Role of \( p \)-Benzoquinone in the Synthesis of a Conducting Polymer, Polyaniline

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ABSTRACT: Polyaniline (PANI) and 2,5-dianilino-\( p \)-benzoquinone both are formed by oxidation of aniline in an acidic aqueous environment. The aim of this study is to understand the impact of addition of \( p \)-benzoquinone on the structure of PANI prepared by the oxidation of aniline hydrochloride with ammonium peroxydisulfate and to elucidate the formation of low-molecular-weight byproducts. An increasing yield and size-exclusion chromatography, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy, and nuclear magnetic resonance analyses of the products show that \( p \)-benzoquinone does not act as a terminating agent in the synthesis of PANI and the content of 2,5-dianilino-\( p \)-benzoquinone increases with the increasing molar concentration of \( p \)-benzoquinone in the reaction mixture, [BzQ]. Regarding the structure of PANI, Raman and UV-visible spectra show that the doping level and the charge delocalization both decrease with the increase of [BzQ], and the FTIR spectra of the PANI bases indicate an increased concentration of benzenoid units at higher [BzQ]. We explain these observations by an increasing concentration of structural defects in PANI chains and propose a 2,5-dianilino-\( p \)-benzoquinone-like structure of these defects present as pendant groups. The bands typical of 2,5-dianilino-\( p \)-benzoquinone-like moiety are observed even in the vibrational spectra of the sample prepared without addition of \( p \)-benzoquinone. This confirms in situ oxidation of aniline to \( p \)-benzoquinone within the course of the oxidation of aniline hydrochloride to PANI.

INTRODUCTION

Polyaniline (PANI),†‡§ one of the most extensively studied conducting polymers, is usually prepared by the oxidation of aniline with ammonium peroxydisulfate (APS).† Oxidation of aniline hydrochloride in aqueous medium leads to a conducting PANI emeraldine salt (conductivity \( \sigma \approx 10^0 \) S cm\(^{-1} \); Scheme 1).

Regarding the reaction course, oxidation of aniline with APS in acidic aqueous media is not a step-growth polymerization because it is assumed that recombination of the radical cations of aniline \( n \)-mers with each other is virtually impossible, as they are insoluble in the reaction system and form a new phase.\(^{2,5} \) However, this reaction is not a typical chain-growth polymerization consisting of initiation, propagation, and termination reactions as well. The oxidation of aniline with APS in acidic aqueous media can be monitored by the pH—time, temperature—time, and open-circuit-potential—time profiles of the reaction course.\(^{2,6,7} \) The in situ measurements provide information that the oxidative polymerization of aniline with APS in the acidic aqueous media typically consists of an initiation reaction, an induction period, and a polymerization phase.\(^{2,3} \) The process of aniline oxidation is exothermic and results in a continuous increase of the acidity of the reaction medium.\(^{2,6} \) Even though a PANI in emeraldine oxidation state is formed by this reaction at the APS-to-aniline mole ratio of 1.25, a higher PANI oxidation state called pernigraniline is formed as an intermediate within the reaction course.\(^{5,7} \)

Information on the kinetic description of the oxidative polymerization of aniline is limited in the literature, as the reaction is heterogeneous and a self-acceleration effect takes place during the polymerization phase.\(^{1,6} \)

Various mechanisms of the oxidative polymerization of aniline with APS in the acidic aqueous media were proposed in the literature (for review, see refs\(^ {1,5,7} \)); from these suggestions, the mechanism proposed by Gospodinova and Terlemezyan\(^ 1 \) with a certain correction fits best the experimental observations: in the first reaction stage, peroxydisulfate anions oxidize neutral aniline molecules which are in equilibrium with anilinium cations. The anilinium cation radicals form dimers which are further oxidized by peroxydisulfate anions to dimer cation radicals which react with the anilinium cation radicals and form trimers which are often reported to be of a phenazine-like...
structure. In the later stage, peroxysulfate ions oxidize growing PANI chains to the pernigraniline oxidation state and anilinium cations are oxidized by protonated diaminobenzquinonoid units to anilinium cation radicals which are connected to the growing PANI chains, that is, the oxidant oxidizes the growing polymer and the molecules of the monomer are oxidized by the polymer. The information on the termination of PANI chain growth is limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited. It has been suggested that the hydrolysis of the terminal amino group in a growing PANI chain to a quinone limited.

The chain growth can simply stop also because of the depletion of the oxidant, peroxysulfate. In such case, termination need not occur and the chain propagation is claimed to be recovered after addition of a new portion of the oxidant, that is, the chains were proposed to be quasi-living.

Chemical oxidation of aniline to p-benzoquinone offers an alternative reaction (Scheme 2) to the oxidative polymerization of aniline, which was used even in the industrial production of p-benzoquinone. According to the electrochemical studies of aniline oxidation, it is expected that p-benzoquinone is a product of hydrolysis of an oxidized aniline dimer, N-phenyl-1,4-benzoquinonedimine. Further, p-benzoquinone smoothly reacts with aniline to form 2,5-dianilino-p-benzoquinone (Scheme 3), and the reaction of 0.2 M aniline hydrochloride with APS is an alternative approach to the oxidation of aniline by a strong oxidant in an acidic medium and the oxidative polymerization of aniline with APS proceeds through a range of pH and oxidation potential values. The in situ formation of p-benzoquinone in the course of PANI synthesis can be hardly excluded. As a result, the in situ-formed p-benzoquinone can play various roles in the oxidation of aniline with APS. By considering the above chemistry, we can expect the following scenarios:

1. p-Benzoquinone reacts with aniline (Scheme 3) and produces 2,5-dianilino-p-benzoquinone as a byproduct without affecting the growth of PANI chains.
2. The growing PANI chains react with p-benzoquinone produced by the oxidation of aniline (Scheme 2) similarly to the reaction of aniline with p-benzoquinone (Scheme 3). Up to two PANI chains could be attached to a single p-benzoquinone molecule. This should result in the termination of the growth of PANI chains and thus in the narrowing of distribution of the molecular-weight values of the formed PANI chains, which might theoretically imply better solubility and processibility of PANI.
3. p-Benzoquinone is incorporated into a growing PANI chain as a comonomer without causing the chain termination.

In order to distinguish among the possible roles of p-benzoquinone in PANI synthesis, we have carried out the “standard” preparation of PANI when 0.2 M aniline hydrochloride is oxidized with 0.25 M APS without the addition of p-benzoquinone and in the presence of p-benzoquinone in the concentrations varying from 0.001 to 0.2 M. The impact of p-benzoquinone on the formation and structure of PANI is elucidated, and the formation of 2,5-dianilino-p-benzoquinone-like oligomers is investigated by means of various spectroscopic methods and size-exclusion chromatography (SEC).

### RESULTS AND DISCUSSION

**Yields, Molecular-Weight Distributions, and Conductivity.** The reactions of 0.2 M aniline hydrochloride with APS yielded dark solids within the whole range of applied concentrations of p-benzoquinone, [BzQ], which varied from 0 to 0.2 M. The yield of PANI prepared without addition of p-benzoquinone equal to 0.81 g of PANI hydrochloride per 1 g of aniline hydrochloride is close to the theoretical value, which is 0.84 g of PANI hydrochloride per 1 g of aniline hydrochloride. The yield of the products prepared in the presence of p-benzoquinone in the concentrations varying from 0.001 to 0.2 M. The impact of p-benzoquinone on the formation and structure of PANI is elucidated, and the formation of 2,5-dianilino-p-benzoquinone-like oligomers is investigated by means of various spectroscopic methods and size-exclusion chromatography (SEC).
Deprotonation to PANI Bases

Conductivity of PANI Salts after Preparation and after

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hydroquinone.\(^2\) The conductivities of PANI bases are of the
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of hydroquinone to the reaction mixtures, which resulted in a

PANI salt prepared by the

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molecular weights,

of applied \([\text{BzQ}]\). Polymeric fractions exhibit weight-average

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weight-average

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and dispersity, \(D = M_w/M_n\) of Polymeric Fraction, and

Conductivity of PANI Salts after Preparation and after

Deprotonation to PANI Bases

Table 1. Yield of PANI Salts Prepared under Various Molar Concentrations of \(p\)-Benzoquinone, \([\text{BzQ}]\), Loss of Mass after Deprotonation, \(\Delta\), Weight-Average Molecular Weight, \(M_w\), and Dispersity, \(D = M_w/M_n\) of Polymeric Fraction, and Conductivity of PANI Salts after Preparation and after Deprotonation to PANI Bases

| \([\text{BzQ}]\) mol L\(^{-1}\) | yield\(^a\), g g\(^{-1}\) monomer | \(\Delta\) wt % | \(10^{-3} M_w\) | \(D\) | conductivity, S cm\(^{-1}\) | salt\(^b\) | base\(^c\) |
|---|---|---|---|---|---|---|---|
| 0 | 0.81 | 20 | 20.2 | 3.4 | 2.76 | 4.2 \times 10^{-10} |  |  |
| 0.001 | 0.81 | 20 | 20.5 | 3.6 | 2.48 | 3.4 \times 10^{-10} |  |  |
| 0.002 | 0.82 | 21 | 17.9 | 3.4 | 2.44 | 5.4 \times 10^{-10} |  |  |
| 0.005 | 0.83 | 21 | 19.2 | 3.4 | 2.75 | 6.4 \times 10^{-10} |  |  |
| 0.01 | 0.84 | 20 | 18.0 | 3.4 | 2.33 | 9.3 \times 10^{-10} |  |  |
| 0.02 | 0.85 | 18 | 22.4 | 3.9 | 2.05 | 1.1 \times 10^{-9} |  |  |
| 0.05 | 0.94 | 20 | 18.4 | 3.5 | 1.60 | 2.8 \times 10^{-9} |  |  |
| 0.1 | 0.94 | 19 | 15.8 | 3.0 | 1.61 | 3.2 \times 10^{-9} |  |  |
| 0.2 | 0.94 | 18 | 20.6 | 3.6 | 2.28 | 3.5 \times 10^{-9} |  |  |

\(^a\)The yield of oxidation product per 1 g of aniline hydrochloride. \(^b\)Measured by van der Pauw method. \(^c\)Measured by two-probe method at voltage 10 V.

exceed the theoretical loss of mass for the deprotonation of

PANI hydrochloride to PANI base, which is equal to 17%.

Molecular-weight distributions obtained by SEC (Figure 1)

reveal the formation of polymeric fractions for the whole range of applied \([\text{BzQ}]\). Polymeric fractions exhibit weight-average molecular weights, \(M_w\) between 15 000 and 23 000 (Table 1) and dispersity, \(D\), between 3 and 4 (Table 1) for all samples. These results clearly prove that \(p\)-benzoquinone does not act as a terminating agent in the growth of PANI chains. Furthermore, samples prepared with \([\text{BzQ}] \geq 0.05 \text{ M}\) exhibit the presence of low-molecular-weight fraction (Figure 1) with \(M_w \approx 200\). Position of the peak of the low-molecular-weight fraction corresponded well with the position of the peak of neat 2,5-dianilino-p-benzoquinone (Figure 1).

Conductivities of the as-prepared samples are of the order of 10\(^9\) S cm\(^{-1}\) (Table 1 and Figure 2A), which is typical of a PANI salt prepared by the “standard” procedure, that is, by the oxidation of 0.2 M aniline hydrochloride with 0.25 M APS in an aqueous environment.\(^5\) No trend in conductivities is observed; they vary within a range of conductivities typical of “standard” PANI synthesis done by different experimentalists.\(^4\) This is in contrast with the addition of various amounts of hydroquinone to the reaction mixtures, which resulted in a decrease in conductivity with an increasing amount of hydroquinone.\(^6\) The conductivities of PANI bases are of the order 10\(^{-10}\)–10\(^{-9}\) S cm\(^{-1}\) independent of the voltage used in a two-point method (Figure 2A); a monotonous increase in conductivity is observed with the increase of \([\text{BzQ}]\). Besides higher conductivity, another interesting effect was observed for increasing \([\text{BzQ}]\): feasibility to measure the conductivity of bases with the van der Pauw method, which is usually not the case for “standard” PANI bases. We speculate that this might be connected with the presence of a low-molecular-weight component (Figure 1A), and it is further discussed in the section Structure of Low-Molecular-Weight Byproducts and Nature of Defects in PANI Chains (see below). A good agreement between the values obtained by the two-probe method and the van der Pauw method indicates low anisotropy in the conductivity of the pellets prepared by pressing these PANI bases.

Figure 1. (A) SEC elution curves and (B) molecular-weight distributions of PANI prepared at concentrations of \(p\)-benzoquinone varying from 0 to 0.2 M and of 2,5-dianilino-p-benzoquinone. The traces are vertically shifted for clarity. Weight-average molecular weights, \(M_w\), and dispersity, \(D = M_w/M_n\), are given in Table 1.

Temperature dependence of conductivity of samples prepared with high \([\text{BzQ}]\) mimics the one for the “standard” PANI (Figure 2B). For evaluation, we followed the approach from ref 26 for composite models because the fit of a single model was not able to cover the whole temperature range successfully. Regarding fitting results, we chose eq 1 as the most appropriate function to fit data.

\[
\sigma(T) = \sigma_0^I \exp \left(-\frac{T_0^I}{T}\right) + \sigma_0^{II} \exp \left(-\frac{T_0^{II}}{T}\right)
\]

(1)

This model assumes the existence of two major contributions to overall conductivity, one is of hopping type\(^2\) and the other is of a more general type following a simple Arrhenius-like model. The adjustable parameters (Table 2) of the model are very similar for all measured samples; hence, increase of \([\text{BzQ}]\) does not affect much the transport-related parameters, such as doping level and disorder.

UV–Visible Spectra. The UV–visible spectra of the protonated forms of the samples (recorded for solution in NMP containing 0.5 vol % of hydrochloric acid) prepared with \([\text{BzQ}]\) varying from 0.001 to 0.2 M (Figure 3A) are of the character typical of the spectrum of the PANI salt prepared without addition of \(p\)-benzoquinone (presented in Figure 3A as well). The spectrum of PANI salt consists of the bands at

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330 and 428 nm and of the band with a maximum in the near-infrared region. The band at 330 nm corresponds to the $\pi - \pi^*$ transitions in benzenoid units, whereas the bands at 428 nm and in the near-infrared region are attributed to polaronic transitions.\textsuperscript{29–31} The spectrum of neat 2,5-dianilino-p-benzoquinone recorded under the same conditions is presented in Figure 3A for comparison.

The spectrum of neat 2,5-dianilino-p-benzoquinone (Figure 3A) consists of the absorption band at 270 nm and the absorption band at 380 nm accompanied by a weak absorption tail in the region from 470 to 620 nm. To assign the absorption bands of 2,5-dianilino-p-benzoquinone, we have performed density functional theory (DFT) calculations, which have shown that the most stable structure of 2,5-dianilino-p-benzoquinone is stabilized by the intramolecular hydrogen bonding N-H⋯O=C (Figure 4A). According to the time-dependent (TD-)DFT calculations, the electronic transition between the molecular orbital energetically below the highest occupied molecular orbital (HOMO-1) and the lowest unoccupied molecular orbital (LUMO) contributes dominantly the main absorption band, which is experimentally observed at 380 nm (Figure 3A) and which occurs at 350 nm in the calculated spectrum (Figure 4B). While the molecular orbital HOMO-1 is delocalized over the whole 2,5-dianilino-p-benzoquinone molecule (Figure 4B), the LUMO is mainly localized on the 2,5-diamino-p-benzoquinone moiety (Figure 4B). The band at 270 nm can be assigned to the $\pi - \pi^*$ transitions in the phenyl rings of 2,5-dianilino-p-benzoquinone.\textsuperscript{25} However, TD-DFT calculations have shown that it is contributed by several transitions between orbitals, which are not localized only on the phenyl rings of 2,5-dianilino-p-benzoquinone.

Inspection of the spectra of the protonated forms of PANI samples (Figure 3A) demonstrate that the increase of [BzQ] in the reaction mixtures is reflected by the following features: (1) intensities of the bands connected with polaronic transitions decrease, (2) the band at 330 nm shifts to higher wavelengths, and (3) the intensity of the band at 270 nm increases with the increase of [BzQ]. These changes can be explained by two parallel processes: the concentration of polarons or the extent of polaron delocalization in PANI chains decreases with the increase of [BzQ].

UV–visible spectra of the bases (Figure 3B) display bands at 334 and 630 nm, which are typical of a PANI emeraldine base. The band at 334 nm is connected with $\pi - \pi^*$ transitions in the calculated spectrum (Figure 4B). The band at 630 nm is connected with $\pi - \pi^*$ transitions in the calculated spectrum (Figure 4B).
benzenoid units and the band at 630 nm with exciton-like transitions in quinone diimino units.\textsuperscript{32,33} The comparison of intensities of these bands shows that the intensity of the band at 630 nm decreases with the increase of [BzQ]. This is connected with a shift of the maximum of the band belonging to the transitions within benzenoid units from 334 nm to the longer wavelengths. In the spectra of the samples prepared with [BzQ] \(\geq 0.05\) M, the band at 630 nm is practically suppressed and the band belonging to the \(\pi - \pi^*\) transitions in benzenoid units is shifted to 342 nm (Figure 3B). The observed differences in spectra are in agreement with changes in the intensities of the bands observed for reduction of PANI emeraldine base to its leucoemeraldine form in NMP solution\textsuperscript{32} and indicate a decreased content of diamino quinonoid units in PANI bases. A comparable decreased content of nonprotonated diamino quinonoid units has been observed for partially self-doped PANI bases.\textsuperscript{31,34} However, the differences in the spectra of PANI bases (Figure 3B) are most probably partially due to the increasing fraction of 2,5-dianilino-p-benzoquinone in the products; the spectrum of 2,5-dianilino-p-benzoquinone recorded under the same conditions is presented in Figure 3B for comparison.

**FTIR Spectra.** The Fourier transform infrared (FTIR) spectroscopy is a bulk method that provides information on a composition of whole samples. The FTIR spectra of the as-prepared samples (Figure 5A) indicate the formation of PANI salt\textsuperscript{35} within the whole range of applied [BzQ]. Additional bands/shoulders at 1444 and 692 cm\(^{-1}\) are resolved in the spectra of the samples prepared with [BzQ] \(\geq 0.02\) M. The detail investigation of the spectra shows that the band connected with quinoid units changes its character with the increase of [BzQ]: a flat maximum between 1577 and 1560 cm\(^{-1}\) is observed for the quinonoid ring-stretching vibrations of the "standard" PANI salt,\textsuperscript{35} and a sharp maximum at 1564 cm\(^{-1}\) is observed in the spectrum of the sample prepared at [BzQ] = 0.2 M. The latter one corresponds to the position in the spectrum of 2,5-dianilino-p-benzoquinone (presented in Figure 5B). Other vibrations of 2,5-dianilino-p-benzoquinone were found in the spectrum of the sample prepared at [BzQ] = 0.2 M as very weak bands.

The FTIR spectra of the bases (Figure 5B) also exhibit bands typical of the "standard" PANI base.\textsuperscript{35} However, a set of additional bands is clearly resolved in the spectra of the samples prepared with [BzQ] \(\geq 0.01\) M. These additional bands are observed at 3236 (for full-range spectra, see Figure S1B in the Supporting Information), 1637, 1569, 1444, 1290, and 1146 cm\(^{-1}\) and their intensities increase with the increase of [BzQ] (Figure 5B). The bands at 3236, 1637, 1569, 1444, and 1290 cm\(^{-1}\) are at the positions of the bands in the spectrum of 2,5-dianilino-p-benzoquinone, which is presented in Figure 4B for comparison.
p-benzoquinone, we assign the band at 3236 cm\(^{-1}\) to the N—H stretching vibration \([\nu(N–H)]\), the band at 1637 cm\(^{-1}\) to the C=O stretching vibration \([\nu(C=O)]\), the band at 1569 cm\(^{-1}\) to the quinonoid ring-stretching vibration, the bands at 1505 and 1491 cm\(^{-1}\) to the benzenoid ring-stretching vibrations, the band at 1444 cm\(^{-1}\) to the C=C stretching of aromatic ring, and the band at 1290 cm\(^{-1}\) to the C=N stretching vibration \([\nu(C=N)]\).\(^{35}\) The last additional band at 1146 cm\(^{-1}\) resolved in the spectra of PANI bases prepared with \([\text{BzQ}]\) ≥ 0.01 M is not observed in the spectrum of 2,5-dianilino-p-benzoquinone. We assign the band at 1146 cm\(^{-1}\) to the mode of B—NH—B (B stands for benzenoid rings) and/or to the C—H in-plane deformation vibrations in the benzenoid rings \([\delta(C–H)]\) of PANI base chains.\(^{35}\) The occurrence of this band and the increase in its intensity with the increase of \([\text{BzQ}]\) indicates the reduced oxidation state of PANI chains. This is consistent with the observation in the UV—visible spectra of PANI bases (see above).

Spectra of solids obtained by evaporation of the ammonia solutions collected after deprotonation of PANI salts (Figure S1C in the Supporting Information) have shown that all the samples were doped by hydrochloric acid and no dependence on \([\text{BzQ}]\) is observed.

**Raman Spectra.** The as-prepared samples were also studied by Raman microspectroscopy. From the view of this method with a spot diameter of few microns, the samples were found to be inhomogeneous. Most of the material consisted of PANI (Figure 6A), but it was possible to find areas where additional bands were clearly resolved in the spectra (Figure 6B).

The Raman spectra of the as-prepared samples excited with the 633 nm laser line display well the level of PANI doping, as nondoped quinonoid sites are resonantly enhanced. In the spectra of the PANI areas (Figure 6A), the intensity of the C=N\(^{\ddagger}\) stretching band at 1336 cm\(^{-1}\) in the delocalized polaron structure\(^{36–38}\) (~ denotes a bond intermediate between a single and a double bond) decreases with the increase of \([\text{BzQ}]\). Simultaneously, the band connected with C=N stretching vibrations in a nondoped quinonoid structure\(^{38–40}\) at 1468 cm\(^{-1}\) increases and the ratio of the C=N stretching vibration bands\(^{36,38,41}\) at 1221 and 1257 cm\(^{-1}\) changes in favor of nondoped quinonoid structures. These observations suggest a gradual change in the structure of formed PANI samples; the doping level of PANI salts as well as the charge delocalization in PANI salts decreases with the increase of \([\text{BzQ}]\). This observation is in agreement with the trends in the UV—visible spectra of protonated forms (Figure 3A), indicating a decreasing concentration of polarons and/or extent of polaron delocalization.

Spectra with the additional Raman bands at 435, 575, and 1650 cm\(^{-1}\) were observed with the 785 nm excitation line (Figure 6B) at some spots of most of the samples including PANI prepared in the absence of p-benzoquinone. The Raman band at 435 cm\(^{-1}\) corresponds to the ring deformation vibration of the benzoquinone ring;\(^{42–45}\) the band at 575 cm\(^{-1}\) to the deformation vibration of a benzenoid ring bonded to a benzoquinone ring;\(^{46}\) and the band at 1650 cm\(^{-1}\) to the C=O stretching vibration.\(^{42}\) The intensities of these bands are not correlated with \([\text{BzQ}]\); they depend rather on the specific spot chosen for measurement. We can only speculate that this is caused by an inhomogeneous distribution of p-benzoquinone in the environment of growing PANI chains. As areas with the bands indicating the presence of p-benzoquinone and benzenoid rings attached to p-benzoquinone were observed even for PANI prepared without addition of p-benzoquinone, we confirm that p-benzoquinone forms in situ during the “standard” synthesis of PANI from 0.2 M aniline hydrochloride and 0.25 M APS in an aqueous environment.

**XPS Spectra.** High-resolution core-level N 1s X-ray photoelectron (XPS) spectra of the bases and of 2,5-dianilino-p-benzoquinone (Figure 7) show different contents of nitrogen atoms in secondary amine —NH— and imine \(\equiv\text{N—}\) configurations in the studied samples. In the N 1s XPS spectrum of the “standard” PANI base (Figure 7), the band related to \(\equiv\text{NH—}\) is observed at 399.0 eV and the band of \(\equiv\text{N—}\) is observed at 397.9 eV.\(^{46}\) Approximately 30% of nitrogen atoms were detected in the \(\equiv\text{N—}\) configuration in the
p-benzoquinone in these samples is expected because of the overstoichiometric yields (Table 1). Moreover, a decreased content of the $\equiv N -$ nitrogens in these samples can also be expected in the structure of these PANI bases, as a lower content of diamino quinonoid units has been observed by UV–visible spectroscopy (Figure 3B).

**Solid-State Nuclear Magnetic Resonance Spectra.** The comparison of solid-state $^{13}$C cross-polarization (CP)/magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectra of the bases and of 2,5-dianilino-$p$-benzoquinone (Figure 8) clearly reflects that the spectral pattern gradually differs depending on [BzQ] in the reaction mixtures. In the absence of $p$-benzoquinone, the signals resonating in the frequency region from ca. 160 to 100 ppm clearly reflect the formation of the “standard” PANI base.47–49 A highly amorphous and disordered character of the formed PANI chains is expected because of the observed broadening of the detected $^{13}$C CP/MAS NMR signals.

For [BzQ] varying from 0 to 0.01 M, there are no apparent changes in the spectral pattern of the synthesized PANI bases except of the observation of a weak and relatively broad signal at ca. 95 ppm. This signal is at the position of the signal of carbon atom C7 of 2,5-dianilino-$p$-benzoquinone (see atom assignment in Figure 8) according to the comparison with the $^{13}$C CP/MAS NMR spectrum of this compound (Figure 8, bottom spectrum). The observed broadening of the recorded signal then suggests rather incorporation of 2,5-dianilino-$p$-benzoquinone into PANI chains than some kind of interactions between 2,5-dianilino-$p$-benzoquinone and PANI chains. In the latter case, we would expect a narrow signal which would be due to the interaction shifted from the
position observed for the neat 2,5-dianilino-p-benzoquinone. However, this signal at ca. 95 ppm becomes narrow for \([\text{BzQ}_0.05] \geq 0.05\) M and a secondary set of narrow signals is superimposed on the broad signals of the PANI base. These narrow and well-separated signals resonating at 179.9, 146.2, 127.9, and 95.3 ppm clearly reflect the formation of 2,5-dianilino-p-benzoquinone, which is in agreement with the results of FTIR spectroscopy. The two-component character of the detected \(^{13}\text{C}\) CP/MAS NMR spectra for \([\text{BzQ}_0.05-0.2] \geq 0.05\) M indicates weak interactions between 2,5-dianilino-p-benzoquinone and the PANI matrix. This finding rather suggests the formation of nano-/micro-segregated domains of 2,5-dianilino-p-benzoquinone dispersed in the PANI matrix, which is in agreement with the inhomogeneity of the samples observed by Raman microspectroscopy.

**Structure of Low-Molecular-Weight Byproduct and Nature of Defects in PANI Chains.** The results described and discussed above have shown that the reaction of aniline hydrochloride with APS in an aqueous environment under various \([\text{BzQ}]\) results in the formation of PANI, whose molecular structure gradually changes with the increase of \([\text{BzQ}]\), and under \([\text{BzQ}] \geq 0.05\) M also results in the formation of a low-molecular-weight byproduct.

The low-molecular-weight byproduct is formed for aniline oxidation carried out with \([\text{BzQ}] \geq 0.05\) M (see SEC elution curves in Figure 1). The positions of peaks of the low-molecular-weight fraction in SEC chromatograms correspond well with the position of the peak of neat, commercially obtained 2,5-dianilino-p-benzoquinone (Figure 1). Both FTIR and solid-state \(^{13}\text{C}\) CP/MAS NMR spectra of the PANI bases prepared with \([\text{BzQ}] \geq 0.05\) M (Figures 5B and 8) exhibit the occurrence of additional bands at the positions corresponding to the positions of the bands of neat 2,5-dianilino-p-benzoquinone. Further, the yields of the products of reactions carried out with \([\text{BzQ}] \geq 0.05\) M (Table 1) exceed the theoretical value for oxidation of aniline hydrochloride to PANI hydrochloride. According to all these facts, we conclude that the low-molecular-weight byproduct is 2,5-dianilino-p-benzoquinone. This is in accord with the fact that the reaction of aniline with p-benzoquinone in the absence of APS provides 2,5-dianilino-p-benzoquinone\(^{13}\) and with the fact that oxidation of aniline with weaker oxidants provides under certain conditions 2,5-dianilino-p-benzoquinone instead of PANI,\(^{24}\) which is due to the in situ oxidation of aniline to p-benzoquinone.

Regarding the structure of PANI, the SEC analysis has shown that the weight-average molecular weights of PANI samples are between 15,000 and 23,000 within the whole range of \([\text{BzQ}]\). According to this, we clearly conclude that p-benzoquinone does not act as a terminating agent in the growth of PANI chains. Employed spectroscopic methods show differences in the structure of PANI samples prepared under various \([\text{BzQ}]\). The observed differences in the spectra are more or less proportional to \([\text{BzQ}]\), and we thus presume formation of structure defects in PANI chains, the concentration of which depends on \([\text{BzQ}]\). Both UV–visible and XPS spectra (Figures 3B and 7) show a decreased content of diamino quinonoid units in PANI bases prepared with higher \([\text{BzQ}]\). Even though this is partially caused by a superposition with the spectrum of the low-molecular-weight byproduct, it is consistent with the information on increased concentrations of benzenoid units in these samples, which is deduced from the occurrence of the band at 1146 cm\(^{-1}\) in the FTIR spectra of PANI bases (Figure 5B). Raman spectroscopy and UV–visible spectroscopy of the PANI salts then provide information on the decreased concentration of polarons and/or the lower extent of polaron delocalization. This is not in contradiction with previous data; as the number of available diamino quinonoid units in PANI chains decreases, the extent of their protonation decreases as well. We speculate that protonation of diamino quinonoid units in PANI chains with structure defects is less thermodynamically favored in comparison to their protonation in an ideal PANI chain. In the previous point, we expect that the formation of diamino quinonoid units is possible in PANI chains with a certain distance between structure defects only.\(^{31,34,50}\) If the distance between the structure defects decreases, the formation of diamino quinonoid units in PANI chains is most probably less thermodynamically favored. Because of this, the decrease of concentration of diamino quinonoid units in PANI chains is connected with the increase of concentration of benzenoid units. According to this, we expect that the structure of PANI samples prepared at higher \([\text{BzQ}]\) is disturbed by structure defects.

A reaction comparable to the reaction of primary amine with p-benzoquinone (Scheme 3) can be suggested for p-benzoquinone and two PANI chains (Scheme 4). Such cross-linking of PANI chains would probably only slightly affect the conductivity of PANI and would lower the extent of polaron delocalization observed in Raman spectra. Both expectations are in agreement with experimental data. However, an increase in molecular-weight values with the increase of \([\text{BzQ}]\) would be expected or maybe an insoluble PANI network would be obtained. Our experimental data do not meet these expectations, and thus, we do not expect cross-linking of PANI chains by 2,5-di(diphenylamino)-p-benzoquinone moieties to be the nature of structure defects in the studied polymers. Furthermore, exposure of “standard” PANI base (\([\text{NH}^+\]) + [==N=] = 0.2 M) to p-benzoquinone (\([\text{BzQ}] = 0.2\) M) in hydrochloric acid (\([\text{HCl}] = 0.2\) M) for 48 hours resulted in formation of a PANI salt which did not exhibit any additional bands in the FTIR spectra.

Hydrogen bonding between the hydrogen of PANI amino group and the carbonyl group of 2,5-dianilino-p-benzoquinone (Scheme 5) might theoretically lower the electron density in PANI chains, which could be reflected as a reduced oxidation state in the UV–visible spectra of the PANI base forms and could cause increased concentration of benzenoid units in the
PANI base chains detected by FTIR spectroscopy. To prove or exclude such nature of structure defects in PANI chains, we have measured the UV–visible spectra in NMP containing 0.5 vol % of triethanolamine and 0.5 wt % of lithium bromide. The obtained spectra (not shown) exhibited a slightly increased (relatively to the band at ≈334 nm) intensity of the band at 630 nm compared to the measurements in solvent without addition of lithium bromide, but its absorbance decreased with the increase of [BzQ] and maintained the trends observed in Figure 3B. As addition of lithium bromide should result in cleavage of hydrogen bonds, we conclude that structural defects have to be attached on PANI backbones by covalent bonds or have to be part of PANI chains which affect both the extent of electron delocalization and PANI oxidation state. On the other hand, hydrogen bonding between PANI and 2,5-dianilino-p-benzoquinone most probably affects supramolecular structure of PANI in solid phase. We speculate that this effect changes the supramolecular structure of PANI bases prepared with [BzQ] ≥ 0.02 M and thus allows measurement of conductivity of these PANI bases by van der Pauw method (see above).

According to the observation of a weak and relatively broad signal at ca. 95 ppm in the 13C CP/MAS NMR spectra of PANI bases prepared with [BzQ] = 0.002–0.02 M (Figure 8), we expect rather an incorporation of 2,5-dianilino-p-benzoquinone-like moiety into PANI chains. Structure units fulfilling this precondition were previously suggested by Venancio et al. (Scheme 6A).51 Regarding the formation of a pendant 5-anilino-p-benzoquinone-2-yl group, we speculate that it generates by a reaction of p-benzoquinone with one molecule of aniline and one PANI chain and the reaction proceeds in analogy with the reaction of p-benzoquinone with two molecules of aniline.

Scheme 7. Assumed Substitution of PANI Chain by the Pendant 5-Anilino-p-benzoquinone-2-yl Group

CONCLUSIONS

The structure and properties of the products prepared by the oxidation of 0.2 M aniline hydrochloride with 0.25 M APS have been investigated under concentrations of p-benzoquinone varying from 0 to 0.2 M. It was shown that p-benzoquinone does not act as a termination agent in the oxidative polymerization of aniline. Formed products consisted of two components: (1) PANI with weight-average molecular weight between 15 000 and 23 000 and dispersity between 3 and 4 and (2) low-molecular-weight byproduct, 2,5-dianilino-p-benzoquinone. The content of 2,5-dianilino-p-benzoquinone increased with the increasing concentration of p-benzoquinone in the reaction medium. This has been deduced from the increasing yield and the SEC, FTIR, XPS, and NMR analyses of the products.

The molecular structure of PANI depended on the amount of p-benzoquinone added into the reaction mixture. Raman spectra have shown that the PANI doping level and the charge delocalization both decrease with the increasing concentration...
of p-benzoquinone. This is in agreement with observations in the UV–visible spectra of both protonated samples and bases, indicating that the chain regularity was disturbed, despite no change in molecular weight was observed. The FTIR spectra of the PANI base forms have shown an increased concentration of benzenoid units in PANI chains. According to the 13C CP/MAS NMR spectra and the FTIR spectra, we assume the presence of the pendant 5-anilino-p-benzoquinone-2-yl group on PANI nitrogen atoms as structure defects, which affects both the geometry of PANI chains and the extent of polaron delocalization. Furthermore, the bands typical of p-benzoquinone were observed even in the Raman spectra of PANI prepared without addition of p-benzoquinone. This confirms in situ oxidation of aniline to p-benzoquinone as an alternative route in the oxidation of aniline hydrochloride with APS leading to PANI.

**MATERIALS AND METHODS**

**Chemicals.** Aniline hydrochloride (98%; Penta, Czech Republic), APS (98%; Lach-Ner, Czech Republic), p-benzoquinone (≥98%; Sigma-Aldrich), hydrochloric acid (p.a., 35%; Lach-Ner, Czech Republic), ammonium hydroxide (p.a., 25%; Lach-Ner, Czech Republic), triethanolamine (p.a.; Lach-Ner, Czech Republic), N,N-dimethyl-2-pyrrolidone (NMP; ≥99%; Carl-Roth, Czech Republic), lithium bromide (Sigma-Aldrich, Czech Republic), and 2,5-dianilino-p-benzoquinone (Specs Research Laboratory, Delft, Netherlands) were used as supplied.

**Preparation.** Aniline hydrochloride (0.2 M) oxidation with APS (0.25 M), that is, at the oxidant-to-monomer mole ratio 1.25, was carried out under various concentrations of p-benzoquinone (0–0.2 M). Briefly, equal volumes (50 mL) of aqueous solution of aniline hydrochloride (20 mmol) and of aqueous solution containing both APS (25 mmol) and p-benzoquinone (0–20 mmol) were mixed in a beaker, briefly stirred and left to react for 24 h at room temperature. The obtained solids were isolated by filtration, rinsed with 0.2 M hydrochloric acid and then with acetone, and dried in air and then over silica gel. Parts of each sample were deprotonated to convert a PANI salt to a PANI base by suspension in a large excess of 1 M ammonium hydroxide for 48 h, subsequently washed with water and acetone, and dried as described above.

**Characterization.** SEC was performed on a Calc 100 chromatograph (Labio, Czech Republic) equipped with a PLgel mixed-C column (Polymer Laboratories, UK) using NMP containing 0.005 g cm−3 of lithium bromide as the eluent at the flow rate of 0.50 mL min−1. Samples in base forms were dissolved in mobile phase containing 0.005 g cm−3 of triethanolamine. Detection of the analytes was done spectrophotometrically at 340 nm. The system was calibrated by polystyrene standards using refractive index detection.

Room-temperature conductivity of PANI salts and some bases was determined by a four-point method in van der Pauw arrangement using a Keithley 220 Programmable Current Source, a Keithley 2010 Multimeter as a voltmeter, and a Keithley 705 Scanner equipped with a Keithley 7052 Matrix Card on PANI powder compressed to pellets of 13 mm in diameter and ≥1 mm thickness with a manual hydraulic press at 530 MPa. A two-point method was used for PANI bases with a Keithley 6517 electrometer/high resistance system at voltages 10, 100, and 1000 V. Before these measurements, circular gold electrodes were deposited on both sides of the pellets. Let us mention that there are principal differences between measurements by the four-point method in van der Pauw arrangement and by the two-point method with circular gold electrodes deposited on both sides of the pellets. The four-point van der Pauw method uses separate voltage and current contacts, which is not the case of the two-point method. The measured current is perpendicular to the axis of cylindrical samples within van der Pauw measurements, whereas it is parallel with this axis for the two-point method. Pellets for measurements are prepared by pressing, and certain anisotropy in resistivity thus has to be expected. Because of this reason, it is useful to compare the results obtained by both methods as they do not describe the same. If the conductivity of samples is low, modified van der Pauw methods have to be used.52

Temperature dependence of the resistivity in the range from about 5 K up to 320 K was measured in a closed-cycle cryostat OmniPlex GMX19 with the second stage of a Model DE-204SL DE-210SF expander and an ARS-10HW helium compressor made by Advanced Research Systems, Inc. As a temperature controller, the LakeShore Model 336 was used. The measured sample was held in a flowing stream of helium vapor, which provides a good control over the temperature homogeneity in the samples. Before temperature measurements, the sample chamber with samples has been evacuated (ca. 0.1–0.01 Pa) for several hours at room temperature (at about 305 K) to get rid of moisture. When the resistivity of the samples is about 105 Ω cm or higher, the four-point van der Pauw method in a modified configuration can be used. The corresponding experimental setup used a Keithley 6220 programmable current source, a Keithley 6485 picoammeter, a Keithley 2000 multimeter, a Keithley 706 scanner equipped with a Keithley 7152L low-current matrix card, and two Keithley 6517B electrometers as high impedance voltmeters. In such configuration, the so-called common-mode current is reduced because low impedance terminals of all devices are not floating but are connected and grounded together. For more details, see ref S2.

UV–visible spectra were recorded on a Lambda 20 spectrometer (PerkinElmer, UK) using quartz cuvettes and PANI solutions in NMP with 0.5 vol % of triethanolamine for PANI bases or in NMP with 0.5 vol % hydrochloric acid for PANI salts. Infrared spectra were recorded using a Thermo Nicolet NEXUS 870 FTIR Spectrometer (DTGS TEC detector; region 4000–400 cm−1; 64 scans; resolution 2 cm−1) in transmission mode in potassium bromide pellets. The spectra were corrected for carbon dioxide and humidity in the optical path. Raman spectra were collected on a Renishaw inVia Reflex Raman spectrometer (Leica DM LM microscope; objective magnification X50) with a HeNe 633 nm laser (holographic grating 1800 lines mm−1) and a near-infrared diode 785 nm laser (1200 lines mm−1) at three different spots of the samples spread on a steel support.

XPS measurements were carried out with a K-Alpha+ spectrometer (Thermo Fisher Scientific, East Grinstead, UK). The samples were analyzed using a micro-focused, monochromated Al Kα X-ray source (400 μm spot size) at an angle of incidence of 30° (measured from the surface) and an emission angle normal to the surface. The kinetic energy of the electrons was measured using a 180° hemispherical energy analyzer operated in the constant analyzer energy mode at 200 and 50 eV pass energy for the survey and high-resolution spectra, respectively. Data acquisition and processing were performed using a Thermo Advantage software. The XPS...
spectra were fitted with Voigt profiles obtained by convolving Lorentzian and Gaussian functions. The analyzer transmission function, Scofield sensitivity factors, and effective attenuation lengths (EALs) for photoelectrons were applied for quantification. EALs were calculated using the standard TPP-2M formalism. The binding energy (BE) scale was controlled by the well-known position of the photoelectron C−C and C−H, C−O, and C(=O)−O C 1s peaks of polyethylene terephthalate and Cu 2p, Ag 3d, and Au 4f peaks of metallic Cu, Ag, and Au, respectively. The BE uncertainty of the reported measurements and analysis is in the range of ±0.1 eV.

Solid-state NMR (ss-NMR) spectra were performed on a Bruker AVANCE 500 WB/US NMR (Karlsruhe, Germany, 2013) at 11.7 T in 4 mm ZrO2 rotors at a MAS frequency of 11 kHz. The 13C CP MAS NMR spectra were measured by applying a $\Delta f(13\text{C})$ field nutation frequency of 62.5 kHz, a contact time of 1 ms, and a recycle delay of 5 s. The number of spectra accumulation was 1k to reach acceptable signal-to-noise ratio. The 13C NMR scale (176.03 ppm) for 13C NMR signals were acquired under the 11 kHz. The 13C CP MAS NMR spectra were measured by applying high-power 1H dipolar decoupling SPINAL 64. Powdered 2013) at 11.7 T in 4 mm ZrO2 rotors at a MAS frequency of sample temperature was kept constant at 295 K. To compensate frictional heating of the sample, active cooling was applied. The actual sample temperature was calibrated by monitoring the $^{207}$Pb chemical shift in Pb(NO$_3$)$_2$ at various temperatures. 55

DFT Calculations. The quantum chemical calculations were performed at the DFT level of theory with the CAM-B3LYP hybrid exchange-correlation functional combined with the 6-311+G(d,p) basis set. The molecular geometry was monitoring the $\Delta f(13\text{C})$ field nutation frequency of 62.5 kHz, a contact time of 1 ms, and a recycle delay of 5 s. The number of spectra accumulation was 1k to reach acceptable signal-to-noise ratio. The 13C NMR scale (176.03 ppm) for 13C NMR signals were acquired under the 11 kHz. The 13C CP MAS NMR spectra were measured by applying high-power 1H dipolar decoupling SPINAL 64. Powdered 2013) at 11.7 T in 4 mm ZrO2 rotors at a MAS frequency of sample temperature was kept constant at 295 K. To compensate frictional heating of the sample, active cooling was applied. The actual sample temperature was calibrated by monitoring the $^{207}$Pb chemical shift in Pb(NO$_3$)$_2$ at various temperatures. 55

FTIR spectra (range 4000−400 cm$^{-1}$): spectra of as-prepared samples (salts), spectra of ammonia-treated samples (bases) with the spectrum of 2,5-dianilino-p-benzoquinone shown for comparison, and spectra of solids obtained by evaporation of the collected ammonia solutions (PDF)

ASSOCIATED CONTENT

Supporting Information
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FTIR spectra (range 4000−400 cm$^{-1}$): spectra of as-prepared samples (salts), spectra of ammonia-treated samples (bases) with the spectrum of 2,5-dianilino-p-benzoquinone shown for comparison, and spectra of solids obtained by evaporation of the collected ammonia solutions (PDF)

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Notes
The authors declare no competing financial interest.

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