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Polymer 46 (2005) 1485–1495

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# Spectroscopic and structural characterization of low molecular weight fractions of polyaniline

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Received 20 May 2004; received in revised form 2 December 2004; accepted 6 December 2004

## Abstract

Detailed characterization of low molecular weight byproducts of oxidative polymerization of aniline is given. Presence of these compounds in the final product of polymerization strongly influences its macroscopic properties, such as density, solubility, etc., and they should be removed for the sake of reproducibility of properties of the polymer. We focused our research on separation and identification of the low molecular weight compounds, which are created during the polymerization process. We also compared the results obtained for room temperature and 0 °C polymerization products. Polymerization at −30 °C was also carried out but only very small amounts of the low molecular weight products were produced.

*Keywords:* Polyaniline; Oligoanilines; Characterization

## 1. Introduction

Designing of polymer materials involves combining of their macroscopic properties and chemical structure. Differently as in metals or ceramics, slight changes in chemical structure of polymer usually induce significant changes in macroscopic properties. For example, linear polyethylene of very high molecular weight is used as a bulletproof material, while the same branched polymer is known as a ‘weak’ material for plastic shopping bags. Therefore, the synthesis route becomes the key factor in the process of obtaining polymers having specified properties.

Polyaniline (PAni) is the most promising conducting polymer, the most often studied and described. It is already produced by several companies and used for antistatic or anticorrosion purposes [1]. Depending on the projected applications, polyaniline in the form of emeraldine can be synthesized chemically [2–12] or electrochemically [13–16]. In special cases, the biochemical method [17–19] or plasma polymerization [20,21] processes are employed. Electrochemical polymerization is used to ensure thin, smooth and uniform layers for use as luminescent diodes, cells or sensors. However, this method cannot be applied when large amounts of the product are required, e.g. in antistatic materials or composites. The most widely used chemical method involves an oxidative polymerization of aniline hydrochloride in the presence of ammonium persulfate followed by deprotonation of the polyaniline hydrochloride with ammonia [3] (the reactions shown in Scheme 1).

Thanks to its simplicity and efficiency, this method is commonly used by nearly all researchers investigating the properties of polyaniline. All the same, products of various syntheses might differ in their average molecular weight, polydispersity index or the crosslinking level, and hence in their conducting properties, solubility and ability to mix with other polymers. Our rigorous and long-term studies lead us to the conclusion that the main reason for the differences between different batches of polyaniline can be connected to a presence of low molecular weight byproducts of polymerization. This problem is examined rigorously in the presented study, and the low molecular weight products are fully characterized. The identification of by-products of aniline polymerization is a major consideration in the light of environmental and work safety regulations. First, because

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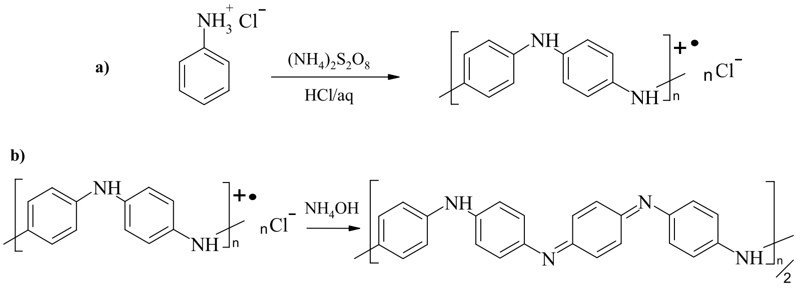
doi:10.1016/j.polymer.2004.12.008



Scheme 1. (a) Oxidative polymerization of aniline, and (b) deprotonaton of polyaniline hydrochloride.

the low molecular weight fractions are most likely removed from the final products as wastes, and second, chemistry researchers and students dealing with this reaction in laboratories should know if they operate with potentially harmful nitrogen containing compounds.

## 2. Experimental

### 2.1. Materials and characterization methods

Aniline was purchased from POCh (Poland) and distilled before use. Elemental analyses were performed using a Perkin Elmer Analyzer CHN S/O 2400. The density of samples was measured with a helium pycnometer Accu-Pyc 1330 (Micrometrics). SEM images were obtained using JSM 5400 Microanalyzer Link ISIS series 300. UV–Vis spectra were recorded on Hewlett–Packard spectrometer. Fourier transform infrared (FTIR) spectra were recorded on a Bio-Rad FTS 60-V instrument with KBr pellets. Raman spectra were recorded on a multichannel Jobin–Yvon T64000 spectrometer. X-ray measurements were made with an FPM Seifert XRD-7 diffractometer.

Matrix Assisted Laser Desorption Ionization-Time of Flight (MALDI-TOF) analysis was made with a Voyager Elite Perspective Biosystem. Electrospray Ionization-Mass Spectrometry (ESI-MS) analysis was performed using a Finningat Mat 95 apparatus.

### 2.2. Oxidative polymerization of aniline

Polymerization of aniline was carried out using the procedure described recently [3], however the reaction temperature was room temperature or 0 °C.

80.5 g (0.3528 mol) of ammonium persulfate was dissolved in 1400 ml of 1 M hydrochloric acid. 140 ml. (1.533 mol) of aniline was dissolved in 2100 ml 1 M hydrochloric acid. Depending on the planned reaction temperature both solutions were cooled down to 0 °C or kept at room temperature. Then the solution of ammonium persulfate was added dropwise to the aniline solution. The reaction is exothermic, hence the oxidant must be added slowly to keep the temperature of the reaction mixture steady. After adding the whole portion of the oxidant the reaction mixture was stirred for additional 1.5 h. The created precipitate of the polymer was filtrated on a Büchner funnel and washed with water to pH 7.

The obtained precipitate of polyaniline hydrochloride was placed in 3500 ml of 0.1 M solution of ammonia (pH 8) and stirred constantly for 15 h. The precipitate of emeraldine base form of polyaniline was then separated and washed thoroughly with distilled water.

$PAni_{-30}$ was synthesized following a procedure described recently [22].

According to the reaction temperature i.e., room temperature, 0 or −30 °C, the investigated samples are marked in the following text as $PAni_{20}$, $PAni_0$ and $PAni_{-30}$, respectively.

### 2.3. Separation of low molecular weight fractions

Low molecular weight compounds were extracted from the obtained emeraldine base by subsequent washing with different organic solvents, such as methanol, chloroform, tetrahydrofuran, benzyl alcohol, and *N*-methyl pyrrolidinone. The extractions were carried out in two parallel ways: (1) polyaniline was placed in a solvent and stirred overnight. Then the polymer was filtrated on a Büchner funnel and washed out with the same solvent until the filtrate became colorless. The filtrates were collected and the solvent evaporated. Black powdery fractions were collected after solvent evaporation. (2) polyaniline powder was placed in a Soxhlet apparatus and extracted with the mentioned solvents until extracts became colorless. In that case *N*-methyl pyrrolidinone was not included because of its high boiling point.

## 3. Results and discussion

### 3.1. Comparison of properties of different batches of polyaniline

The polymerization process of aniline was repeated more than twenty times. Standard characterization of the polymerization products, including elemental analysis, FTIR, X-ray powder diffraction, do not reveal major differences between the products (Fig. 1), yet in the light

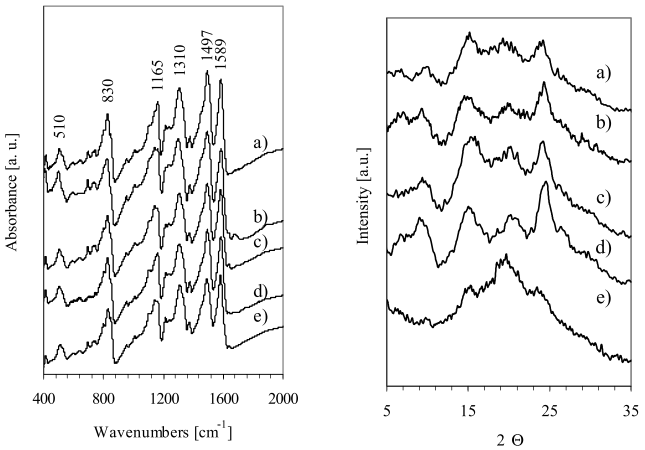


Fig. 1. FTIR spectra (left) and diffraction patterns (right) of five different batches of emeraldine base. The final products of polymerization were purified in different ways: (a) washed with water, (b) methanol, (c) chloroform, (d) chloroform in Soxhlet apparatus, (e) diethyl ether.

of the materials engineering and their intended applications the differences seem considerable. For example, the density of five independently derived samples of emeraldine base would range from 1.3423–1.3679 g cm$^{-3}$. Certain differences in the morphology of the samples were also observed (Fig. 2). As the consequence, the processability parameters are not fully reproducible. For example, differences in polymer plasticity were observed and the obtained samples would differ in their plasticity threshold, viscosity and flow curve characteristics.

All these observations lead to the conclusion that elimination of low molecular weight products of the reaction is the necessary condition for ensuring reproducibility of final properties of the polymer. The compounds can be easily separated from polyaniline by the extraction method because, unlike the polymer, they are soluble in organic solvents. Solvents that we used in the extraction process are chemically neutral to polyaniline, this group includes, methanol, chloroform, tetrahydrofuran and benzyl alcohol. *N*-metylpyrrolidinone regarded as the best solvent of polyaniline with the large molecular weight [23–27] was also used for the sake of comparison.

Acidic solvents like *m*-cresol, trifluoroacetic acid, or hexafluoropropanol were not applied. These solvents easily react with polyaniline on account of their acid properties, producing salts. In the consequence, the relationship between the polymer solubility and molecular weight is not straightforward.

The pattern of polyaniline solubility in methanol and chloroform is similar for both PAni$_{20}$ and PAni$_{0}$, no matter what the process temperature, however solubility of PAni$_{0}$ is greater. Polyaniline solubility in tetrahydrofuran and benzyl alcohol is enhanced in the case of PAni$_{20}$. PAni$_{-30}$ was found insoluble in any of the used solvents.

In both cases solubility depends on the type of solvent in the following order: MeOH < CHCl3 < THF < BzOH < NMP. Proportions of the individual fractions are indicated in Fig. 3. GPC of the obtained fractions carried out in tetrahydrofuran shows that the average molecular mass of extracted products will not exceed several thousand Da.

The overall content of soluble fractions does not exceed 40% by weight for PAni$_{20}$ and 20% by weight for PAni$_{0}$ (see also our recent paper [28]). Elemental analysis of individual

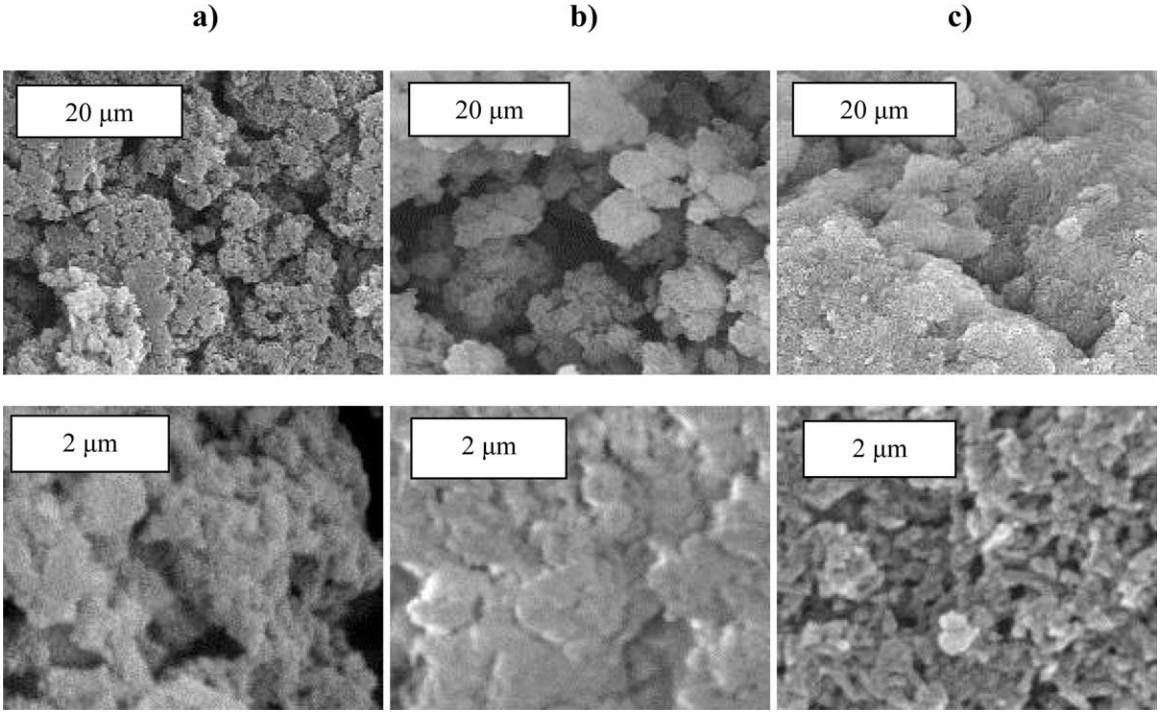


Fig. 2. SEM photos of emeraldine base powder treated with: (a) water, (b) chloroform (c) Soxhlet extraction with chloroform.

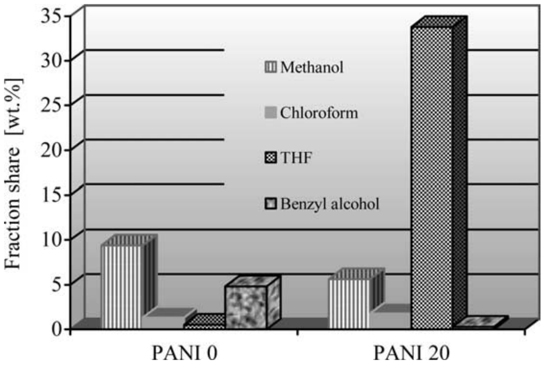


Fig. 3. Content of fractions obtained by subsequent extraction with organic solvents.

fractions did not reveal any impurities associated with the presence of ammonium persulfate—an oxidizer, or ammonium sulfate, a reaction product.

Compounds making up the individual fractions were analyzed by FTIR, Raman spectroscopy, UV–Vis, MALDI-TOF, ESI, XRD methods.

### 3.2. *Characterization of low molecular weight products*

#### 3.2.1. *FTIR and Raman spectroscopy*

FTIR spectra of derived fractions of $PAni_{20}$ and $PAni_0$ are shown in Fig. 4, respectively. Band assignment is based on data available in literature. Of particular interest are bands characteristic of emeraldine and aromatic amines [29–42] and so are the bands associated with specific vibrations of oligoanilines [43–49]. The position of the latter is associated both with the length of the oligoaniline chain and the type of substitution on the aromatic ring. Spectra of individual fractions vastly differ from that of polyaniline. They contain more bands and the spectrum of $PAni_{20}$ appears to display more diverse features than that of $PAni_0$. Characteristic bands present in all spectra excluding that of high-molecular-weight polyaniline are: 696, 754, 1026, 1178, 1380, 1446 $cm^{-1}$. The bands at 696 and 754 $cm^{-1}$ are characteristic of mono-substituted aromatic rings and are associated with deformative vibrations out of plane C–C (696 $cm^{-1}$) and outside the plane C–H (754 $cm^{-1}$) of benzenoid ring. Since mono-substituted rings are always terminal in the chain, the bands associated with them are clearly visible only in spectra of short-chain oligoanilines containing up to five aniline units [43,48,50]. As the chain length increases, their intensity continues to decrease till they wholly fade out in the polymer spectrum. Both bands are best visible for all fractions of $PAni_{20}$ whilst in the case of $PAni_0$ their intensity diminishes for the subsequent fractions. No matter what the temperature of polymerization, spectra of a large molecular weight polymer remaining after the fractionating process (in Fig. 5—$PAni_{20}$ and $PAni_0$) are identical and do not contain any bands characteristic of oligomers. Band assignment for polyaniline is shown in Table 1. All bands visible in spectra are compiled in Table 2 and the vibration modes are provided. These bands are characteristic of oligoanilines. Table 2 provides also the references where all the investigated spectra are discussed.

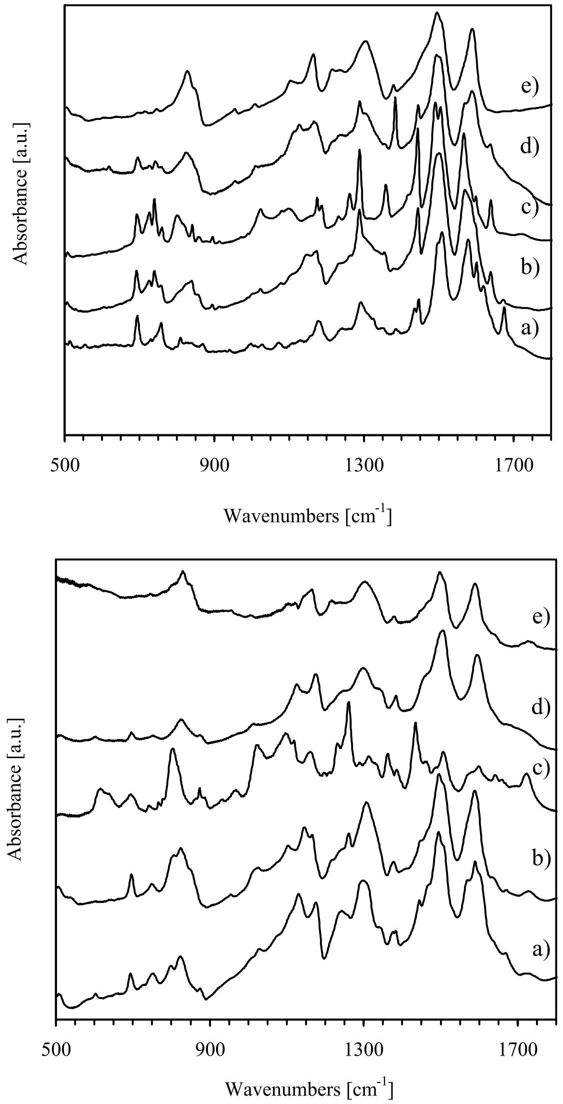


Fig. 4. FTIR spectra of fractions obtained by subsequent extraction of polyaniline synthesized at room temperature (top) and 0 °C (bottom) with (a) methanol, (b) chloroform, (c) THF, (d) benzyl alcohol, (e) PAni after extraction.

Raman spectra of all fractions are identical and do not differ from those of polyaniline. That means that the fractions contain compounds made from aniline segments. Since their vibrations are resonance-excited the chain length cannot be precisely established by this method. One has to bear in mind that the obtained spectra are characteristic of emeraldine—an oxidized form of oligoanilines, and of polyaniline. They contain no narrow bands at 1000 $cm^{-1}$ characteristic of oligomeric derivatives of leucoemeraldine, such as B2, B3, B5 [50–52]. That means that in those process conditions the synthesized oligomers contain at least one quinoid chain. In accordance with the data from

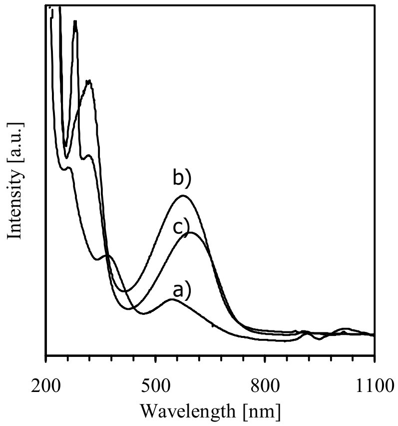


Fig. 5. UV–Vis spectra of PAni fractions obtained by extraction with (a) methanol, (b) THF, (c) $CHCl_3$.

literature the bands appearing in Raman spectra are assigned as follows: 1161 $cm^{-1}$—deformative vibrations of the quinoid ring, 838 $cm^{-1}$—deformative vibrations of amine groups, 1216 $cm^{-1}$—stretching of C–N, 1417 $cm^{-1}$—stretching C=C in the quinoid ring, 1470 $cm^{-1}$—stretching of C=N, 1580 $cm^{-1}$—stretching of C–C.

### 3.2.2. UV–Vis spectroscopy

Emeraldine shows very strong absorption in two areas, with the maximums at 320–330 and 600–660 nm. The first band is assigned as the exciton transition $\pi \rightarrow \pi^*$, the other is associated with the transition of benzenoid rings into quinoid rings $B \rightarrow Q$ [33,34,53–55]. These transitions occur in most oligoanilines [45,46,56–59] and the actual locations of the peak at 600 nm depend on the length of the oligomer chain [42,55,56] and on the number of reduced and oxidized rings [60]. For example, in the trimer BQB the transition band $B \rightarrow Q$ occurs at the wavelength 450 nm, in the tetramer BQBB −570 nm, in BQBQ—590 nm, in a pentamer BQBQB—593 nm and in the nonamer with the formula B8Q1—∼620 nm, in a hexadecamer of emeraldine −610 nm. No absorption in the range 550–659 nm is reported in leucoemeraldine oligomers containing only benzenoid rings (the UV–Vis spectrum of B5 contains only one band at 333 nm) [61,62]. Depending on the degree of oxidization (in other words on the number of quinoid rings in the oligomer molecule) the absorption peak at ∼300 nm is shifted. In this case, increased degree of oxidization brings about the shift of the absorption peak towards the lower wavelengths. For example, B5 absorbs at 333 nm whilst BBQBB—at 310 nm [61].

Comparison of spectra of derived fractions (Fig. 5) with the data available in literature affords us a conclusion that all fractions contain oligomers in an oxidized form since they absorb the UV radiation over the range 440–720 nm. The absorption peak shifts from 560 nm for a fraction containing MeOH, through 592 nm for a fraction containing $CHCl_3$, right to 610 nm for THF, which implies that subsequent fractions contain larger and larger molecules.

### 3.2.3. X-ray diffraction

The presence of oligoanilines in the product of the polymerization process is confirmed by the X-ray diffraction analysis (Fig. 6). Diffraction patterns of polyaniline with a large molecular weight tend to display a broad amorphous halo over the range $2\Theta = 9 \div 27°$ and three distinct peaks at the angles $2\Theta = 15, 20, 24°$ [63]. The relative intensity of these peaks might differ, depending on the conditions of the polymerization process.

A distinctive feature of diffraction patterns of large-molecular weight polyaniline is the absence of sharp peaks. Such peaks occur in the diffraction patterns for the first three fractions and are typical of oligoanilines [45,64].

Similar to FTIR spectra, diffraction patterns reveal that analogous fractions might have different properties depending on the temperature of polymerization. Diffraction patterns for $PAni_{20}$ exhibit more Bragg peaks than $PAni_0$ patterns. The peaks tend to disappear as molecular weight increases, hence it appears that polymerization at room temperatures promotes frequent chain terminations and generates oligomers containing more than ten rings. In the case of polyaniline synthesized at 0 °C, low-molecular weight compounds are produced such as B2, B3 or BQB (wholly rinsed with methanol), and oligomers containing up to twenty rings in their molecules. The letter compounds are

Table 1
Assignment of IR bands to specific vibrations in polyaniline (Q = quinoid ring, B = benzenoid ring)

| Wavenumbers [$cm^{-1}$] | Characteristic vibrations of polyaniline functional groups |
|---|---|
| 830 | C–H in *p*-substituted benzenoid ring; out of plane bending |
| 960 | Quinoid ring in plane deformations |
| 1111 | Benzenoid ring deformations |
| 1167 | N=Q=N stretching and C–H in plane bending |
| 1220 | C=N=C stretching |
| 1254 | C–N in plane stretching |
| 1308 | C–N in secondary aromatic amines; asym. Stretching |
| 1392 | C–N in QBQ; stretching |
| 1499 | C–C stretching in benzenoid ring, |
| 1506 | N–H bending |
| 1593 | C=N and C=C stretching in quinoid ring |

Table 2
Assignment of IR bands to specific vibrations of oligoanilines. (Q = quinoid ring, B = benzenoid ring)

| Wave-numbers [cm$^{-1}$] | Fraction[a] | Specific vibrations of functional groups | Oligoanilines[b] | Literature |
|---|---|---|---|---|
| 696[c] | All | C–C out of plane deformation in monosubstituted aromatic ring | B4Q1, B3Q2, B2Q1, B3, B2, B5, B7, BQ(16-mer) | [42,47,50,55] |
| 726, 742, 756 | All PAni$_{20}$ | C–H out of plane bending in monosubstituted aromatic ring | B2Q1, BQ(16-mer) B2, B3, B5, B7 | [42] |
| 827 | All PAni$_0$, and MeOH of PAni$_{20}$ | C–H out of plane bending in *para*-substituted ring | B3Q2, B4Q1, B3 B2Q1, B3Q2, B3 | [50] |
| 805 | All PAni$_0$, and THF PAni$_{20}$ | Benzenoid ring in plane deformation | B2, B3, B5, B7 | [42,50] |
| 843 862 | All PAni$_{20}$, and THF PAni$_0$ | Quinoid ring out of plane deformation + benzenoid ring in plane deformation + C–H bending in monosubstituted ring | B2Q1, B3Q2, B4Q1, B2, B3, B5, B7 | [50] |
| 875 | MeOH and $CHCl_3$ of PAni$_{20}$ | N–H out of C–N–C plane bending; only in reduced forms of oligomers; shifts toward lower wavenumbers with the increase of number of rings | B2, B3, B7 | [47, 50] |
| 1030 | All, most intensive for THF fraction | Aromatic ring deformations | B2, B3 | |
| 1100 | $CHCl_3$ | Benzenoid ring deformations, and N–H bending | B2, B3, B5, B7 | [42] |
| 1138[c], 1149[c] | $CHCl_3$ | C–H bending and C–C stretching in monosubstituted ring | B3, B5, B7 | [42] |
| 1250 | All | C–N stretching | B3, B5 | [42] |
| 1291 | $CHCl_3$, THF, BzOH | C–H bending and C–C stretching | B5 | [42] |
| 1340 | $CHCl_3$, THF, BzOH | C=N stretching sym. | B2–NH$_2$, B2Q1 | [42,47] |
| 1380 | All | Quinoid ring deformation | BQB, B3 | [50] |
| 1447 | All | C–H and N–H bending | B2, B3, B5, B7, BQB | [42] |
| 1603 | MeOH, THF | Benzenoid ring stretching | B2Q1, B4Q1 | [42] |
| 1639 | All PAni$_{20}$ | NH$_2$ stretching sym. | B2–NH$_2$ | [47] |

[a] Fraction in whose spectrum the given band is present.
[b] The band was observed in the spectra of the listed oligoanilines.
[c] The intensity of the band decreases with increase of length of oligoanilines.

dissolved in chloroform and in tetrahydrofuran. Diffraction patterns for the fraction THF PAni$_0$ exhibit identical peaks as PAni$_{20}$, yet of lower intensity, which suggests that the compounds which gave rise to them are present in small amounts only. All diffraction patterns for PAni$_0$ exhibit an amorphous 'halo', characteristic of longer molecules in which structure ordering is hindered.

### 3.2.4. Mass spectrometry

The results outlined above afford us a conclusion that reasonably large quantities of oligomers are produced during the polymerization of polyaniline. However, accurate identification using the described methods requires that individual compounds be first separated. Even though feasible, this procedure seems time-consuming and discouraging.

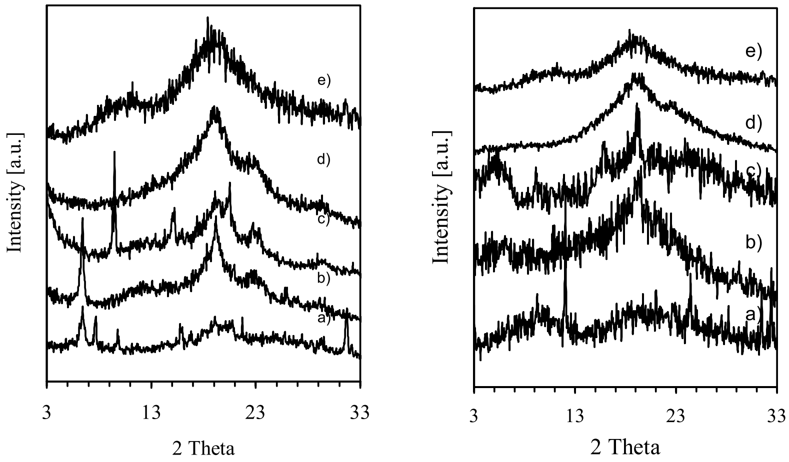


Fig. 6. Diffraction patterns of polyaniline fractions obtained by extraction with (a) methanol, (b) chloroform, (c) THF, (d) benzyl alcohol, (e) NMP. Left diagram—PAni synthesized at room temperature, right—PAni synthesized at 0 °C.

In the last few years new methods were developed whereby the molecular weight is determined on the basis of mass spectrometry (MS) [65,66]. Molecules are not fragmented, instead 'soft' ionization is used involving the absorption of hydrogen cation. Thus obtained mass spectrum allows the accurate identification of emerging ions and hence the structure of the intact molecules. The methods have been recently utilized for soluble oligomers of polyaniline [69,70].

Low-molecular weight polyaniline fractions are investigated by mass spectrometry based approaches: MALDI-TOF and ESI-TOF. The MALDI method is convenient because the investigated substance, thanks to the absorbed radiation energy, is transformed into the gaseous phase, i.e. sublimes. Since individual oligomers do not differ in polarity but in the actual number of repeat segments, the difference in the amount of energy required for sublimation is proportional to the molecular weight. Accordingly, sample separation is accurate and efficient. Besides, detection of molecules through measurement of time of flight also utilizes the relationship between the ion speed and their mass. The MALDI method produces only unipositive ions, which vastly facilitates the interpretation of thus obtained spectrum. The ESI method yields chiefly multiple ions. In most mass analyzers ion separation is closely associated with the ion mass to charge ratio $m/z$. A chief benefit is that the ESI method permits the easy registering of signals from large molecular weight ions even in analyzers with a small measurement range.

### *3.2.5. Determination of molecular mass of oligomers by laser desorption ionization*

Figs. 7–9 show mass spectra of polyaniline fractions obtained by the MALDI-TOF method. It is worthwhile to mention at this point that aromatic amines, such as *p*-nitroaniline are widely applied in MALDI method as base matrices while phenols and carboxyl acids are used as acid matrices [67]. Acids, however, react with polyaniline and oligoanilines, producing salts and cannot be applied. Because molecules are activated with the UV laser, and both polyaniline and oligoanilines are strong absorbents of UV radiation, they may absorb sufficient energy for desorption and ionization and therefore an additional matrix was not required in our experiments.

All measurements for the given fraction were taken for the four independent samples: two samples of $\mathrm{PAni}_0$ and two of $\mathrm{PAni}_{20}$.

Spectra of fractions processed from methanol (Fig. 7) contain several peaks, differing in intensity. The effects of process temperature on the amounts of reaction products with low molecular weight are clearly revealed. It appears that tetrameter B–N=Q=N–B–NH–B with a molecular mass 348 ($m/z=349$), which in those process conditions creates an ion 1+ is the low molecular weight compound produced in the process of polymerization conducted at 0 °C. The remaining peaks have low intensity, which implies that other compounds are present in small amounts only. In the spectrogram of $\mathrm{PAni}_{20}$ the predominant peak at $m/z=365$ might be assigned to the tetrameter containing four nitrogen atoms and having the structure: B–N=Q=N–B–NH–B–$NH_2$ or B–NH–B–NH–B–N=Q=NH ($M=364$). This is not surprising since the tetrameter is an equivalent of the smallest repeat unit of emeraldine. On account of the fact that the first of these structures enables further chain increase while the other does not, the latter structure seems more likely to occur. The remaining four peaks differing in intensity, revealed in the mass spectrum $\mathrm{PAni}_{20}$ are: $m/z=$ 260, 290 and 454 attributable to the trimers B–NH–B–NH–B, $NH_2$–B–NH–B–NH–B–$NH_2$ and $NH_2$–B–N=Q=N–B–$NH_2$ and the pentameter B–N=Q=N–B–N=Q=N–B–$NH_2$ or B=Q=N–B–NH–B–N=Q=NH.

Peaks in the spectra of $\mathrm{PAni}_{20}$ are grouped in multiples, implying that all subsequent oligomers are produced which differ not only in the number of segments $C_6H_4$–NH– or –$C_6H_4$=N– but also in the oxidation level and the type of terminal groups. It looks that the process of polymerization at the room temperature leads to more frequent chain termination, as the result the peak intensity is enhanced. The

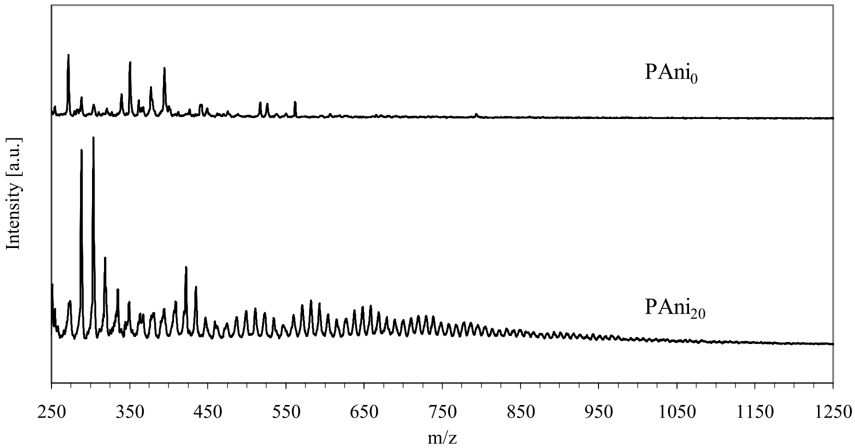


Fig. 7. MALDI-TOF spectra of methanol processed fractions of polyaniline.

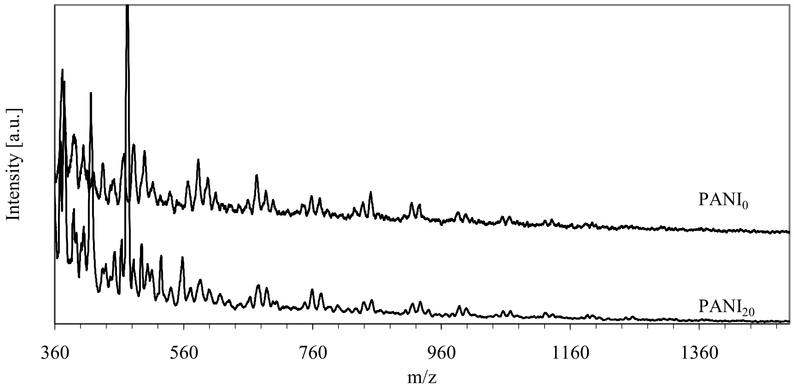


Fig. 8. MALDI-TOF spectra of chloroform processed fractions of polyaniline.

peak configuration in the spectrum PAni$_0$ displays less regular features, indicative of selective production of certain oligomers only.

No matter what the polymerization temperature, the extraction of the final product with methanol leads to the washing out oligomers containing up to ten aromatic rings. The peak values of *m*/*z* agree very well in the spectra of all the fractions processed from methanol, which indicates that in all cases the same low-molecular weight compounds are produced. However, the quantity of these compounds gets lower when the process temperature is decreased.

The *m*/*z* values at which peaks occur in the spectrum of PAni$_0$ are: 260, 274, 285, 290, 303, 316, 332, 349, 363, 378, 394, 408, 423, 429, 438, 454, 469, 484, 499, 514, 529, 545, 560, 575, 590, 605, 620, 650. The assignation of all *m*/*z* values to ions of particular oligomers is provided in Table 3 as supplementary information to this article.

Fractions processed by chloroform extraction always produce a nearly identical mixture, no matter what the process temperature (see the spectra in Fig. 8). The only peak absent in PAni$_0$ is the one at $m/z=446$ dominating in the spectrum PAni$_{20}$. This peak, however, cannot be assigned to an ion 1+ of any oligomer. In both spectra multiplets are clearly visible, with the peak-to-peak distance $m/z=90$ (equivalent of a repeat unit –$C_6H_4$=N–). The difference in *m*/*z* values between peaks within one multiple is 14 or 15, which is a rough equivalent of the molecular mass of the group =N– or –NH–. Subsequent peaks in the spectrum PAni$_0$ occur at the following *m*/*z* values: 363, 378, 389, 414, 427, 441, 454, 469, 505, 531, 546, 560, 571, 636, 707, 725, 740, 802, 816, 830, 906, 921, 997, 1012, 1087, 1102, 1177, 1192, 1268. The *m*/*z* values are assigned to ions of particular oligomers in Table 3 as supplementary information to this article.

To the chloroform solution pass oligomers with the molecular mass 360–1200 Da. However, polymerization at room temperature produces large amounts of lower molecular weight compounds (less than 550 Da) and relatively small amounts of oligomers containing 7–12 aromatic rings. Lowering the process temperature to 0 °C vastly reduces the amounts of by-products other than regular oligomers with the oxidation level of pernigraniline or emeraldine and the molecules are terminated either by two amine groups, two aromatic rings or by a phenyl at one end and an amine group at the other.

Mass spectra of fractions obtained by extraction with tetrahydrofuran seem to confirm the previous conclusions drawn on the basis of spectral analysis and X-ray patterns. Oligomers containing 17–25 repeat units –$C_6H_4$–NH– or –$C_6H_4$–N= are produced only during the polymerization

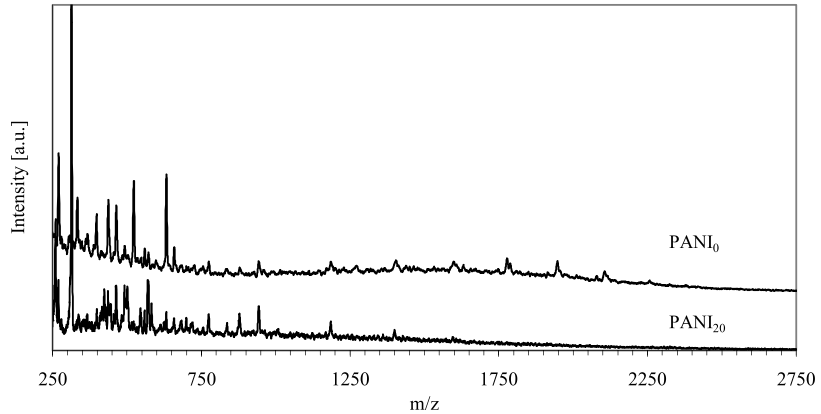


Fig. 9. MALDI-TOF spectra of tetrahydrofuran processed fractions of polyaniline.

conducted at 0 °C. In the case of the fraction $PAni_{20}$, the highest $m/z$ value at which a low-intensity peak occurs is at 1831, associated with a pentadecamer. Like in fractions processed from chloroform, the predominant peak occurs at a very low $m/z=294$. This peak is absent in the $PAni_0$ fraction and no oligomer can be assigned. The remaining higher-intensity peaks coincide with those visible in the $PAni_0$ spectrum, though they might vary in intensity. These peaks occur at $m/z$ values: 268, 301, 319, 338, 360, 377, 394, 413, 437, 486, 504, 534, 572, 590, 673, 725, 945, 1167, 1387 and at 1422, 1600, 1819, 2040, 2261 (these are present only in the spectrum of $PAni_0$).

### 3.2.6. *Determining the molecular mass of low molecular weight products by the ESI-MS method*

For the sake of comparison, mass spectra of $PAni_0$ fractions were collected using the ESI method. These spectra are shown in Fig. 10. Spectra of fractions processed in methanol extraction perfectly coincide with the analogous MALDI spectra and the $m/z$ values at which subsequent peaks occur are identical. That means that low molecular weight compounds washed out with methanol, i.e. oligoanilines containing up to 7 aromatic rings have a tendency to single ionization. However, peak intensities in ESI spectra are different than that in MALDI. The maximum intensity peak in the ESI spectrum occurs at $m/z=378$ and not at 364, as in the MALDI spectrum. This peak is associated with a pernigraniline-type maximally oxidized form of tetramer NH=Q=N–B–N=Q=N–B–$NH_2$ ($M=377$). Further high-intensity peaks in the ESI spectra occur at $m/z=393$, 408, 423, 469, 484. Differences in peak intensity for the same $m/z$ values are attributable to the measurement methodology, which might indicate that mass spectra are insufficient to find the sample composition in quantitative terms. On the other hand, an excellent agreement between $m/z$ values in the two methods proves the adequacy of mass spectrometry in qualitative identification of chemical composition of a sample.

The ESI spectrum of the fraction processed from chloroform displays more peaks than the analogous MALDI spectrum. There are not only those peaks where the $m/z$ values coincide with those in MALDI spectra, but a whole group of other peaks of variable intensity, following the Gauss pattern. It is diagnostic of creation of many ions of the same compound though differing in charge. As the fraction processed from chloroform is a mixture of a great number of compounds, the peaks in the ESI spectrum are so densely packed. Full interpretation of this spectrum presents certain difficulties, nonetheless most peaks are easily assigned to the ions: $m/z=551 \rightarrow$ ion $2^{+}M=1100$, $m/z=595 \rightarrow$ ion $2^{+}M=1191$, $m/z=664 \rightarrow$ ion $2^{+}M=1326$. For the specific assignment of molecular weights to chemical formulas of compounds see Table 3 in supplementary information.

ESI and MALDI spectra for fractions processed from tetrahydrofuran extraction are quite different. The ESI spectrum has few interesting features. There is one very intensive peak at $m/z=673$ and several lower intensity peaks at $m/z=219$, 268, 357, 454. All these peaks are present in the MALDI spectrum, too. The fact that the ESI spectrum has fewer features than in MALDI is attributable to the tendency for protonation of only 50% of nitrogen atoms in longer oligoaniline chains. Accordingly, the longest oligomer registered in the MALDI spectrum is the one containing 20 nitrogen atoms with $M=1833$ which, upon attracting ten ions H+, produces the peak at $m/z=184$, i.e. outside the measuring range. On the other hand some peaks might have very high intensity due to possible superposition of peaks from ions varying in molecular mass and in charge. For example, the peak at $m/z=357$ is assigned to the ion 1+ of the compound with $M=357$ and to the ion 3+ of the compound with $M=1068$. The peak 454 may be assigned either to the ion 2+ of the compound with $M=906$ or to the ion 3+ when $M=1359$.

This observation is confirmed by the ESI spectrum of a fraction processed from *N*-methylopyrrolidinone. This spectrum is most characteristic of polymers. Two series of peaks are easily distinguished, their intensity following the Gaussian curve pattern. One peak series has a maximum at $m/z=639$, the other enveloping lower-intensity peak is shifted by a constant value. This feature is diagnostic of the presence of two kinds of polymer molecules differing in their terminal groups only. The structure of thus separated polymers suggests that these are molecules containing terminal phenyl or amine groups at both ends. The subsequent peaks in the series are assigned to the subsequent, multiple charged, protonated, apparent molecular ions of polyaniline $[M+zH^{+}]$, their intensities following the statistical distribution. The analysis of the mass spectrum indicates that the peak at $m/z=507$ is assigned to the ion 18+, peaks at $m/z=551$ are associated with the ion 17+, those at $m/z=595$ are assigned to the ion 16+ and those at $m/z=639$—to the ion 15+. The ion charge and the $m/z$ value being known, the molecular mass of the polymer is easily calculated. It is about 10,000 Da, hence the longest chain will contain 100–110 repeat units. When the molecule is protonated in 50%, which is fully consistent with the tendency of polyaniline to produce polaron form, the $m/z$ value for such polaron equals $10{,}000/50=200$. Apparently the single most intensive peak in the spectrum occurs at $m/z=199$.

### 3.2.7. *Assigning chemical structures to the m/z values*

Nearly all $m/z$ values at which peaks occur in the $PAni_0$ spectra can be assigned chemical structures belonging to two groups. The first group includes oligoanilines with a high level of oxidation characteristic of pernigraniline and emeraldine. Derivatives of leucoemeraldine are rather rare. It is understandable since the polymerization process is conducted in the oxidizing conditions. Depending on the type of terminal groups, three groups of oligoaniline molecules are distinguished: those terminated with two

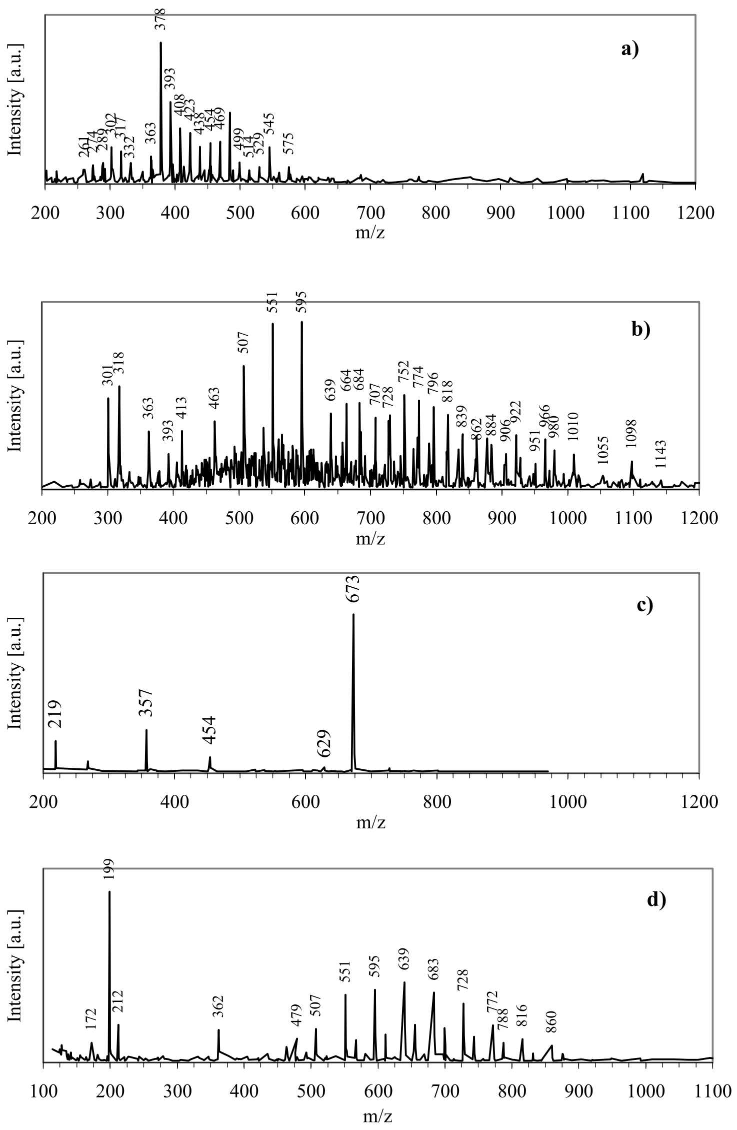


Fig. 10. ESI-MS spectra of $PAni_0$ fractions obtained by extraction with (a) methanol, (b) chloroform, (c) tetrahydrofuran, (d) *N*-methylpyrrolidinone.

phenyls, those with two terminal amine groups and those having a phenyl group at one end and an imine group =HN at the other. The presence of three types of oligoanilines shows that termination of a growing polyaniline chain involves elimination of the terminal group $-NH_2$, producing molecules terminated by two aromatic rings or interchain transfer of an amine group, thereby producing molecules terminated by two amine groups. In some cases a radicalcation is not formed on the nitrogen atom present in an amine group, instead the amine group is oxidized forming an imine group and a growing chain is deactivated. Nearly one half of compounds processed from methanol extraction can be assigned as the typical products of amine oxidation—nitro and nitroso compounds. Such products can be created in acid environment in the presence of a powerful oxidizer, such as $K_2Cr_2O_7$ or $H_2O_2$ in which amines are oxidized to hydroxyloamines and then to nitro and nitroso compounds, following the reaction [68]:

$$Ar{-}NH_2 \rightarrow Ar{-}NHOH \rightarrow Ar{-}NO \rightarrow Ar{-}NO_2$$

Analogous conditions prevail in the aniline polymerization environment. A portion of amine groups are oxidized forming stable nitroso and nitro compounds. In the presence of oxidizers hydroxyloamines are rather unstable. The summary of compounds presented in Table 3 (supplementary information) reveals that chiefly small molecules containing up to six aromatic rings are oxidized forming nitro and nitroso compounds.

## 4. Conclusion

Full characterization of low molecular weight byproducts of oxidative polymerization of aniline is described. The compounds were extracted from the final product of polymerization with organic solvents such as, methanol, chloroform, tetrahydrofuran, and benzyl alcohol. FTIR, Raman, XRD, UV–Vis, and mass spectrometry methods were used to identify the compounds. Basing on the obtained results we can state that the low molecular weight byproducts are oxidized forms of oligoanilines containing up to twenty aniline units, and products of oxidations of amines, i.e. nitro- and nitroso-derivatives of oligoanilines.

## Acknowledgements

This work was supported by WIMiC AGH (Grant no. 10.10.160.675).

## Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2004.12.008.

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