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## Oxidative polymerization of aniline: a new area in cationic polymerization

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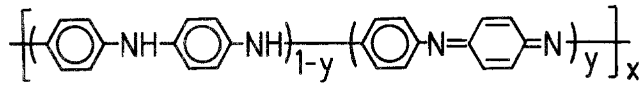
Based on the analysis of the authors' own experimental data on the chemical oxidative polymerization of aniline (ANI), as well as on the results of other authors on the electrochemical oxidation of ANI and the electrochemical response of the polyaniline (PANI) film obtained, the conclusion has been drawn that the polymerization of ANI can be considered both as a cationic polymerization and as a normal redox process. Summarizing, the conditions of initiation, propagation and termination of the chains can be expressed by the value of the electrochemical potential (EP) of the system. When the EP is kept at a value higher than *c.* 0.55 V, the polymerization can be regarded as a living cationic polymerization. In this case, PANI with an oxidation state (OS) higher than emeraldine is obtained. Thermodynamically reversible termination takes place when the EP of the system drops to a value less than *c.* 0.5 V. In this case, the oxidative polymerization of ANI can be regarded as a quasi-living cationic polymerization, and PANI of emeraldine OS is obtained.

**(Keywords: polyaniline; dispersion; cationic polymerization)**

### *Introduction*

Polyaniline (PANI) was recently rediscovered as a novel conducting polymer. It can be obtained by the chemical or electrochemical oxidation of aniline (ANI) in acidic aqueous media[1–23]. The general structure of PANI may be presented as follows:



where $y$ accounts for the oxidation state (OS) of PANI. The conducting form is associated with emeraldine OS where $y \sim 0.5$.

We have studied in detail the chemical oxidative polymerization of ANI[24–32], showing for the first time that the propagation and termination of PANI chains are determined by the OS of the chains and pH of the medium[24–26,31].

In this paper, the conditions determining the elementary steps of the polymerization process, namely initiation, propagation and termination of the chains, are expressed using values of the electrochemical potential (EP) of the system. For that purpose we reconsidered our conclusions on the mechanism of the oxidative polymerization of ANI, as well as the results of other authors on the anodic oxidation of ANI[33,34] and on the electrochemical preparation and investigation of PANI[12–23], from the viewpoint of a typical redox process. Taking into account that our previous investigations indicated the cationic mechanism of the chain growth, this paper is a first attempt to express the conditions for cationic polymerization in terms of the EP of the system.

A detailed description of the materials and experimental methods used was given in our previous communications[24,26,27]. For that reason an experimental section is not included in this paper.

### *Results and discussion*

*Initiation.* Analyzing the results from cyclic voltammograms for electropolymerization of ANI (for the first cycle)[13–15] and for anodic oxidation of the dimer *p*-aminodiphenylamine (PADPA)[5,33,34], it is seen that, while the EP of the system, corresponding to the oxidation of ANI in a strongly acidic medium, is about 0.9 V (*versus* saturated calomel electrode, as throughout this paper), the EP corresponding to the oxidation of PADPA is considerably lower (*c.* 0.55 V). Therefore, the formation of PADPA can be regarded as an initiation stage of the ANI polymerization. The substantial difference in EP, corresponding to the oxidation of ANI and PADPA (and of longer chains, as shown later), allows us to suggest that the formation of new growing sites (i.e. PADPA) is possible only at the initial stage of polymerization. Hence, it is hard to expect the formation of new active sites at the chain propagation step, the growth of the already existing active species being much more probable at this stage.

A considerably lower EP, corresponding to the oxidation of PADPA as compared to ANI, is the exact reason for the instant oxidation of PADPA to its oxidized form, *N*-phenyl-1,4-benzequinone diimine (PBQ), which we have identified at the initial stage of the oxidative polymerization of ANI[24].

As evident from our investigations[24–26], the oxidation of ANI to PBQ proceeded not only in acidic media, but also in neutral and alkaline media when ammonium peroxydisulfate (the oxidation potential of which does not depend on the pH of the medium) was used. It is reasonable to suggest that EP, corresponding to the oxidation of ANI, has to decrease on increasing the pH

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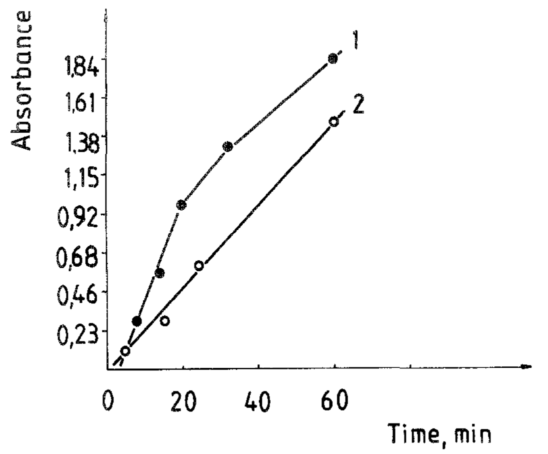

**Figure 1** Time dependence of the absorbance at 420 nm (characteristic of PBQ) at different pH values of the medium: 1, pH 9.0; 2, pH 4.5 (concentration of ANI, 0.04 mol $l^{-1}$, molar ratio of OX/ANI = 1, concentration of PVAL, 2 wt%, temperature, 23°C)

of the medium due to its deprotonation (p$K_a$ of ANI is 4.6). Duic and Mandic[15] have indeed found that the EP, corresponding to the oxidation of ANI, decreased by 50–60 mV/pH. As a consequence, the rate of PBQ formation has to increase on increasing the pH of the medium, as was actually found in our experiments (*Figure 1*).

Therefore, the conditions for initiation of the oxidative polymerization of ANI can be expressed by the EP value of the system: in strongly acidic media it is about 0.9 V and drops on increasing the pH of the medium. Thus, the most favourable conditions for initiation of the oxidative polymerization of ANI exist in neutral and even in alkaline media rather than in strongly acidic media.

*Chain propagation and termination.* As we have shown previously[24–26,31], the reduction step determining the propagation of the polymer chain starting from PBQ proceeded solely in acidic media. This enabled us to suggest that the active site is the nitrenium cation and hence the polymerization of aniline is cationic.

Moreover, the reduction of PBQ proceeded[25] only at a pH lower than 2, while the reduction of longer chains took place at pH < 6 and when their OS is higher than emeraldine (i.e. $0.5 < y \leqslant 1$).

Let us try to express the same conditions in terms of EP by using results from cyclic voltammograms for the anodic oxidation of PADPA[33,34] and cyclic voltammetry of PANI films[15–23]. According to these results, in strongly acidic media (pH $\sim$ 0) PBQ can be obtained at an EP of *c.* 0.55 V; PANI in emeraldine OS ($y \sim 0.5$), in an intermediate OS ($0.5 < y < 1$) and in pernigraniline OS ($y = 1$) can be obtained at an EP of about 0.25–0.5 V, 0.55–0.75 V and 0.75 V, respectively.

Analyzing these results, the following statements may be made:

1. Chain propagation can be divided into at least two stages depending on the EP of the system: PBQ reduction and growth of longer oxidized chains ($0.5 < y \leqslant 1$). This confirms our previous similar suggestion[25] based on different conditions (in respect to pH) necessary for the reduction of PBQ and of longer chains.
2. Chain propagation takes place when the EP of the system is in the range of 0.55–0.75 V.
3. When the EP is kept constant in the above region, the conditions necessary for living polymerization exist, i.e. the chains will keep growing until exhaustion of the monomer. However, the OS of PANI obtained will always be higher than emeraldine.
4. Decreasing the EP of the system to *c.* 0.5 V (corresponding to emeraldine OS at pH $\sim$ 0) brings about a termination of the chain growth, as this oxidation potential is insufficient for ANI oxidation. In this case, the PANI obtained will be in emeraldine OS and the polymerization itself can be regarded as quasi-living. Actually, this equilibrium is thermodynamically reversible, i.e. the chains can be reactivated by increasing the EP of the system to more than 0.55 V.
5. The polymer chains can be reactivated by increasing the electrode potential in the case of electrochemical polymerization, or by addition of oxidant in the case of chemical polymerization of ANI.
6. Reactivation of the polymer chains is also possible by treatment of PANI in emeraldine OS in neutral and alkaline media, as we have shown previously[24,31]. As we have suggested, in that case the oxidation of PANI can be caused by the presence of traces of the oxidant[24,31] (or even by the dissolved oxygen), due to a considerable decrease in the EP corresponding to PANI in emeraldine OS as a result of its deprotonation. Actually[16,17], the EP corresponding to PANI in emeraldine OS decreases from 0.3 V at pH 0 to −0.2 V at pH 9. The easy oxidation of PANI in emeraldine OS on treatment in neutral and particularly in alkaline media allows the subsequent reduction (propagation) due to the presence of reducer (ANI) to proceed on reacidification.

In conclusion, it can be stated that the oxidative polymerization of ANI is a cationic polymerization, where the conditions of initiation, propagation and termination of the chain can be expressed by the EP of the system. When EP was kept at a value higher than 0.55 V, the polymerization can be regarded as a living cationic polymerization. In this case the kinetic chain preserves its growing capability and grows until the exhaustion of the monomer. The OS of PANI obtained has to be higher than emeraldine. The thermodynamically reversible termination takes place under conditions when the EP of the system drops to a value less than 0.5 V. In this case the oxidative polymerization of ANI can be regarded as a quasi-living cationic polymerization. As a result, PANI in emeraldine OS is obtained.

The consideration of the oxidative polymerization of ANI as a redox process holds opportunities for a proper selection of comonomers and copolymerization conditions. The oxidation potential may be regarded as a basic criterion of the comonomer activity.

### *Acknowledgement*

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