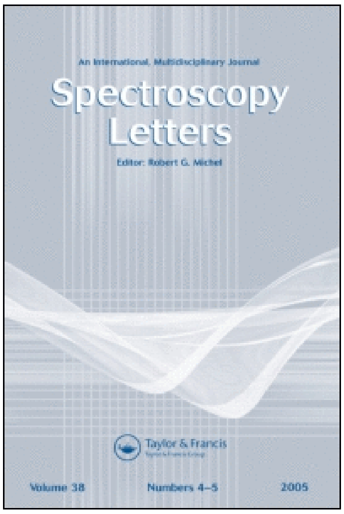

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Electrochemical Synthesis and Structure of Poly(2-Methyl-1-naphthylamine) Films

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ABSTRACT

A novel polymer, poly(2-methyl-1-naphthylamine), which was synthesized electrochemically at various temperatures from a solution containing 2-methyl-1-naphthylamine, acetic acid and sodium acetate, was characterized by IR spectroscopy. The structural conclusions were based on comparisons of polymer spectra with the IR-spectrum of the monomer, 2-methyl-1-naphthylamine. IR spectroscopy indicates that the electropolymerization proceeds via the $-NH_2$ groups and that the poly(2-methyl-1-naphthylamine) structure consists of imine ($-N{=}C$) and amine ($-NH-C$) links between naphthalene rings as well as a free methyl groups in the chains. An analysis of the ''substitution pattern''

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region in the polymer's spectra suggests that the polymer molecules were formed via mixed N–C(4), N–C(5) and N–C(7) linkages between repeated units. The ratio of between the 1645 and 1620 cm^{-1} peak areas decreases with increased temperature during synthesis, indicating that 25°C is the best temperature to obtain higher molecular weights.

Key Words: IR-spectroscopy; Electrosynthesis; Polymer film; Poly(2-methyl-1-naphthylamine).

INTRODUCTION

In the last decade increasing attention has been paid to the electrochemical polymerization of polynuclear aromatic amines (1-naphthylamine,[1–3] 1-aminoanthracene,[4] 1,5-diaminonaphthalene,[5] 5-amino-1-naphthol,[6,7] 1-amino-9,10-anthracenedione[8] as well as to IR and Raman-spectral properties of obtained polymers.[1–7] These polymers were considered for applications such as chemical sensors[2] (for example, they have a good response on pH changes) corrosion protectors[5] or electrochromic devices.[1] In our previous paper,[3] investigations on the structure of poly (1-naphthylamine) gave different results than those already reported by other authors, particularly concerning the types of the linkages between the repeated units. Continuing our investigations, in this work we studied the effect of introduction of a methyl group in the 1-naphthylamine molecule on the structure of polymerization products, especially on the types of the linkages between the repeated units. Why did we chose the methyl group? Bearing in mind previous results relating to the familiar class compounds, poly (methyl-aniline)s,[9,10] we presumed that the electropolymerization of ring-substituted 1-naphthylamine will be favored in general by an electron-donor substituent, such as a methyl group, which, when introduced in the *ortho*-position, should facilitate the oxidation of the monomer. The second reason for choosing the methyl group as a ring substituent was stereochemical in nature. Namely, simple stereochemical considerations led us to the conclusion that the methyl group, as the smallest alkyl group, would make the weakest steric hindrance and provide the growth of longer chains than in the cases of other alkyl-ring substituents. Additionally, on the basis of some previous reports on alkyl-ring derivatives of conducting polymers,[9,11,12] we expect several advantages of the poly (alkyl substituted 1-naphthylamine)s such as: an improvement in processability and crystallinity, better solubility in common organic solvents, and better stability than the corresponding unsubstituted polymers.

To our knowledge, there are no reports related to the chemical and electrochemical polymerization of 2-methyl-1-naphthylamine, (2-Me-1-NPA). Within this study poly(2-methyl-1-naphthylamine), p(2-Me-1-NPA), films were prepared on a platinum electrode, by a potentiostatic method, from an acidic solution at several temperatures. Their structure was investigated by infrared spectroscopy, using the spectrum of the monomer for comparison.

EXPERIMENTAL

2-Me-1-NPA, purum $\geq 98.0\%$ (Fluka), sodium acetate, p.a. 99.0% (Fluka) and acetic acid, puriss p.a. $\geq 98\%$ (Reanal), were used as purchased. Lithium perchlorate, purum p.a. $\geq 98\%$ (Fluka), was dried before use to reduce water content to $<0.1\%$.

The working electrode was a platinum plate with a 1.8 cm^2 working area. Before use, the working electrode was heated in a reducing propane/butane flame and then polished by fine emery paper No1200. The counter electrode was a platinum foil. A thermostated single-compartment cell containing 10 ml of the solution was used. The composition of solution used for electropolymerization was 0.05 M 2-Me-1-NPA/5.0 M CH_3COOH/0.05 M CH_3COONa (pH 3). Films of p(2Me-1-NPA) synthesized at different temperatures are marked in the following manner: temperature 25°C—sample A; 30°C—sample B; 45°C—sample C and 60°C—sample D. The polymer films were synthesized using a potential pulse of 0.9 V vs. saturated calomel electrode (SCE). The potentiostatic pulse duration was about two hours. The resultant p(2-Me-1-NPA) films were dark, compact, uniform and very adherent to the platinum support. After the synthesis the polymer films were washed with distilled water and activated in $HClO_4$/$LiClO_4$ (pH 1.3) solution by cycling 80 times between -0.1 and 0.5 V vs. SCE at a scan rate of 50 mV/s, again washed with distillated water and then dried. A PAR Model 273 potentiostat/galvanostat was used for electrochemical experiments.

The IR-spectra of polymers were recorded on a dispersive IR spectrophotometer Perkin Elmer 983 G by use of the KBr-pellet technique. Before pelletization each polymer was scraped from the platinum support and ground in a mortar together with KBr. The IR-spectrum of liquid monomer, 2-Me-1-NPA, was recorded using KRS-5 windows. Band fitting was performed with the Jandel Scientific Peakfit program, version 3.11B for DOS. Absorbance spectra in the spectral range 1700–1520 cm^{-1}, with a subtracted baseline, were processed. Smoothing procedures were not used.

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RESULTS AND DISCUSSION

965–650 cm^{-1} Range—The ''Substitution Pattern''-Range

The IR-spectra of the monomer, 2-Me-1-NPA, and as-formed p(2-Me-1-NPA) samples (A, B, C and D) in the 1800–400 cm^{-1} range are given in Figure 1. It can be seen that infrared spectra of the polymer samples have well-defined band structures indicating polymer chains in ordered states.[13] The analysis of the 965–650 cm^{-1} range provides information on substitution on the aromatic nucleus. This frequency range corresponds to aromatic C–H out-of-plane angular bending, γ (C–H).[14–16] 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, but in the case of a single hydrogen atom the relevant bands may be weaker and their position variable.[16,17] The bands of monomer 2-Me-1-NPA and polymer samples (A, B, C and D) are listed in Table 1, with their estimated intensities and corresponding types of substitution at the naphthalene rings of the polymers. Both monomer and polymer spectra were analyzed in terms of the number of adjacent hydrogen atoms remaining in the rings, considering each ring separately.

In the 2-Me-1-NPA spectrum two bands from γ (C–H) vibrations due to four adjacent aromatic hydrogen atoms on one nucleus[14,16] are present: a very strong one at 736 cm^{-1} and a medium to strong one at 776 cm^{-1}. Two very strong bands at 856 cm^{-1} and 796 cm^{-1} in the spectrum of 2-Me-1-NPA correspond to C–H out-of-plane vibrations of two adjacent aromatic H atoms present on the second nucleus.[14]

In polymer spectra the band at 696 cm^{-1} of medium intensity can be attributed to aromatic γ (C–H) of three adjacent hydrogen atoms,[16] i.e. to 1, 2, 3-substitution. This substitution pattern is consistent with N–C(5) bonding between monomer molecules. The strong band at ~745 cm^{-1} in polymer spectra can be assigned to C–H out-of-plane deformation vibrations of four adjacent aromatic H atoms, i.e. 1, 2-disubstitution[14,16] on one ring. This type of substitution is consistent with N–C(4) coupling between monomer molecules. Furthermore, this band can be also attributed to 1, 2, 3-(3 adjacent H atoms on one nucleus) or 1, 2, 3, 4-substitutions (2 adjacent H atoms) on naphthalene aromatic rings.[14,16] In spectra of 1,2,3,4-substituted polymers a weak band in the 750–700 cm^{-1} range sometimes occurs,[16] but in this case it is most probably overlapped with the above mentioned stronger bands due to out-of-plane CH bending absorption of four and/or three adjacent aromatic H atoms. Combination of 1,2,3- and 1,2,3,4-substitutions corresponds to

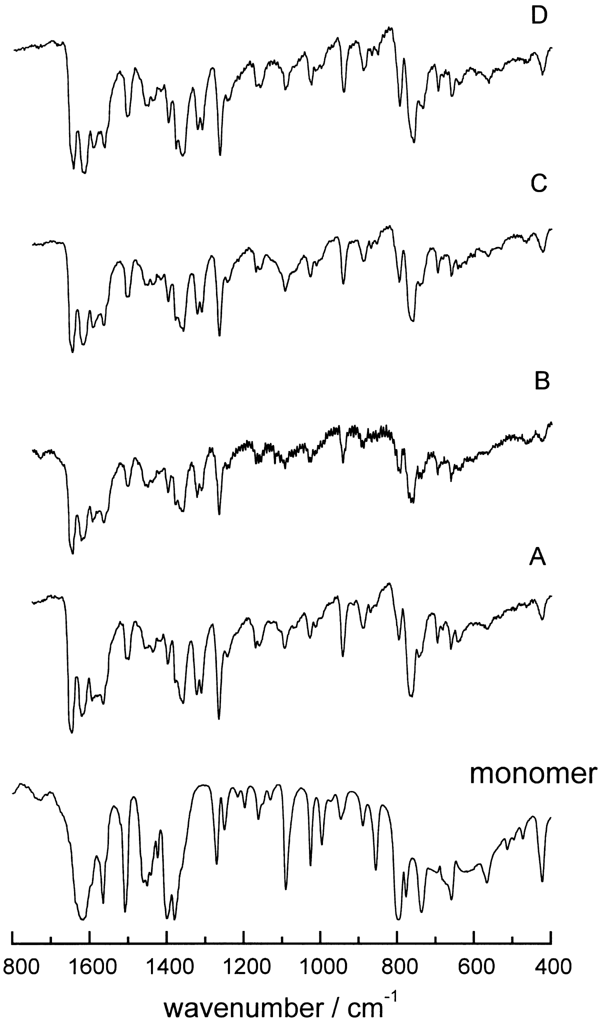

Figure 1. IR-spectra of 2-Me-1-NPA and p(2-Me-1-NPA) samples A, B, C and D in 1800–400 cm^{-1} range.

N–C(5) coupling route (although 1,2,3,4-substitution also fits N–C(7) coupling route).

A strong (or very strong) band in all p(2-Me-1-NPA) spectra around 760 cm^{-1} originates from an aromatic γ (C–H) vibrations of the 1,2- or/ and 1,2,3-substitution patterns,[14–16] which are consistent with N–C(4) and

Table 1. Out-of-plane deformation vibration, γ(C–H), for 2-methyl-1-naphthylamine and poly(2-methyl-1-naphthylamine) samples.[a]

Wavenumber/cm^{-1}					
	p(2-Me-1-NPA)				
2-Me-1-NPA	A	B	C	D	Type of substitution in any aromatic ring in polymer samples
698 w	696 m	696 m	696 m	696 m	1,2,3
736 vs	744 m-s	746 m	743 m-s	737 m-s	1,2 or/and 1,2,3 or/ and 1,2,3,4
	766 vs	764 s	761 s	761 vs	1,2 or/and 1,2,3
776 m-s					
796 vs	797 m-s	794 m	797 m-s	796 s	1,2,3 or/and 1,2,3,4
856 vs	850 w		850 w	853 w	1,2,4 or/and 1,2,3,4,5
	875 w		867 w	868 w	1,2,4 or/and 1,2,3,4,5
889 m	889 m	889 w	890 m	891 m	1,2,4 or/and 1,2,3,4,5
946 m	943 s	943 m	942 m	942 s	1,2,3,4

[a]Abbreviations used are: vs, very strong; s, strong; m, medium; w, weak.

N–C(5) coupling ways between 2-Me-1-NPA molecules, respectively. The medium to strong band at about 795 cm^{-1} corresponds to 1,2,3,4- and 1,2,3-substitution.[14–16]

The band observed at 850 cm^{-1} in polymer spectra is weak in contrast to the very strong band at 856 cm^{-1} in the monomer spectrum cited above. As the intensity of the γ (C–H) bands falls off along with the reduction of the number of adjacent hydrogen atoms,[14,16] this band is attributed to one isolated ring hydrogen atom, i.e. to 1,2,4- and/or 1,2,3,4,5-substitution. This is consistent with N–C(7) and N–C(4) coupling ways, respectively.[14,16] The same types of substitution can be attributed to the weak band at ~870 cm^{-1} and to the medium intensity band at ~890 cm^{-1}. The medium band at ~942 cm^{-1} can be attributed to 1,2,3,4-substitution[15] in the naphthalene derivative ring, consistent with N–C(5) and N–C(7) coupling route.

On the basis of the previous analysis of substitution on the naphthalene nuclei (bearing in mind that the combination of 1,2,3,4,5- and 1,2-substitution corresponds to N–C(4) coupling way, 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 corresponds to N–C(7) coupling way) we can conclude that the p(2-Me-1-NPA) molecules were formed via mixed N–C(4), N–C(5) and N–C (7) bonding between the 2-Me-1-NPA molecules. In the 965–650 cm^{-1} range, IR spectra of the electropolymerized 2-methyl-1-naphthylamine films contained more bands (eight) than the spectra of electropolymerized 1-naphthylamine films,[2,3] (three or four). However, the comparison of the types of substitution at the naphthalene rings of these two polymers[3] indicated that the methyl group had no significant influence on coupling routes between repeated units, and that in both cases, macromolecules were formed by mixed coupling ways: N–C(4), N–C(5) and N–C (7). Structural schemes proposed for poly (2-methyl-1-naphthylamine) with N–C(4), N–C(5) and N–C (7) coupled units are presented on Figures 2–4.

1700–970 cm^{-1} Range

The main bands of poly(2-methyl-1-naphthylamine) film spectra in the 1700–970 cm^{-1} region and their assignments are listed in Table 2.

The very strong band at 1645 cm^{-1} for all polymer samples is assigned to the stretching vibration of C=N bond of aromatic amines[2,5,16,18,19] and it is absent in the monomer spectrum. The appearance of this band in spectra of p(2-Me-1-NPA) films, synthesized at all applied temperatures, indicate head-to-tail coupling during the electrooxidation of 2-Me-1-NPA, and formation of the polymer structure containing imine –N=C links

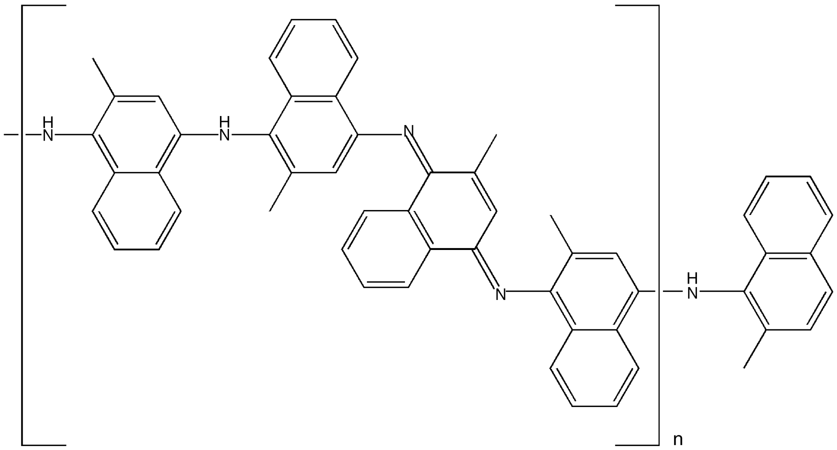

Figure 2. Structural scheme proposed for poly(2-methyl-1-naphthylamine) with N–C(4) coupled units.

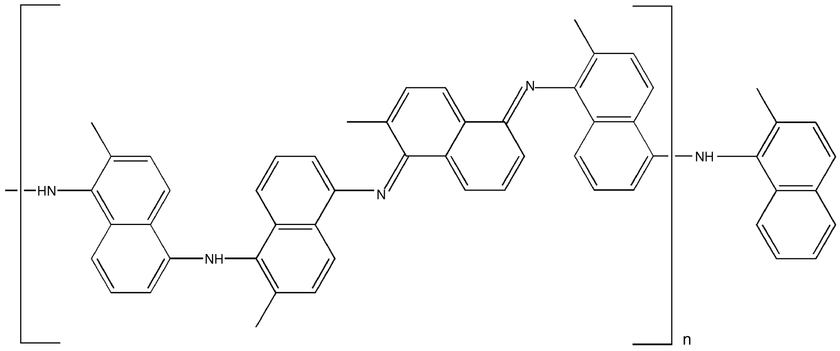

Figure 3. Structural scheme proposed for poly(2-methyl-1-naphthylamine) with N–C(5) coupled units.

between naphthalene nuclei (quinone type structure), as it is shown in Figures 2–4.

The bands due to the naphthalene ring skeletal stretching modes[15,16,18,20] were observed at 1594, 1565, 1503, 1438 and 1399 cm^{-1}. The band at 1503 cm^{-1} can be assigned as aromatic ring stretch of the benzenoid form.[5] It was considerably weaker in all polymer spectra comparing to the corresponding band in the monomer spectrum. The very

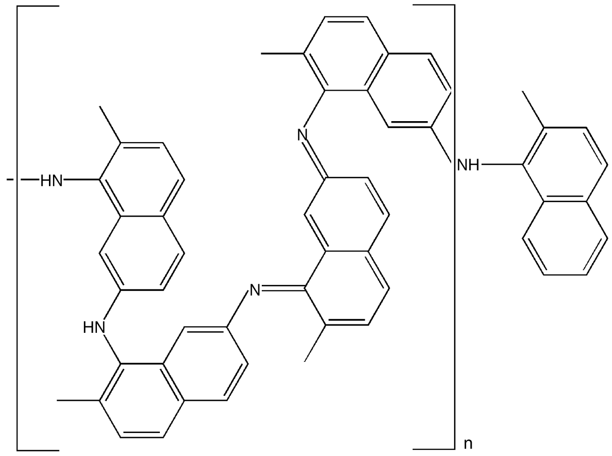

Figure 4. Structural scheme proposed for poly(2-methyl-1-naphthylamine) with N–C(7) coupled units.

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Table 2. IR-spectral data (cm^{-1}) of the monomer 2-Me-1-NPA and polymer p(2-Me-1-NPA) in the 1700–970 cm^{-1} range.[a]

Wavenumber/cm^{-1}					
Compound					
	p(2-Me-1-NPA)				
2-Me-1-NPA	A	B	C	D	Assignment
	1646 vs	1645 vs	1646 vs	1645 vs	ν (C$=$N)
1617 vs	1620 s	1623 s	1618 s	1615 s	β_s (NH$_2$)
1596 sh	1594 m-s	1595 s	1593 s	1592 s	Aromatic ring C$=$C stretch
1565 vs	1565 s	1565 s	1565 s	1563 s	Aromatic ring C$=$C stretch
1508 vs	1503 m-s	1503 m	1505 m-s	1506 s	Aromatic ring C$=$C stretch
1454 s	1457 w-m	1458 m	1454 w-m	1454 m	δ (CH$_3$) or/and aromatic ring C$=$C stretch
1441 s	1437 w-m	1440 w-m	1438 w-m	1435 w-m	Aromatic ring C$=$C stretch or/and δ (CH$_3$)
1424 s					
1399 vs	1399 m	1399 m	1398 m	1398 m-s	Aromatic ring C$=$C stretch
1380 vs	1379 s	1380 m-s	1379 s	1380 s	δ (CH$_3$)
	1358 s	1361 s	1358 s	1362 s	δ (CH$_3$) or/and ν (C$_{\text{arom}}$–N)
	1323 s	1323 m-s	1322 s	1323 s	ν (C$_{\text{arom}}$–N)
	1310 s	1312 m-s	1310 s	1311 s	ν (C$_{\text{arom}}$–N)
1270 s	1265 vs	1265 vs	1265 vs	1265 s	ν (C$_{\text{arom}}$–N)
1250 m-s	1243 m	1239 w	1244 m	1243 m	δ (C–H)
1197 w-m					δ (C–H)
	1170 m		1170 m	1171 m	δ (C–H)
1162 m	1160 m	1161 w-m	1161 m	1160 m	δ (C–H)
1131 w					δ (C–H)
1090 vs	1094 m	1093 w-m	1094 m-s	1095 m	δ (C–H)
1025 s	1028 m	1028 w-m	1028 m	1025 m	δ (C–H)
996 m-s	1014 w		1012 w	1016 w-m	δ (C–H)

[a] Abbreviation used are: vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; ν, stretching vibrations; δ, in-plane deformation vibrations; β_s, scissoring vibration mode.

strong band at 1593 cm^{-1} can be attributed to the aromatic ring stretch of the quinoid form.[5]

The strong band at ~1620 cm^{-1} was interpreted as scissoring mode β_s of the NH_2 group.[2,9,15,16,18,21,22] This band is characteristic for primary amines and it arises from the polymer chains terminations. This fact indicated that the degree of the polymerization of the p(2-Me-1-NPA) was relatively small. The ratio of the 1645 and 1620 cm^{-1} peak areas decreased with increasing synthesis temperature, although at 30 and 45°C it was approximately the same, Table 3. This has shown that longer chains of electropolymerized 2-methyl-1-naphthylamine are obtained at lower temperatures, i.e. that a temperature of 25°C is the most suitable for obtaining higher molecular weights.

The bands at 1457 and 1379 cm^{-1} are attributed to the methyl group angular bending (asymmetrical bending,[18] δ_{as} (CH_3) = 1457 cm^{-1} and symmetrical bending,[23,24] δ_s (CH_3) = 1379 cm^{-1}). Unlike the spectrum of monomer, where only one very strong band at 1379 cm^{-1} is present, in the spectra of polymers A, B, C and D a strong band was found at ~1360 cm^{-1} and a weaker one at ~1379 cm^{-1}. The intensity of the band at ~1379 cm^{-1} (compared to the intensity of 1360 cm^{-1} band) is rising with increasing the polymerization temperature. The most probable assignment of the 1360 cm^{-1} band is $\delta(CH_3)$[21,23] although it may be due to C–N stretch of aromatic amino groups.[2,5,24]

In the 1240–960 cm^{-1} range, the bands originate from aromatic C–H in-plane deformation vibrations, δ(C–H), the positions of which vary with the type of substitution arrangement.[14,16] In the case of the polymers an additional band at 1170 cm^{-1} was observed, while bands of the monomer at 1197 and 1216 cm^{-1} were absent in the polymer spectra.

The strong bands in p(2-Me-1-NPA) spectra at 1323 and 1310 cm^{-1} were not observed in the monomer spectrum. They may be assigned as C–N

Table 3. Band fitting results for β_{NH2} and $\nu_{C=N}$ bands at different temperatures. G1 and G2 are Gaussian amplitude functions referring to these bands, respectively.

	G1		G2		
t/°C	Position/ cm^{-1}	Half-width/ cm^{-1}	Position/ cm^{-1}	Half-width/ cm^{-1}	G2/G1 area ratio
25	1618.8	29.8	1648.5	17.2	0.67
30	1618.8	30.6	1648.0	19.2	0.61
45	1618.2	30.0	1648.1	17.1	0.60
60	1617.4	30.4	1647.2	18.3	0.54

stretching vibrations of the secondary aromatic amino group.[2,4,5,16,19,21,25] These bands indicate the formation of (–NH–C) units in polymer structure. The band at 1265 cm^{-1} in the spectra of all polymer samples is attributed to C–N stretch of primary aromatic amines[16,21,25] and corresponds to the band at 1270 cm^{-1} observed in the monomer spectrum.

3500–2500 cm^{-1} Range

Spectra of the electropolymerized 2-methyl-1-naphthylamine obtained at different temperatures, in the 3500–2500 cm^{-1} range, are presented in

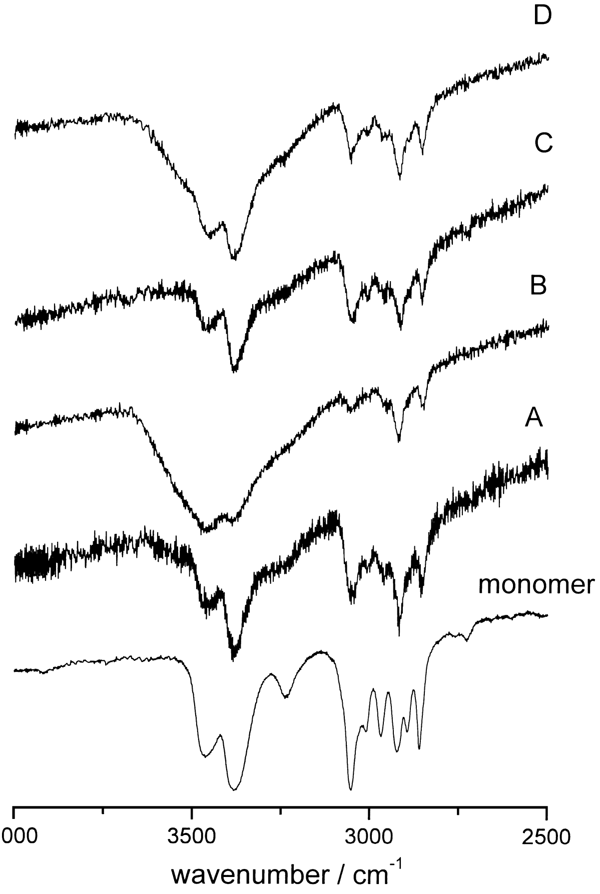

Figure 5. IR-spectra of 2-Me-1-NPA and p(2-Me-1-NPA) samples A, B, C and D in the 3500–2500 cm^{-1} range.

Figure 5. The main IR bands in this range for 2-Me-1-NPA and p(2-Me-1-NPA) and their assignments are given in Table 4. In the IR spectra of the 2-Me-1-NPA and p(2-Me-1-NPA) the symmetric and antisymmetric N–H stretching modes were assigned to the bands at 3383 (ν_s (N–H)) and 3460 cm^{-1} (ν_{as} (N–H)) respectively.[16,18,24] The bands of the polymers were broader compared to the monomer. The presence of these bands in the IR spectra of p(2-Me-1-NPA) is in accordance with above mentioned indications about relatively short polymer chains, i.e. quite a high fraction of NH_2 groups originated from the polymer chains terminations. Regarding the fact that secondary amines have only one band due to N–H stretching in the same wavenumber region where primary amines have two bands,[16] the fraction of terminal NH_2 groups cannot be determined.

The band at 3236 cm^{-1}, which is weaker than ν_s (N–H) and ν_{as} (N–H), was observed in the monomer IR spectrum. This frequency could be interpreted as an overtone of the deformation vibration $\delta(NH_2)$ the fundamental of which occurred at ~1620 cm^{-1}.[24] It was absent in IR spectra of polymers. The bands at 3050 and 3005 cm^{-1} observed in the monomer and polymer spectra were assigned as aromatic ν (C–H) stretching modes.[13,16,18,20]

In the range 2970–2850 cm^{-1} peaks at ~2960, 2916 and 2850 cm^{-1}, due to the (C–H) stretch in methyl group,[15] were observed in spectra

Table 4. Assignment of IR-spectral data for monomer 2-Me-1-NPA and polymer p(2-Me-1-NPA) samples in the 3500–2500 cm^{-1} range.[a]

Wavenumber/cm^{-1}					
Compound					
	p(2-Me-1-NPA)				
2-Me-1-NPA	A	B	C	D	Assignment
3463	3460	3460	3460	3451	ν_{as} (N–H)
3383	3386	3386	3382	3386	ν_s (N–H)
3236					Overtone of $\delta(NH_2)$[b]
3052	3050	3050	3050	3050	ν (C–H) aromatic
3010			3008	3005	ν (C–H) aromatic
2967	2958	2954	2958	2963	ν (C–H) in CH_3
2920	2916	2916	2916	2916	ν (C–H) in CH_3
2892					ν (C–H) in CH_3
2859	2852	2847	2852	2852	ν (C–H) in CH_3

[a] Abbreviation used are: ν_{as}, antisymmetric stretching vibration; ν_s, symmetric stretching vibration; δ, deformation vibration; ν, stretching vibrations.
[b] See explanation in the text.

of p(2-Me-1-NPA) films. The vibrations at ~2960 cm^{-1} (2967 cm^{-1} for monomer) and 2916 cm^{-1} (2920 cm^{-1} for monomer) correspond to antisymmetric C–H stretch modes ν_{as} (C–H) in the methyl group.[13,15,25] The band at 2847 or 2853 cm^{-1} for polymers (2859 cm^{-1} for monomer) was designated as symmetric stretching vibration ν_s (C–H) in methyl group.[13,21,22,24]

CONCLUSION

2-Methyl-1-nahthylamine was polymerized electrochemically on a platinum electrode from the acidic aqueous solution containing 2-methyl-1-nahthylamine and the structure of obtained polymer films was studied by IR-spectroscopy. Generally, infrared spectra of poly(2-methyl-1-naphthylamine) films consist of a well-defined band structure and indicate a relatively small degree of polymerization. IR spectroscopy indicates that electropolymerization occurs via the $-NH_2$ groups of monomer molecules, and that the resultant polymer contains free methyl groups in chains. On the basis of the analysis of the substitutions on the aromatic nuclei it can be concluded that the poly(2-methyl-1-naphthylamine) films were formed via mixed N–C(4), N–C(5) and N–C(7) bonding between the repeated units. The polymerization temperature affects the IR spectra of the electropolymerized 2-methyl-1-naphthylamine mostly by changing the ratio of the ν(C=N) and β (NH_2) band areas. This ratio is inversely proportional to the temperature of synthesis indicating that the longest chains of the electropolymerized 2-methyl-1-naphthylamine are obtained at 25°C, i.e. at the lowest used temperature.

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