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Electropolymerization mechanism of *N*-methylaniline

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Abstract

A poly(*N*-methylaniline) (PNMA) film was obtained by chronoamperometry on tin oxide (TO) in dimethylformamide DMF containing 0.5 M sulphuric acid. The PNMA film formation was monitored by in situ UV–vis spectroscopy. A detailed electropolymerization mechanism and reaction pathway of *N*-methylaniline (NMA) is proposed based on mass spectroscopy (MS) and NMR analysis. The NMA repeating units (both in the film and in the soluble part) were found to be partially dealkylated during electropolymerization. NMA was also electropolymerized in different solvents such as propylene carbonate (PC) and acetonitrile (ACN). Our results show that protonation is not a necessary condition to initiate the electropolymerization of NMA, but it may play a key role for the propagation of longer conjugated chains. The influence of solvents on the film formation and the function of protons are discussed in this paper.

Keywords: Poly(*N*-methylaniline); Electropolymerization mechanism; In situ UV–vis spectroscopy; NMR; MS

1. Introduction

Poly(*N*-methylaniline), PNMA is one of the most important polyaniline, (PANI) derivatives. It has received increasing attention during the recent years due to its unique properties like low oxidation potential, solubility in organic solvents and its strongly reduced pH sensitivity relative to PANI [1–4]. In contrast to the detailed studies on the properties of PANI and its derivatives, much less attention has been paid to the fundamental mechanism of its film growth and nucleation [5–9]. There are only a few reports to the best of our knowledge on the mechanism of the anodic reactions of *N*-substituted anilines in the literature. Some of them to be mentioned are the ESR experiments of Watanabe et al. indicating that the radical sites of poly(*N*-alkylaniline), like PANI, are localized at the nitrogen atom [10], while Baughman et al. found that the radical cations are not fully localized on nitrogen [11]. Galus et al. proposed that the initial anodic oxidation of NMA is followed up by a tail-to-tail coupling leading to the formation of *N*-substituted benzidine [12]. Hambitzer et al. reported based on mass spectra the presence of a radical species in electropolymerization of both aniline and NMA. They found that the main product in the reaction was a dealkylated dimer of NMA, i.e. the tail-to-tail coupled benzidine and that the by-product was the head-to-tail coupled species [13,14]. Benzidine was also found as the main product in the anodic oxidation of *N*,*N*-dialkylanilines in 0.1 M NH_4OAc [15]. Comisso et al. [16] polymerized NMA electrochemically in aqueous acidic solutions. The reaction was described as a coupling of radicals via head-to-tail at the *para* position leading to a high degree of polymerization. The formation of hydrazobenzene as a result of head-to-head coupling of anilines was reported to take place especially at high pH conditions [17]. A general EC mechanism in the electro-oxidation of *N*-substituted anilines was proposed by Malinauskas and Holze using in situ UV–vis spectroscopy [18,19].

In this paper, we extend our previous study on the electropolymerization of NMA in organic media [3] to comprise both the soluble part and the formed PNMA film. The main focus has been on synthesis of a PNMA film from sulphuric acid in DMF. An electropolymerization mechanism and reaction pathway for

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NMA is proposed based on MS and NMR spectroscopic data. The role of protons and the influence of solvents on electrodeposition will be discussed.

2. Experimental

2.1. Chemicals

N-Methylaniline (NMA) (98.0%), methanesulfonic acid (MSA) (≥99%), lithium perchlorate ($LiClO_4$) (>98%) and dimethylformamide (DMF) (>99.8%) were obtained from Fluka. Propylene carbonate (PC) (99.7%) and acetonitrile (ACN) (99.8%) were from Aldrich, and sulphuric acid (95–97%) from J.T. Baker. All chemicals were used as received.

2.2. In situ UV–visible spectroscopy

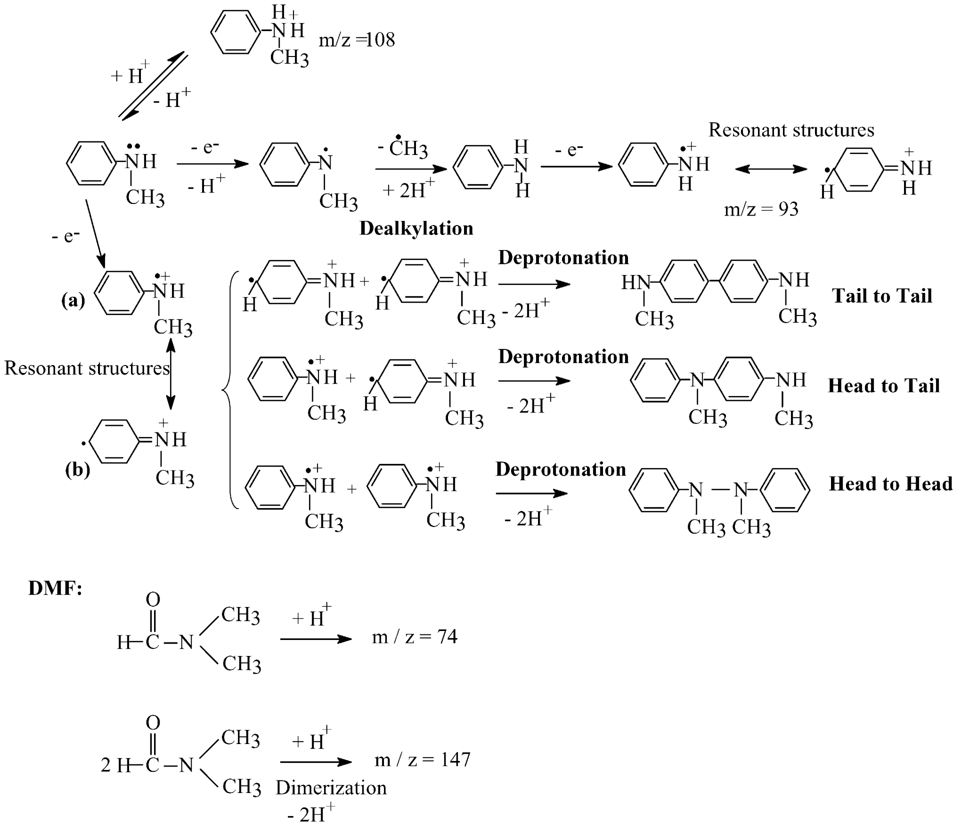
NMA was electropolymerized by chronoamperometry in a three-electrode configuration in a standard 10 mm quartz cuvette with the UV–vis spectra taken in situ. The UV–vis transmission spectra were recorded with a Hitachi U-2001 spectrophotometer. The electropolymerization was performed either at 450 or 750 mV and spectra were recorded both during polymerization and at the open circuit potential after the polymerization. A tin oxide, TO glass (thickness: 4 mm) served as working electrode, WE, a Pt and a Ag|AgCl wire were used as counter electrode CE and reference electrode RE, respectively. Prior to each measurement the TO glass was rinsed with acetone and an excess of deionised water. The background spectra were always recorded with two blank TO glasses before the polymerisation was started.

2.3. Cyclic voltammetry

The cyclic voltammetric (CV) measurements made to establish the oxidation potentials of NMA in different solvents were also performed in a three electrode cell with a TO glass as the WE, a Pt wire as CE and a Ag/AgCl wire as RE. The electropolymerisation of NMA was done in DMF, PC and ACN containing 0.5 M NMA and 1.0 M MSA by potential scanning between 0 and 1 V, at a scan rate of 50 mV/s. The potential was controlled with an Autolab (PGSTAT 20) potentiostat. Prior to all measurements the solutions were purged with nitrogen and the solutions were blanketed with nitrogen during the experiments.

2.4. NMR and mass spectroscopy

For NMR spectroscopic analysis the films were dissolved in chloroform, the solvent was evaporated and the residues were dissolved in DMSO-d_6. The signal of DMSO was used as an internal chemical shift standard ($\delta_H = 2.5$ ppm and $\delta_C = 39.5$ ppm). The ^1H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker AV-600 spectrometer at 600.13 and 151.91 MHz, respectively. The NMR signal assignments were based on chemical shifts and H–H and H–C correlation spectroscopy (COSY, HSQC and HMBC).



Scheme 1. (a) Initiation mechanism of the electrochemical oxidation of NMA and (b) protonation and dimerization of DMF.

The mass spectrometric analyses were performed on a Agilent 1100 Series LC/MSD SL Trap system (Agilent Technologies, Espoo/Esbo, Finland) equipped with an electrospray source and operated in the positive mode. Nitrogen was used both as nebulizer gas (15 psi) and as drying gas (5 mL/min) heated to 325 °C. The capillary exit offset was 128.5 V with skim 1 set at 40.0 V. The maximum ion accumulation time was 2000 μs and the target value was 30 000. Full mass spectra were recorded between m/z 50 and 800 with collision induced dissociation (CID) experiments coupled with multiple tandem mass spectrometry (MS^n) employing helium as collision gas. The fragmentation amplitude was varied between 0.8 and 1.0 V. The samples were introduced to the source by a syringe pump at a flow rate of 5 μL/min of a concentration of about 5 μg/mL. The solvent was a 1/1 mixture of 10 mM ammonium acetate and acetonitrile.

3. Results and discussion

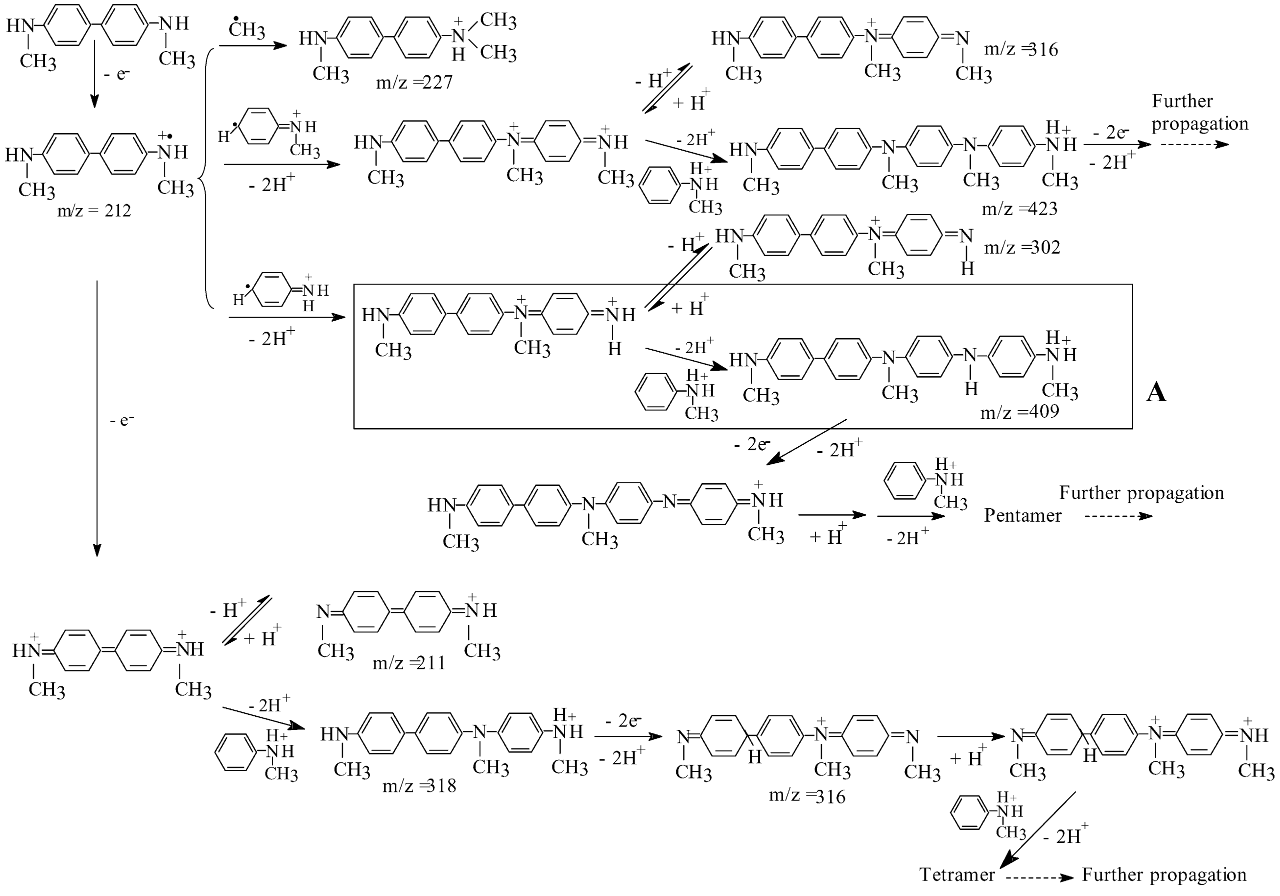
Aniline couples mainly tail-to-tail, and head-to-tail under acidic conditions [20]. These two possibilities should also exist for NMA, additionally the head-to-head coupling reported for aniline polymerization at high pH values can take place [17].

It is generally accepted that, like aniline, *N*-methylaniline is first oxidized to a radical cation [14], which will exist in various resonance stabilized structures. In Scheme 1, the resonance structures of possible radical cations (a) and (b) are drawn, that can propagate for longer conjugated chains. The head-to-tail and tail-to-tail dimers easily undergo further coupling reactions leading to longer conjugated chains drawn in Schemes 2 and 3. Whereas the head-to-head form, hydrazonbenzene is difficult to form into a polymer at concdictions with high pH.

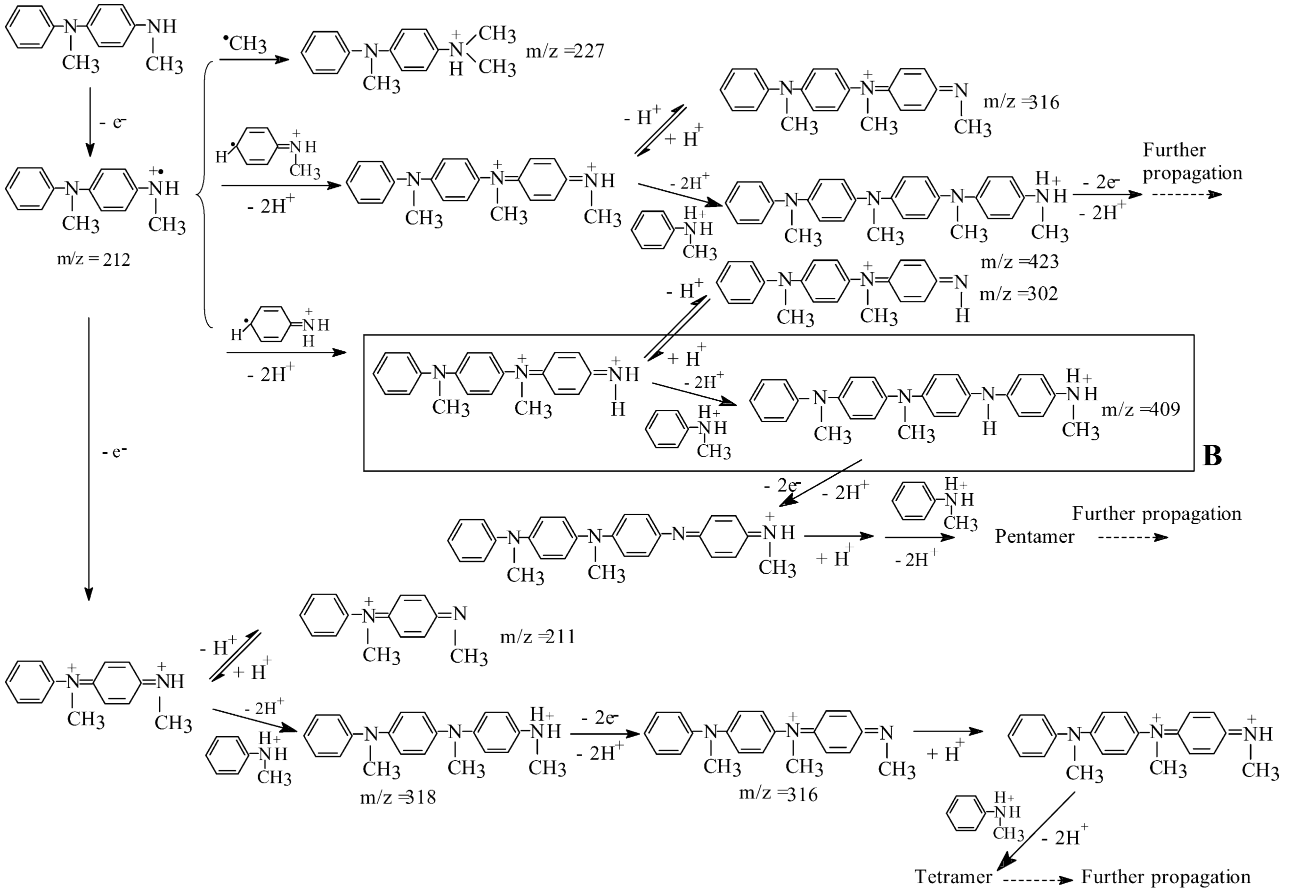
Due to the fact that the NMA monomer intermediate species are instable their isolation and detection has been difficult. During the past years there has been a considerable discussion of which intermediate is present.

Once the dimer is formed, it is rapidly oxidized to a quinoid dication, Schemes 2 and 3. Since the oxidation potentials of both dimers (tail-to-tail, head-to-tail), Scheme 1, are lower than that of the NMA monomer [16] there are different possibilities for the following chemical coupling reactions, which are drawn in Schemes 2 and 3. First, the initiated dimer radical cations can couple with various radicals in the solution forming neutral oligomers. Second, the oxidized quinoid dimer dication may be reduced by a monomer to form a neutral trimer. These reactions, which are drawn based on the MS results might exist as competing reactions for the synthesis of longer conjugated chains of PNMA.

In situ UV–vis measurements were performed in 0.5 M NMA dissolved in 0.5 M H_2SO_4-DMF. The UV–vis spectra were recorded at 450 mV for 10 min (solid lines) and thereafter at open circuit potential (E_{ocp}) (dotted lines), shown in Fig. 1.



Scheme 2. Chain propagation of the tail-to-tail dimers. m/z values are shown for species that were observed in the mass spectrum in Fig. 2.



Scheme 3. Chain propagation of the head-to-tail dimers. *m/z* values are shown for species that were observed in the mass spectrum in Fig. 2.

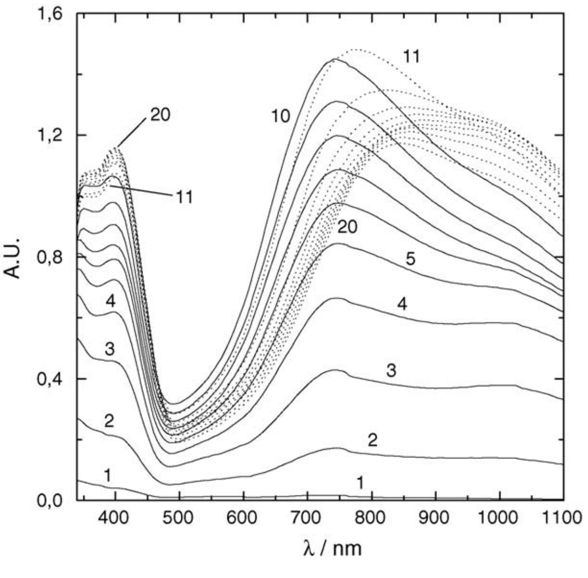


Fig. 1. The UV–visible spectra recorded of the film formation during potentiostatic polymerisation of 0.5 M NMA in 0.5 M H_2SO_4-DMF. The spectra were first recorded every minute for 10 min at 450 mV (solid lines) and then for 10 min at E_{ocp} (dotted lines).

It has been reported that the radical cations of aromatic amines show a characteristic absorption at 450 nm in aqueous solutions [18,19,21,22]. These radical cations are, however, quickly consumed during the polymerisation of NMA in DMF (Fig. 1) and therefore difficult to detect. The wavelength region where the cation is absorbing is in our case dominated by the presence of the absorbance at 400 nm (Fig. 1). This absorbance maximum is growing in intensity with increasing polymerisation time and can be attributed to the conducting emeraldine form of PNMA [16]. The absorbance maximum at 740–750 nm can, on the other hand, be attributed to localized polarons like in PANI [23]. It has been shown that during doping of PANI, the intensity of the absorption band from the localized polarons decrease and the free charge carrier tail associated with the delocalized polaron band (at 1000 nm) increasing steadily in intensity into NIR region [23,24]. Zimmermann et al. assigned an intense band at 750 nm to an interband transition of the diimine structures [25]. According to the results reported by Comisso et al. [16] based on the in situ UV-spectra of a PNMA film, the peak at 740–750 nm could be assigned to the fully oxidized pernigraniline form. In our case short fully oxidized oligomers would give rise to this absorbance. Dao et al. [28] characterized by UV-spectroscopy chemically synthesized poly(*N*-alkylanilines), which were solubilized in ACN solution or casted as films. They assigned the absorbance maximum at 730 nm to a transition of the highly distorted polaron lattice caused by the steric effect

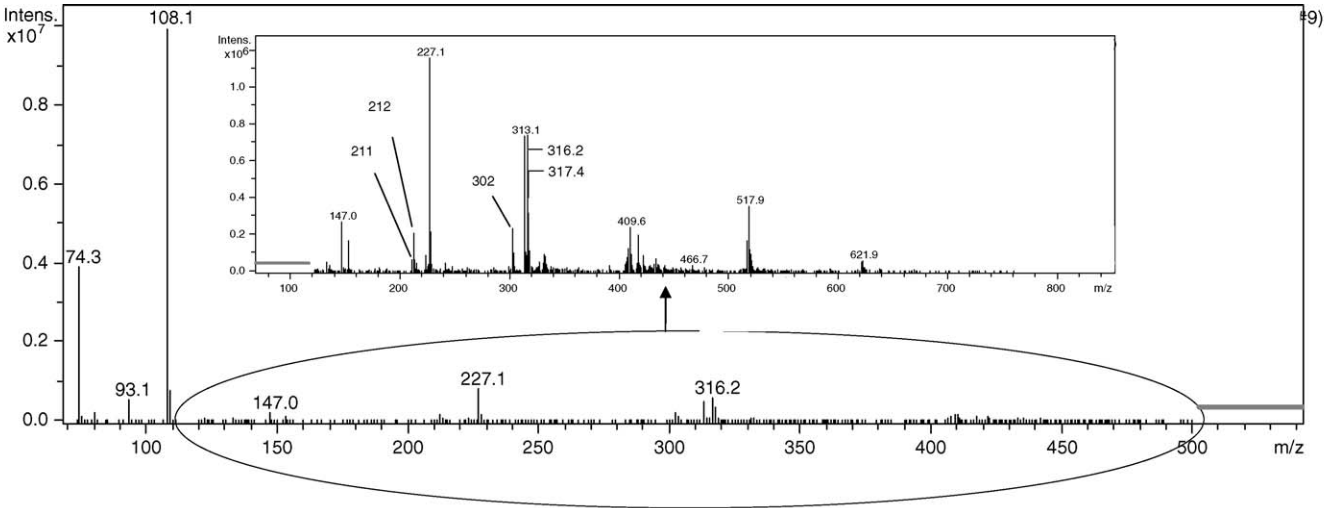


Fig. 2. Mass spectrum of the soluble fraction obtained during electropolymerization of 0.5 M NMA at 450 mV in 0.5 M H_2SO_4-DMF.

induced by the *N*-substituted group. According to their observation, the sharp absorption peak at 720 nm shows that polarons in solution are strongly localized in comparison with those in the film. After the polymerisation, when the electrode is kept at the E_{ocp}, the absorbance maximum observed at 740–750 nm shifts to 840–850 nm and a minor absorbance maximum becomes clearly visible at 1000 nm. The delocalized polaron will result in stronger interchain interactions, which leads to better charge transport. The maximum at 1000 nm has been assigned to free charge carriers [26] and originates together with the band at 400 nm from the conducting emeraldine form of the oligomeric species [16]. The spectrum that is recorded after 10 min at E_{ocp} (Fig. 1, #20) indicates that the charge delocalization increases during the open circuit conditions. It should, however, be pointed out that the polymerization results in simultaneous formation of a dark green PNMA film and a great amount of soluble reaction products.

3.1. Polymerization mechanism of NMA

A reaction scheme of the proposed polymerization mechanism of NMA is presented in Schemes 1–3. The electropolymerization of 0.5 M NMA in 0.5 M H_2SO_4-DMF, resulted in a film but also in a dark green soluble fraction. Both the film and the soluble fraction were analyzed by MS and NMR.

The mass spectrum of the soluble fraction is shown in Fig. 2 and possible structures corresponding to the main peaks are shown in Schemes 1–3. In the spectrum from the soluble fraction no signals from the highly reactive monomer cation ($m/z = 107$) or from the dicationic dimer ($m/z = 106$) could be observed. But instead a signal from the protonated NMA monomers ($m/z = 108$) was observed. The dicationic dimers are probably very reactive, and are quickly consumed during electropolymerization and are therefore not detected in the soluble fraction. The m/z values of 302 and 409 in Scheme 3 confirm the presence of aniline units in the PNMA oligomers, probably as a result of dealkylation. This is in good agreement with the NMR results showing that 3% of the NMA units were dealkylated. Since electrospray ionization is an extremely soft ionization technique, the possibility of dealkylation in the MS source can be ruled out. Dealkylation of NMA has also previously been reported by Strassen and Hambitzer [14].

The peak at $m/z = 211$ can be assigned to the dimer and the more abundant signal at $m/z = 227$ to the *N*,*N*′-dimethyldimer as shown in Schemes 2 and 3. This was confirmed by further bombardment with higher energy resulting in the loss of a methyl group ($m/z = 211$). The MS analyses showed that the soluble fraction of the polymerization contained mainly monomers, dimers, trimers and trace amounts of tetramers. This is probably due to the fact stated for other polymers that at a critical length, the dissolved oligomers aggregate, and then precipitate at the surface of the working electrode. In accordance with the polymerization mechanism of PANI it can be assumed that during the electrosynthesis the oxidized oligomers [27] can catalyze the oxidation of the monomers or neutral oligomers present in the solution. The oxidized oligomers are simultaneously reduced to lower oxidized states, see the reaction path A and B in Schemes 2 and 3. With the growth of the chains, the oligomers are more easily oxidized and more susceptible to nucleophilic attack [28].

For NMR analysis (^{1}H NMR, ^{13}C NMR and 2D NMR) the PNMA film was dissolved in chloroform, thereafter the solvent was evaporated and the samples were finally dissolved in deuterated DMSO. The ^{1}H NMR spectrum is shown in Fig. 3. The NMR data indicate that the main component in the mixture is a dimer, formed by head-to-head coupling of NMA. The ^{1}H NMR spectrum displays a triplet at $\delta = 7.44$ ppm ($J = 7.5$ Hz) and a doublet at $\delta = 7.25$ ppm ($J = 7.5$ Hz). The latter signal is overlapping a triplet at $\delta = 7.24$ ppm ($J = 7.5$ Hz). The pattern is characteristic of protons in monosubstituted benzene rings. The corresponding methyl group singlet is found at $\delta = 2.89$ ppm. In addition to these signals, a weak doublet is shown at $\delta = 7.33$ ppm ($J = 7.5$ Hz). H–H and H–C correlation spectra showed that this proton signal was coupled to a signal overlapped by the signals centered at $\delta = 7.24$ and 7.25 ppm.

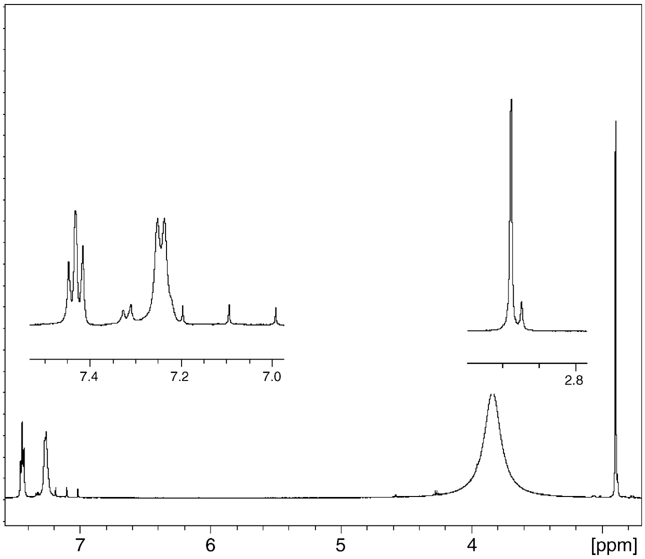


Fig. 3. The ^{1}H NMR spectrum (600 MHz, DMSO-d_6) of the film made from a solution of 0.5 M NMA dissolved in 0.5 M H_2SO_4-DMF. The electropolymerization was made potentiostatically at 750 mV.

The pattern indicates a *para*-disubstituted aromatic ring which could be part of an oligomeric structure formed by head-to-tail coupling. The corresponding methyl group singlet is found at $\delta = 2.88$ ppm. The aromatic signals of a monosubstituted end-group could not be observed as they probably were overlapped by the signals of the head-to-head dimer. A very weak singlet is observed at $\delta = 3.95$ ppm. This signal showed connectivity (HSQC) to a carbon signal at $\delta = 39.8$ ppm and based on the chemical shifts the signals could be due to a methyl group in a quinoid structure, the aromatic signals of which are not detected due to their low intensity. A very coarse estimation of the relative amounts of different units based on signal integration showed that the ratio of *mono*- to *para*-disubstituted units in the mixture was close to 10:1. The 1:1:1 triplet signal centered at $\delta = 7.10$ ppm is due to the ammonium protons in protonated amino groups. A rough estimation based on the integral values of aromatic versus methyl protons indicated some dealkylation (ca. 3%).

3.2. *Influence of solvents and of protons*

Fig. 4(a) and (b) shows the in situ UV–vis spectra when NMA was electropolymerized in 1.0 M MSA-DMF and 1.0 M MSA-PC. The potential was kept at 750 mV for 10 min (solid lines) following another 10 min at E_{ocp} (dotted lines). The absorbances recorded in PC and in ACN (not shown in the figure) are much lower than in DMF and water. The formation of intermediates is facilitated in DMF and water, which might be due to the higher degree of dissociation of MSA in these solvents, resulting in a higher proton concentration. The dissociation constants are listed in Table 1.

At the applied potential of 750 mV a well defined band at 450 nm assigned to the radical cations increases in intensity with time in the PC solution, Fig. 4(a). During E_{ocp} the absorbance from the radical cations decreases and a weak absorbance maximum evolves at 380 nm. No absorbance band could however be observed at 1000 nm. When the electropolymerization of NMA is made in DMF, absorbance bands at 390, 725 and 1000 nm appear simultaneously in the spectra in Fig. 4b. All bands decrease during E_{ocp}, especially the peak at 725 nm. In neither case (polymerization in PC and DMF) a PNMA film could be formed. It seems that the increasing bands at 400 and 1000 nm during E_{ocp} in some cases indicates the film formation. As far as ACN containing 1.0 M MSA was concerned, the results were similar to those from PC, no film was formed, and no band from free charge carriers appeared at 1000 nm.

The donor number (DN) is related to its electron donating capability, i.e. the solvent basicity. The DN numbers [32] of the discussed solvents are listed in Table 2.

Table 1
The dissociation constants of H_2SO_4 and MSA in different solvents [29]

Acid/base	Solvent			
	ACN	PC	DMF	H_2O
H_2SO_4				
pK_{a1}	7.8	8.4	3.1	Strong
pK_{a2}	25.9		17.2	1.96
MSA	10.0	8.3	3.0	Strong

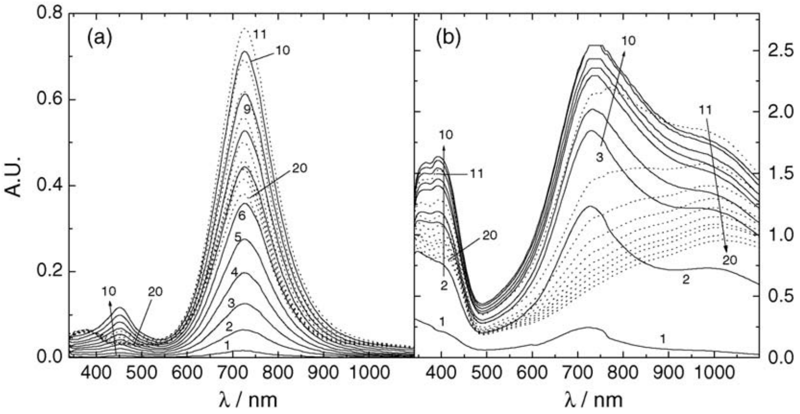


Fig. 4. The UV–vis spectra recorded at 750 mV during potentiostatic polymerisation of 0.5 M NMA in (a) 1.0 M MSA-PC and (b) 1.0 M MSA-DMF. The spectra were first recorded every minute for 10 min at 750 mV (solid lines) and then for 10 min at E_{ocp} (dotted lines).

Table 2
Physical parameters of different solvents [29]

	Solvents			
	H_2O	DMF	PC	ACN
DN	33.0	26.6	15.1	14.1
Conductivity ($S\,cm^{-1}$)	6×10^{-8}	6×10^{-8}	1×10^{-8}	6×10^{-10}
Viscosity (cP)	0.890	0.802	2.53	0.341

The acid–base properties of the solvents may affect the deprotonation process during the PNMA film formation. Thus H_2O and DMF (both have relatively high DN) offer an optimum 'basic' atmosphere at appropriate acid concentrations that promotes formation of longer conjugated PNMA by permitting deprotonation of the intermediates.

A second parameter influencing film formation might be the dissociation capability of the acid–solvent systems. As shown in Fig. 5, the first oxidation potentials of 0.5 M NMA in 1.0 M MSA-DMF and 1.0 M MSA-H_2O are much lower than for 1.0 M MSA solutions of ACN and PC. This might be due to the higher degree of dissociation of the acids in H_2O and DMF in comparison to ACN and PC, Table 1, which enhances the ionic conductivity during electropolymerization of the DMF and water solutions, pH is simultaneously lowered, which also facilitates the polymerization process. Table 2 shows that the conductivity of DMF and H_2O are the same, while that of ACN is much lower. A third parameter influencing the electropolymerization is the viscosity of the solution that might change the diffusion conditions for the formed intermediates. The dissociation constants, conductivity values and the viscosity are given in Tables 1 and 2.

Miras et al. synthesized an electroactive PANI film in proton free ACN solutions [30,31]. All their experimental results indicated that protonation of aniline is not necessary for polymerization of aniline. Our MS analysis for the soluble fraction of PNMA showed that although protonation is also not necessary for initiation of NMA, it might influence its further propagation.

We have therefore also carried out in situ UV–vis experiments in a proton free system containing 0.5 M NMA and 0.5 M $LiClO_4$ in DMF. The potential was kept at 750 mV for 10 min and the UV–vis spectra were recorded every minute are shown as solid lines, the spectra taken at E_{ocp} as dotted lines in Fig. 6. In this case there was no film formed on TO. The colour of the soluble product is purple instead of the blue or green colour usually observed under acidic conditions. The solution has an absorbance maximum at 550 nm, which is characteristic for the pernigraniline base form of PANI [32–34]. The solution colour changes to blue when acid is added. This indicates presence of the fully oxidized pernigraniline form when NMA is oxidized in proton free DMF. In the absence of protons, the reaction products will accumulate at the surface of the TO electrode, giving rise to an absorbance maximum at 550 nm. In the presence of protons, the violet coloured unprotonated pernigraniline form may possibly be protonated, like PANI, to the blue coloured pernigraniline salt form, which oxidizes the neutral monomers forming longer conjugated chains. The pernigraniline form will simultaneously be reduced to the emeraldine form. PNMA will be formed on the working electrode if the reaction conditions (e.g. solvent, acid and substrate material) are suitable for nucleation. The MS results for the purple solution showed only a small amount of dimers $m/z = 211, 212$.

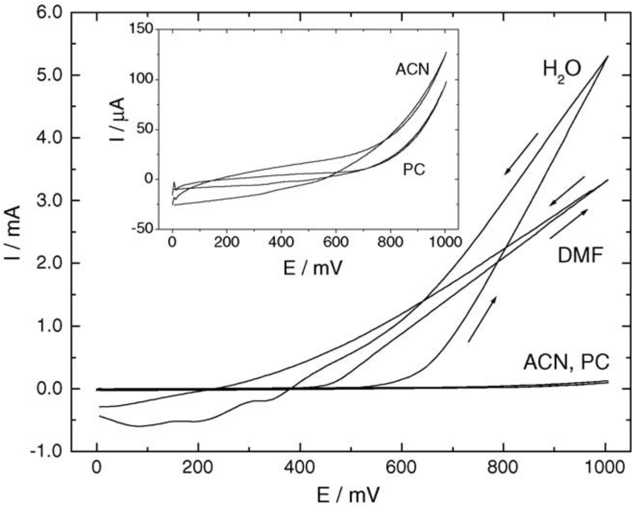


Fig. 5. Oxidation potentials of 0.5 M NMA on TO in water, DMF, ACN and PC containing 1.0 M MSA, $v = 50$ mV/s.

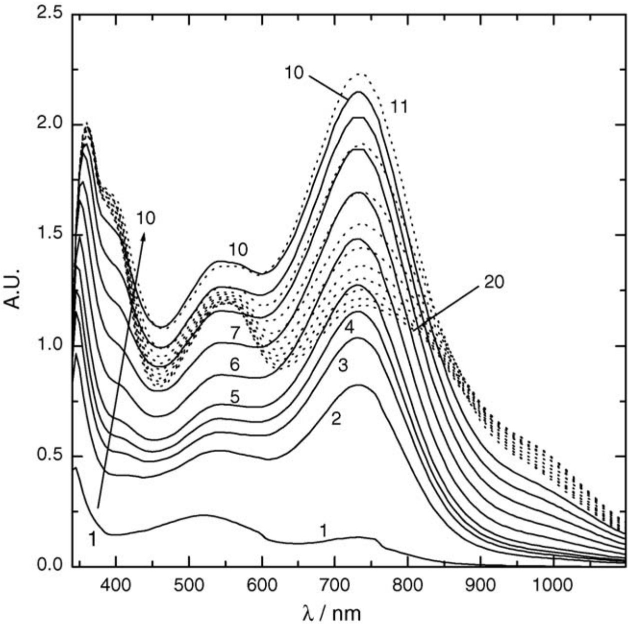


Fig. 6. The UV–visible spectra recorded at 750 mV during potentiostatic polymerisation of 0.5 M NMA in 0.5 M $LiClO_4$-DMF. The spectra were first recorded every minute for 10 min at 750 mV (solid lines) and then for 10 min at E_{ocp} (dotted lines).

4. Conclusions

Electropolymerization of NMA in a 0.5 M H_2SO_4-DMF solution starts with formation of oligomers in solution. A dark green film is deposited on the tin oxide electrode surface. MS analysis reveals that the soluble fraction of the polymerisation products consisted mainly of monomers, dimers and trimers. Only trace amounts of tetramers and pentamers was detected with MS indicating that above a critical chain length, insoluble oligomers will form and deposit on the electrode surface. The NMR analysis showed also that the PNMA film consisted of head-to-head, tail-to-tail and head-to-tail coupled *para*-substituted benzene rings. The aniline units, which were formed during dealkylation, cannot only be found in the PNMA film, but also in the soluble fraction. An electropolymerization mechanism of NMA in 0.5 M H_2SO_4-DMF is proposed in this paper based on these results.

The PNMA film was not completely stable when conditioned in DMF after the polymerization, but seemed to be stable in an aqueous solution of 0.5 M H_2SO_4. The stability was, however, not studied in more detail.

The donor number of the solvent and proton concentration can be considered as important parameters for a successful polymerization of NMA in organic solvents. A better understanding of the electropolymerization mechanism will be helpful in predicting possible reaction pathways, in choosing a suitable reaction medium and in modifying the properties of the conducting polymer product. It will eventually establish the optimum experimental conditions to obtain desired conducting polymer films from PANI derivatives.

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