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A new approach to the study of oxidative polymerization of aniline and transformations of polyaniline. Support by means of the Hueckel method

N. Gospodinova*, L. Terlemezyan and P. Mokreva
Institute of Polymers, Bulgarian Academy of Sciences, BG-1113, Sofia, Bulgaria

and A. Tadjer
Faculty of Chemistry, Sofia University 'St. Kliment Ohridski', BG-1126, Sofia, Bulgaria

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An interrelationship between the mechanism of aniline polymerization and the direction of redox processes with participation of polyaniline chains on the one hand, and the π-electron energy of oligoanilines with various numbers of units, degrees of oxidation and protonation on the other hand, has been found for the first time. Calculations performed using the Hueckel method revealed that the difference in the π-electron energy of the oxidized and reduced forms of the chain correlated very well with the experimentally determined electrochemical potential for the respective redox transition. It is suggested that the Hueckel method can be used for investigation of the electrochemical activity of conjugated polymers obtained by oxidative polymerization, as well as for studying the mechanism of the latter. Copyright © 1996 Elsevier Science Ltd.

(Keywords: polyaniline; polymerization mechanism; Hueckel method)

Introduction

In our previous communications we have shown that the oxidative polymerization of aniline (ANI) should be regarded first of all as a redox process[1-3], the mechanism of which determines to a great extent the activity of polyaniline (PANI) chains in the redox-processes[1-5], i.e. their electrochemical activity. It is well known[6] that the electrochemical potential (E) of a redox transition correlates fairly well with the difference in the π-electron energy, ΔE_π, of the oxidized and the reduced forms of a given conjugated molecule. Thus the aim of this work is to establish an interrelationship between the experimentally found mechanism of oxidative polymerization of ANI and the electrochemical activity of PANI on the one hand, and the change in the π-electron energy of the chains as a result of the redox transitions, which simulate real redox processes, on the other.

Experimental

Reagent-grade ANI (Fluka) was vacuum distilled prior to use. All other reagents were also purchased from Fluka and were used as received.

PANI dispersions were prepared as described previously[7,8] by oxidative polymerization of ANI in 5 M formic acid using poly(vinyl alcohol-*co*-acetate) as steric stabilizer and $(NH_4)_2S_2O_8$ as oxidant. In order to obtain the potential (temperature)—time profile of the oxidative polymerization of ANI, the process was performed at an ANI concentration of $0.83\,mol\,l^{-1}$ and an equimolar ratio of oxidant/ANI. The PANI dispersion for investigation of PANI oxidation at various pH values of the medium (the initial PANI dispersion) was obtained at an ANI concentration of $0.2\,mol\,l^{-1}$ and a molar ratio of oxidant/ANI = 0.5. The increase of pH of the medium was attained by the addition of 0.5 and 3 M solutions of NaOH to the initial PANI dispersion. The oxidation of PANI was performed by adding various amounts of oxidant (depending on the pH of the medium) to the initial PANI dispersion.

The values of E and temperature during the oxidative polymerization of ANI, and of E and pH during the oxidation of PANI, were recorded using simultaneous *in situ* potential and pH measurements of the reaction medium and registration of the temperature during the processes. A microprocessor-based pH meter (HI 8417, Hanna Instruments) complete with combined pH and redox (platinum–calomel) electrodes was used in these measurements.

The calculations of E_π of oligoanilines with various numbers of units n, varying degree of oxidation (number of π-electrons involved in the redox transition, m) and different levels of protonation were performed using the Hueckel method. For model compounds and during analysis of the results obtained, the following assumptions were made:

1. the basicity of the imine nitrogen atoms is substantially higher than that of the amine nitrogen;
2. the oligoanilines with $n > 8$ reproduce to a great extent the characteristics of PANI.

The redox transitions were simulated as processes of electron detachment or acceptance, which concern mainly the population of the frontier molecular orbitals. We assume that the adopted model gives a relevant (from the standpoint of the π-electron) description of the formation of propagating active sites. In the protonated forms of oxidation states the imine nitrogen was regarded as a cation-radical of amine type. The calculations for the oxidation of protonated forms were

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* To whom correspondence should be addressed

performed stepwise, but since the Hueckel method is unable to distinguish between the ionization potential of two electrons in the same molecular orbital, ΔE_π has the same value for each pair of electrons detached from a monomer unit. This is why curves 2 and 4 in *Figure 3* are dashed. Standard parameters were used[6].

Results and discussion

In our previous paper[3] it was supposed that the oxidation of ANI into the nitrenium cation (or cation-radical) at $E = 0.9$ V, accompanied by instant formation of the dimer *p*-aminodiphenylamine (PADPA), can be regarded as the initiation step of ANI polymerization, since oxidation of the dimer proceeds at substantially lower E. The calculations performed in this work reveal that initial oxidation ($m = 1$) of the dimer, trimer, tetramer,..., polymer and any higher degree of their oxidation (up to $m = n$) are characterized by lower ΔE_π, compared with the oxidation of ANI (*Figure 1*).

Considerably lower E, corresponding to the oxidation of PADPA, is the reason for registration of its oxidized form *N*-phenyl-1,4-benzequinone diimine (PBQ) as early as in the first minute of the polymerization process. It was recorded in our previous studies by means of electronic absorption spectroscopy (EAS)[1–3] while other authors[9] proved the presence of PBQ by the appearance of a characteristic anodic peak in the cyclic voltammogram even at the first scan, i.e. in ~15 s from the beginning of the electrochemical oxidation of ANI.

Only a few attempts at measuring E during the chemical oxidative polymerization of ANI by means of a redox electrode have been described so far[10,11]. However, as noted by some authors[11], this method gave a good measure of the end of the reaction but the beginning of the reaction was hard to discern. In the present study we have succeeded for the first time in recording E corresponding to PBQ formation (i.e. to the oxidation of PADPA) by means of a redox electrode, using high initial concentration of the reactants (*Figure 2*, curve 1). It is worth noting the fairly good coincidence of the E value for PBQ found by other authors[9] and that in our study (amounting to ~0.4 V at pH 2, see *Figure 2*, curve 1).

The propagation of the polymer chains proceeds by a redox process between the growing chain (as oxidant) and ANI (as reducer) with addition of the monomer to the chain end. The high concentration of a strong oxidant, $(NH_4)_2S_2O_8$, at the initial stage of the polymerization enables the fast oxidation of oligo- and polyaniline, as well as their existence (and consequently their registration) in the oxidized form. This is the explanation for the presence of oxidized oligomers and pernigraniline (the fully oxidized form of PANI) at the initial stage of polymerization, as recorded by means of EAS in our previous investigation[1]. The results presented in *Figure 2* show an increasing E of the system at this stage, starting from 0.4 V corresponding to PBQ, up to 0.7 V corresponding to pernigraniline. It is noteworthy that this dependence correlates fairly well with the dependence of ΔE_π (corresponding to the highest degree of oxidation ($m = n$) of oligo- and polyaniline) on the length of the chain n, presented in *Figure 1* (curve 3).

Keeping a high degree of oxidation (and consequently a high concentration of imine bonds) of the growing chains at the initial stage of the polymerization creates favourable conditions for hydrolysis of imine bonds. As we have shown previously[8], this process is endothermic. Obviously, the effect of hydrolysis prevails over the effect of polymerization (exothermic) in the overall thermal effect, thus resulting in the overall endothermic effect recorded at the initial stage of the process (*Figure 2*, curve 2).

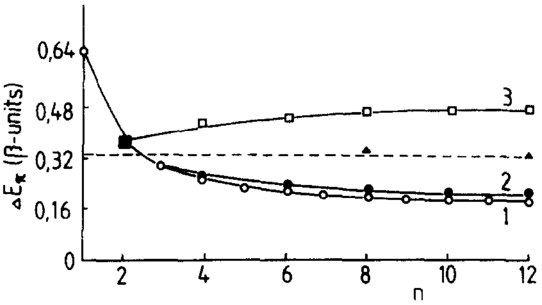

Figure 1 Calculated change of the π-electron energy E_π (β units) on increasing the number of monomer units, upon: (1) detaching the first electron ($m = 1$) from the fully reduced form; (2) detaching the nth electron from the deprotonated oxidized form; (3) detaching the nth electron from the protonated oxidized form; (Δ) detaching the $[(n/2)+1]$th electron from the protonated emeraldine form (dashed line corresponds to the ΔE_π level of this transition)

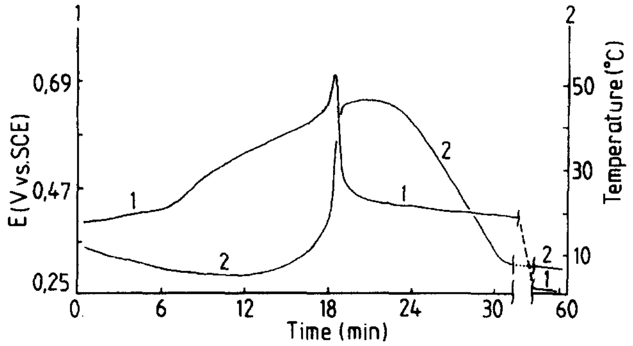

Figure 2 Experimental potential–time (1) and temperature–time (2) profiles of oxidative polymerization of aniline (aniline concentration of 0.83 mol l^{-1}, equimolar ratio of oxidant/aniline)

When the equilibrium E ($E = 0.7$ V)—which depends on the oxidation potentials and the concentrations of the oxidized PANI chains and oxidant—has been attained, reduction of PANI chains with addition of ANI was predominantly observed. This was evident by the lowering of E of the system and by the exothermicity of the process (*Figure 2*). The system reached a new equilibrium at $E = 0.25$ V, corresponding to the emeraldine (EM) degree of oxidation of PANI chains. The oxidation potential of PANI chains in this degree of oxidation is insufficient for the addition of ANI, as we have shown previously[1–5]. The same conclusion can be drawn when analysing the results shown in *Figure 1* (curve 3 and dashed line). It is seen that ΔE_π corresponding to the oxidation potential of PANI in EM degree of oxidation is lower than that of the oxidized forms of oligo- and polyaniline (starting from PBQ), which are active in chain growth. Besides, the chains of oligo- and polyaniline are active not only in the highest degree of oxidation (i.e. when $m = n$, see *Figure 1*, curve 3), but also in intermediate steps between the EM and the highest degree of oxidation (i.e. when $m > (n/2) + 1$, see

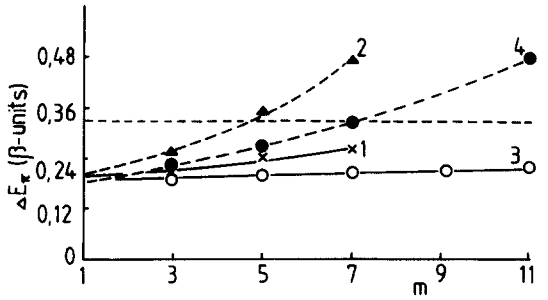

Figure 3 Calculated change of E_π (β-units) on increasing degree of oxidation (number of detached electrons, *m*) of chains of various numbers of monomer units (*n*): (1) $n = 8$, deprotonated form; (2) $n = 8$, protonated form; (3) $n = 12$, deprotonated form; (4) $n = 12$, protonated form. The dashed line parallel to the abscissa is at the same level of ΔE_π as in *Figure 1*

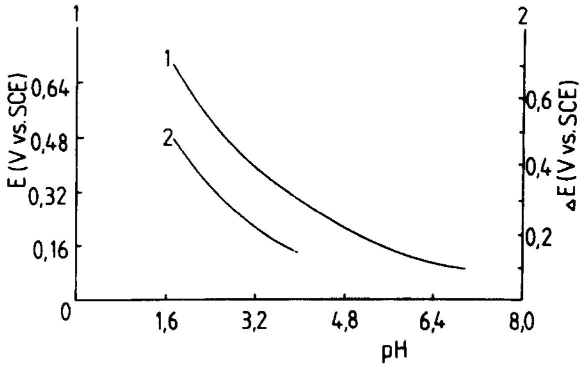

Figure 4 Experimental dependence of the electrochemical potential E corresponding to pernigraniline (1) and difference of the electrochemical potentials between pernigraniline and emeraldine ΔE (2), on pH of the medium

Figure 3, curves 2, 4 and the dashed line parallel to the abscissa), which correspond to the previously[1-5] suggested $-N=/-N< > 1$.

The relatively low oxidation potential of PBQ explains the so-called induction period of ANI polymerization observed by some authors[12]. The increase of the oxidation potential of the oxidized forms of oligoaniline on increasing the length of the growing chains is most likely the reason for autoacceleration in the reaction kinetics, characteristic of oxidative polymerization of ANI[11,12].

As we have shown previously[1-5], the reduction of growing chains with addition of ANI was controlled not only by their degree of oxidation but also by the pH of the medium, which determines the level of protonation of the chains. Thus, the reduction rate decreased on increasing the pH of the medium from 0 to 6, and in neutral and alkaline media reduction did not proceed, i.e. the polymerization process was terminated. In order to explain this phenomenon we suggest that the oxidation potential of oligo- and polyaniline chains depends on both the degree of oxidation and the level of protonation of the chains. Thus, decreasing the level of protonation on increasing the pH of the medium brings about a lowering of the oxidation potential of the chains. This results not only in retardation or even impossibility of chain growth, but also in their easy oxidation by traces of oxidant, or even by atmospheric oxygen.

The results presented in *Figures 1*, *3* and *4* show that both the calculated values of ΔE_π and the experimentally found E for the corresponding redox process decrease considerably on deprotonation of PANI chains, i.e. on increasing the pH of the medium. The deprotonation of PANI chains, according to the calculations (*Figure 1*, curves 1 and 2; *Figure 3*, curves 1 and 3), also results in narrowing of the potential window in which PANI transition from the fully reduced (leucoemeraldine) to the fully oxidized (pernigraniline) form takes place. This corresponds very well to the experimental data from electrochemical oxidation of PANI[13], as well as to the dependence of the transition of PANI from EM to pernigraniline on pH of the medium (*Figure 4*, curve 2) presented in this study.

Analysis of investigations on the mechanism of oxidative polymerization of pyrrole[14] and thiophene[15] and the electrochemical activity of the polymers obtained, leads us to suggest that the approach described in the present communication can be extended to study the oxidative polymerization of these monomers. This will be the subject of our further investigations.

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