ratio for both low and high molecular weight emeraldine base (EB).

Table 2 reports the peaks area ratio between 2° groups, 1° groups and imines.

Table 2: peaks area ratio between 2° groups, 1° groups and imines by ^{15}N NMR spectra and average number (N°) of repeat units.

Kind of PANI	Ratio of peak areas			N° repeat units
	Imine	2° amine	1° amine	
Low Mw EB	1.4	14.0	1.0	28
High Mw EB	12.4	31.0	1.0	63

Assuming one $–NH_2$ final group for each polymeric chain, it is possible to calculate 28 aniline repeat units for low Mw EB and 63 for high Mw EB.

However, higher Mw values were obtained by GPC technique, as shown in Table 3.

Table 3: average Mw by GPC and average number (N°) of repeat units.

Kind of PANI	Mw	N° repeat units
Low Mw EB	131710	151
High Mw EB	32320	346

The higher values of repeat units calculated by GPC could be justified if the polymerization occurs also at 2- and 4- positions. However, a more reasonable explanation could be related to an overestimation of these values due to aggregation phenomena of the polymeric chains in solution. Moreover, the reference standard used is not totally comparable to PANI in terms of hydrodynamic radius and chains flexibility.

Despite the difficulties and limitations associated with these techniques, also in this case the efforts devoted by the authors usefully contributed to the understanding of the PANI structure.

5.3 Molecular weight by MS

Mass spectrometry represents the technique of choice for the determination of molecular weights of small and large molecules. Thanks to the possibility to choose accurately the type of source and analyzer, different experiments can be carried out allowing numerous and different information not only on the Mw but also on the molecular structure.

Figure 2 shows a simplified scheme of a mass spectrometer and reports the main ion sources and analyzers used.

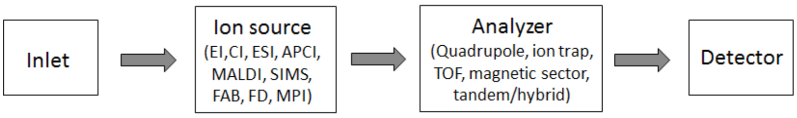


Figure 2: Scheme of a mass spectrometer and the most common ion sources and analyzers used (EI= electron ionization; CI= chemical ionization; ESI= electrospray ionization; APCI= atmospheric pressure chemical ionization; MALDI= matrix assisted laser desorption ionization; SIMS= secondary ion mass spectrometry; FAB= fast atom bombardment; FD= field desorption; MPI= multiphoton ionization).

Concerning the characterization of polymers and macromolecules, among the ion sources ESI, APCI, MALDI, SIMS and FAB are the most common techniques that allow to obtain useful information on the materials avoiding strong fragmentation phenomena.

The latter aspect is crucial for those materials such as polymers consisting of numerous identical or very similar repeat units.

For these molecules, in fact, an excessive fragmentation prevents obtaining useful information on their original structure.

For the characterization of PANI and PANI derivatives, many approaches have been applied. However, because of the low solubility of the polymer in the common solvents used for MS experiments, the obtained results mainly concern the most soluble oligomers.

Before delving into the results achieved so far with this technique, a look at the main reaction mechanisms involved in PANI synthesis is necessary to understand and appreciate more the results obtained by MS.

Even though scientists agree that the reaction mechanisms involved in PANI synthesis by both chemical and electrochemical methods are very similar, actually only for the electrochemical way the reactions involved in the aniline polymerization were proved.

The polymerization mechanism consists in three main steps: (i) initiation, (ii) chain propagation and (iii) termination [50].

(i) *Initiation*. During the first step of the reaction aniline monomer undergoes oxidation reaction on the surface of the electrode producing aniline radical cations (Figure 3).

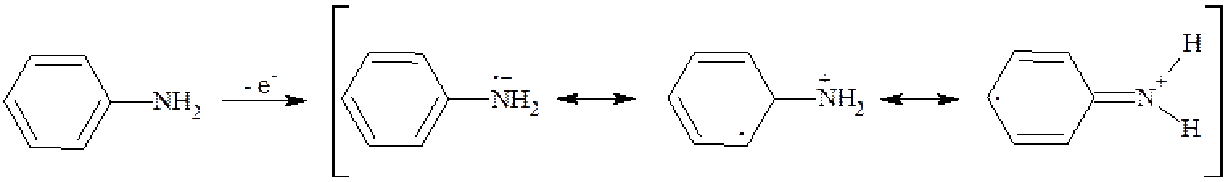


Figure 3: aniline radical cations formation.

Aniline radical cation has different resonant forms that can differ for their reactivity. However, all of them can react with other radical species by coupling reaction. By the removal of two protons and by the re-aromatization of the rings, they lead to dimeric species (Figure 4) on whose nature depends the progress of the polymerization reaction.

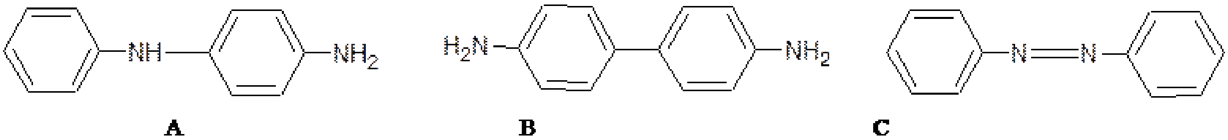


Figure 4: A) N-4(aminophenyl)aniline, B) benzidine, C) trans-azobenzene.

Unlike trans-azobenzene, both benzidine and N-4(aminophenyl)aniline can initiate the polymerization reaction.

(ii) *Chain propagation.* As for aniline monomer, also dimers can be oxidized on the surface of the electrode producing radical cations that can react with aniline monomers or other dimers leading to oligomers and PANI. During the propagation step, these species can undergo further oxidation reactions leading to PANI with different oxidation states (Figure 1).

(iii) *Termination*. The last step of the reaction is not clear and has never been completely demonstrated. Only a few hypotheses have been formulated based on hydrolysis processes or on the stop of the reaction because of steric hindrance on the polymeric chains.

MS technique allowed to confirm the reaction mechanism of PANI synthesis.

The main advantage of the SIMS technique typically consists in providing molecular information of the surface investigated.

In this regard, the work of Chan and coworkers is one of the first attempts to apply SIMS in static mode to the investigation of three chemically prepared PANIs doped by HCl, HBr and HF [14]. By the study of negative mass spectra of PANI-HF, the following species (Figure 5) were assigned to the peaks at 181, 183, 260 and 262 Da.

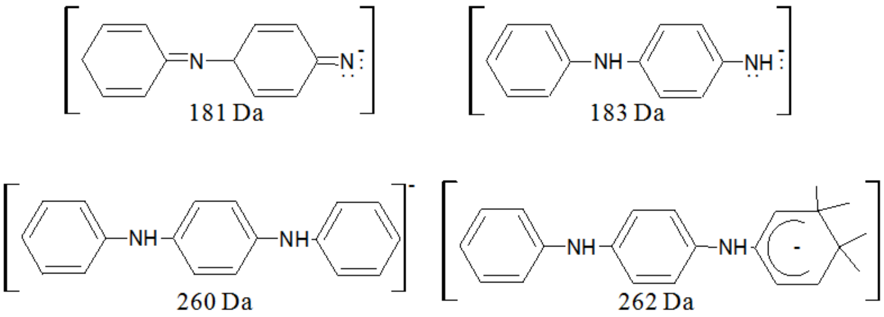
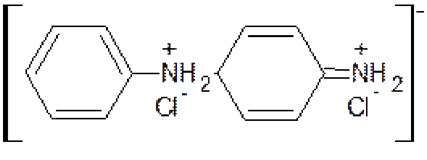


Figure 5: molecular structures assigned to the peak at 181, 183, 260 and 262 Da in the negative mass spectrum of PANI-HF.

No meaningful assignments were reported for PANI-HBr, while in the case of PANI-HCl the triplet at 255, 257 and 259 Da was assigned to the benzenoid-quinoid structure reported in Figure 6.



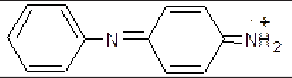
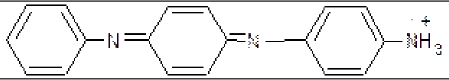
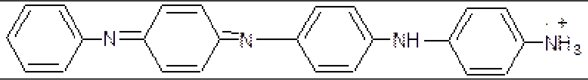
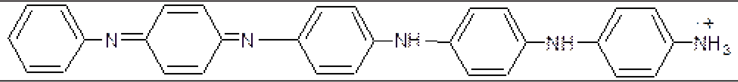
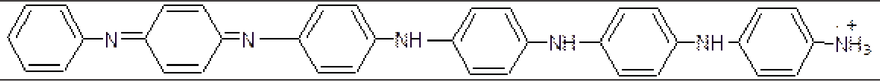
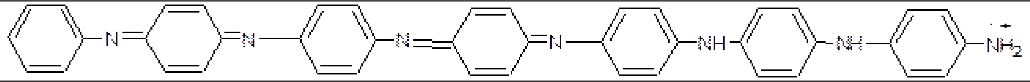
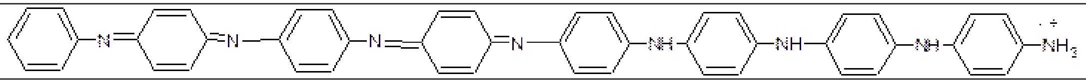
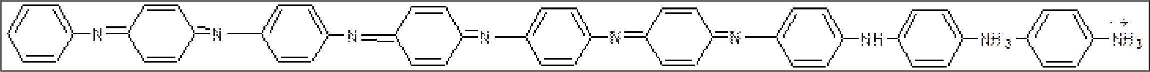
255, 257, 259 Da

Figure 6: molecular structure assigned to the peak at 255, 257 and 259 Da in the negative mass spectrum of PANI-HCl.

Although today the existence of these structures could seem obvious, at that time it strongly contributed to the characterization of the material supporting the results obtained by other researchers independently [51-54].

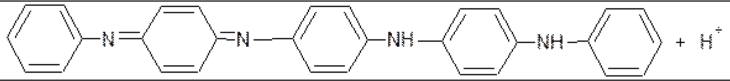
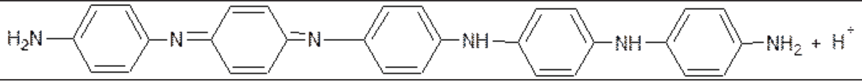
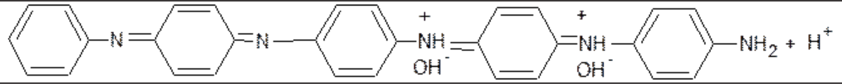
Low Mw oligomers of PANI were properly synthesized by Dolan and Wood and analyzed by ESI/MS technique using tandem mass spectrometry (MS/MS) experiments for the identification of the end groups [16]. The ESI mass spectrum of the soluble fraction allowed to identify oligomers up to 9-mer. The main peaks showed differences of 91 m/z or multiple of this repeat unit. Table 4 displays the identified PANI structures.

Table 4: proposed molecular structures assigned to the peaks in the ESI/MS spectrum of PANI oligomers.

Proposed structure	m/z
	182
	274
	365
	456
	547
	636
	727
	816

Along with these main structures, additional secondary series were observed in the ESI/MS spectrum that did not show an equal number of nitrogen and aromatic rings. These secondary compounds could derive from loss of amine or terminal phenyl groups, as elsewhere reported [13, 15, 19]. The proposed structures are summarized in Table 5.

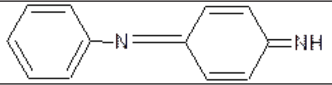
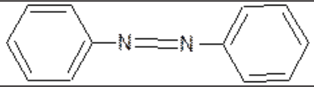
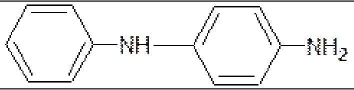
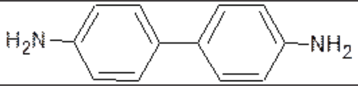
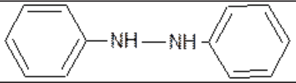
Table 5: proposed molecular structures of the secondary ions in the ESI/MS spectrum of PANI oligomers.

Proposed structure	m/z
	441
	471
	490

This kind of experiment does not allow to determine the exact sequence of benzenoid and quinoid units. Therefore, in order to verify the proposed structures tandem MS experiments were carried out on the main peaks. From the study of tandem mass spectra, the molecular structures reported in Tables 4 and 5 were confirmed.

A more sophisticated approach was developed by Deng and coworkers in 1999 [17], consisting in a thin-layer electrochemical flow cell coupled on-line with ESI-MS able to characterize the soluble components produced during the aniline electrochemical polymerization using H_2O and H_2O/CH_3OH (1:1 volume ratio) as the solvents, at different pH values. Dimeric species and oligomers up to 10-mer were characterized in terms of molecular weight and redox-state distribution and the main results are reported in Table 6.

Table 6: molecular structures and m/z values of dimers at different pH values.

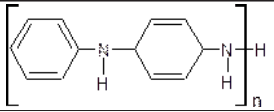
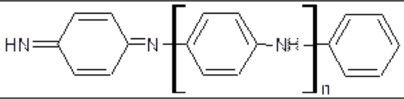
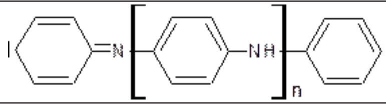
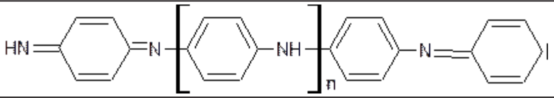
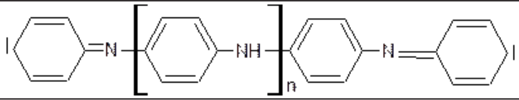
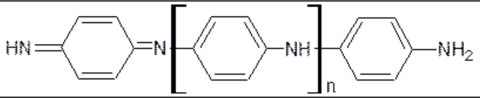
Proposed structure	M+H m/z	pH
	183	4 and 9
	183	9
	185	4 and 9
	185	4
	185	9

It is evident that the kind of dimeric species produced during the aniline electrochemically polymerization and their oxidation state are strictly related to the pH of the solution. Moreover, useful information on the redox state of oligomers up to 10-mer were reported.

Chemically and electrochemically PANI was also analyzed by multiphoton ionization (MPI) mass spectrometry [15]. MPI is a soft ionization technique able to lead to a few fragments if compared to EI. Numerous groups of ions were obtained. The main peak of each group differs from the main ion of the following and the subsequent group by 91 m/z, corresponding to the C_6H_5N unit.

Table 7 reports the identified main ions of each group.

Table 7: molecular structures of the main ions for each group determined by MPI.

Proposed structure	m/z	n
	93+91n	0-8
	182+91n	0-8
	167+91n	0-8
	271+91n	0-7
	256+91n	0-6
	197+91n	0-6

Oligomers up to 20-mer were observed by field desorption (FD) mass spectrometry [13]. In this case aniline was electrochemically polymerized on the conducting carbon-whisker-FD emitter working as the anode.

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI/MS) is described as a useful technique for polymer characterization [55]. It gives information on repeat units, end groups and molecular weights distribution of polymers. However, a critical point of this technique is the sample preparation. Choosing the most appropriate matrix is the most important aspect. In fact, it has to provide the ionization of the sample and has to be compatible with it also in the solid state. Moreover, the matrix has to show high electronic absorption at the used laser wavelength (typically 337 nm) in order to desorb and ionize the sample efficiently. Concerning the characteristics of the solvent, it has to ensure compatibility between sample and matrix. Folch *et al*. applied the laser desorption/ionization and MALDI mass spectrometry to the investigation of PANI, using 2,5-dihydroxybenzoic acid as the matrix and exploring different solvents (tetrahydrofuran, N, N-dimethylformamide, methanesulfonic acid and 1-methyl-2-pyrrolidone) [19]. Working in the absence of any matrix, 1-methyl-2-pyrrolidone allowed to ionize higher molecular weight oligomers than the other solvents, thanks to its high solvent power. However, the acidic properties of methanesulfonic acid led to more defined peaks, corresponding to oligomers up to 10-mer, both for emeraldine and pernigraniline, operating whether in the absence and in the presence of matrix.

Secondary peaks around the more intense ones that differ for ±1 mass unit suggested the presence of oligomers having different oxidation degree (benzenoid/quinoid ratio).

From these results it was possible to conclude that, despite the MALDI/MS is the main technique for the polymers characterization, it fouls in the case of PANI because of its very low solubility in common matrices and solvents. In fact, similar information was obtained by ESI/MS.

In order to overcome these drawbacks, Dolan and Wood proposed an innovative alternative solventless approach consisting in the mixing and grounding in a mortar the sample and the matrix (gentisic acid (2,5-dihydroxybenzoic acid), dithranol or 7,7,8,8-tetracyano-quinodimethane) together. Even though oligomers up to 1700 Da were identified by this method, longer polymeric chains were not ionized [16].

Pyrolysis-GC/MS technique was also employed for the study of thermal degradation of PANI produced by both chemical and electrochemical aniline polymerization.

The investigations of Borrós Gómez and Folch demonstrated the high thermal stability of both emeraldine and pernigraniline synthesized by the chemical way [18]. In fact, after heating at high temperature dimers and oligomers were not detected. In particular, the lack of benzidine and trans-azobenzene demonstrated that head-to-head and tail-to-tail polymerizations contribute very little to PANI formation.

Thermal degradation of electrochemically prepared HCl- and HNO_3-doped PANI in form of films was also described [21]. Concerning PANI-HNO_3, the decomposition of the material in two steps, at around 320 and 440°C, was justified with the presence in the polymer of chains with different molecular weights. Moreover, the authors demonstrated the formation of nitro-aniline and chloro-aniline structures during the electropolymerization process, while the CO_2 evolution at elevated temperatures indicates oxidation process on the backbone of the polymer when the polymerization reaction is carried out in the presence of HNO_3.

CONCLUSIONS

The present paper summarized an overview of research studies carried on the characterization of PANI. Each technique applied to the PANI characterization allowed to clarify some aspects of its structure and to understand the reaction mechanism. If on the one hand ^{15}NMR investigations definitively defined the presence and the number of primary amines groups on the polymeric chains, on the other hand by MS experiments the different oxidation states of the polymer were clearly identified. Moreover, MS allowed to add crucial information on the reaction mechanism of aniline polymerization. Light scattering seems to offer a greater chance of success because it does not require the use of proper reference standards and does not show limits related to the ionization of long chains.

Recent advances in analytical technologies in terms of sensitivity could strongly and positively contribute to face this issue by different and innovative approaches. In this regard, online MS techniques that allow to follow the growth of the polymer during the polymerization reaction could permit to obtain more information on longer oligomers.

However, despite the important progress made so far, the knowledge of the molecular weight of PANI is still an unresolved question that will continue to excite the future researchers.

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