

Chemical oxidative polymerization of aniline in aqueous medium without added acids

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Chemical oxidative polymerization of aniline in aqueous dispersion stabilized by poly(vinyl alcohol coacetate) in initially neutral and alkaline media was studied by electron absorption spectroscopy and *in situ* pH measurements. It was shown that polyaniline could be obtained only under conditions when the initial stage of polymerization (formation of oxidized dimer) results in a decrease of pH to values lower than about 2.

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

Introduction

In a typical synthesis, the oxidative polymerization of aniline (ANI), both chemical and electrochemical, proceeds in a strongly acidic medium¹. The mechanism of polymerization is still the subject of debate due to the experimental difficulties in identifying the reaction intermediates, associated with the high reaction rate and insolubility of the reaction products (even those with low degree of polymerization) in most organic solvents. We have succeeded in preparing stable aqueous dispersions of polyaniline (PANI), with spherical particles smaller than 200 nm, using poly(vinyl alcohol coacetate) (PVAL) as a steric stabilizer^{2,3}. This enabled us to follow easily both the formation of intermediates *in situ* and their transformation on changing pH of the medium by electron absorption spectroscopy (e.a.s.). Based on the results obtained, we proposed a mechanism of oxidative polymerization of ANI accounting for the dependence of the main steps of polymerization (oxidation and reduction) both on pH of the medium and oxidation state (OS) of the chain^{4,5}. The oxidation step takes place in the whole pH range, its rate in acidic medium being lower than in neutral and alkaline media. The reduction step, determining the polymerization rate and consisting of addition of ANI (reducer) to the propagating chains, proceeds only in acidic medium, when the OS of polymer chains is higher than emeraldine.

An exception is the reduction stage of dimer (*p*-aminodiphenylamine) formation. It was shown⁴ that this stage and the following oxidation, resulting in formation of *N*-phenyl-1,4-benzoquinone diimine (PBQ), took place in the whole pH range. Since these processes are accompanied by proton abstraction of concentration in proportion to the ANI concentration, it could be supposed that PANI synthesis could proceed not only in acidic, but also in initially neutral and even slightly alkaline media.

In this paper, experimental results on chemical oxidative polymerization of ANI in initially neutral and alkaline media are presented and discussed for the first time. They add to the elucidation of the previously suggested⁴ mechanism of polymerization of ANI.

Experimental

PANI dispersions were prepared by oxidative polymerization of ANI at 20°C as described previously^{2,3}, but without addition of acid. For alkalization of the reaction system, 1–10 M solutions of sodium hydroxide were used. The initial pH value (pH₀) was determined immediately after addition of ANI and oxidant (ammonium peroxodisulfate) to the aqueous solution of PVAL.

In situ pH measurements of the reaction mixture were performed in parallel with e.a.s. investigations of reaction intermediates. Spectra were recorded on a Specord M42 (Carl Zeiss, Germany).

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

Results and discussion

Polymerization of ANI at pH₀ values of 11.0, 8.0 and 6.0 was performed at a molar ANI concentration of 0.2 (molar ratio ANI/oxidant=1). The results from pH measurements, performed *in situ* during polymerization, are presented in *Figure 1*. Samples for e.a.s. were taken during the synthesis at selected time intervals. Spectra of the registered intermediates, referred to as A, B and C, are shown in the insert in *Figure 1*. The points where the corresponding intermediates have been detected by e.a.s. are denoted in *Figure 1* by the same symbols (A, B and C).

In the whole pH₀ range studied, at the initial stage of the process (*Figure 1*, curves 1–3, points A) formation of intermediate A, absorbing at 420 nm (*Figure 1*, spectrum A), was observed, which was assigned previously^{4,6} to PBQ.

Formation of this intermediate was accompanied by a sharp drop in pH of the medium. When pH₀ was 11.0 (*Figure 1*, curve 1) the final pH after polymerization reached a value of 4.5, and the absorption spectrum of the final product was analogous to the spectrum of PBQ.

However, when the reaction started at pH₀ = 8.0 and 6.0 (*Figure 1*, curves 2 and 3), and final pH values below about 2 were reached, we observed consecutive formation of products B and C (*Figure 1*, spectra B and C) after the initial formation of PBQ; products B and C could

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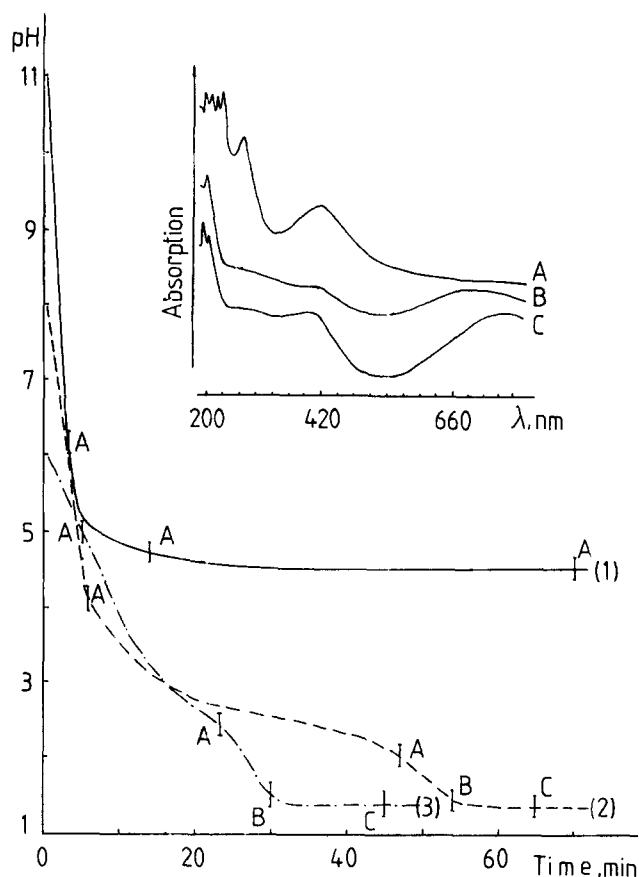


Figure 1 Variation of pH during the polymerization of ANI at different initial pH values (pH_0). Concentration of PVAL, 10 wt%; initial concentration of ANI, 0.2 mol l^{-1} ; molar ratio of ANI/oxidant = 1; $t = 20^\circ\text{C}$. (1) $\text{pH}_0 = 11.0$; (2) $\text{pH}_0 = 8.0$; (3) $\text{pH}_0 = 6.0$. A, B and C: points where samples for e.a.s. were taken. Insert: electron absorption spectra of intermediates A, B and C, corresponding to points A, B and C

be identified as PANI with OS higher than emeraldine, the extent of oxidation being decreased from B to C.

As was shown previously^{4,5}, propagation of PANI chains through reduction with ANI became possible at $\text{pH} \leq 6$. In the case of PBQ, this process obviously proceeded with a perceptible rate at pH less than about 2, as shown above. This could probably be explained by the substantial difference in the chemical

potential of the system in cases of the oxidized dimer (PBQ) and the products of longer chains.

Synthesis of PANI in initially slightly alkaline, neutral and slightly acidic media, at monomer concentration of 0.2 mol l^{-1} , resulted in a polymer of conductivity two orders of magnitude lower than those of PANI, obtained in initially strongly acidic medium. Thus, conductivity of films cast from PANI dispersions prepared at pH_0 ranging from 8.0 to 6.0, was measured to be about $10^{-3} \text{ S cm}^{-1}$, while a value of $10^{-1} \text{ S cm}^{-1}$ was measured when the polymerization started at $\text{pH}_0 < 1$. The same dependence was observed when precipitation polymerization of ANI was carried out under analogous conditions, but in the absence of PVAL; then conductivity was enhanced from $10^{-1} \text{ S cm}^{-1}$ (at $\text{pH}_0 = 8.0\text{--}6.0$) up to 10^1 S cm^{-1} (at $\text{pH}_0 < 1$). Obviously, as shown above, when the polymerization started at higher pH values the extent of reduction corresponding to emeraldine OS of PANI, which is relevant to the highest conductivity, could not be reached.

In conclusion, it could be stated that oxidative polymerization of ANI proceeds not only in strongly acidic medium, but also in initially slightly alkaline, neutral and slightly acidic media, under conditions when PBQ formation results in a decrease of pH of the medium to values lower than about 2. Therefore, in the mechanism of oxidative polymerization of ANI at least three stages could be identified:

1. initial stage of PBQ formation taking place over the whole pH range;
2. reduction of PBQ proceeding only at pH lower than 2; and
3. propagation of longer chains taking place at $\text{pH} \leq 6$.

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