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Electrochemical polymerization of 2-methyl-1-naphthylamine

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Summary

2-methyl-1-naphthylamine has been electropolymerized from the acidic aqueous solutions by three different synthetic routes. The polymerization products, deposited at a platinum working electrode as very adherent films, were characterized by cyclic voltammetry (CV), infrared spectroscopy (IR) and gel permeation chromatography (GPC). In a strongly acidic medium, the products display redox properties, in a form of two well-defined redox pairs with the formal potentials at 0.19 V and 0.47 V vs. SCE. IR-spectroscopy indicated that the polymerization occurs *via* the $-NH_2$ groups, by different coupling ways: N-C(4), N-C(5) and N-C(7), as well as that ClO_4^- ions incorporate themselves into the product of electropolymerization. GPC of the polymerization products evidenced oligomeric chains with molar masses up to 1600 g/mol as main species.

Introduction

In recent years electroconductive polymers based on aromatic amines have attracted considerable interest particularly as new electronic materials [1]. They have been synthesized either chemically [2], or electrochemically involving anodically induced polymerization [3,4]. Among aromatic amine polymers, polyaniline has been studied most frequently [5,6]. Less attention has been dedicated to the polynuclear aromatic amines. For instance, there exist in the literature only the reports on electrochemical polymerization of 1-naphthylamine [7-9], 1-aminoanthracene [10], 5-amino-1-naphthol [11] and 1, 5-diaminonaphthalene [12]. Electroactive polymers based on polynuclear aromatic amines are considered as candidates for corrosion protectors [12], chemical sensors [7] or electrochromic devices [8]. The main advantage of electrochemical polymerization over the chemical one is the possibility to control the polymer film thickness by means of Faraday laws.

This work presents the continuation of our previous investigations relating to electropolymerization of 1-naphthylamine. In our previous paper [9], it has been predicted on the basis of quantum-chemically assisted stereochemical analysis of the possible structural subunits of the poly(1-naphthylamine), that the most stable N-C(4) coupled product is not planar, and that the more planar structures of N-C(5) coupled product, characteristic of lower stability, may be formed. Because of that, in comparison to polyaniline, the diminished electronic conductivity and shorter chains of poly (1-naphthylamine) are to be expected. We extended our investigations to the class of alkyl-ring substituted 1-naphthylamines, which, to our knowledge, were not studied from the viewpoint of electropolymerization.

It is known that by appropriate choice of substituents particular physical and chemical properties of polymerized aromatic amines may be attained, which extend the domain of their application. For instance, ring-substituted polyanilines display better solubility, stability, processability or crystallinity [4,5] in comparison to the unsubstituted polyaniline, but, on the other hand, ring-substituted poly (alkylanilines) exhibit reduced both molar mass and electric conductivity [4,5]. Bearing in mind the published data on the similar class of compounds [4], we expected that the polymerization of the 1-naphthylamine may be generally favored if an electron-donor substituent (such as the methyl group) is introduced in ortho position. Therefore, we started the investigations of alkyl-substituted 1-naphthylamines polymerization on the example of 2-methyl-1-naphthylamine.

To our knowledge, there is no report relating to the electrochemical and chemical polymerization of 2-methyl-1-naphthylamine (2-Me-NPA). The aim of our work was to polymerize the 2-methyl-1-naphthylamine by electrochemical polymerization under various conditions, and to study electrochemical behavior and structure of obtained polymerization products using appropriate measuring techniques: cyclic voltammetry (CV), infrared spectroscopy (IR) and gel permeation chromatography (GPC).

Experimental

Chemicals and instrumentation

2-Methyl-1-naphthylamine (purum ≥ 98.0 %, Fluka), sodium acetate (p.a. 99.0 %, Fluka), acetic acid (puriss p.a. ≥ 98 %, Reanal), and tetrahydrofuran, (THF), (99,9 % HPLC grade, Sigma-Aldrich) were used as received. Lithium perchlorate (purum p.a.≥ 98 %, Fluka), was dried before use to reduce water content to less than 0.1 %. A PAR model 273 potentiostat/galvanostat was used for both electropolymerization and cyclovoltammetric investigations. The infrared spectra of monomer and polymer were recorded using an IR spectrophotometer Perkin Elmer 983 G. The spectra were recorded by KBr-pellet technique. Before pelletization, the polymerization product was scraped from the platinum support and ground in a mortar together with KBr. The IR-spectrum of liquid monomer was recorded using KRS-5 windows. The gel permeation chromatography (GPC) measurements were carried out using the Labio, (Czech Republic) device equipped with refractometric detector. The separation system consisted of 600 x 7.5 mm PL gel column of porosity 500 Å (Polymer Laboratories), and it was calibrated with polystyrene standards. Tetrahydrofuran was used as a mobile phase with a flow rate 1 ml/min. For the purposes of chromatography the 2% (w/v) solutions of the polymerization products in THF were used, which were prepared by intensive stirring with an electromagnetic stirrer at room temperature for about 30 min. Toluene in low concentration (2% v/v) was used as an internal standard.

Electrochemical polymerization

The electrochemical experiments were carried out in a thermostated three-electrode cell. The working electrode was a platinum plate of 1.8 cm^2 working area, which was heated in a reducing propane/butane flame and polished by fine emery paper No 1200 before use. Saturated calomel electrode (SCE) was used as reference electrode, and the counter electrode was a platinum foil. The electropolymerization was carried out at a constant potential 0.9 V vs. SCE during 80 minutes. Polymerization conditions and the ways of the treatment of the film covered working electrode are given in Table 1. For the further studies films of freshly electropolymerized 2-Me-1-NPA, being firmly attached on a platinum support, were washed with distilled water to remove the excess of the electrolyte.

Table 1. Polymerization conditions and the treatment of the electropolymerized 2-Me-1-NPA films (abbreviated as Pt-film electrode).

Procedure	Polymerization conditions					Treatment of the Pt – film electrode
	Electrolyte composition	T / °C	pH	Potential [V]	Time [min]	
1	0.1M monomer CH_3COOH CH_3COONa	45	3	0.9	80	Pt-film electrode was only washed with distilled water and dried on the air
2	0.05M monomer CH_3COOH CH_3COONa	45	3	0.9	80	Washed Pt-film electrode was cycled 80 times between – 0.1 V and 0.5 V in 0.1 M $HClO_4$ + 0.1 M $LiClO_4$ solution (pH 1) without monomer
3	0.05M monomer CH_3COOH CH_3COONa	45	5	0.9	80	Washed Pt-film electrode was cycled 80 times between – 0.1 V and 0.5 V in 0.1 M $HClO_4$ + 0.1 M $LiClO_4$ solution (pH 1) without monomer

Results and discussion

Polymerization of 2-methyl-1-naphthylamine started immediately upon the potential of 0.9 V was applied to the working electrode, resulting in a black deposit. After 80 min, a smooth and adhesive film covering the entire Pt surface was developed. During potential pulse application, the anodic current density decreased fastly within the first minute, (from 5 to 0.5 mA/cm^2), but after this initial drop the current decreased much slower. In order to investigate the redox properties, the films of electropolymerized 2-Me-1-NPA on a Pt-support were washed thoroughly with distilled water and transferred into supporting electrolyte solution, which did not contain monomer. Figure 1a displays the consecutive cyclic voltammograms of the electropolymerized 2-Me-1-NPA film (synthesized by the procedures 2 or 3 described in Table 1.) in a very acidic solution, 0.1 M $HClO_4$ + 0.1 M $LiClO_4$. One can see from this picture that one deals with a redox polymer. At initial potential scans, the anodic and cathodic peak currents were quite low, but during continuous cycling, up to approximately 80 cycles, the peak currents increased and finally attained a constant height. This behavior noted in a very acidic solution indicates that the kinetics of the oxidation and reduction process is sensitive to the presence of H^+ ions in solution. The formal potential of the electropolymerized 2-Me-1-NPA amounts to 0.13 V vs. SCE.

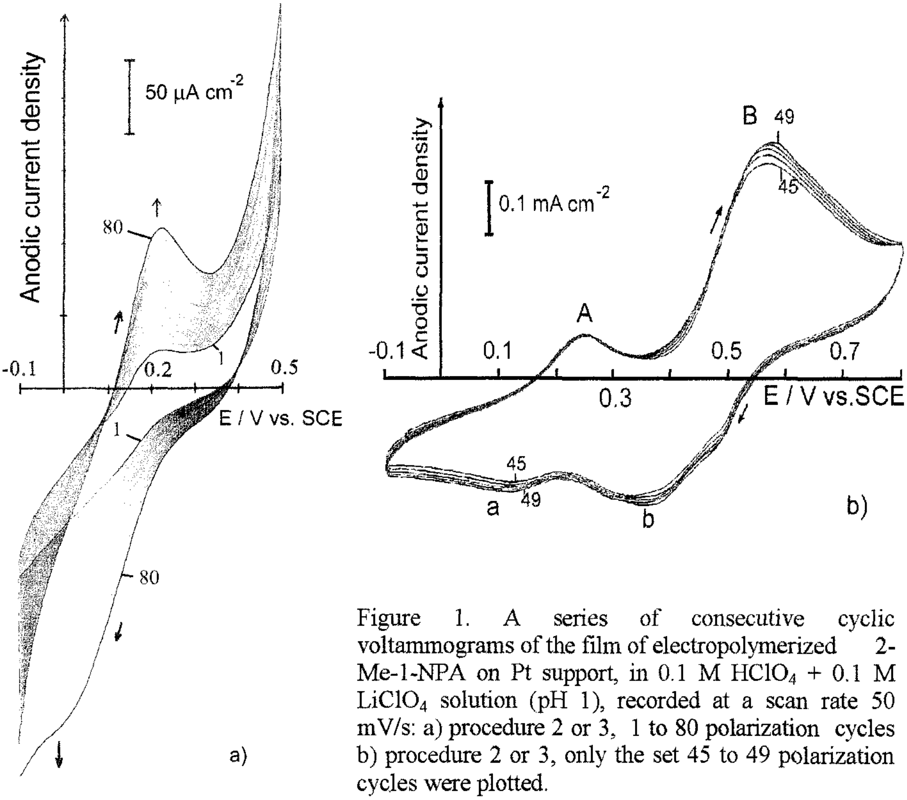

Figure 1. A series of consecutive cyclic voltammograms of the film of electropolymerized 2-Me-1-NPA on Pt support, in 0.1 M $HClO_4$ + 0.1 M $LiClO_4$ solution (pH 1), recorded at a scan rate 50 mV/s: a) procedure 2 or 3, 1 to 80 polarization cycles b) procedure 2 or 3, only the set 45 to 49 polarization cycles were plotted.

Figure 1b shows the cyclovoltammograms of the electropolymerized 2-Me-1-NPA (synthesized by the procedures 2 or 3, Table 1) recorded upon enlarging anodic potential to 0.8 V. As a result of enlargement a new pair of current peaks (designated as B and b) appears. The formal potentials of the first and the second redox couple are 0.19 and 0.47 V vs. SCE, respectively. This electrochemical behavior resembles the one of polyaniline [5] and poly (2-methyl aniline) [6] electrosynthesized in 2 M HBF_4 and 2M HCl aqueous solutions, respectively.

The IR-spectra in a 1800 – 400 cm^{-1} wave number range of the electropolymerized 2-Me-1-NPA (procedures 1,2 and 3) are shown in Fig. 2. The band at 1641,1646 or 1638 cm^{-1}, for films obtained by the procedure 1,2 and 3, respectively, may be assigned to the stretching vibration of C=N bond of aromatic amines [8, 13-15], ν (C=N). This band was not observed in the spectrum of monomer, and it indicates that the polymerization occurs *via* the $-NH_2$ groups, as well as that the structure containing imine (–N=C) links between naphthalene nuclei (quinone type of the structure) did appear. It was the strongest in the case when the procedure 2 was applied. The very strong, or strong, band at ~1615 cm^{-1} appears in all polymerization products spectra as well as in the spectrum of monomer. It may be assigned to scissoring mode β_s (NH_2) [8, 14], characteristic of primary amines and it may arise from the polymer chains terminations. This is an indication of a relatively low polymerization degree. The bands due to the naphthalene ring C-C skeletal stretching modes [14] were observed at 1594, 1565, 1503, 1438 and 1399 cm^{-1} in the spectra of all films. The bands at ~ 1450 and ~1375 cm^{-1} are due to the methyl group angular bending $\delta(CH_3)$ (the asymmetrical vibration [16], δ_{as} (CH_3) ~1450 cm^{-1} and the symmetrical vibration [16], δ_s (CH_3) = 1375 cm^{-1}). Three peaks positioned at 2960, 2916 and 2850 cm^{-1} in the spectra of both monomer and polymerization products obtained by all three procedures additionally confirmed the presence of a methyl group [16], the band at 2960 cm^{-1} being most useful for diagnosis. The most probable assignment of the band at 1360 cm^{-1} is C-N stretch of secondary aromatic amino groups [8,13,16]. In the spectrum of the polymerization product synthesized by the

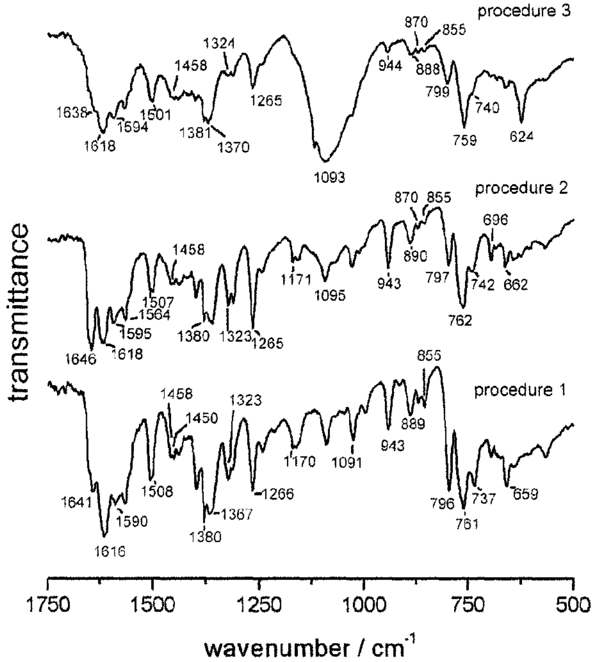

Figure 2. The IR-spectra of the electropolymerized 2-methyl-1-naphthylamine films obtained by different procedures described in Table 1.

procedure 3, a very strong and broad band at 1089 cm^{-1} (dominant band) together with a strong band at 622 cm^{-1}appeared, which were attributed to perchlorate anions [17]. These two bands were not present in spectra of polymerization products obtained by procedures 1 and 2. It can be concluded that ClO_4^- ions are incorporated into the matrix of 2-Me-1-NPA (synthesized by procedure 3) under additional cyclic polarization treatment in $HClO_4$ + $LiClO_4$ solution. The bands at 1320 and 1310 cm^{-1} observed in spectra of electropolymerized 2-Me-1-NPA were not present in the spectrum of monomer. These bands may be assigned to C-N stretching vibrations of secondary aromatic amino group [8,11,13-15] and indicate both the formation of amine (-NH-C) units in polymerization product structure, and polymerization route *via* the $-NH_2$ groups. The band at ~1263 cm^{-1} in the spectra of polymerization products obtained by all procedures is attributed to C-N stretch of primary aromatic amines [14,16] and corresponds to the band at 1270 cm^{-1} observed in the monomer spectrum. It may correspond to the terminal NH_2 groups in polymerization products.

Table 2. Out-of-plane deformation vibration, γ (C-H), for monomer and polymerization products and the type of substitution in any aromatic ring in polymerization products[a]

Monomer	Polymerization products obtained by different procedures			Assignment and type of substitution in any aromatic ring of naphthalene in polymerization products
	Procedure 1	Procedure 2	Procedure 3	
946 m	943 s	943 s	944 m	γ (C-H) 1,2,3,4
889 m	889 m	890 m	888 m	γ (C-H) 1,2,4 or/and 1,2,3,4,5
	869 m	870 w	870 w	γ (C-H) 1,2,4 or/and 1,2,3,4,5
856 vs	855 m	855 w	855 w	γ (C-H) 1,2,4 or/and 1,2,3,4,5
796 vs	796 vs	797 s	799 s	γ (C-H) 1,2,3 or/and 1,2,3,4
776 m-s				
	761 vs	762 vs	759 vs	γ (C-H) 1,2 or/and 1,2,3
736 vs	737 s	742 m	740 sh	γ (C-H) 1,2 or/and 1,2,3 or/and 1,2,3,4
698 w	696 w	696 m	697 w	γ (C-H) 1,2,3

[a] Abbreviations: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder

965 – 650 cm^{-1} frequency range corresponds to aromatic C-H out-of-plane angular bending, γ (C-H) [14], and provides information about the substitution on the aromatic nucleus. It is known that rules based on benzene substitution are generally valid for groups of two, three, or four hydrogen atoms in the naphthalene nucleus [14]. The wave numbers of γ (C-H) bands of monomer and polymerization products and the types of substitution [14] at the naphthalene rings, are listed in Table 2. Considering that the combination of 1,2,3,4,5- and 1,2- substitution may correspond to N-C(4) type of coupling, the combination of 1,2,3,4- and 1,2,3- substitution is consistent with N-C(5) linkages and the combination of 1,2,3,4- and 1,2,4- substitution may correspond to N-C(7) coupling, it can be concluded that the most probable coupling routes during polymerization were N-C(4), N-C(5) and N-C(7).

Figure 3. illustrates GPC distribution curves for electrochemically polymerized 2-Me-1-NPA using three described procedures. For all polymerization conditions oligomers with molar masses up to ~1600 g/mol are main species. The trimers, tetramers, pentamers and hexamers are distinctly resolved for all synthetic procedures. The dimers are detected in the cases of procedures 1 and 2. The chains of higher molar

masses appeared only as a broad peak centred at $\sim$ 13700 g/mol in the case of the procedure 2. This may be related to the very strong ν(C=N) band observed in its IR spectrum, which indicates better electronic conductivity. The more favorable pH value of the synthesis solution and the cyclic polarization post-treatment of the film in $HClO_4 + LiClO_4$ solution may be responsible for obtaining these longer chains. By our knowledge, there is only one report in the literature about molar mass of electropolymerized 1-naphthylamine [9], where GPC performed on the THF-soluble fractions of polymerization product yielded one broad peak, which suggested an average chain lenght of about four repeated units. Thus one may conclude that both the introduction of the CH_3 group in the 1-naphthylamine molecule, and the use of a suitable electropolymerization procedure may result in a higher degree of polymerization.

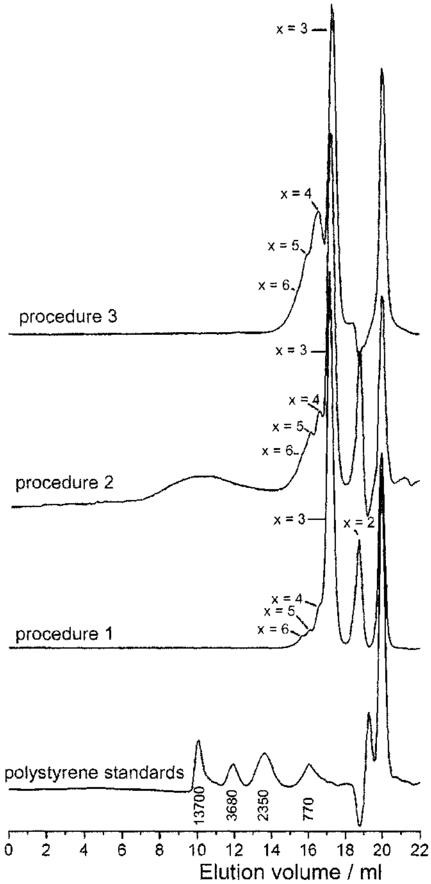

Figure 3. GPC distribution curves for the films of electropolymerized 2-Me-1-NPA (the procedures of synthesis are described in Table 1); solvent THF; temperature 25 °C; toluene peak appears at eluation volume of 20 ml; *x* designate the number of the repeated units in the electropolymerized 2-Me-1-NPA.

Stereochemistry ofers the most probable explanation of relatively short chain lengths. Here we confirmed our earlier predictions [10] that there is a low probability of formation of lengthy chains. However, in spite of the fact that the chains are short, the dissolution of polymerization products was not observed during the electropolymerization procedure (contrary to the case of poly(2-methoxyaniline)[18] and polyaniline obtained in acetic acid [7], molar masses of which amunted to $\sim$ 2000 g/mol) and the polymerization resulted in a very adherent and compact films on platinum support. In addition, the electropolymerized 2-Me-1-NPA displayed advantage in the fact that its consistency may be adjusted. Namely, after wetting it with the solvent such as ethyl alcohol, electropolymerized 2-Me-1-NPA become elastic and can be protracted into threads. This characteristic offers the possibility of material shaping and mechanical deposition on different supports.

Conclusions

Electrochemical polymerization of 2-methyl-1-naphthylamine in acidic aqueous solutions leads to the formation of very adherent films at a platinum support. In an acidic aqueous solution (pH 1), electropolymerized 2-methyl-1-naphthylamine displays redox properties manifested as two redox pairs of defined formal potential. IR spectra indicated that 2-methyl-1-naphthylamine polymerization is of the type head-to-tail, and that different sites of the naphthalene rings take part to link the repeated units mutually. Perchlorate anions may be incorporated in polymerization products by *dc* polarization. GPC measurements evidenced that oligomers with the molar masses up to 1600 g/mol were dominant species in the polymerization products.

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