

POLYANILINE: FORMS AND FORMATIONJaroslav STEJSKAL^a, Pavel KRATOCHVIL^a and Aubrey D. JENKINS^b^a *Institute of Macromolecular Chemistry,**Academy of Sciences of the Czech Republic, 162 06 Prague 6, Czech Republic*^b *School of Chemistry and Molecular Sciences,**University of Sussex, Falmer, Brighton BN1 9QJ, U.K.*

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Dedicated to Dr Blahoslav Sedlacek on the occasion of his 70th birthday.

The forms of polyaniline, viz. pernigraniline, emeraldine and leucoemeraldine, their mutual transformations and their roles in the chemical polymerization of aniline, are discussed. Absorption spectra of its various protonated forms and corresponding bases are reported. A simple reaction scheme is proposed to account for the colour and acidity changes during polymerization.

Polyaniline^{1,2} (PANI) has properties that are not often found with other polymers – it is electrically conducting and coloured. Moreover, polyaniline exists in a variety of forms which differ in degree of oxidation or extent of protonation, or both. A description of these forms, their basic properties and their roles in the formation of polyaniline are briefly outlined in this paper. A scheme of interrelated structures, which accounts for the spectrophotometric observations, is proposed and discussed.

Polyaniline is prepared by chemical or electrochemical oxidation of aniline. In chemical oxidation by strong oxidizing agents in aqueous acids, PANI is obtained as an insoluble fine precipitate. When this reaction is carried out in the presence of a suitable steric stabilizer, e.g., poly(vinyl alcohol), dispersions of submicrometre particles composed of a polyaniline core and a stabilizer shell can be prepared^{3,4}. Such dispersions, rather than true solutions, can conveniently be used in the spectrophotometric characterization of PANI (refs^{5,6}); this approach has been used in the present study.

EXPERIMENTAL

A stock solution of poly(vinyl alcohol) (degree of polymerization 1 600; type 72 000 by Fluka, Switzerland) was added to an aqueous solution of aniline hydrochloride and the mixture was cooled to 0–2 °C. An aqueous solution of ammonium peroxydisulfate was introduced to start polymerization. The final concentrations of the components were: 0.2 M aniline hydrochloride, 0.1 M ammonium peroxydisulfate and 2 wt.% poly(vinyl alcohol).

The changes of acidity during the oxidation of aniline were followed with a PHM64 Research pH Meter, Radiometer, Denmark, using a glass electrode with a calomel reference.

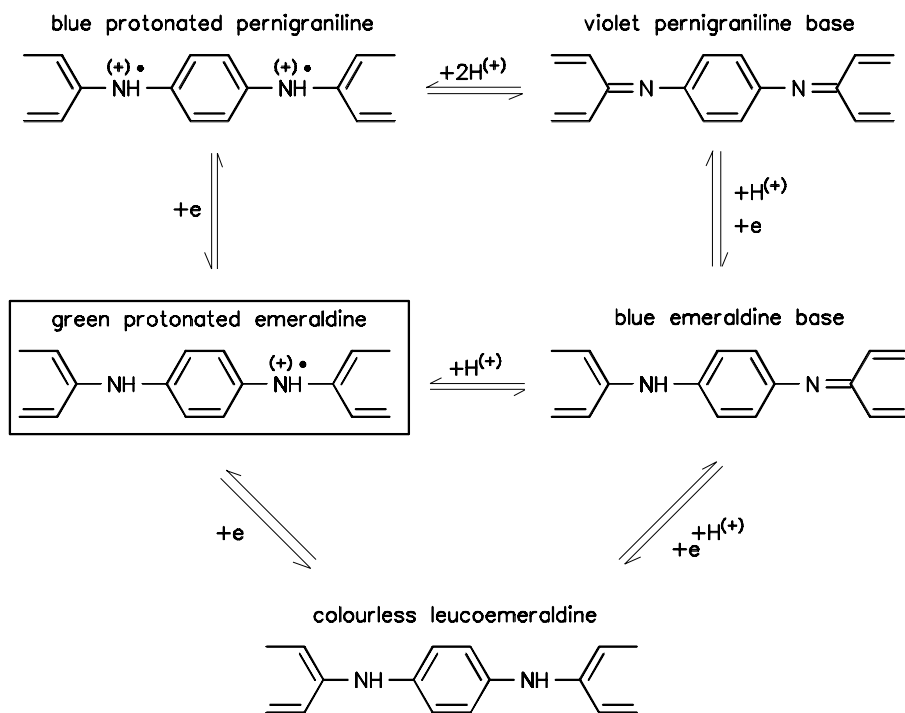
After dilution with excess of hydrochloric acid or ammonium hydroxide, the optical absorption of the reaction mixture or of the dispersion was recorded with a Hewlett-Packard 8451A diode-array spectrophotometer.

RESULTS AND DISCUSSION

Polyaniline Forms

For the discussion of polyaniline forms and their interconversions, the following Scheme 1 is proposed.

The most important form of PANI, protonated emeraldine, is produced by the oxidative polymerization of aniline in aqueous acids. Its characteristic green colour is the reason for its name. It is electrically conducting (conductivity^{7,8} $\sigma \approx 10^{-2}$ – 10^0 S cm⁻¹), due to the presence of cation radicals⁹ in its structure (Table I). The positive charge on aniline units is balanced by negatively-charged counterions, typically chloride anions. This form of PANI is stable. It is, however, difficult to process as it deprotonates and



SCHEME 1

decomposes below a softening or melting point. With the exception of concentrated sulfuric acid, it is insoluble in any solvent¹⁰. The problem of limited processibility can be addressed by the preparation of PANI dispersions. Alternatively, instead of inorganic counterions, PANI may contain anions derived from bulky organic acids, e.g., dodecylbenzenesulfonic or camphorsulfonic acid. Such salts are soluble in some organic solvents^{11,12}.

Protonated emeraldine converts to the blue emeraldine base in alkaline medium. This, probably best-known, transition proceeds⁶ at pH \approx 6–7. The emeraldine base has the same number of unprotonated imine and amine groups^{9,13}; it is electrically non-conducting. Unlike the protonated form, it is partially soluble in some organic solvents, e.g., in *N*-methylpyrrolidone.

Emeraldine can be reduced to colourless and electrically non-conducting leuco-emeraldine by phenylhydrazine¹⁴ or hydrazine¹⁵. The latter procedure was used in the determination of molar mass of polyaniline by light scattering¹⁵ in order to remove the colouration, and thus undesirable optical absorption, of emeraldine solutions.

The oxidation of emeraldine by strong oxidizing agents, e.g., ammonium peroxydisulfate or hydrogen peroxide, yields the fully oxidized form of polyaniline, pernigraniline (Scheme 1). The conversion to pernigraniline is completed in strongly acidic media typically in seconds but may take hours in alkaline systems. Protonated pernigraniline most likely exists in the dication diradical form^{1,16}. It is again blue, but of a different shade compared with that of the emeraldine base. The differences between the absorption bands of the two blue forms can be seen in Fig. 1 and in Table I.

The pernigraniline base is violet (Scheme 1, Table I). The absorption peaks¹⁷ correspond well to those of pernigraniline prepared electrochemically^{18,19}. The acid–base transition of pernigraniline proceeds in strongly acidic region, at pH \approx 0–1. Because of the variety of coloured forms and their interconversion, polyaniline is a good candidate for application in electrochromic devices²⁰.

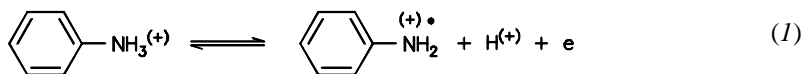
TABLE I
Colouration, corresponding absorption maxima λ_{\max} (in nm), and the occurrence of polyaniline forms

Polyaniline	Protonated form	Base
Pernigraniline	blue	violet
	$\lambda_{\max} = 350, 690$	$\lambda_{\max} = 340, 540$
	pH < 0.5–1	pH > 0.5–1
Emeraldine	green	blue
	$\lambda_{\max} = 350, 430, 810$	$\lambda_{\max} = 340, 610$
	pH < 6–7	pH > 6–7

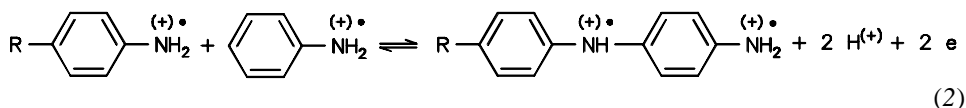
Formation of Polyaniline

The following reactions are proposed to account for the colour and acidity changes observed during the oxidation of aniline:

The polymerization of aniline by oxidizing agents proceeds in acidic media where it exists mainly as an anilinium cation. The aniline cation radical is assumed to be the first product of aniline oxidation^{1,16,21-23}:



Aniline cation radicals then recombine into benzidine or *N*-phenyl-*p*-phenylenediamine^{16,24} (*p*-semidine) or they participate in the growth of a polyaniline chain :



R = H or pernigraniline chain

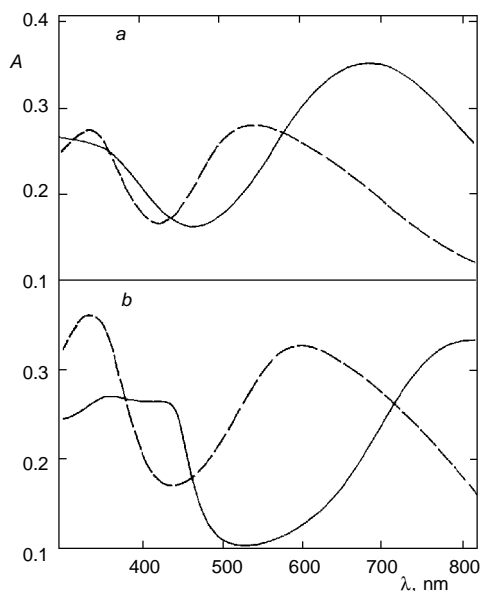
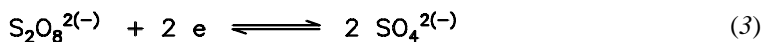


FIG. 1

Absorption spectra of **a** pernigraniline and **b** emeraldine (both $7.7 \cdot 10^{-3} \text{ mol l}^{-1}$) in the protonated form (in 1 M hydrochloric acid; full lines) and of the bases (in 1 M ammonium hydroxide; broken lines). Emeraldine was oxidized to pernigraniline by addition of an equimolar amount of ammonium peroxydisulfate

A transparent blue colouration, observed in the early stages of oxidation, corresponds to the formation of low-molecular-weight cation radicals, the structure of which is not exactly known. Later on as the polymerization proceeds, the reaction mixture becomes deep blue. A comparison of the spectra recorded during the polymerization (Fig. 2) with those of the PANI forms (Fig. 1) indicates that the deep blue colouration corresponds to the protonated pernigraniline structure¹⁷ in its dication diradical form^{1,16,25}. Also, when a drop of a polymerizing mixture is diluted with an alkali, a brilliant violet colouration of the pernigraniline base is observed (Figs 1 and 2), as expected. The protons released during the oxidation, according to Eqs (1) and (2), are responsible for the decrease of pH during the oxidation of aniline^{17,26} (Fig. 3).

The electrons abstracted from aniline in the above oxidation processes are consumed in the reduction of oxidizing agents, e.g., peroxydisulfate to sulfate:



If all the oxidizing agent has been consumed while reduced and unreacted aniline is still present, pernigraniline takes over the role of oxidant and becomes reduced to emeraldine:

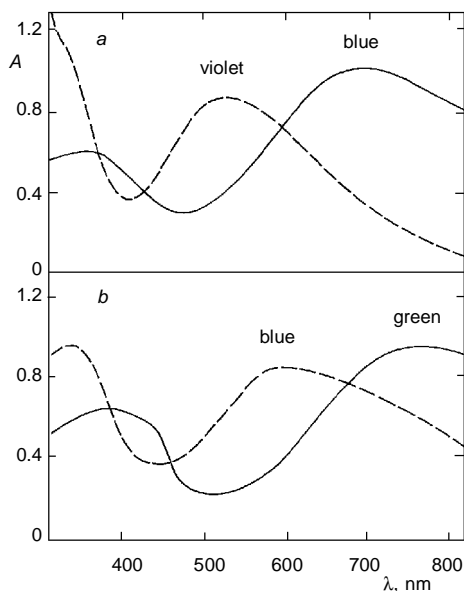
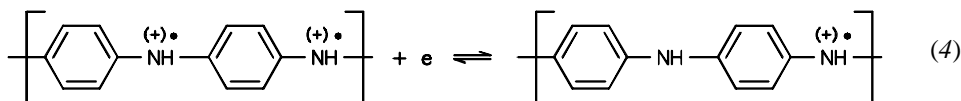


FIG. 2
Absorption spectra recorded during *a* the blue and *b* the green stage of the dispersion polymerization of aniline hydrochloride. The reaction mixture was diluted 60 times with 1 M hydrochloric acid (full lines) or alkalinized with 1 M ammonium hydroxide (broken lines) prior to measurement of the spectra. Cell thickness, 0.1 cm. (Taken from ref.¹⁷.)

The oxidative polymerization of aniline thus proceeds until all the pernigraniline has been converted to emeraldine. The colour of the reaction mixture quickly turns green during this stage (Fig. 2), but additional, less pronounced changes in the spectra can be recorded on a scale of hours⁶. Protons produced during this polymerization step result in another decrease of pH (Fig. 3). The polymerization stops after the final product, stable protonated emeraldine, has been produced. A more or less deep minimum is observed on the time dependence of pH at this point.

Preliminary EPR experiments showed that the number of radicals increases during the polymerization but it does not change during the blue-to-green transition. This supports the idea that the protonated pernigraniline itself is able to act as an oxidizing agent in the polymerization of aniline. As it becomes reduced by aniline according to Eq. (4), aniline is at the same time polymerized according to Eqs (1) and (2). Pernigraniline, containing one cation radical for each aniline unit, becomes converted into two equivalents of emeraldine, having one cation radical per two aniline units. The number of cation radicals thus remains constant during this reaction phase. Pernigraniline seems to be able to act as a mediator^{17,27} in electron-transfer processes during the polymerization of aniline²⁷. The ability of pernigraniline to oxidize aniline may be responsible for the autoacceleration effect observed during the polymerization^{17,28}. Autoacceleration is reflected, e.g., by an exponential increase of the number of released protons, i.e., by the linear decrease of pH during the polymerization stage (Fig. 3).

The protonated pernigraniline is unstable and, especially in the presence of excess oxidizing agent, it converts into colourless low-molecular-weight oxidation products (1,4-benzoquinone or its derivatives), typically within tens of minutes in dilute PANI

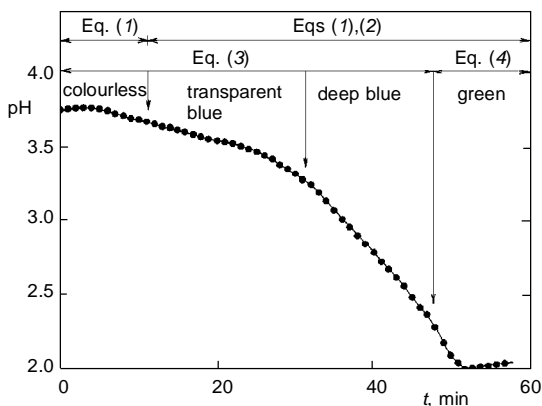
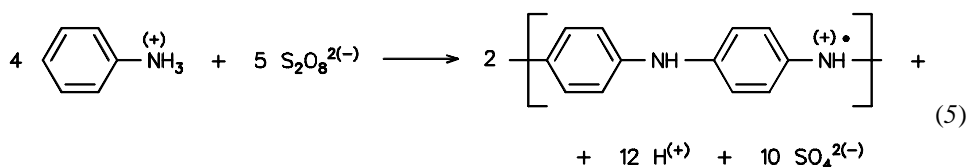


FIG. 3

Acidity changes and the colouration of the reaction mixture observed during the dispersion polymerization of aniline hydrochloride. The reactions governing the individual phases are given at the top of the Figure

dispersions. Much slower decomposition, typically on a scale of hours, occurs also with the pernigraniline base.

The redox processes outlined by Eqs (1)–(4) proceed simultaneously, their mutual balance being dependent on the concentration of the components during the polymerization. The reactions governing the individual stages are denoted in Fig. 3. To sum up, for an addition of one aniline molecule to the growing chain, three electrons have to be abstracted, according to Eqs (1) and (2). For the final reduction of pernigraniline to emeraldine, according to Eq. (4), one electron has to be added per two aniline units. Consequently, the net balance amounts to 2.5 electrons, which are removed by ammonium peroxydisulfate according to Eq. (3). Thus 1.25 mol of ammonium peroxydisulfate is expected to be needed for the polymerization of 1 mol of aniline into emeraldine^{28,29}:



If peroxydisulfate has been used in excess of the stoichiometric ratio, there may still be unreduced pernigraniline present after all the aniline has been consumed. The conversion of the blue colour to green is then slow, unlike the preceding case, as blue pernigraniline decomposes into colourless low-molecular-weight products and only the green colouration of emeraldine remains. With a large excess of oxidant, only brownish decomposition products are obtained.

Open Problems

There are several points which challenge further investigation. In the discussion of their thermochemical measurements, Fu and Elsenbaumer²⁹ reported that polymerizations which start at initial pH < 1.9 (and the pH becomes even lower during the polymerization¹⁷) proceed in a single fast step, while in less acidic media (initial pH > 4.3) a much slower two-step mechanism is observed. However, the reaction heat produced during the polymerizations is exactly the same, regardless of pH. They concluded that the polymerization kinetics are very different as a result of the change in the acidity of the reaction medium. Such a conclusion could be explained by the fact that in strongly acidic mixtures, with pH < 0.5–1, pernigraniline exists mostly in a protonated state while in less acidic media the degree of protonation might be substantially lower. Considering the mechanism of chain growth postulated in Eq. (2), the protonation of pernigraniline may be of crucial importance for the progress of polymerization.

From measurement of the visible spectra of pernigraniline at various pH values, it can be concluded that the pernigraniline base becomes significantly protonated only at $\text{pH} < 0.5\text{--}1$ (Table I). It should be noted that, during polymerization, protonated pernigraniline is also produced in less acidic media, e.g., at $\text{pH} \approx 2\text{--}3.5$ in the case of a simple polymerization of aniline hydrochloride (Fig. 3). Under these conditions pernigraniline is expected to deprotonate to its base; however, this has never been observed. Possibly, the polymerization (and thus the formation of the protonated form according to Eq. (2)) is much faster than deprotonation; also the subsequent reduction to emeraldine according to Eq. (4) could be preferred to the alternative deprotonation according to Scheme 1.

Although the equations describing the polymerization of aniline seem to be straightforward, the rate of the individual reactions and their mutual balance may be controlled by more subtle effects. It has been reported in several cases that the presence of PANI accelerates the polymerization of aniline^{17,23}. Also, the presence of low-molecular-weight compounds, which form cation radicals on oxidation, increases the rate of PANI formation²⁷; *p*-phenylenediamine, its *N*- or *N,N'*-substituted derivatives or benzidine, may serve as examples^{27,29,30}. Such compounds may play the role of mediator in electron-transfer processes^{27,31}, and they may increase the reaction rate, just as catalysts affect the rate of chemical reactions.

We have also observed that potassium thiocyanate effectively blocks the progress of polymerization. This compound is known to reduce the extent of hydrogen bonding in aqueous solutions. Structures based on hydrogen bonding or aniline/polyaniline charge-transfer complexes may thus participate in the molecular mechanism of the oxidation.

CONCLUSIONS

During the oxidative polymerization of aniline, the growth of polyaniline chains proceeds in the protonated pernigraniline dication diradical form. The progress of polymerization in the pernigraniline form and the subsequent reduction to the emeraldine cation radical by excess aniline explains the observed colour and acidity changes. The preparation of polyaniline dispersions facilitates the investigation of both the forms and formation of polyaniline by UV-VIS spectroscopy.

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