On the mechanism of oxidative polymerization of aniline

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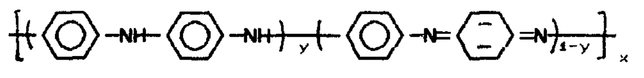
Oxidative polymerization of aniline in aqueous dispersion stabilized by poly(vinyl alcohol coacetate) was studied *in situ* by electron absorption spectroscopy. A mechanism is proposed, accounting for the dependence of the main polymerization steps (oxidation and reduction) on both the pH of the medium and the oxidation state of the chain.

(Keywords: polyaniline; dispersion; electron absorption spectroscopy; mechanism of polymerization)

Introduction

Polyaniline (PANI) can be obtained by the chemical or electrochemical oxidation of aniline (ANI) in acidic aqueous medium[1–11]. The general structure of PANI may be presented as:



where $(1-y)$, or the corresponding ratio of imine to amine nitrogens (I/A), accounts for the oxidation state (OS) of PANI shown as no. 6 in *Table 1*. The conductive form of PANI is associated with emeraldine OS.

The mechanism of oxidative polymerization of ANI (both chemical and electrochemical) has been studied by many authors[1–8]. However, the results are quite controversial and the mechanism is still being debated due to the experimental difficulties in identifying the reaction intermediates associated with: (1) high reaction rate of the precipitation polymerization of ANI; and (2) insolubility of the reaction products, even those with a low degree of polymerization, in most organic solvents. Many authors[5,7,8] identified *p*-aminodiphenylamine (PADPA) as a soluble intermediate. In the electrochemical polymerization of ANI, Genies and Tsintavis[2] used electron absorption spectroscopy to observe *in situ* a soluble intermediate absorbing at 420 nm, which was assigned to nitrenium cation $C_6H_5\overset{+}{N}H$. Wei *et al.*[5], based on their own experimental results and those of other authors[2], have proposed the most generalized mechanism for polymerization of ANI, in wich the rate-determining step is the formation of PADPA. Propagation of the polymer chain proceeds by consecutive oxidation step (starting with PADPA) and reduction step by addition of ANI to the growing chain end.

However, the following questions still remain:

—What is the difference in the reaction conditions determining the main steps (oxidation and reduction), and thus their separation in order to identify the reaction intermediates?

—Why was PANI in emeraldine OS always obtained in oxidative polymerization, instead of fully reduced (leucoemeraldine) OS as Wei's mechanism[5] suggested?

MacDiarmid *et al.*[6] have found that pernigraniline (the fully oxidized form of PANI) is formed at the initial stage of oxidative polymerization of ANI, followed by reduction to emeraldine OS by addition of ANI, present in the reaction system, to the growing chain. However, the authors did not comment on the notable fact that termination of polymerization and isolation of pernigraniline took place via alkalization of the reaction mixture.

We have succeeded in preparing stable aqueous dispersions of PANI with spherical particles of less than 200 nm using poly(vinyl alcohol coacetate) (PVAL) as a steric stabilizer[12,13]. Using electron absorption spectroscopy it was easy to follow both the formation of intermediates *in situ* and their transformation (as well as the interconversions of the final product) on changing the pH of the medium. Based on the results, a mechanism of oxidative polymerization of ANI, except the formation of PADPA, is proposed.

Experimental

PANI dispersions and free-standing films cast from them were prepared as described previously[12,13] and studied by electron absorption spectroscopy. Both dispersions and aqueous solutions, in which the free-standing films were immersed, were acidified and alkalized by means of 1–4 molar solutions of HCl and NaOH. After equilibrating at different pH values, spectra were recorded on a Specord M42 (Carl Zeiss) apparatus.

Conductivity measurements of free-standing films cast from dispersions were performed using the four-probe technique; these films contained both PANI and PVAL.

Results and discussion

Figure 1a presents the absorption spectra of intermediates obtained at the initial stage of ANI polymerization. Spectra A* and C* were taken *in situ* at different time intervals (1 to 10 min) during the polymerization of ANI in acidic medium (pH ≈ 0), and A, B and C are the spectra of corresponding samples after alkalization of the reaction systems up to pH 11. The absorption spectra of

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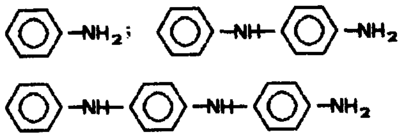
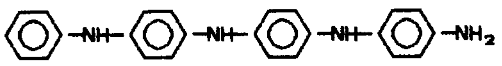
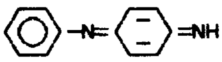
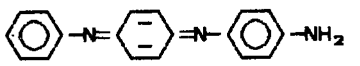
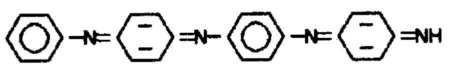
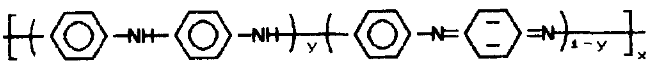
Table 1 Absorption bands of the reaction products of oxidative polymerization of aniline

No.	Products		λ_{max} (nm)	Ref.
1			280–300	14
2			310	14
3			288, 420 (A*, A)	14
4			300–310, 590 (B)	14
5			288, 310, 476	
6				9–11
6a	$1-y=0.97$	Pernigraniline OS	283, 327, 530 (C)	
6b	$0.5<1-y<0.97$		330, 530–800 (C*)	
6c	$1-y\approx0.5$	Emeraldine OS	330, 420, 800	
6d	$1-y\approx0$	Leucoemeraldine OS	330	

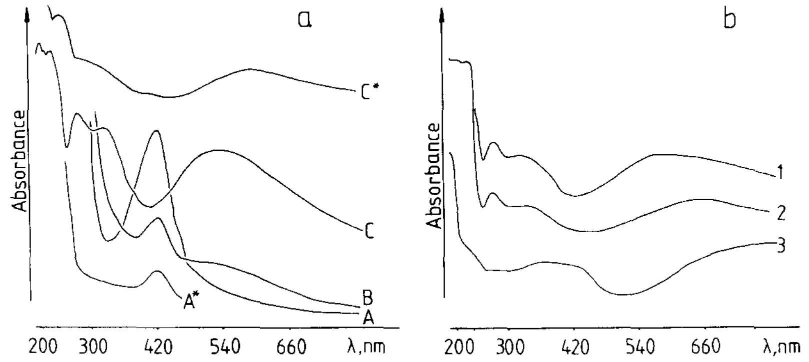
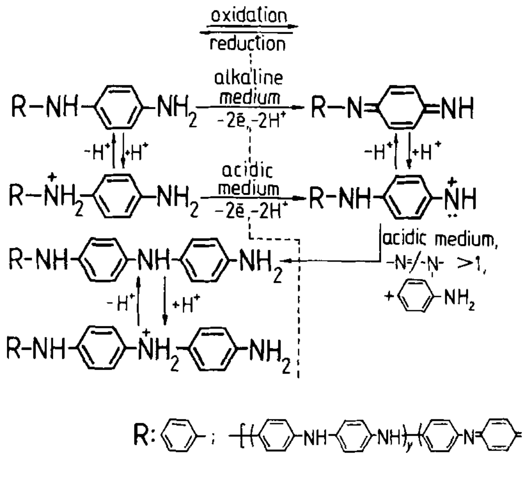


Figure 1 Electronic absorption spectra of aniline oligomers and polymer. (a) During polymerization for different time intervals: A*, 1–2 min; C*, 8–10 min; A, 1 min; B, 5 min; C, 8 min; A* and C* at pH≈0; A, B and C at pH 11. (b) Final product at different pH values: 1, 11; 2, 6; 3, 0

PANI dispersion as a final product of polymerization at pH 0 (curve 3) and the same product at pH 6 (curve 2) and pH 11 (curve 1) are shown in *Figure 1b*.

Spectra were analysed using available data on absorption of oligomers[14] and PANI of different OS[9–11]. The analysis enabled us to suggest that the products presented in *Table 1* were formed during the polymerization of ANI. Oxidized products ($1-y>0.5$ or $I/A>1$) as oligomers (A, A*, B) and polymer (C, C*) were found at the initial stage of polymerization in the whole pH range studied. This proves that the rate of oxidation is higher than the following reduction, as could be assumed from the experimental results of MacDiarmid *et al.*[6]. The absorption spectra showed that the products A, B and C were stable in the pH range from 11 to 7. However, on acidification to pH≤6, polymerization continued and PANI in emeraldine OS ($1-y\approx0.5$ or $I/A\approx1$) was obtained (*Figure 1b*, curve 3). The termination of the polymerization in alkaline and neutral media at the stage of oxidized products (A, B and C) and restarting of the process in acidic medium is very important. It shows that the reduction step takes place solely in acidic medium. Therefore, the chain propagation, starting from PADPA, can proceed as presented in *Scheme 1*, where the reactivity of propagating active sites depends on the electrochemical potential of the chain, i.e. both on the OS of the chain and on the pH of the medium. Obviously, in alkaline and neutral media this potential is not sufficient for propagation of the chain through reduction with ANI. It is noteworthy that MacDiarmid *et al.*[6], proving that pernigraniline is formed at the initial stage of the oxidative polymerization of ANI, terminated the reaction (in fact the reduction) by alkalizing the reaction system. But they did not pay attention to this experimental fact.

An exception is the formation of product A, which continued in neutral and alkaline media, resulting in an increase of absorption at 420 nm. Registration of an intermediate, absorbing at 420 nm in alkaline and neutral media, enabled us to suggest that this product does not correspond to the nitrenium cation, as stated by Genies and Tsintavis[2]. Moreoever, using a similar



Scheme 1

technique[15] (oxidation of ANI or PADPA in neutral or alkaline medium), Cao *et al.*[15] prepared *N*-phenyl-1,4-benzequinone diimine (i.e. oxidized PADPA) which, according to the absorption spectra, is identical to our product A.

The mechanism of chain propagation that we propose could also be illustrated by the following experiment. Using electron absorption spectroscopy we followed *in situ* the OS of PANI during the polymerization of ANI by step-wise addition of oxidant (OX), starting with an excess of reducing agent (ANI), and reaching an excess of OX. Furthermore, after addition of each portion of OX and equilibration, free-standing films were cast from the corresponding dispersion. Electrical conductivity, σ, of the films depends both on the content of the conductive constituent (PANI) in its blend with PVAL, and on the OS of PANI.

PANI was characterized by emeraldine OS ($1-y\approx0.5$) (*Figure 1b*, curve 3) in a dispersion prepared with a large excess of reducing agent (ANI), at a molar ratio of OX/ANI = 0.2 (*Figure 2*, point 1). On adding the next portion of OX (*Figure 2*, point 2) product C* (*Figure 1a*) was formed instantly, followed by reduction to emeraldine OS (*Figure 1b*, curve 3). Similar processes were observed up to a molar ratio of OX/ANI = 1.8. In this range of OX/ANI ratios, adding OX leads to an immediate oxidation of PANI from emeraldine OS ($1-y\approx0.5$) to a higher OS ($1-y>0.5$), followed by reduction back to emeraldine OS ($1-y\approx0.5$), caused by the ANI present in the system. The increased OX/ANI ratio up to 1.1 (*Figure 2*, point 4) probably leads to a sharp increase of the yield of PANI in emeraldine OS, i.e. to increasing content of the conductive constituent in the polymer blend, thus enhancing the electrical conductivity (*Figure 2*, points 1–4). In the range of molar ratio of OX/ANI from 1.1 to 1.8, the conductivity of PANI obtained was also fairly high (*Figure 2*, points 5–7). But on further addition of OX, when its large excess was reached at molar ratios of OX/ANI from 1.8 to 3.4 (*Figure 2*, points 8–12), the reducing agent available had been gradually exhausted, and finally (*Figure 2*, point 12) PANI in fully oxidized pernigraniline OS ($1-y\approx1$), corresponding to product C (*Figure 1a*), was formed. This results in a sharp decrease of conductivity (*Figure 2*, points 8–12). The fully oxidized product could be reduced in acidic medium (pH$\approx$0) up to emeraldine OS by addition of ANI, or up to emeraldine and leucoemeraldine OS by adding another reducing agent such as $Na_2S_2O_3$ or KI. However, without additional ANI or another reducing agent we did not observe reduction of this product up to emeraldine OS in acidic medium (1M HCl). This is inconsistent with the statement of Masters *et al.*[9] that interconversion of pernigraniline to emeraldine takes place on exposure to 1M HCl due to reductive ring chlorination.

Our experiments showed that pernigraniline prepared by polymerization of ANI in acidic medium using a large excess of OX (*Figure 2*, point 12) retained its OS, as seen from the absorption spectra, not only in acidic but also in neutral and alkaline media. On the contrary, in products of emeraldine OS ($1-y\approx0.5$) (*Figure 2*, points 1–7) or intermediate OS ($0.5<1-y<1$) (*Figure 2*, points 8–11), post-polymerization redox processes, resulting in changes of the OS of PANI, could proceed. The presence of both ANI (40–80 wt% of the initial amount) and OX in these products allowed us to separate the main steps of the post-polymerization redox process by changing the pH of the medium. *Figure 1b* shows absorption spectra of products obtained by varying the pH of PANI dispersion (corresponding to point 1 in *Figure 2*).

When a dispersion containing PANI in emeraldine OS (*Figure 1b*, curve 3) was alkalized to pH 11, the polymer was instantly oxidized up to the highest (under these experimental conditions) OS and product C* was obtained (*Figure 1a*; *Table 1*, no. 6b). Obviously, the electrochemical potential of the polymer chains decreased on the deprotonation resulting from alkalization. So they could be oxidized by the OX present in the system. Product C* was stable in the pH range from 11 to 7. At pH 6 reduction taking place due to the presence of ANI as a reducing agent, could already be observed (*Figure 1b*, curve 2). At pH$\approx$0 the highest degree of reduction under these conditions, i.e. emeraldine OS (*Figure 1b*, curve 3), was reached.

Therefore, in acidic medium the oxidation step of polymerization has to be followed by a reduction step, accompanied by consumption of the reducing agent (ANI) present. The oxidized product obtained after exhaustion of ANI has to be stable in the whole pH range. As mentioned above, this was actually proved for pernigraniline obtained in acidic medium (*Figure 2*, point 12).

In conclusion, it could be stated that the oxidative polymerization of ANI proceeds by successive steps of

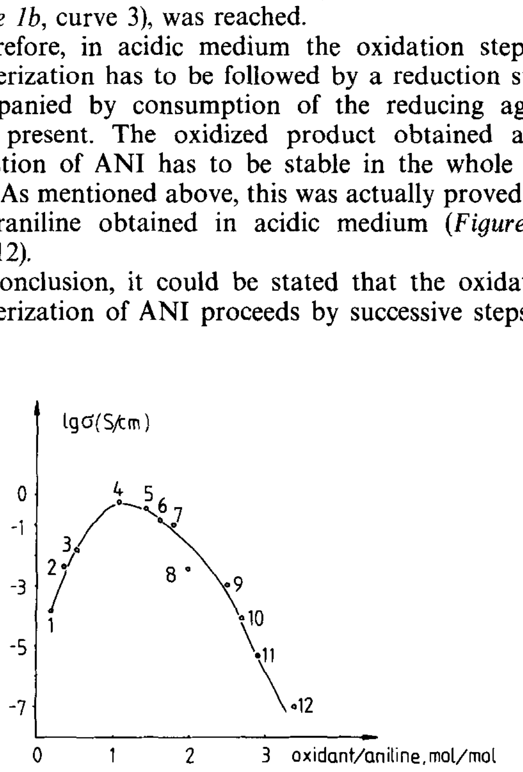


Figure 2 Conductivity of (PANI + PVAL) films *versus* OX/ANI ratio (calculated to initial ANI concentration) on step-wise adding of OX during the ANI polymerization. (Polymerization mixture contained 2 wt% ANI, 10 wt% PVAL in 2.3 M HCl)

oxidation and reduction. The oxidation step takes place in the whole pH range, while the reduction step, accompanied by addition of ANI (reducing agent) to propagating chains, proceeds only in acidic medium, when the OS of the polymer chain is higher than emeraldine OS (i.e. $0.5 < 1 - y < 1$, or $I/A > 1$). Equilibrium occurs when the electrochemical potential of the chain is not high enough for the reduction (addition of ANI) to proceed, and it is not low enough for oxidation by the available OX to take place. At $pH \approx 0$ and OX/ANI molar ratio not higher than 1.5–1.8 this equilibrium corresponds to the emeraldine OS of the chain, i.e. to the conducting form of PANI. The experimental data of other authors[16–19] concerning the dependence of conductivity on the conditions of polymerization confirm that PANI of fairly high conductivity could be prepared only under the conditions described above.

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