CONDUCTING POLYMERS PREPARED BY OXIDATIVE POLYMERIZATION: POLYANILINE

N. GOSPODINOVA*, L. TERLEMEZYAN

Institute of Polymers, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Abstract – Polyaniline (PANI) is one of the most intensively investigated polymers during the last decade. The establishment of the scientific principles allowing regulation of its properties, determining the potential application areas (alternative energy sources and transformers, media for erasable optical information storage, non-linear optics, membranes, etc.) is an important scientific problem. We have shown for the first time that the behavior of this polymer is subject to the same basic principles as the polymerization process itself. Both the polymerization of aniline and the subsequent transformations of polyaniline have to be regarded as typical redox processes, where the direction and establishment of equilibrium are dependent on the oxidation potentials and concentrations of the reactants (and also on pH of the medium, affecting the values of oxidation potential of the reactants). Such an approach allows us to identify the oxidative polymerization of aniline (and presumably of thiophene and pyrrole) as a new area in cationic polymerization, wherein the conditions of initiation, propagation and termination of the chains can be expressed by means of the electrochemical potential of the system. Furthermore, this allows an elucidation of the key problems related to the main types of transformations of this polymer (the so-called oxidative and non-oxidative doping of polyaniline). It also gave us a reason to suggest a novel original classification of the numerous potential application areas of PANI.

1. INTRODUCTION

The continuously growing interest in the study of PANI may be illustrated by the following statistical data: while during the period 1986–1989 there were 948 published papers and patents worldwide, for the last 3-year period (1993–1995) only the papers amount to 1143. This interest is caused, on the one hand, by diverse, but also unique properties of PANI, allowing its potential applications in various fields, such as energy storage and transformation (alternative energy sources, erasable information storage, non-linear optics, shielding of electromagnetic interference), as well as catalysts, indicators, sensors, membranes of precisely controllable morphology, etc. On the other hand, although some industrial companies have put a lot of effort into the development of some applications of this material, there exist too many ambiguities about PANI. They are related to both the mechanism of polymerization and the polymer structure (including its transformations), determining the material properties.

The main results from the PANI investigations, presented most comprehensively in the review articles[1–9], can be summarized by the following picture. PANI exists in three well defined oxidation states: leucoemeraldine, emeraldine and pernigraniline (Fig. 1). Leucoemeraldine and pernigraniline are the fully reduced (all the nitrogen atoms are amine) and the

---

*To whom all correspondence should be addressed.

C O N T E N T S

fully oxidized (all the nitrogen atoms are imine) forms, respectively, and in emeraldine the ratio $-\overset{|}{N}-/-N=$ is ~0.5. Starting from the electrically insulating leucoemeraldine, electrically conducting emeraldine can be obtained by standard chemical or electrochemical oxidation, as with other conducting polymers. But, upon further oxidation a second redox process occurs, which yields a new insulating material, pernigraniline. In addition to this unusual behavior, a decrease of conductivity by ten orders of magnitude is obtained just by treatment of the conducting emeraldine in neutral or alkaline media. Protonation induces an insulator-to-conductor transition, while the number of π-electrons in the chain remains constant. A lot of work has been devoted to the study of this unusual transition. The mechanism of oxidative polymerization of aniline, which always results in a conducting emeraldine PANI, appears also to be ambiguous.

In this review article we do not aim at solving, and even at showing, all the ambiguities about PANI. We shall try to present a novel approach to the study of this polymer, which, naturally, may also have some defects, but, in our opinion, will contribute to clarify the picture. The key point is that PANI is regarded as a polymer, the behavior of which is subject to the same principles as the polymerization process itself. This is the essential difference
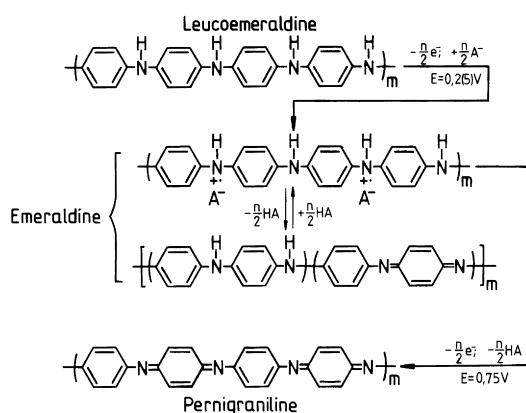

Fig. 1. Generalized scheme of the oxidative and non-oxidative (protonic acid) doping of polyaniline: n, number of aniline units, $m = 4n$.

between PANI and conventional polymers, the polymerization mechanism of which affects their properties in as much as it influences the microstructure, the molecular weight and the molecular weight distribution. Therefore, the mechanism of the oxidative polymerization of aniline is the clue for understanding the transformations of PANI, and hence its properties and application spectrum.

Based on numerous works by other authors and our own results, we tried for the first time to present the mechanism of aniline polymerization as subject to the principles of the redox processes, i.e. such processes, where the direction and establishment of the equilibrium depends on the oxidation potentials and the concentrations of the reactants (and also on pH of the medium, affecting the oxidation potentials of the reactants). In a similar way the behavior of PANI, which determines its potential applications, was treated also for the first time. Namely, all the transformations of PANI, irrespective of the method employed (standard chemical or electrochemical oxidation and reduction, variation of pH of the medium, effects of various types of energy), appear to be redox processes with participation of PANI chains, the oxidation potential of which is determined by the degree of oxidation (i.e. the oxidation state) and protonation.

2. MECHANISM OF OXIDATIVE POLYMERIZATION OF ANILINE

The mechanism of oxidative polymerization of aniline is still debatable. This polymerization has been assigned to the oxidative category since it is concomitant with the oxidation of aniline by means of standard methods of chemical or electrochemical oxidation. (It has to be noted that such an oxidation does not necessarily result in formation of polymer; thus, e.g. polymer was not formed when the potential was kept at the level required for oxidation of aniline [10–13].) The consideration of the mechanism of oxidative polymerization of aniline as a redox process, however, has been limited basically to the initial stage of the process [14–18], while at further stages a kinetic approach, which is characteristic of polymerization studies, has been used [14,15,17,19–36]. Even the potential profiles (typical electrochemical method) of aniline polymerization have been discussed mainly from the viewpoint of the rate differences of the various stages of polymerization (the corresponding sections of the profiles) [15,28,33,36], rather than from the standpoints typical of the redox processes, viz. establishment of the equilibrium electrochemical potential during such a process.

Let us now consider in detail the most generalized mechanism of aniline polymerization suggested by Wei et al. [14,17,21,28], based mainly on kinetic studies of the electrochemical polymerization of aniline (see Fig. 2). In the last paper [28], while studying the potential profile of the polymerization process, they introduced some corrections in this scheme, referring to the process as 'non-classical chain polymerization' (or something between a classical step-growth polymerization and a classical chain-growth polymerization). According to the authors, ''the slowest step in the polymerization of aniline is the oxidation of aniline monomer to form dimeric species (i.e. p-aminodiphenylamine, PADPA, N-N'-diphenylhydrazine and benzidine), because the oxidation potential of aniline is higher than those of dimers, subsequently formed oligomers and polymer. Upon formation, the dimers are immediately oxidized and then react with an aniline monomer via an electrophilic aromatic substitution, followed by further oxidation and deprotonation to afford the trimers. This process is repeated, leading eventually to the formation of PANI''.
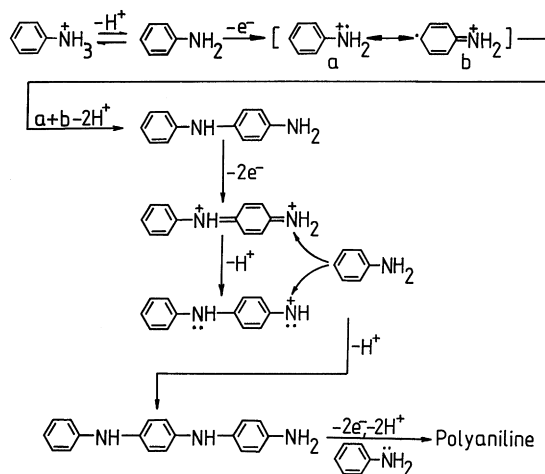
Fig. 2. Mechanism of the polymerization of aniline, proposed by Wei et al.[14,17,21].

In our opinion, there are several fundamental contradictions and discrepancies in this consideration. Thus, the authors took the view of Genies and Lapkowski[37], that the oxidation of aniline up to the dimer occurred by formation of nitrenium cation ($C_6H_5NH^+$). Genies and Lapkowski, however, as early as in the initial few seconds of the polymerization process, have already observed in situ by means of electronic absorption spectroscopy (EAS), a soluble intermediate absorbing at 420 nm, which has been assigned to $C_6H_5NH^+$. In fact, the oxidation of aniline up to the dimer formation is not the slowest step in the polymerization, but appears to be the step requiring the highest electrochemical potential, E, of the system. The term 'rate-determining step' is related to the polymerization stage (as we have concluded from the analysis of[28]), which is characterized by increasing E of the system from 0.4 to 0.78 V (versus saturated calomel electrode, as throughout this paper). Several authors[23,33], while studied the kinetics of the process by calorimetry, considered this period even as an induction period. Thus, according to Wei, at this stage various oxidized oligomeric species and pernigraniline have been formed (pernigraniline formation has been first shown by Manohar et al.[38]).

The unclear point is why the electrochemical potential increases at this stage and why this stage is the slowest (i.e. rate-determining) step. But, according to the authors themselves[17], the oxidation potential of oligo- and polyanilines, M_x, decreases as x increases. Further, the questions on what is dependent the oxidation potential of the 'oxidized M_x', and most important, which M_x is able to add the next monomer molecule, have not been addressed at all. In fact, at this point we approach the key problem in elucidation of the mechanism of oxidative polymerization of aniline, which has not as yet been solved in either of the mechanisms proposed, namely:

1. what forces the oligo- and polyaniline chains to grow and why does propagation terminate when the emeraldine oxidation state of PANI has been reached?
2. what are the basic factors determining the 'activity' of the growing chain in the monomer addition? In our opinion, the ambiguities in the oxidative polymerization of aniline arise

from the application of an approach typical of the investigation of the polymerization processes, to a process wherein the driving force is the difference in the oxidation potentials of the reactants (oxidant − aniline, oxidant − oligomeric or polymeric chain, oligomeric or polymeric chain − monomer).

We hope that our investigations[39−45] during recent years contribute substantially in solving this problem. As mentioned above, we considered the process of oxidative polymerization of aniline from the viewpoint typical for the usual redox processes. Namely, we tried for the first time to express the conditions, determining the elementary steps of the polymerization process, viz. initiation, propagation and termination of the chains, using the values of the electrochemical potential of the system. In order to employ such an approach and to prove its conformity with the real situation, we used both experimental and theoretical methods.

In our experiments we used methods allowing to change and to record the electrochemical potential of the system and the oxidation state of oligo- and polyaniline chains. We followed by in situ potential- and pH-measurements of the reaction medium and by EAS both the formation of intermediates in situ and their transformations during the changes of the electrochemical potential of the system (changes in pH of the medium and in the concentrations of oxidants and reducers in the system). This became possible due to our success in preparation of stable (in the whole pH range) aqueous dispersions of PANI with particles smaller than 200 nm[46−49] using poly(vinyl alcohol coacetate) as a steric stabilizer.

To obtain theoretical support for the proposed mechanism, we performed for the first time calculations by the Hueckel method[42], taking into account the well known fact[50] that the electrochemical potential of the 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. We performed calculations of E_π of oligoanilines of various numbers of units, n, degree of oxidation (number of π-electrons involved in the redox transition, m) and degree of protonation. For the model compounds and during the analysis of the results obtained, the following assumptions have been accepted:

- the basicity of the imine nitrogen atoms is substantially higher than that of the amine nitrogen;
- the oligoanilines of $n > 8$ 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 π-electron standpoint) description of the formation of a propagating particle. In the protonated forms of oxidation states the imine nitrogen was regarded as a cation-radical of the amine one. The calculations for the oxidation of protonated forms were done 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. That is why curves 2 and 4 in Fig. 8 are dashed. Thus, the mechanism of oxidative polymerization of aniline can be presented as follows.

2.1. *Initiation*

As mentioned above, the oxidation of aniline into nitrenium cation (or cation-radical) at $E{\sim}0.9$ V was accompanied by an instant formation of the dimer PADPA. Analyzing the
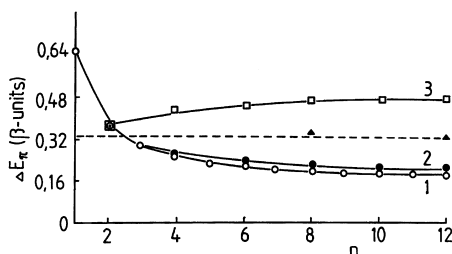
Fig. 3. Calculated change of the π-electron energy, ΔE_π (β-units), on increasing the number of monomer units, upon: (1) detaching the first electron ($m = 1$) from the fully reduced form; (2) detaching of the nth electron from the deprotonated oxidized form; (3) detaching of the nth electron from the protonated oxidized form; (Δ) detaching of $(n/2 + 1)$th electron from the protonated emeraldine form (dashed line corresponds to the ΔE_π level of this transition)[42].

results from cyclic voltammograms for electropolymerization of aniline (for the first cycle) and for anodic oxidation of PADPA[10,12,17], it is seen that, while E of the system, corresponding to the oxidation of aniline in an acidic medium, is about 0.9 V, E corresponding to the oxidation of PADPA is considerably lower ($\sim$0.4–0.5 V). Therefore, the formation of PADPA can be regarded as an initiation stage of the aniline polymerization.

Actually, the initial oxidation ($m = 1$) of the dimer, trimer, tetramer,..., polymer and any higher degree of their oxidation (up to $m = n$) were characterized by lower ΔE_π, as compared to the oxidation of aniline (Fig. 3).

The substantial difference in the electrochemical potentials, corresponding to the oxidation of aniline 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.

The considerably lower electrochemical potential, corresponding to the oxidation of PADPA as compared to aniline, is the exact reason for the instant oxidation of PADPA to its oxidized form, N-phenyl-1,4-benzequinonediimine (PBQ), which we have identified at the initial stage of the oxidative polymerization of aniline by using EAS[40,41,43].

Fig. 4 presents the absorption spectra of intermediates obtained at the initial stage of aniline polymerization[40]. Spectra A* and C* were taken in situ at different time intervals during the polymerization of aniline in acidic medium (pH$\sim$0) and A, B and C are the spectra of corresponding samples after alkalization of the reaction systems up to pH$\sim$9. Spectra of intermediates formed during aniline polymerization taking place in initially alkaline and neutral media, are shown in Fig. 5[41]. It can be stated that the intermediate A, absorbing at 420 nm (Fig. 4, spectrum A*), which has already appeared in the first minute of the reaction, does not correspond to $C_6H_5NH^+$ as stated by Genies[37], but can be assigned to PBQ, since a similar absorption appears also in neutral and alkaline media (Figs 4 and 5, spectrum A). Using the well known[51] oxidation of aniline in neutral or alkaline medium, Cao et al.[52] obtained PBQ, the absorption spectrum of which is identical to our spectrum A. Next to our papers, the authors[23] also revealed that in neutral and alkaline media an absorption at about 430 nm appeared at the initial stage of polymerization. Further evidence that the
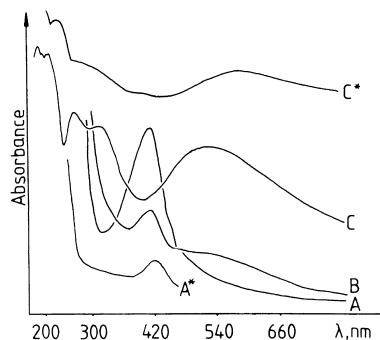
Fig. 4. Electronic absorption spectra of aniline oligomers and polymer during polymerization for different time intervals: A*, 1–2 min; C*, 8–10 min; A, 1 min; B, 5 min; C, 8 min; A* and C* at pH~0; A, B and C at pH~9[40].
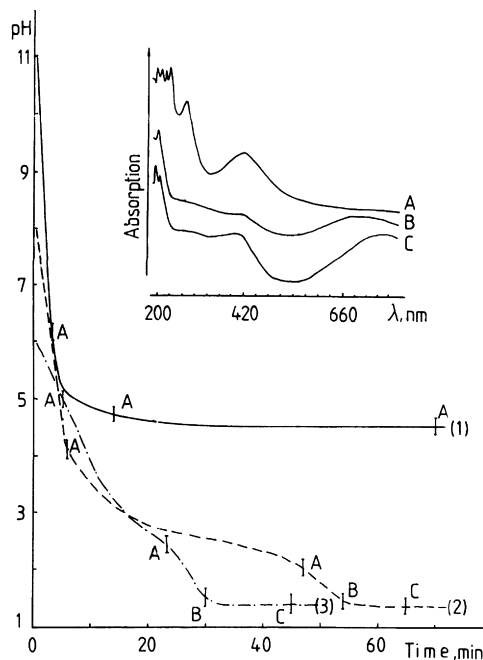
Fig. 5. Variation of pH during the polymerization of aniline starting at different initial pH values (pH_0). Concentration of poly(vinyl alcohol coacetate), 10 wt%; initial concentration of aniline, 0.2 mol l^{-1}; molar ratio of aniline/oxidant, 1; $T = 20°C$; pH_0 values: 11, 8 and 6 for curves 1, 2 and 3, respectively. A, B and C: points where samples for EAS were taken. Insert: electronic absorption spectra of intermediates A, B and C, corresponding to points A, B and C[41].

Fig. 6. Experimental potential–time (1) and temperature–time (2) profiles of oxidative polymerization of aniline. Concentration of poly(vinyl alcohol coacetate), 10 wt%; aniline concentration, 0.83 mol l^{-1}; equimolar ratio oxidant/aniline[42].
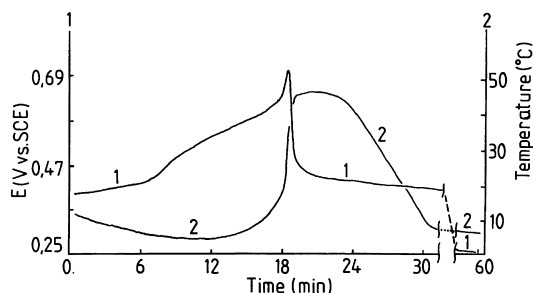
product absorbing at about 420 nm is PBQ is the value of E, which we have registered at the stage of polymerization corresponding to formation of A (Fig. 6, curve 1)[42].

As noted previously[33], the method of measuring E during the chemical oxidative polymerization of aniline by means of redox electrode, gives a good indication of when the reaction ends, but the beginning of the reaction is hard to discern.

We have for the first time succeeded in recording E, corresponding to PBQ formation (i.e. to the oxidation of PADPA) by means of redox electrode, using high initial concentrations of the reactants (Fig. 6). It is worth noting the fairly good coincidence of the E value found by other authors[10,12,17] for PBQ and that obtained in our study (about 0.4 V at pH~2, see Fig. 6, curve 1).

As mentioned above, the oxidation of aniline to PBQ occurred not only in acidic medium, but also in neutral and alkaline media, when ammonium peroxidisulfate (the oxidation potential of which does not depend on the pH of the medium) was used. It is reasonable to suggest that the electrochemical potential, corresponding to the oxidation of aniline, has to decrease on increasing the pH of the medium due to its deprotonation (pK_a of aniline is 4.6). Duic and Mandic[18] have indeed found that E, corresponding to the oxidation of aniline decreased by 50–60 mV/pH. As a consequence, the rate of PBQ formation has to increase on increasing pH of the medium, as was actually found in our experiments (Fig. 7)[43].

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

As can be expected, each additive of lower oxidation potential as compared to aniline (which is able to add aniline), has to reduce the electrochemical potential of the initiation and consequently to accelerate the process. Support of this assumption can be found in Refs.[14,17,19,21,28]. Using such an additive, the polymerization can be initiated or accelerated by oxygen or another mild oxidant, which has been actually observed in[14,20]. The results seem reasonable[21], showing that the initial stage of polymerization of substituted anilines (where the initiation contributes substantially) is faster for the monomers of lower oxidation potential. Hence, in case of copolymerization the chain should start exactly from those monomers.
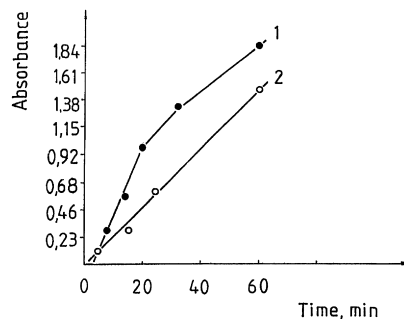
Fig. 7. Time dependence of the absorbance at 420 nm (characteristic of PBQ) at different pH values of the medium: 1, pH 9.0; 2, pH 4.5. Concentration of aniline, 0.04 mol l^{-1}; molar ratio of aniline/oxidant, 1; concentration of poly(vinyl alcohol coacetate), 2 wt%; $T = 23°C$[43].

It is worth noting that, besides PADPA, two other types of dimer can be formed upon oxidation of aniline (as shown in Wei's mechanism[14,21]): benzidine and N,N-diphenylhydrazine. It is well known that considerable amounts of benzidine (over 25% of the total amount of PADPA and benzidine)[10] were formed at pH values lower than 0, while N,N-diphenylhydrazine was formed in strongly alkaline medium[53]. Whereas the oxidized form of benzidine is capable of taking part in chain propagation, formation of azobenzene results in inhibition of polymerization.

2.2. *Chain propagation and termination*

The propagation of polymer chains proceeds by a redox process between the growing chain (as an oxidant) and aniline (as a reducer) with addition of 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 explains the presence of oxidized oligomers and pernigraniline at the initial stage of polymerization (see Fig. 4). Spectra were analyzed using available data on absorption of oligomers[52] and PANI of different oxidation state. The results presented in Fig. 6 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 chain length, n, presented in Fig. 3 (curve 3).

The high degree of oxidation (and consequently a high concentration of the imine bonds) of the growing chains at the initial stage of the polymerization, favors the hydrolysis of imine bonds. As we have shown in our investigations[44], this process is endothermic. Obviously, the effect of hydrolysis prevails over the effect of polymerization (exothermic) in the overall thermal effect, thus resulting in an overall endothermic effect, which was actually recorded at the initial stage of the process (Fig. 6, curve 2).

When the equilibrium electrochemical potential ($E \sim 0.7$ V), corresponding to pernigraniline degree of oxidation, has been established, reduction of PANI chains with addition of
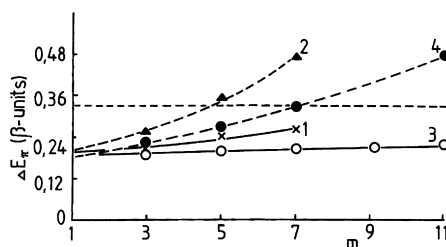
Fig. 8. Calculated change of E_π (β-units) on increasing degree of oxidation (number of detached electrons, m) of chains of various number of monomer units (n): 1, $n = 8$, deprotonated form; 2, $n = 8$, protonated form; 3, $n = 12$, deprotonated form; 4, $n = 12$, protonated form. The dashed line parallel to the abscissa is at the same level of ΔE_π as in Fig. 3 [42].

aniline was predominantly observed. This was evident by the lowering of E of the system and by exothermic effect of the process (Fig. 6, curve 1).

The system reached a new equilibrium at $E \sim 0.25$ V, corresponding to emeraldine degree of oxidation. The oxidation potential of PANI chains in this degree of oxidation is insufficient for the addition of aniline. The same conclusion can be drawn, when analyzing the results shown in Fig. 3 (curve 3 and dashed line). It is seen that ΔE_π, corresponding to the oxidation potential of PANI in emeraldine degree of oxidation is lower, as compared to 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 Fig. 3, curve 3), but also in intermediate steps between the emeraldine and the highest degree of oxidation (i.e. when $m > n/2 + 1$, see Fig. 8, curves 2, 4 and the dashed line parallel to the abscissa), which correspond to the previously suggested $-N=/-N- > 1$.

The relatively low oxidation potential of PBQ explains, in our opinion, the so-called induction period of aniline polymerization, observed by some authors[23,33]. The increase of the oxidation potential of the oxidized forms of oligoaniline on increasing length of the growing chains from PBQ to pernigraniline, is most likely the reason for autoacceleration in the reaction kinetics, which several authors[24–26,28,33] related to the formation of pernigraniline.

As we assumed in our first paper on the mechanism of polymerization[40], the reduction of growing chains with addition of aniline was controlled not only by their degree of oxidation, but also by the pH of the medium, which determines the degree of protonation of the chains. Thus, more time was necessary for the equilibrium E in the redox process between the growing chain and aniline to be reached, on increasing the pH of the medium from 0 to 6, and in neutral and alkaline media reduction did not occur, i.e. the polymerization process was terminated.

We have already shown[40] that the oxidative polymerization of aniline can be terminated by increasing the pH higher than 6 and reinitiated on acidification of the medium. (It is note-worthy, however, that Manohar et al.[38], proving that pernigraniline has been formed at the initial stage of the aniline polymerization, terminated the reaction, in fact the reduction, by alkalizing the reaction system. But they pay no attention to this experimental fact.) The only exception appeared to be the process of PBQ formation, which proceeds, as shown above, even favorably in neutral and alkaline media.
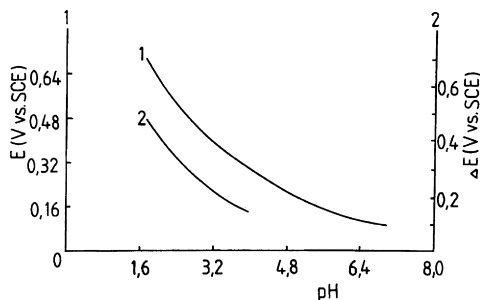
Fig. 9. Experimental dependence of the electrochemical potential, E, corresponding to pernigraniline (1) and the difference of the electrochemical potentials between pernigraniline and emeraldine, ΔE, (2), on pH of the medium[42].

In order to explain the observed termination of polymerization in neutral and alkaline media, we have suggested that the oxidation potential of oligo- and polyaniline chains depends not only on the degree of oxidation, but also on the degree of protonation of the chains. Thus, a decreasing degree 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 Figs 3, 8 and 9 show that both the calculated values of ΔE_π and the experimentally found E for the corresponding redox process, decreased considerably on deprotonation of PANI chains, i.e. on increasing pH of the medium. The deprotonation of PANI chains, according to the calculations (Fig. 3, curves 1 and 2; Fig. 8, curves 1 and 3), results also in a narrowing of the potential window in which the transition of PANI from the fully reduced (leucoemeraldine) into the fully oxidized (pernigraniline) form takes place. This corresponds very well to the experimental data from electrochemical oxidation of PANI (e.g.[54]), as well as to the dependence of the transition of PANI from emeraldine to pernigraniline on the pH of the medium (Fig. 9, curve 2), presented in this study.

The dependence of the oxidation potential of PANI chains (and hence, their ability to take part in various redox processes) on the degree of oxidation and protonation, determines to a great extent the behavior of the polymer, which will be discussed in more detail in the sections 'Electrochemical activity of polyaniline' and 'Emeraldine base–emeraldine salt transition'.

It is very important to note that two substantially different stages can be distinguished in the process of chain propagation: propagation of PBQ and growth of longer chains. This is most pronounced and informative when the polymerization proceeds in initially alkaline, neutral or slightly acidic media. We have first shown the existence of these two stages, following the pH changes during the aniline polymerization under the above mentioned conditions[41]. The process of PBQ formation and the increase of its concentration in the system was accompanied by a decrease of the medium pH (Fig. 5), which is indicative of considerably lower basicity of PBQ, as compared to aniline. As seen from Fig. 5, the propagation of PBQ (the first stage of the chain propagation) started only when the pH dropped below about 2, in contrast to the propagation of longer chains, which took place at pH < 6.

Hence, the possibility of initiation of the aniline oxidative polymerization in the whole pH range, which results in the formation of PBQ, having substantially lower basicity than aniline, allowed, under conditions leading to a decrease of pH below about 2, the polymerization of aniline to be carried out both in aqueous and non-aqueous media without added acids. Whether the necessary pH will be attained will depend on both PBQ concentration and the protophilicity of the solvent. Results from the study of electrochemical synthesis of PANI in organic solutions[55–58], as well as chemical synthesis of the polymer at low acid concentrations[23] confirmed our observations and conclusions.

Thus, the authors[58] have found, that 1,2-dichloroethane is a more effective solvent for the preparation of PANI without proton donor, as compared to acetonitrile and propylene carbonate, which are characterized with higher donor number (protophilicity). In the presence of the last solvents, in the author's opinion, the chain propagation will be inhibited until the proton concentration near the working electrode becomes higher. The period required for the increase in proton concentration near the working electrode, was referred to by the authors as induction time.

The two steps in the course of aniline polymerization at pH $\geq$ 4.2, have also been found by the authors[23] by using solution calorimetry. Each of these steps gives off varying amounts of heat, the second being substantially higher. There is a long 'delay' between the first heat evolution and the second. This 'delay time' is clearly dependent on the pH of the reaction medium: the increase of initial pH results in prolongation of the 'delay time'. In our opinion, the reaction period, named by the authors as 'delay time', corresponds to the period of PBQ accumulation, which, according to our observations, is accompanied by decrease of pH down to about 2, after which the chain propagation starts. Similar dependence of this period duration on the initial pH of medium is also seen in Fig. 5 (curves 2 and 3).

The process of PANI chain propagation, as a redox process between the growing chain and aniline [Fig. 10, eq. (3)], will take place until their oxidation potentials have not been equilibrated. This occurs on reaching the emeraldine oxidation state of the PANI chains. The corresponding potential, according to our investigations, as well as numerous studies on electrochemical oxidation of PANI, is approximately 0.2–0.25 V (at pH~1). (It has to be noted that we are not speaking of standard oxidation potential, which has to be determined under standard conditions using very precise experimental technique. For that reason, we specified the potential range corresponding to a defined redox transition. The same holds true in respect of all other potential values.) Hence, it can be supposed that the same electrochemical potential is characteristic also of the redox transition related to the oxidation of aniline upon its addition to the PANI chain [Fig. 10, eq. (1)]. The PANI chains are capable of growing when their oxidation potential is higher than 0.2(5) V, which takes place on keeping the following two conditions: oxidation state of the chains higher than emeraldine (i.e. =N–/–N– > 1) and pH of the medium lower than 6 (except for the growth of oxidized dimer, where pH of the medium has to be lower than 2) [as shown in Fig. 10, eq. (3a) and eq. (3b)].

Considerably lower electrochemical potential of the redox process concerning addition of aniline to the polymer chain, as compared to the potential relevant to its initiation (E~0.9), as well as the lower E necessary for oxidation of PANI chains (even to the highest oxidation state), determine the chain-growth type of the process. Namely, after the dimer formation, for the oxidant is more favorable to oxidize the dimer, trimer, tetramer...polymer, and for the monomer is more favorable to be added to the chain rather than to form new active sites. The
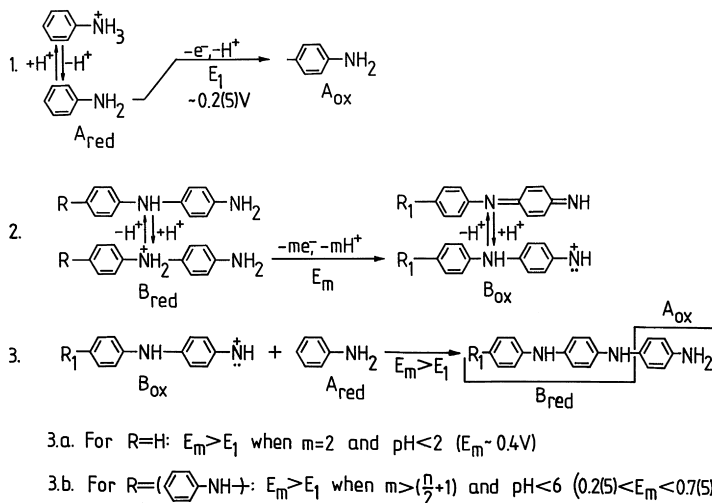
Fig. 10. Proposed mechanism of the chain propagation for the polymerization of aniline based on[39–43,45]. n, number of aniline units; m, number of electrons involved in the redox transition ($m = 2,4…n$); E_m, electrochemical potentials of the system, corresponding to each of $n/2$ redox transitions; A_{red} and A_{ox}, reduced and oxidized forms of the monomer, respectively; B_{red} and B_{ox}, reduced and oxidized forms of oligo- and polyaniline.

growing sites in this polymerization appear to be, most probably, nitrenium cations, since the chain propagation occurs solely in acidic medium, as shown above.

Therefore, the oxidative polymerization of aniline can be regarded as a new area in cationic polymerization, since the conditions of initiation, propagation and termination of the chains can be expressed by means of the electrochemical potential of the system. Moreover, this polymerization appears to be a living polymerization, since during the chain propagation all the chains are thermodynamically equivalent with respect both to the monomer addition (since they have the same oxidation potential) and the termination. The termination is a result of the establishment of thermodynamic equilibrium in the redox process corresponding to the chain propagation. Classical living polymerization, completing with total exhaustion of the monomer, is possible when the oxidation potential of the chains is kept higher than 0.2(5) V. The oxidation state of the resulting PANI, however, is also higher than emeraldine.

The higher the oxidation potential of the growing chains, the faster the equilibrium in the redox process determining chain growth is reached. This should be detected as an enhanced rate of polymer formation. Such an 'accelerating' effect in aniline polymerization should show, for example, dimers (able to add aniline) of oxidation potential higher than that of PBQ, but naturally lower than E of aniline oxidation. Actually, results from investigations of aniline polymerization in the presence of aromatic additives[14,19,25,28] confirmed this assumption, additives with oxidation potential in the range of 0.6–0.7 V showing an accelerating effect.

A similar approach can be used in the study of polymerization of substituted anilines and their copolymerization with aniline. Indeed, comparing the cyclic voltammograms of PANI and its derivatives with the kinetics of polymerization of aniline and the respective monomers[15,21], it can be seen that the polymerization rate is higher with the monomers

possessing higher oxidation potential of the growing chain (particularly dimer and pernigraniline).

Further, in aniline copolymerization with substituted anilines, the growing chains of which (e.g. in pernigraniline oxidation state) possess lower oxidation potential than the fully oxidized PANI, a lower rate of the process should be observed, as compared to PANI, which was actually found[15]. It can be supposed that tailor-made copolymers of aniline and its derivatives of predicted composition and sequence distribution could be obtained by regulating the potential window, where the copolymerization will take place.

The main conclusion to be drawn from the above discussion can be formulated as follows. Consideration of aniline polymerization first of all as a redox process, implies PANI should be regarded as a compound characterized by a sequence of defined oxidation potentials. Their values are determined by the degree of oxidation and the degree of protonation of the chain. In its turn, the value of the oxidation potential of PANI chains determines the direction of the redox processes with their participation. Thus, the oxidative polymerization of aniline appears to be a particular case of *demonstration of the electrochemical activity of polyaniline*. Detailed analysis of the current state of investigations on the electrochemical activity of PANI will be presented in the section 'Electrochemical activity of polyaniline'.

We find it necessary, however, to discuss in advance the influence of hydrolysis on the oxidative polymerization of aniline. The mechanisms of the two processes are not interrelated. Nevertheless, in our opinion, the hydrolysis has also to be regarded from the standpoints of the suggested approach.

3. INFLUENCE OF HYDROLYSIS ON THE OXIDATIVE POLYMERIZATION OF ANILINE

As far as the authors are aware, there are only a few data on the influence of hydrolysis of the imine nitrogen–carbon bonds on the chemical polymerization of aniline. Thus, elemental analysis data of PANI, prepared by chemical oxidative polymerization at high HCl concentration (2–4 M) have revealed a deficit of nitrogen atoms (with respect to carbon atoms) which equaled the number of oxygen atoms introduced into the chain[59]. This was explained by the hydrolysis of imine nitrogen–carbon bonds, which may result in either chain breaking [Fig. 11, eq. (1)] or nitrogen elimination if an end-group is involved [Fig. 11, eq. (2)]. The hydrolysis that occurred in more acidic media became significant for PANI exhibiting a higher oxidation state than that of emeraldine.

The mechanism of hydrolysis in the processes of electrochemical and chemical oxidation of aniline has been studied in detail under conditions when PANI has not been formed, i.e. at constant electrode potential higher than 0.75 V[11–13]. The oxidation of aniline under these conditions resulted in the formation of PBQ and was accompanied by hydrolysis of the PBQ formed.

Summarizing the experimental results from the electroanalytical studies, preparative electrolysis and preparative chemical oxidation of aniline in 0.5 N and 6 N H_2SO_4, Hand et al.[13] suggested the following mechanism of formation and hydrolysis of PBQ [Fig. 11, eq. (3)].

However, this mechanism was based on the identification of the final products and on Hueckel molecular orbital (HMO) calculation of the fully protonated diimine, but not on the experimental observations of the intermediates. Intermediates both in this mechanism (hydrolysis in position 2), as well as in the only plausible alternative mechanism (hydrolysis
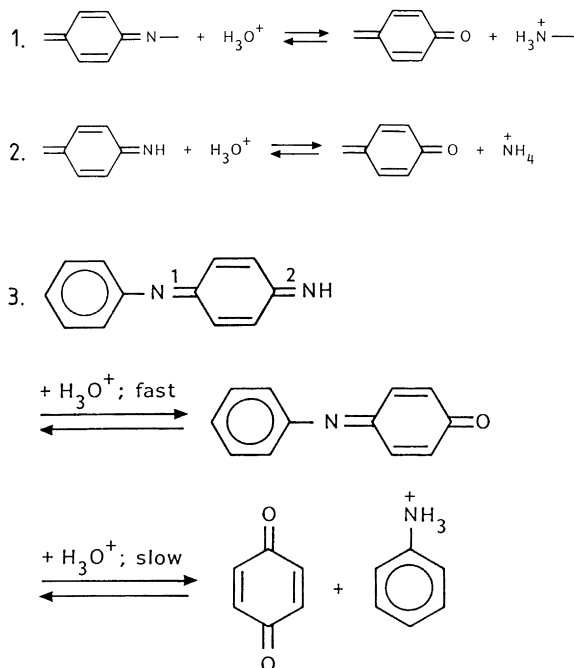
Fig. 11. Hydrolysis of imine nitrogen–carbon bonds in polyaniline (1, 2) and in N-phenyl-1,4-benzoquinonediimine (3).

in position 1) have not been detected. In view of the experimental evidence, or the lack thereof (especially the absence of either intermediate) it was not possible to determine which mechanism was operative, though according to Hand et al. on the basis of HMO calculations[13], the former was favored.

Summarizing the data on the mechanism of oxidative polymerization of aniline and on the concomitant hydrolysis presented above, it can be stated that under certain conditions the hydrolysis competes with the polymerization. Such conditions, in our opinion, appear to be mainly the potential window, pH of the medium and temperature of polymerization.

The influence of the last parameter is associated with the opposite thermal effects of the two processes: exothermic polymerization and endothermic hydrolysis.

Only recently have publications appeared, wherein the authors have tried to estimate the extent of influence of hydrolysis on the process of PANI synthesis[35,60,61]. In both cases the ratio between hydrolysis and polymer chain growth has been studied in electropolymerization of aniline in presence of strong acids (sulfuric acid and perchloric acid). The authors[35], using the mechanism suggested by Hand, have assumed that hydrolysis proceeds most probably at the stage of PBQ formation. After the polymer formation (in pernigraniline form), hydrolysis is not likely to take place due to the presence of aniline. That means that according to the authors, it is very likely that PANI in pernigraniline form will attach an aniline molecule rather than water molecule. The authors[60] have also considered the competitive power of hydrolysis in respect to polymerization from the viewpoint of the concentration ratio of the participants in competing reactions. In our opinion, such an approach is not quite correct for
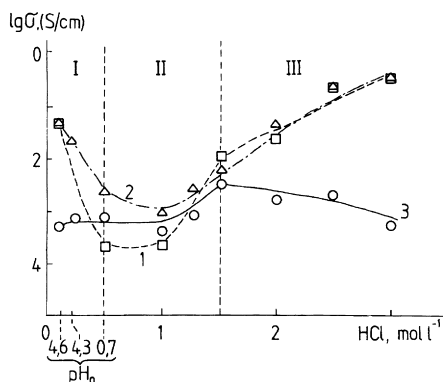
Fig. 12. Conductivity of composite (PANI + poly(vinyl alcohol coacetate)) films versus HCl concentration in the polymerizing mixture at various initial temperatures, T_0: curve 1 ($\square$), 2°C; curve 2 ($\triangle$), 4°C; curve 3 ($\bigcirc$), 30°C. Concentration of aniline, 0.2 mol l^{-1}; aniline/oxidant molar ratio, 1; concentration of poly(vinyl alcohol coacetate), 10 wt% [44].

the same reasons stated above in the discussion of polymerization mechanism. We attempted to avoid these shortcomings in a study of the influence of hydrolysis on the polymerization of aniline[44], the results being shown below.

We estimated the influence of hydrolysis on the process of oxidative polymerization of aniline by the effect of the above mentioned parameters on the yield of PANI. The yield was evaluated by the conductivity of composite films cast from aqueous dispersions of PANI prepared by polymerization of aniline in the presence of poly(vinyl alcohol coacetate). The plots of conductivity of films vs HCl concentration and T_0 presented in Fig. 12, revealed three regions of HCl concentration, differing in the extent of its effect on the yield of the conducting constituent. In the first region (I), the initial values of pH of the reaction system were changed within wide limits: from $pH_0 = 4.6$ for 0.1 M HCl to $pH_0 = 0.7$ for 0.5 M HCl. In the slightly acidic region (pH > 4) the conductivity of the films increased considerably (about two orders of magnitude) on decreasing the initial temperature, T_0, from 30 to 4–2°C, whereas at pH~0.7 the influence of temperature was not substantial (compare curve 3 with curves 1 and 2 in region I of Fig. 12), and even decreasing T_0 did not result in increased conductivity of the films. This last tendency of relatively low yield of PANI and its independence on temperature was observed also in the second region (II) of HCl concentration (from 0.5 to 1.5 M). Further increase of HCl concentration (region III, Fig. 12) resulted in a situation analogous to the slightly acidic region, i.e. decreased T_0 resulted in an abrupt increase in conductivity of the films obtained (compare curves 1 and 2 with curve 3 in region III, Fig. 12).

Based on these results it can be supposed that the hydrolysis effect is substantial in the whole range of HCl concentration studied. However, the strong hydrochloric acid is not suitable for elucidation of the influence of hydrolysis on the PANI yield. First, a variation of its concentration in a very narrow range results in an abrupt change of pH_0 of the medium; secondly, as a strong acid it does not possess a buffering ability. Thus, it is not possible to keep a constant pH in a certain time interval during polymerization in the presence of hydrochloric acid.
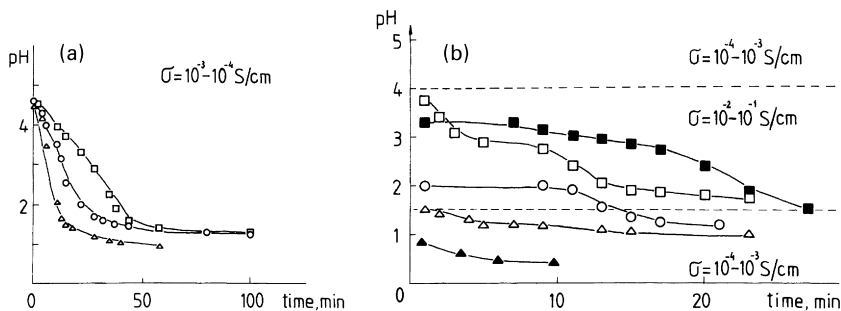
Fig. 13. (a) Variation of pH during the polymerization of aniline in the presence of: 0.1 M formic acid ($\square$), 0.1 M hydrochloric acid ($\triangle$), 0.15 M orthophosphoric acid ($\bigcirc$). Concentrations of aniline, poly(vinyl alcohol coacetate) and molar ratio aniline/oxidant as shown in Fig. 12; $T_0 = 23°C$ [44]. (b) Variation of pH during the polymerization of aniline in the presence of: 1 M monochloroacetic acid ($\square$), 1 M orthophosphoric acid ($\triangle$), 1 M formic acid ($\blacksquare$), 5 M formic acid ($\bigcirc$), 0.5 M hydrochloric acid ($\blacktriangle$). Concentrations of aniline, poly(vinyl alcohol coacetate) and molar ratio aniline/oxidant as shown in Fig. 12, $T_0 = 23°C$ [44].

However, it was interesting to find exactly the ranges of pH (but not the concentration of a particular acid) where the influence of hydrolysis on the chemical oxidative polymerization of aniline is most pronounced, as pH can be regarded as a parameter summarizing the influence of both the concentration and the strength of the acids and bases present in the system. For that purpose we studied the polymerization of aniline at different initial pH values, pH_0, from 5 to 0 and for various rates of change of pH during the process. For that reason, except for the strong hydrochloric acid, various other acids of pK_a in the range of 2–5 (orthophosphoric, monochloroacetic, formic, acrylic, and acetic acids) were used. The most illustrative results are shown in Fig. 13a and 13b.

Based on these results, three main pH regions differing by the extent of the influence of hydrolysis on the yield of PANI can be distinguished. In the first region ($pH_0 > 4$) (Fig. 13a) the effect of hydrolysis is substantial, as judged by the low conductivity ($\sigma = 10^{-3}$–10^{-4} S/cm) of the films obtained from dispersions prepared at $T = 23°C$. The conductivity of these films increased considerably (about two orders of magnitude) on decreasing the initial temperature from 23 to 4–2°C. In the second range, $1.5 < pH_0 < 4$ (Fig. 13b), films of higher conductivity ($\sigma = 10^{-2}$–10^{-1} S/cm) can be obtained at $T_0 = 23°C$ and the conductivity of the films does not depend on polymerization temperature in the whole range studied ($T_0 = 2$–30°C). These experimental facts suggest the negligible effect of hydrolysis on the yield of PANI in this pH range. In the third range ($pH_0 < 1.5$) a strong influence of hydrolysis on the yield of PANI similar to that described above for slightly acidic medium ($pH_0 > 4$), was observed.

All these experimental results can be explained as follows. As shown above, at the initial stage of the process (8–10 min at room temperature), oxidized oligomers and pernigraniline have been formed consecutively. It is natural to suggest that, exactly at this stage of the polymerization process, the hydrolysis of imine nitrogen–carbon bonds would have the most substantial effect.

Further, as mentioned above, reduction of PBQ proceeded at a measurable rate only at pH < 2, in contrast to the longer oxidized chains where reduction took place at higher pH
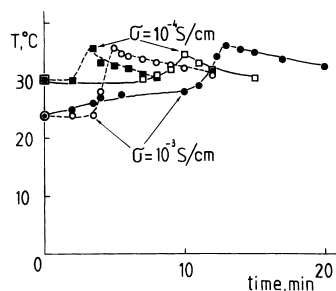
Fig. 14. Variation of temperature during the polymerization of aniline at different HCl concentrations: ●,□, 0.1 M; ○,■, 3 M. Concentrations of aniline, poly(vinyl alcohol coacetate) and molar aniline/oxidant ratio as shown in Fig. 12[44].

values as well. Therefore, in polymerization of aniline under conditions when $pH_0 \gg 2$, an initial time interval should exist (before reaching the value of $pH \sim 2$) when PBQ formation and its hydrolysis take place, but reduction practically does not occur. This actually occurred when polymerization took place at $pH_0 > 4$, i.e. at low concentration of the acid (Fig. 13a). Evidence that in polymerization at $pH_0 > 4$, hydrolysis considerably affects the yield of the conductive constituent (and thus the conductivity of the films obtained), is the above discussed dependence of the yield of PANI on the T_0.

Additional confirmation of the suggestion that hydrolysis affects mainly the initial stages of polymerization (at $pH_0 > 4$ the stage of PBQ formation) is decreased conductivity of the film obtained by polymerizing aniline in 0.1 M HCl at $T = 23°C$ ($\sigma = 10^{-3}$ S/cm), as compared to a similar film obtained at $T = 30°C$ ($\sigma = 10^{-4}$ S/cm) under conditions when the highest polymerization temperature, T_{max}, is equal in both cases (Fig. 14). When polymerization (initial stage) proceeds at $pH_0 < 4$, and especially at $pH_0 \sim 2$, conditions exist that are probably more favorable for reduction than for hydrolysis both of PBQ and of longer oxidized chains. Such conditions could be created when acids of medium strength (formic, mono-chloroacetic) were used. In a fairly large range of concentration they correspond to the above stated conditions in respect to pH_0 ($1.5 < pH_0 < 4$). Under those conditions pH at the initial stage was kept between 4 and 1.5 due to buffering ability of these acids. As a result, films of conductivity 10^{-2}–10^{-1} S/cm were obtained (Fig. 13b). As a consequence of the negligible effect of hydrolysis on the yield of PANI under these conditions, the conductivity of the films does not depend on polymerization temperature in the whole range studied ($T = 2$–$30°C$).

When the polymerization took place in initially strongly acidic medium, conditions were again created where hydrolysis and reduction proceeded as competitive processes. As a result, films prepared at $pH_0 < 1.5$ and $T = 23°C$ revealed conductivity in the range of 10^{-3}–10^{-4} S/cm (Fig. 12, regions II and III; Fig. 13b). It is worth noting, however, that the dependence of the PANI yield on the reaction temperature, which in our opinion is an indirect measure of the influence of hydrolysis on the process of aniline polymerization, differs considerably in the pH ranges $0 < pH_0 < 1$ (concentration of HCl 0.5–1.5 M) (Fig. 1, region II) and $pH_0 \sim 0$ (HCl concentration higher than 1.5 M) (Fig. 1, region III).

As seen from Fig. 12, the increase in conductivity of the films on decreasing T_0 was observed only at HCl concentration higher than 1.5 M (region III). According to our statement, the hydrolysis in this pH range is competitive with polymerization. The decrease of T_0
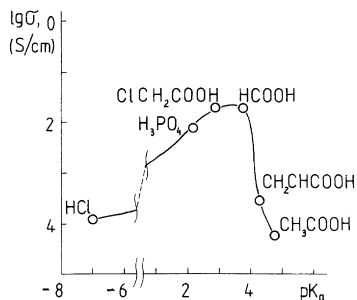
Fig. 15. Conductivity of composite (PANI + poly(vinyl alcohol coacetate)) films cast from dispersions, prepared in 1 M solution of various acids versus pK_a of the acids. Concentrations of aniline, poly(vinyl alcohol coacetate) and molar aniline/oxidant ratio as shown in Fig. 12, $T_0 = 23°C$[44].

down to 2–4°C allows PANI of high yield (conductivity 10^{-1} S/cm) to be obtained even in a strongly acidic medium. By analogy with slightly acidic medium ($pH_0 > 4$), in this case temperature affects most considerably the initial stage of polymerization too, i.e. the yield of PANI is affected by T_0. Thus, the increase of T_0 from 23°C to 30°C when polymerization took place in 3 M HCl, resulted in decreased conductivity of films from 10^{-3} to 10^{-4} S/cm (Fig. 14).

In the concentration range 0.5–1.5 M HCl (Fig. 12, region II), however, the change of T_0 from 2 to 30°C practically did not change the conductivity of films; a conductivity of 10^{-3}–10^{-4} S/cm was observed even at low temperature, with a following slight increase at the border line between regions II and III.

Probably, the range $0 < pH_0 < 1$ corresponding to II is not only characterized by the substantial effect of hydrolysis on the yield of PANI, but also is not favorable for the polymerization of aniline itself, which results in a lower yield of PANI. Similar results have been obtained by Duic and Mandic[18] when the electrochemical polymerization of aniline at different pH_0 values was studied.

Another approach we have used to illustrate the dependence of PANI yield on pH_0 and on the pH range where the initial stage of the polymerization proceeds was polymerizing aniline in 1 M solution of acids of different pK_a values: hydrochloric, orthophosphoric, monochloroacetic, formic, acrylic, acetic. This selection of acids of different strength enabled us to cover all the pH ranges, using the same (1 M) concentration.

Thus, the dependence of the conductivity of films, prepared at $T_0 = 23°C$ by using 1 M solutions of the above-mentioned acids, on their pK_a (Fig. 15), reflects the influence of the pH range where the polymerization takes place on the PANI yield. The dependence obtained reflects in a generalized form the information presented in Fig. 13a and 13b. It enabled us to draw the conclusion that in the presence of acids of medium strength ($2 < pK_a < 4$) the influence of hydrolysis on the polymerization of aniline was reduced to a minimum, and films of the highest conductivity were obtained.

Therefore, the following ranges of pH_0, which differ in the extent of the influence of hydrolysis on the oxidative polymerization of aniline can be distinguished:

- at $pH_0 > 4$ and $pH_0 < 1.5$ hydrolysis has a profound effect and cooling to at least 5°C is a necessary condition for its elimination;

- at $1.5 <$ pH$_0 < 4$ the effect of hydrolysis is negligible and polymerization with a high yield occurs in a wide range of temperature; as the pH of the medium decreases during oxidative polymerization of aniline, it is advisable to use acids of medium strength ($2 < pK_a < 4$) in order to keep a nearly constant pH value at the initial stage of the polymerization (stage of oxidized products).

In conclusion it is noteworthy that kinetic characteristics of the polymerization process of aniline such as changes in temperature and electrochemical potential, weight of the product obtained, overall current density and/or film charge, cannot reflect the actual mechanism of polymerization, when the hydrolysis effect has not been taken into account. Very often, however, studies of the polymerization kinetics aimed to elucidate the mechanism have been performed by electrochemical (for example[29–31]) or calorimetric[23,33] methods. Besides, the influence of hydrolysis (the mechanism of which has nothing in common with the polymerization mechanism) on the molecular mass and molecular mass distribution of PANI, does not allow these characteristics to be employed in the elucidation of the mechanism of polymerization, except for the cases when the conditions of the process studied minimize this side reaction.

Further, the influence of hydrolysis should be taken into account in investigations of the electrochemical activity of PANI as well.

4. ELECTROCHEMICAL ACTIVITY OF POLYANILINE

The key problem in understanding the physical and electrochemical properties of PANI appears to be the investigation of its electrochemical activity, i.e. the establishment of the basic principles of the redox processes determining the changes of oxidation state of the polymer. A lot of studies on the electrochemical properties of PANI (for example[2–4,8,62,63]) have been directed toward both the examination of the redox processes themselves and the preparation of PANI of defined oxidation state. The basic methods for investigation of the electrochemical activity of PANI are various kinds of voltammetry.

The existing concept based on these investigations, presented by the generalized scheme in Fig. 1, can be briefly formulated as follows.

- PANI exists in three well defined oxidation states: leucoemeraldine, emeraldine and pernigraniline. Cyclic voltammetry actually reveals two redox processes (or the so-called oxidative doping of polyaniline). They correspond to the transitions from leucoemeraldine to emeraldine and from emeraldine to pernigraniline, although the existence of a limited potential window of conducting state (emeraldine) and the corresponding three-state switching, have been regarded as a surprising behavior, as compared to the conventional semiconductors[8].
- The electrochemical activity of PANI (evaluated by the positions of the oxidation and reduction peaks, the shape of the transitions, anodic and cathodic charge) depends mainly on the pH of the medium; in neutral and alkaline media PANI loses its electrochemical activity.

However, the results of detailed studies of the redox behavior of PANI reported recently have necessitated a critical attitude towards the above mentioned statements[64–76]. Thus, the authors[64–70] have convincingly shown that:

- the redox behavior of PANI is characterized by a fundamental asymmetry;

- during oxidation the PANI system is far from equilibrium, while during reduction it is much closer to equilibrium;
- the oxidation peak current depends on both the 'wait-time' of the PANI electrode at the negative potential and the sweep rate, the so-called 'memory effect';
- the oxidation process is completed, but reduction is not entirely completed on the timescale of cyclic voltammetry;
- the reduction transient is more rapid than the oxidation one;
- PANI does not lose its electrochemical activity in neutral and alkaline media; merely, there are two prerequisites for its registration: (a) higher sweep rate (100 V/s), so that the timescale of the experiments is in the millisecond range, and (b) preliminary keeping (for a few minutes) of the PANI coated electrode at proper negative potential (from -0.2 to -0.8 V on increasing pH from 3.2 to 9.3).

It is worth noting that, in spite of the above cited statements, for the main question 'why do oxidation and reduction occur by different pathways?', Peter et al.[65] offered a 'geometrical' explanation: the nucleation and growth of a separate phase with different chemical potential on oxidation and progressive contraction of a network of this separate phase on reduction, respectively.

This suggestion is quite provisional even for explanation of the different pathways of the transitions and does not explain at all the observed difference in the rates of the oxidation and reduction processes, as well as their dependence on pH of the medium. Further, registration of the so-called 'blue products' in the range of the second peak of the cyclic voltammogram, is usually explained by reference to the coexistence of PANI chains of different oxidation states (pernigraniline and emeraldine)[76,77]. This explanation corresponds also to the growth of a separate phase with defined chemical (more precisely electrochemical) potential.

It is also noteworthy that the oxidation of PANI, which has been recorded by Peter et al. as complete on the timescale of cyclic voltammetry, was really complete only in the time intervals mentioned. So, for pernigraniline[78] and for the 'blue products'[79] as well, relaxation (reduction) to emeraldine was observed under conditions of open-circuit experiments, when the observation time considerably exceeded the timescale of cyclic voltammetry.

The only assumption, allowing the explanation of the above described observations within the framework of the existing concept, is the possibility of coexistence of separate phases of different electrochemical potentials (viz., leucoemeraldine/emeraldine and emeraldine/pernigraniline) at a defined electrode potential.

In our opinion, a more likely explanation is the possibility of not only two, but a sequence of $n/2$ redox transitions in PANI, leading to the formation of products of gradually changing degree of oxidation, which is excluded according to the existing concept. The registration of the whole spectrum of redox transitions (or products of gradually changing degree of oxidation) would prove unequivocally our alternative concept. The possibility of recording of these products (or corresponding transitions) is determined by their stability towards reactions changing their oxidation potential (redox processes concomitant to the electrode processes) and hence by the conditions of investigation of the electrochemical activity of PANI.

The possibility of the occurrence and the direction of redox processes with participation of PANI chains depended on the oxidation potential of PANI chains (determined by the oxidation state and the degree of protonation) and the oxidation potentials and the concentrations of oxidants and reducers present in the system (or the electrode potential in the case of electro-

chemical processes). The chain growth, which is in fact a redox process between an oxidant (PANI chain) and a reducer (aniline), resulting in addition of aniline to the chain, takes place when E of the system is higher than 0.2(5) V. Thermodynamic control of the chain propagation and termination suggested a possibility for the presence of residual monomer (and oxidant in case of standard chemical oxidation) in the polymer.

Consequently, the redox processes with participation of PANI, occurring at defined electrode potential by interaction not only with an electrode (anode or cathode upon oxidation and reduction, respectively), but also with other oxidants and reducers present in the system (oxygen, aniline), have to affect the main characteristics of voltammograms related to the electrochemical activity of PANI.

Extending our investigations on the mechanism of aniline polymerization, we have simulated the conditions usually used in the study of the electrochemical activity of PANI[45]. Using oxidants and reducers (instead of working electrode) for oxidation and reduction of PANI, we were able to avoid the occurrence of the possible electrode effects, viz. formation and growth of separate phases with defined electrochemical potential. The values of the electrochemical potential during the oxidation or reduction were recorded using in situ potential measurements.

Using this approach we tried to formulate a new concept of the electrochemical activity of PANI, based on answers to the following questions:

- which are the processes revealed in the voltammetric study of PANI; how are they related to the electrochemical activity of the polymer?
- which are the factors affecting the actual electrochemical activity of PANI and how it can be recorded?

Thus, we have studied the processes of oxidation and reduction of PANI under conditions simulating those of voltammetry. The choice of the potential window between 0.2(5) and 0.75 V corresponding (at pH 0–1) to the region between the two peaks and to the second peak in the cyclic voltammogram, was prompted by the following considerations. Firstly, in this very region PANI reveals its surprising behavior and secondly, objective experimental obstacles exist associated with the maintenance of low E values (lower than 0.2 V) at pH 0–1, corresponding to the region before the first peak in cyclic voltammogram of PANI.

Oxidation of PANI in the range of E between 0.2(5) and 0.75 V (pH~1, room temperature) was performed by gradually adding increasing amounts of strong oxidant, $(NH_4)_2S_2O_8$, into PANI dispersion containing the polymer in emeraldine oxidation state (see point A in Fig. 16a and Fig. 17, corresponding to the values of λ_{max} and E of the initial system, respectively). Initial PANI dispersion was prepared by oxidative polymerization of aniline at 20°C in 5 M formic acid at aniline concentrations of 0.2 mol/l and oxidant/aniline molar ratio of 0.5, using poly(vinyl alcohol coacetate) as the steric stabilizer and $(NH_4)_2S_2O_8$ as the oxidant[44,46]. The non-equilibrium behavior of the oxidation process in the region of E values of 0.2(5)–0.75 V was evidenced by the relaxation of the system (except for a very high excess of oxidant), with respect to both E and oxidation state of PANI, from a state intermediate between emeraldine and pernigraniline, into a state corresponding to emeraldine (Figs 16 and 17). Besides, the process itself and the registration of PANI in intermediate oxidation state during our experiments cannot be explained by the formation and growth of a phase of defined electrochemical potential, as suggested by Peter et al.[64,65] and other authors[71,72,77].

The only logical explanation of the observed processes appears to be the occurrence, under
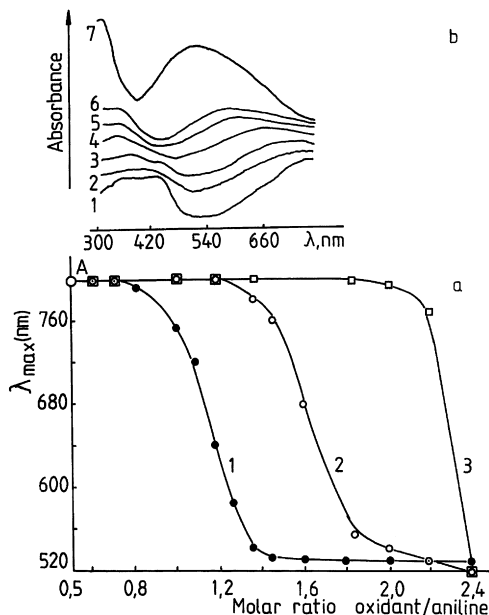
Fig. 16. (a) Dependence of λ_{max} in the visible range of the electronic absorption spectrum of PANI on the molar ratio oxidant/aniline at different times of oxidation: 1, 5 min; 2, 60 min; 3, 24 h. (b) Electronic absorption spectra of polyaniline at different oxidation states: 1, emeraldine; 2–6, "blue products"; 7, pernigraniline[45].
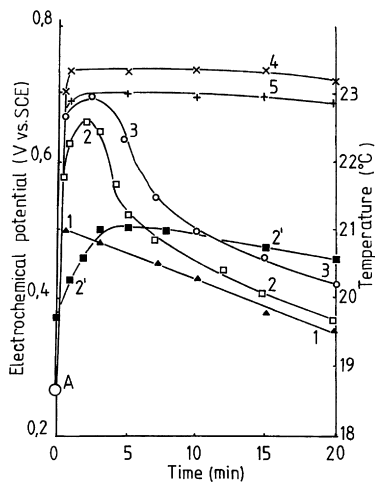
Fig. 17. Electrochemical potential–time (curves 1–5) and temperature–time (curve 2′) profiles of the PANI oxidation at different oxidant/aniline molar ratios: 1, 0.6; 2 and 2′, 0.8; 3, 1.1; 4, 1.45; 5, 2.4[45].

the given conditions, both of oxidation of PANI chains and their subsequent reduction (with addition of aniline), which is in fact a polymerization (post-polymerization) process. Therefore, the conditions determining the ability of the system to oppose the oxidation (i.e. to relax into a state corresponding to emeraldine oxidation state), should be the same as the above mentioned conditions of aniline polymerization.

Thus, if the real electrochemical activity of PANI in the potential window between 0.2(5) V and 0.5 V has been obscured by the post-polymerization, its registration should be possible by elimination of the influence of this concomitant redox process. Hence, on changing the experimental conditions of cyclic voltammetry from favorable to unfavorable for post-polymerization (exhausting the monomer, increasing the pH and the sweep rate, decreasing the temperature), a tendency to a monotonic shape of anodic transition has to appear.

Similar consideration can also be used for the other potential regions, where PANI reveals its electrochemical activity. In the range of low potentials ($E < 0.2$ V), it is possible for oxidation of PANI by oxygen to occur, while at $E > 0.5$ V the electrode processes can be accompanied by hydrolysis of PANI. Therefore, registration of the real electrochemical activity of PANI in these cases is also possible only upon elimination of the concomitant processes. We will try to prove all these assumptions by our own experiments and also the results of other authors set forth below.

(1) The possibility for occurrence of post-polymerization is related, first of all, to the presence of residual monomer in PANI of emeraldine oxidation state resulting from oxidative polymerization of aniline. The presence of residual monomer in the polymer obtained by electrochemical and chemical (even in homogeneous conditions) polymerization has been noted by some authors[80,81]. On the one hand, this results from the thermodynamic control of propagation and termination of PANI chains, as mentioned above. On the other hand, the very presence of residual monomer determines the stability of emeraldine oxidation state in a quite wide potential range (0.2–0.5 V), and also the well known stability of voltammetric characteristics upon multicycling (up to 10^6 cycles) in the potential range mentioned[3]. In this range oxidation of aniline cannot occur. PANI chains, however, are oxidized into an oxidation state higher than emeraldine (see Fig. 17, curve 1). Then, they are able to interact with the monomer (by adding it) and to restore the emeraldine oxidation state. Actually, the absence of residual monomer in PANI films (prepared for example using the Langmuir–Blodgett technique[82,83]) resulted in obtaining PANI in the pernigraniline oxidation state. Hence, PANI when devoid of its own protector (aniline), can be oxidized easily (e.g. by atmospheric oxygen). An excess of proper reducer has to be added in order for the emeraldine oxidation state to be kept. This excess must be considerably higher, since, in contrast to the aniline, the typical reducer ($E < 0.2$ V) will react not only with the oxidized PANI chains, but also with the 'external' oxidant providing the range $0.2 < E < 0.5$ V.

Actually, after adding a high excess of oxidant into PANI in emeraldine oxidation state (i.e. creating conditions for complete exhaustion of the monomer), in reversal of the electrochemical potential of the system into emeraldine oxidation state, we used different reducers ($Na_2S_2O_3$ and ascorbic acid) (Fig. 18). As seen, in order for the emeraldine oxidation state of PANI chains to be reached and also to be kept for a long time, a very high (in respect of the stoichiometry) excess of reducer is needed.

The low oxidation potentials of PANI in emeraldine and lower than emeraldine oxidation
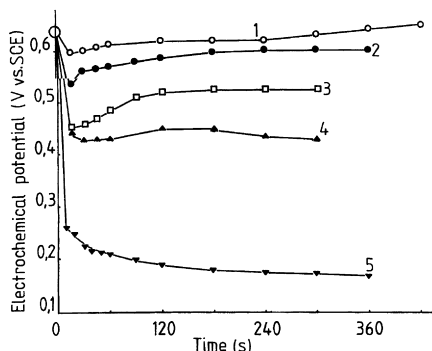
Fig. 18. Electrochemical potential–time profile of the reduction of preliminary oxidized PANI (molar oxidant/aniline ratio of 2.4) with different reducer/aniline molar ratios: 1, 0.36; 2, 0.57; 3, 0.65; 4 and 5, 1.2. Curves 1–4 correspond to $Na_2S_2O_3$ and curve 5 corresponds to ascorbic acid[45].

states, even in acidic medium, suggest the easy oxidation of these products (even from atmospheric oxygen). This appears to explain the dependence of the anodic peak current on the sweep rate[69,70,83], the 'memory effect'[64–70] (which in our opinion reflects the dependence of the degree of reduction of PANI on the 'wait-time' of PANI coated electrode at negative potential), as well as the obligatory presence of an excess of strong reducer in order for leucoemeraldine to be obtained. Moreover, prolonged keeping of leucoemeraldine is possible only in an inert atmosphere (e.g.[84]).

(2) Evidence that the observed relaxation appears to be a post-polymerization can be illustrated by our following experiments, and also by the results of other authors. As seen (Fig. 17, curve 2′), the relaxation process was accompanied by an exothermic effect, which is characteristic of aniline polymerization. Study of the thermal effects concomitant to electrochemical oxidation of PANI revealed similar exothermic effect in the potential range mentioned (0.2 V $<$ E $<$ 0.5 V)[85].

Further, the post-polymerization has to result in an increasing yield of PANI. With the polymer blends PANI + poly(vinyl alcohol coacetate) studied, this should give rise to a higher content of the conductive constituent, thus enhancing the electrical conductivity. We have observed increased conductivity of two orders of magnitude (from 10^{-3} to 10^{-1} S/cm) in films cast from PANI dispersions obtained upon increasing molar ratio oxidant/aniline from 0.5 to 0.8 (corresponding to an increase of the PANI content from 7 to 12 wt%). Still further, Aoki et al.[71,72] studied the growth of conducting zone in PANI film in the range of electrode potential 0.22–0.5 V. The authors mentioned that iterative switching up to 0.6 V resulted in a gradual decrease in the growth rate. In our opinion, the experimental facts described can be explained by post-polymerization and gradual exhaustion of the monomer upon iterative switching up to a potential higher than 0.5 V. According to the authors themselves, however, after the percolation threshold potential, which was determined to be 0.22 V, growth of the conducting zone into the insulating zone occurred. In fact, this explanation also suggested coexistence of separate phases with different electrochemical potentials at a defined electrode potential. Pistoia[73] has shown that, if the PANI electrode is conveniently polarized and then left on open circuit, polymer growth occurs in the absence of current. The author even

referred to this phenomenon as 'post-polymerization effect', which was most pronounced when the electrode has been polarized at 0.5 V.

(3) In the potential range 0.5 V $< E <$ 0.75 V (oxidant/aniline molar ratio of 0.8–2.2) the relaxation time increased considerably and real conditions for registration of the so-called 'blue products' (530 nm $< \lambda_{max} <$ 800 nm) and pernigraniline ($\lambda_{max} =$ 530 nm) were created (Fig. 16). These products have been observed in the region of the second oxidation peak of the cyclic voltammograms. However, the conditions used in our experiments allowed us to assert that these products did not result from coexistence of PANI chains (or separate phases) in emeraldine and pernigraniline oxidation state, as was suggested previously[64–68,76,77], but from PANI chains in intermediate oxidation states between emeraldine and pernigraniline.

Much longer times of relaxation of these products into emeraldine oxidation state, as compared to the timescale of cyclic voltammetry, made possible their recording and explained their above-mentioned ability to restore the emeraldine oxidation state upon keeping for several hours under open-circuit conditions[78,79].

The termination of post-polymerization (relaxation) of the 'blue products' and pernigraniline by removal of the electrolyte may be supposed to be a prerequisite for obtaining these products. Under the conditions used, we succeeded in obtaining products characterizing by 530 nm $< \lambda_{max} <$ 800 nm and corresponding electrical conductivity in the range 10^{-7}–10^{-2} S/cm, when films cast from PANI dispersions (prepared at oxidant/aniline molar ratio of 1.8–2.2) were dried for 2 h at room temperature.

Obviously, when the drying conditions of the 'blue products' and pernigraniline (pH, temperature, duration) are favorable for post-polymerization, the dry product will possess lower oxidation state, as compared to the corresponding wet product. Possibly, such a post-polymerization during the transition from 'wet state' to 'dry state' has been actually observed by the authors[86], which have found that pernigraniline oxidation state is unstable and cannot be obtained in the dry state.

Upon oxidation of PANI at $E >$ 0.5 V (particularly at $E >$ 0.7 V), conditions arise for hydrolysis of $\rangle$C=N– bonds, which results in chain breaking, leading to formation of PANI chains of various length, as well as of low-molecular-weight products such as benzoquinone and aniline[13,60,61,77]. Most probably, the aniline thus formed is a reducer for the 'blue products' and pernigraniline, obtained in this potential range.

By the influence of hydrolysis during prolonged cycling in the potential range $-$0.2–0.8 V (sweep rate of 30 mV/s, more than 20 cycles), the authors[77] explained the decrease of anodic peak current. Further, the authors[81] have also shown that the decrease in anodic peak current and in anodic charge depended on the positive potential 'limit', as well as on the duration of cycling. Thus, at $E =$ 0.98 V the anodic charge decreased for 10 min by several orders of magnitude.

A similar decrease in oxidizing capacity of the system (corresponding to lowering of the anodic charge) was observed in our experiments upon oxidation of PANI at $E >$ 0.7 V. The increase in duration of the oxidation process (i.e. the increase of the extent of hydrolysis of PANI chains) up to 1 h brought about a considerable increase of the extent of reduction of PANI upon adding an equal amount of reducer, $Na_2S_2O_3$ (Fig. 19). This fact showed a decrease in oxidizing capacity of the system with the time of oxidation, which could be explained by exhaustion of the oxidant during the post-polymerization. As was supposed above, the aniline required for the occurrence of this process is a product of PANI hydrolysis.
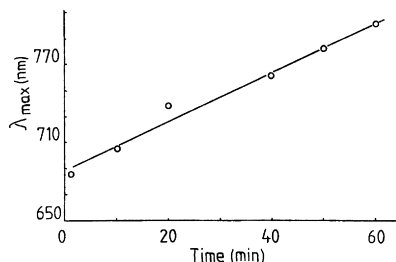
Fig. 19. Dependence of λ_{max} in the visible range of the electronic absorption spectrum of PANI reduced by using molar $Na_2S_2O_3$/aniline ratio of 0.93 on the time of preliminary oxidation at a molar oxidant/aniline ratio of 2.4[45].

The influence of hydrolysis can also explain the decrease in the electrochemical potential of the system, in spite of the enhanced concentration of oxidant, as seen from Fig. 17, curves 4 and 5.

It can be supposed that by adding aniline to such a system the more competitive process of polymerization can suppress the hydrolysis. Actually it was found[87] that PANI is more stable with respect to hydrolysis in an aniline-containing solution.

However, under the conditions of cyclic voltammetry in the range of the second anodic peak, the hydrolysis probably prevails over the post-polymerization. This has to influence the overall thermal effect of the electrode processes. Indeed, the authors studying the thermal effects accompanying the cyclic voltammetry study of PANI have recorded an endothermic change in the range of the second peak of the cyclic voltammogram[85]. As we have shown above, this endothermic effect is characteristic of hydrolysis[44].

(4) The relaxation process (post-polymerization) is very fast in the potential range 0.2(5) V $< E < 0.5$ V. For that reason, the influence of relaxation has been recorded not only by using millielectrodes, but also when ultramicroelectrodes have been used[65,69,70,83]. Nevertheless, it is worth noting that in both cases the increasing sweep rate resulted in a tendency to a monotonic shape of the anodic transient as we have suggested above.

(5) As we have mentioned above, the possibility of post-polymerization decreased as pH of the medium increased up to 6. This is associated with decreasing oxidation potential of the PANI chains as a result of deprotonation. As is evident from the above results (see Fig. 9), even pernigraniline turned from an oxidant into a reducer on increasing pH. This has to result in both a narrowing of the potential window corresponding to the emeraldine oxidation state (where the post-polymerization can compensate the anodic oxidation), and also in a simultaneous shift of the cyclic voltammograms into the range of lower potentials, which have been observed in the papers[88,89]. In neutral and alkaline media (including aprotic solvents) post-polymerization does not occur, i.e. a monotonic oxidation of PANI (from leucoemeraldine into pernigraniline) in the range of low potentials should be observed, as was actually found[57,67,90]. The ease of oxidation of PANI in alkaline and neutral media (it can be oxidized even by the atmospheric oxygen) accounts both for the special technique, required for the registration of the electrochemical activity of PANI under those conditions (see above), and for the electrochemical activity of PANI (in fact its oxidizability) in neutral and alkaline media, observed by the authors[91–94], instead of the expected absence of electrochemical activity.

(6) It can be expected that when the cyclic voltammograms are taken at lower temperature, the rate of post-polymerization and particularly of hydrolysis will decrease. Thus, the effect of lowering the temperature on the characteristics of the voltammograms has to be analogous to increasing sweep rate or pH, i.e. a tendency to monotonic shape of anodic transient has to appear. Such a change of the shape of transients on decreasing the temperature of recording of the cyclic voltammograms from 27 to $-53°C$, was actually observed by Peter et al.[65].

In conclusion, it can be stated that the conditions of study of the electrochemical activity of PANI by cyclic voltammetry allow the occurrence (and hence, recording) not only of the anodic and cathodic processes with participation of PANI themselves, but also of concomitant redox processes, as follows:

- oxidation of PANI chains in the range of low potentials ($E < 0.2$ V) by atmospheric oxygen;
- reduction with addition of aniline (post-polymerization) at $E > 0.2(5)$ V, which compensates entirely the oxidation (on the timescale of the cyclic voltammograms) in the potential range $0.2(5)$ V $< E < 0.5$ V.

The occurrence of the mentioned processes during the recording of the conventional cyclic voltammograms determines:

- the non-equilibrium behavior of the oxidation transition and its lower rate as compared to the reduction transition;
- completion of oxidation only on the timescale of the cyclic voltammetry and incomplete occurrence of the reduction transition under the conditions of conventional cyclic voltammetry;
- existence of a limited potential window (instead of defined potential) of the emeraldine oxidation state and the three-state-switching behavior;
- dependence of the electrochemical activity on the pH of the medium.

Hence, the conventional cyclic voltammograms appear to be a total effect of both the electrode processes with participation of PANI (i.e. its electrochemical activity) and the concomitant redox processes, taking place during their registration. Therefore, the concept based on the analysis of results from conventional cyclic voltammetry does not reflect the actual electrochemical activity of PANI.

Thus, a real estimate of the electrochemical activity of PANI is possible only when all the above mentioned processes have been eliminated, i.e. complete absence of aniline in non-aqueous electrolyte and inert atmosphere. The monotonic oxidation and reduction transients appear to be a real effect of the electrochemical activity and they imply that on oxidation (and reduction) of PANI from leucoemeraldine to pernigraniline (and vice versa) not only two, but $n/2$ redox processes exist, associated with the existence of $n/2$ oxidation states of PANI where the degree of oxidation (–N–/–N= ratio) changes gradually.

After the completion of our work[45] on the above presented concept, a paper of McCoy et al.[95] appeared, showing convincingly for the first time that ''polyaniline is best described as having access to a continuum of states of charge on a molecular level, ranging from 0 to 1 electron per aniline repeat unit rather than mixtures of the three states'', evidenced by study of potential-dependent nucleophilicity of PANI. This strongly supports the novel concept presented in this paper.

5. 'EMERALDINE BASE–EMERALDINE SALT' TRANSITION IN POLYANILINE

One of the most important conclusions which can be drawn from the results presented and discussed so far can be formulated as follows: PANI in emeraldine oxidation state, even in the protonated form, exhibits low oxidation potential, i.e. appears to be a typical reducer.

In order to keep such an easily oxidizable product unaffected, an 'internal protector' and relevant pH of the medium are required. On increasing the pH from 0 to 6, oxidation of PANI (by residual oxidant or atmospheric oxygen) proceeds increasingly easily and its reduction (i.e. aniline addition) takes place with increasing difficulty. On each pH value the system reaches an equilibrium state corresponding to a defined oxidation state of PANI. The higher the pH of the medium and the higher the oxidant concentration (or the anode potential), the higher the oxidation state of PANI. It has to be noted that the redox processes with participation of PANI are accompanied by changes in pH of the medium. Thus, when the system does not contain a buffer, not only the initial pH, but also the pH value corresponding to the equilibrium state, must be taken into account. Further, the increase of pH up to values higher than 6 (the upper statement about pH is also valid) precludes the possibility of the PANI reduction with addition of aniline. For that reason, PANI will be oxidized into different equilibrium oxidation states depending on the oxidation potential and concentration of the oxidant present in the system (residual oxidant and oxygen). When the oxidation potential of those oxidants is not pH dependent, the equilibrium oxidation state of PANI will be invariable in the whole pH range corresponding to neutral and alkaline media.

Actually, when PANI (as aqueous dispersion or film cast therefrom) was titrated using solutions of pH 0–11, we obtained all the spectrum of the 'blue products' (Fig. 20), similar to the above described, i.e. corresponding to oxidation states between emeraldine and pernigraniline. At each pH value, the oxidation of PANI can be performed up to the highest degree of oxidation (pernigraniline), when upon increasing pH an oxidant of regularly decreasing amount was added. As evident from the results on oxidation, shown in Fig. 9, the electrochemical potential of the system, corresponding to the pernigraniline formation, actually dropped as pH increased.
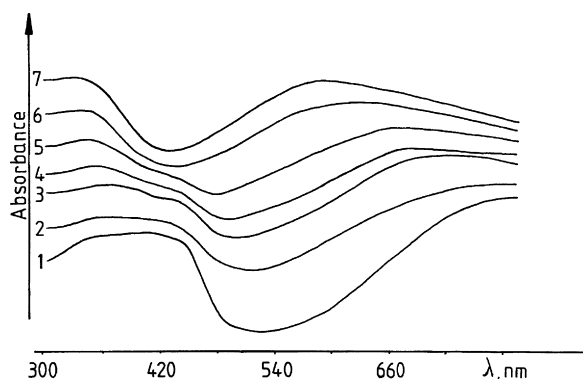

Fig. 20. Electronic absorption spectra of polyaniline dispersion at different pH values: 1, 0.6; 2, 1.2; 3, 3; 4, 4; 5, 5; 6, 6; 7, 9.

The 'blue products' and pernigraniline, formed in neutral and alkaline media on acidification to pH $<$ 6, are capable of reduction with addition of aniline, until the equilibrium oxidation state of PANI is reached.

Oxidation of PANI in acidic medium (the process was described in detail in the section 'Electrochemical activity of polyaniline'), in the potential range where the 'internal protector' aniline has already been exhausted, resulted in formation of the same (in respect to the electronic absorption spectra) 'blue products' and pernigraniline. Naturally, the neutralization of thus obtained oxidized forms of PANI in neutral and alkaline media and the subsequent acidification did not result in changes of their oxidation state and of the corresponding electronic absorption spectra of those products.

Analogous considerations allowed us to suggest[39] an alternative concept of the transition 'emeraldine base–emeraldine salt'. According to this concept, PANI in emeraldine oxidation state is oxidized when treated in neutral or alkaline medium (pH $>$ 6), and the 'emeraldine base' thus obtained (a blue product characterized by λ_{max} in the visible range of 620 nm) in fact does not represent the emeraldine oxidation state, but appears to be PANI in an intermediate oxidation state between emeraldine and pernigraniline. (In the same paper we have assumed that the electronic absorption spectrum of PANI reflects first of all its oxidation state.)

According to the existing concept, suggested by MacDiarmid et al.[1,96], the changes in PANI structure which appeared on treatment of the polymer of emeraldine oxidation state in media of various pH, and which affected its electronic absorption spectrum and the conductivity, can be explained by the different degree of protonation of the imine nitrogen atoms in PANI of emeraldine oxidation state. The highest degree of protonation, and the highest conductivity, respectively, were attained at pH 0–1, i.e. when the emeraldine salt was formed, while the deprotonated form of the emeraldine salt, viz. the emeraldine base, which appeared to be an insulator, was formed in neutral (or alkaline) medium. The transition 'emeraldine base–emeraldine salt' was called non-oxidative (protonic acid) doping. This conclusion served as a basis for the existing viewpoint of the transition from the conducting to the non-conducting form of PANI: unlike all other conducting polymers, conductivity of PANI depends on two variables, namely the degree of oxidation and the degree of protonation. Therefore, two types of PANI doping, oxidative and non-oxidative doping, respectively, could be distinguished.

Hugot-Le Goff et al.[97], simultaneously with us, while studying the possibilities of optical multichannel analysis for following the kinetics of color changes in electrochromic experiments of PANI, have stated fundamental (according to the authors themselves) speculations! The main point of those speculations is that the oxidation of leucoemeraldine in emeraldine base necessarily goes through the intermediate emeraldine salt, which, in fact, coincides with our statement that the 'emeraldine base' is characterized by a higher oxidation state than emeraldine.

The investigations of Kang et al.[86,98–100] on the processes of PANI protonation–deprotonation, especially in their last papers[99,100], evidenced that on deprotonation an increase in the oxidation state occurred, while with subsequent acid treatment the oxidation state lowered. This also supports the concept suggested by us.

Possibly, it is necessary here to stress the significance of the problem of precise determination of the PANI oxidation states. While choosing the proper methods, the possibility of changes in the oxidation state during the analysis has to be taken into account, which is impossible without expertise in the field of electrochemical activity of PANI.

We cannot but agree with Kang et al.[86] that elemental analysis does not provide an accurate indication of the chemical structure, and common spectroscopic techniques, such as infrared and electronic absorption spectroscopies, only give a fairly qualitative indication of the oxidation state of PANI. Even X-ray photoelectron spectroscopy does not allow precise resolution of the peaks corresponding to imine and amine nitrogen[89]. According to these authors, a more quantitative technique is the titration of PANI (for example with TiCl$_3$). In our opinion, the most considerable errors may arise under the conditions used in the last method. For that reason, we consider that despite being only qualitative, the most realistic information is offered by electronic absorption spectroscopy.

In conclusion to this section, it has to be noted that the redox behavior of PANI cannot be considered apart from the pH of the medium, and the influence of the pH of the medium on PANI properties cannot be examined without taking into account the redox processes with participation of the polymer. The pH value of the medium appears to be one of the main parameters to affect significantly the direction of redox processes with participation of PANI, and thus the oxidation state of the polymer, which determines its properties.

6. POLAR AND HYDROGEN-BONDING INTERACTIONS IN POLYANILINE AND THEIR POSSIBLE EFFECTS ON ITS TRANSFORMATIONS

Strong polar and hydrogen-bonding interactions in all forms of PANI have been proved by many authors[101-115]. The long known 'interaction' of PANI with water[101,104,107-115] appears to be a consequence of those interactions. The exposure to water vapor results, for example, in reversible enhancement of the PANI conductivity with approximately one order of magnitude. MacDiarmid et al.[101] suggested that solvated water molecules reduced the electrostatic interactions leading to greater charge delocalization, thus increasing conductivity. Shacklette et al.[109] confirmed this idea based on experimental and theoretical evidence. They suggested describing the interaction of PANI with organic solvents and with conventional polymers, i.e. the solubility and dispersibility of PANI, by polar and hydrogen-bonding interactions.

An opinion also exists that the interaction of water (and organic solvents of general formula R–OH) is not limited solely by the hydrogen-bonding interactions. Thus, the authors[104,110-112] have supposed that the interaction of water molecules with the PANI backbone obeys the same mechanism as that of protonic acid doping of PANI. According to these authors, a general scheme for the interaction of water with polymer backbone includes two stages: (i) hydrogen-bonding of the water molecule to the nitrogen atom; (ii) dissociation of the adsorbed molecule and protonation of the polymer chain. The authors, however, have offered these mechanisms, following the behavior of PANI upon thermal treatment (thermogravimetric and calorimetric measurements)[112] and upon polarizing by a.c. voltage in the frequency range 10^{-1}–10^5 Hz at a temperature between $-100°C$ and $+100°C$[111]. In the last paper, the changes of electric behavior of PANI under the influence of applied electric field revealed that the variation of both the acid and the water concentration in PANI caused similar changes of the electric behavior, thus indicating a similar mechanism of interaction of water and acid molecules with the polymer backbone.

Hence, the changes of PANI, identified by the authors[111] as the transition 'emeraldine base–emeraldine salt' under the influence of water molecules, does not proceed under

equilibrated ambient conditions, but appear to be effected by an electric field of defined frequency and by thermal treatment.

It is noteworthy that many data exist showing that the changes in PANI structure, discernible by variation of either spectral characteristics or conductivity, occur under the influence of light[116–118] (i.e. of electromagnetic field of optical frequency) or heat[116,117,119–121]. These phenomena will be discussed in more detail in the next section. A general feature of all the mentioned works is, however, that the changes in PANI structure have not been considered in conjunction with the redox processes with participation of PANI.

Thus, summarizing the information described in this section, the following suggestions and conclusions can be drawn.

1. PANI is a polar and hydrogen-bonding material and hence, during its preparation and subsequent treatment with various chemical compounds, it can take part in strong hydrogen-bonding and polar interactions with corresponding compounds like aniline, water, acids, solvents etc. These compounds can be retained between the PANI chains due to those interactions.
2. Under defined external conditions PANI can take part in redox-processes (oxidation upon interaction with oxidants, including atmospheric oxygen, and reduction upon interaction with aniline) with some of the mentioned compounds included in it.
3. Defined external conditions appeared to be either the presence of electrolyte or defined air humidity. In fact, this concerns the possibility of occurrence of redox processes with participation of PANI. The oxidation state of PANI chains to be reached is determined by the direction of those processes.
4. It can be suggested that except under the conditions mentioned, a possibility of occurrence of redox processes with participation of PANI arises also upon releasing of other reactants in the redox processes (oxidant, aniline, acid, water), bounded with PANI by means of polar and hydrogen-bonding interactions. Such a release can be a result of the effect of defined energy, such as heat or electromagnetic field of certain frequency.

7. CLASSIFICATION OF THE POTENTIAL APPLICATIONS OF POLYANILINE

Analysis of the literature data concerning the potential applications of PANI showed that they are related to the ability of the polymer to change the oxidation state, irrespective of the effect, which induces this change (referred to hereafter as change-inducing effect): standard chemical or electrochemical oxidation and reduction, variation of pH of the medium, effect of various types of energy. Variation of the oxidation state results in changes of the whole spectrum of chemical, physicochemical and physical properties of the polymer: oxidation potential, light absorption, dielectric constant, refractive index, pK_a, conductivity, crystallinity, dimensionality, etc.

In our opinion, all the potential applications of PANI can be classified into two large groups. In the first group, PANI is not required to respond quickly towards the change-inducing effect, but rather to retain the result of this effect, which means that the polymer has to retain its performance in a defined time interval (i.e. to exhibit a 'memory' in respect of e.g. charge, optical image etc.). In the second group of applications the polymer is required to reveal rapid change of defined property as a result of the change-inducing effect.

In a separate group we have classified the application areas which are not directly related to the change in the oxidation state of PANI. Thus, e.g., a change in oxidation state, which means a change at molecular level, results in a change in supramolecular structure (from entirely amorphous into partially crystalline). Nevertheless, detachment of the third group is quite provisional, since, depending on whether the given change-inducing effect must be accumulated or has to provoke a fast response, the corresponding materials have to be assigned to the first or to the second group.

PANI-based materials assigned to the first group conform to the ability of the polymer to accumulate and transform energy (including optical frequencies), and hence, to memorize (erase) information. This ability allows PANI to be used as an electrode in rechargeable batteries, in corrosion protection, in electrochromic displays and windows, in photovoltaic cells and transistors, as a medium for photoelectric devices and light (laser) induced erasable information (image) storage, as electromembranes, etc.

Most of the papers in this area have been devoted to the investigation of PANI as a battery electrode. Although PANI can serve both as cathode (leucoemeraldine) and anode (perni-graniline), it has been studied mostly as a cathode. As a medium in such batteries the following have been studied: aqueous[122–125,127] and non-aqueous ($LiClO_4$ in propylene carbonate or its mixture with ethylene carbonate)[122,125,126,130] electrolyte solutions, and recently also solid electrolytes (polyethylene oxide with $LiClO_4$[128,129] or with H_3PO_4[129]; acrylonitrile–methacrylate copolymer with $LiBF_4$, $LiPF_6$ or $LiCF_3SO_3$[131,132,136]). Very recently, composite battery electrodes of PANI associated with sulfur compounds (dimer-captans) have been suggested[131–135]. It was found that the slow redox reaction of the dimer-captan at room temperature was accelerated in PANI matrix.

Analysis of the cyclic voltammograms reveals that charging and discharging processes occur in the range of ± 1 V, the corresponding potentials being dependent on the type of electrolyte and mostly on pH of the medium. While the discharge capacity does not depend substantially on the type of electrolyte and amounts to 100–150 Ah/kg, the number of the cycles increases drastically on changing the aqueous electrolyte (16–30 cycles depending on pH of the medium) with non-aqueous (over 100 cycles) and solid (250 cycles) electrolytes. These variations have to result from the difference in electrochemical activity and chemical stability of the electrode material in different media.

The lack of systematic studies on the electrochemical activity of all the oxidation states of PANI has to be noted. Recently, however, there has been growing interest in the study of the chemical stability of PANI, namely the influence of hydrolysis of the polymer on the performance of PANI films. Hydrolytic instability probably limits the use of PANI as an anode material.

PANI coatings can provide significant corrosion protection to steel (and copper) exposed to severe corrosion environments. This protection extends to exposed areas of bare steel that are galvanically coupled to the PANI coated steel. It appears to be electrochemically driven, being derived from both anodic and cathodic polarization. Passivation was found to occur by the formation of an oxide layer induced by contact with PANI[137–139].

The processes of electrochemical oxidation (reduction) of PANI in the range of applied potential of ± 1 V are concomitant with changes in the optical absorption spectrum in the visible range (400–800 nm). The electrochromism of PANI, predominantly in aqueous[77,79,145], but also in non-aqueous[78] and solid[140,141] electrolytes, has been the subject of numerous investigations. The study of electrochromic transformations is a very important point in the elucidation of the question of activity of various oxidation states of the polymer,

since it couples the electronic absorption spectrum with the applied potential at a defined pH of the medium.

The electrochromism of PANI and the related differences in the visible light transmission (up to 40% at 580 nm[78] and up to 70% at 800 nm[140]) led to the development of electrochromic displays and windows (in conjunction with complementary electrochromic material as tungsten oxide[140–142,146] or tungsten oxide and Prussian blue[143,144]), the last popularly called 'smart windows'. The 'optical memory' of those products and the cycle life of the devices should depend again on the activity of PANI in different oxidation states.

As mentioned above, the variation of PANI structure (in our opinion, the variation of the oxidation state), leading to a change in the optical absorption in the visible range, can also be a result of thermal effects[116,117,119–121]. The thermochromism of PANI should be accompanied by changes in electrical conductivity, as was actually observed by the authors[116,117]. The variation of PANI spectral characteristics in the visible range, which in our opinion reflects the direction of the redox processes with participation of PANI (oxidation or reduction), depends on the conditions of thermal treatment: temperature range, humidity, etc. It is worth noting that the potential applications of thermochromism, except to the first group of our classification, could be assigned also to the second group, since the changes occur rapidly and the corresponding fast response can be used, for example, in sensors.

The variation of oxidation states on charging and discharging, with concomitant diffusion of ions into and from the polymer, makes PANI useful as ion-exchange material[146–151] controllable by the electrochemical potential of the system. Conductive stationary phase consisting of glassy carbon particles was modified with PANI film to add selectivity to the electrochemical separation of anionic compounds[152,153].

As can be expected, PANI reveals ion exchanging and ion separating properties without applied potential as well. Actually, PANI has been used as anion exchange material[154–156], the ion exchange capacity being dependent on the 'history' of the polymer (i.e. on the characteristics set up during synthesis[155]), and also on its transformations, occurring after treatment at various pH (viz. the so-called degree of protonation[154]). We suppose that both the 'history' of the polymer and its transformations upon a change in pH of the medium affect, first of all, the oxidation state, which determines the value of pK_a and the ion separating properties of PANI, respectively.

The ability of PANI to change its electron-donating or electron-accepting properties depending on the oxidation state, renders it a promising material as a component of p–n heterojunctions, the second component being an inorganic semiconductor[157–160]. I–V and C–V characteristics of heterojunction p-PANI/n-Si[158,159], p-PANI/n-In$_2$S$_3$[160] and of PANI with other metal sulfides (CuS, CuZnS$_2$, CuCdS$_2$)[157] have been described.

PANI heterojunctions, like all other p–n heterojunctions, are sensitive to sunlight, which makes them suitable for photovoltaic cells (solar cells). Study of photoelectric characteristics of p-PANI/n-Si junction[159] has shown that the photocurrent spectrum of the junction and the optical transmission spectrum of p-PANI film occur in the same range of the photon energy (1.8–2.8 eV), i.e. the PANI film in the heterojunction offers a window for photons of energy in the range 1.8–2.8 eV.

Poly(o-methylaniline) (and hence PANI as well) can be reversibly transformed from p-type into n-type. Study of photoelectrochemical properties of PANI-containing heterojunction has demonstrated that this reversible transition depends on the applied potential and pH of the medium, the photocurrent of p-PANI being much less as compared to the n-type[158].

Light-emitting devices (LEDs) have been made using PANI spin cast on poly(ethylene terephthalate) substrate or a combination of PANI and indium–tin oxide as the transparent hole-injecting anode and poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] as the active layer[161–164]. LED has also been made by closely contacting an n^+-type porous silicon film with chemically polymerized PANI inside the pores[165–167]. Sulfonated PANI and poly(p-phenylene vinylene) multilayer heterostructure LED has been prepared using electrostatic self-assembly technique[168].

Photoinduced redox processes in PANI film containing potosensitive oxides (titanium dioxide and tungsten trioxide) and corresponding changes in the electronic absorption spectrum have permitted the formation of an erasable light image by illuminating (including by laser) the film in both aqueous and non-aqueous solutions containing an alcohol as a hole scavenger. Turning back the electrochemical potential of the system by polarizing the film at e.g. 0.5 V vs SCE in the dark, is enough to erase the light image[92,169–171].

Inorganic–organic conducting polymer composite systems with controllable electrical and optoelectronic properties are of current interest for applications including electrochromic displays, rechargeable batteries, membranes and sensors. Methods of intercalation of the organic guests into inorganic hosts have been described in[172–178]. Aqueous dispersions of PANI have been mentioned as promising in this respect.

Of particular interest is the very large capacity of PANI to absorb and reflect electromagnetic radiation by changing its dielectric constant on interaction with energy of radiowave–microwave–millimeter wave range[179–181]. This makes PANI an appropriate candidate to shield electromagnetic interference (where PANI approaches the shielding efficiency of copper[179,182–185]), in the design of microwave absorbers for stealth purposes and in areas involving remote heating of materials and surfaces (e.g. joining of plastics)[179,186,187]. Dependence of the electric behavior of PANI on the frequency of the electric field and the temperature[110–112], allows PANI application possibilities in this area to be extended, designing materials which are effective in a defined temperature–frequency range.

As mentioned above, the fast response of PANI to variation of the change-inducing effect is the basis of the second group of potential applications as indicators[154], electrochemical sensors[188–192], including 'artificial muscle'[193–195], and as catalysts[91,196–202]. Thus, variations in anodic (cathodic) current due to redox processes with the substrate, make it appropriate for use in e.g. gas sensors[189,191] and biosensors[190,191]. All-plastic electromechanical actuators ('artificial muscle') have been constructed based on electrochemomechanical deformations of PANI films (expansion and contraction on oxidation and reduction, respectively)[193–195]. Color changes caused by changes in the pH of the medium related to the processes of protonation–deprotonation in emeraldine oxidation state as mentioned above, allow PANI to be used as an 'acid–base' indicator[154].

Due to the reversible redox processes PANI has been suggested as a versatile catalyst in dehydrogenative (and/or decarboxylative) oxidation of benzylamines and 2-phenylglycine into corresponding imines and in combination with cuprous chloride or ferrichloride for dehydrogenation of cynnamyl alcohol into cynnamaldehyde possibly due to complexation. Reversal to the active (oxidized) form of PANI has been performed by oxidation with oxygen[91].

By coupling the metal reduction process in acid solutions with an increase in the oxidation state of PANI, and the subsequent reduction of the oxidized polymer in acidic media, spontaneous and self-sustained electroless precipitation of precious metals, such as gold and palladium, in their elemental form has been readily achieved[197,198].

Such a spontaneous deposited thin noble metallic layer can be used as an electrode for subsequent Cu electro-plating. On the other hand, in metallization of printed circuit boards, PANI film can be used as an electrode for the electrolytic deposition of Cu on the trough holes[196].

Electrodes modified by platinum particles dispersed inside a PANI film have shown high activity with respect to electrocatalytic oxidation of methanol and other C1 molecules (such as formaldehyde and formic acid)[200].

PANI protonated with 12-tungstophosphoric acid has been used in catalytic conversion of isopropanol into acetone[199].

Due to its response to an electromagnetic field in the optical regime, PANI itself is appropriate as a medium for erasable optical information storage[179,203–206] (which can be assigned to the first group of potential applications) and also in non-linear optics[207,208,220] (which belongs to the second group). The application of PANI for erasable optical information storage is determined by the existence of long-lived (several hours at low temperature) photoinduced excitations near $1.4–1.5$ eV[179,203–206] in the absorption spectra, which also possess spin[1/2] see Refs. [179,205,206]. It is well known that absorption in this range is characteristic of the PANI conducting form referred to as emeraldine salt according to MacDiarmid. It was suggested that these long-lived photoinduced excitations in pernigraniline base and emeraldine base are composed of neutral solitons and neutral polarons (confined neutral solitons pair) stabilized by ring twist and interchain interactions[179,206]. We rationalize these photoexcitations in pernigraniline base and emeraldine base as having occurred from post-polymerization analogous to the transition emeraldine base–emeraldine salt on changing pH of the system.

Papers[116–118] appeared recently on changes (similar to those described above) in the near-infrared excited resonance Raman spectra of PANI (excitation wavelength of 1064 nm), which evidenced a broadening of the frequency range of light response of PANI.

PANI membranes for gas[209,210] and neutral solute[211,212] separations can be assigned to a separate group in our classification, where the respective applications are not related directly to the change in oxidation state. Their selectivity is based on precise control of the morphology changes due to oxidation–reduction[212] and protonation–deprotonation[209,211] processes.

Finally, applications based solely on the electrical conductivity of PANI are also worth noting[179–181,213–219], such as conductive coatings useful in a variety of applications, including static charge dissipation (antistatic coatings)[213–215]. Three years ago it was announced[216] that the group Zipperling and Kessler, Americhem and Allied Signal Corp. produced $20\,000$ m^2 of transparent antistatic PANI layers monthly.

The requirement for conductivity span a very wide range from as low as 10^{-8} S/cm for electrostatic elimination up to values greater than 10^4 S/cm for commercially useful light-weight conducting wires. Because of the commodity nature of metals, particularly copper, it is unlikely that PANI or any conducting polymer, will replace conductive metals in the near future. But nevertheless, it has to be noted, that the intrinsic electrical conductivity of metallic PANI has been estimated to be ca. 10^7 S/cm.[180]. Conductivities of the order of 300 S/cm have been measured for stretch-oriented free-standing PANI films[217]. The three-dimensional nature of metallic state has been demonstrated by the correlation of low temperature dielectric response with the parallel and perpendicular crystalline domain lengths obtained from X-ray data. The charge localization to delocalization transition depends on the polymer processing[180].

Conducting polymers, including PANI, are inherently anisotropic materials. When the macromolecular chains are well oriented, metallic conducting polymers are highly dichroic over a wide spectral range from the near infrared through the far infrared. Thus, highly oriented, metallic conducting polymers are analogous to wire grid polarizers, but with the anisotropy on the molecular scale. PANI should, therefore, be an excellent candidate as a material for infrared polarizers for operation over a broad spectral range[221].

REFERENCES

1. MacDiarmid, A. G., Chiang, J. C., Richter, A. F., Somasiri, N. L. D. and Epstein, A. J., in *Conducting Polymers*, ed. L. Alcacer. Reidel Publishing Co., Dordrecht, 1987, pp. 105–120.
2. MacDiarmid, A. G. and Epstein, A. J., *Faraday Discuss. Chem. Soc.*, 1989, **88,** 317–332.
3. Genies, E. M., Bogly, A., Lapkowsky, M. and Tsintavis, C., *Synth. Met.*, 1990, **36,** 139–182.
4. Yang, R. Cz. Ch., in *Large-area Chromogenics; Materials and Devices for Transmittance Control*, ed. C. M. Lampert and C. G. Granqvist. SPIE Optical Engineering Press, Bellingham, Washington, 1990, pp. 335–365.
5. MacDiarmid, A. G. and Epstein, A. J., *Macromol. Chem., Macromol. Symp.*, 1991, **51,** 11–28.
6. MacDiarmid, A. G., in *Conjugated Polymers and Related Materials: the Interconnection of Chemical and Electronic Structure*, ed. W. R. Salaneck and I. Lundstrom. Oxford Scientific Press, 1992.
7. MacDiarmid, A. G. and Epstein, A.J., in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*, ed. J. L. Bredas and R. R. Chance. Kluwer Academic, 1990.
8. Travers, J.-P., Genoud, F., Menardo, C. and Nechtschein, M., *Synth. Met.*, 1990, **35,** 159–168.
9. Lux, F., *Polymer*, 1994, **35,** 2915–2936.
10. Bacon, J. and Adams, R. N., *J. Am. Chem. Soc.*, 1968, **90,** 6596–6599.
11. Leedy, D. W. and Adams, R. N., *J. Am. Chem. Soc.*, 1970, **92,** 1646–1650.
12. Hand, R. and Nelson, R. F., *J. Am. Chem. Soc.*, 1974, **96,** 850–860.
13. Hand, R. and Nelson, R. F., *J. Electrochem. Soc.*, 1978, **125,** 1059–1069.
14. Wei, Y., Jang, G.-W., Chan, Ch.-Ch., Hsuen, K. F., Hariharan, R., Patel, S. A. and Whitecar, C. K., *J. Phys. Chem.*, 1990, **94,** 7716–7721.
15. Mattoso, L. H. C., Manohar, S. K., MacDiarmid, A. G. and Epstein, A. J., *J. Polym. Sci.*, 1995, **33,** 1227–1234.
16. Shim, Y.-B., Won, M.-S. and Park, S.-M., *J. Electrochem. Soc.*, 1990, **137,** 538–544.
17. Wei, Y., Tang, X., Sun, Y. and Focke, W. W., *J. Polym. Sci.*, 1989, **27,** 2385–2396.
18. Duic, L. and Mandic, Z., *J. Electroanal. Chem.*, 1992, **355,** 207–221.
19. Yang, C.-H. and Wen, T.-C., *J. Appl. Electrochem.*, 1994, **24,** 166–178.
20. Kitani, A., Kaya, M., Yano, J., Yoshikawa, K. and Sasaki, K., *Synth. Met.*, 1987, **18,** 341–346.
21. Wei, Y., Hariharan, R. and Patel, S. A., *Macromolecules*, 1990, **23,** 758–764.
22. Toshima, N. and Yan, H., *Bull. Chem. Soc. Jpn.*, 1995, **68,** 1056–1063.
23. Fu, Y. and Elsenbaumer, R. L., *Chem. Mat.*, 1994, **6,** 671–677.
24. Stejskal, J., Kratochvil, P. and Jenkins, A. D., *Collect. Czech. Chem. Commun.*, 1995, **60,** 1747–1755.
25. Stejskal, J., Kratochvil, P. and Spirkova, M., *Polymer*, 1995, **36,** 4135–4140.
26. Stejskal, J., Spirkova, M. and Kratochvil, P., *Acta Polymer*, 1994, **45,** 385–388.
27. Volkov, A., Tourillon, G., Lacaze, P.-C. and Dubois, J. E., *J. Electroanal. Chem.*, 1980, **115,** 279–291.
28. Wei, Y., Hsueh, K. F. and Jang, G.-W., *Polymer*, 1994, **35,** 3572–3575.
29. Koenig, U. and Schultze, J. W., *J. Electroanal. Chem.*, 1988, **242,** 243–254.
30. Schultze, J. W. and Thyssen, A., *Synth. Met.*, 1991, **41–43,** 2825–2830.
31. Tsakova, V., Milchev, A. and Schultze, J. W., *J. Electroanal. Chem.*, 1993, **346,** 85–97.
32. Gumbs, R. W., *Synth. Met.*, 1994, **64,** 27–31.
33. Fong, Y. and Schlenoff, J. B., *Polymer*, 1995, **36,** 639–643.

34. Kulikov, A. V., Kogan, Ya. L. and Fokeeva, L. S., *Synth. Met.*, 1993, **55–57,** 1023–1028.
35. Duic, L., Mandic, Z. and Kovac, S., *Electrochim. Acta*, 1995, **40,** 1681–1688.
36. Davied, S., Nicolau, Y. F., Melis, F. and Revillon, A., *Synth. Met.*, 1995, **69,** 125–126.
37. Genie, E. M. and Lapkowski, M., *J. Electroanal. Chem.*, 1987, **236,** 199–208.
38. MacDiarmid, A. G., Manohar, S. K., Masters, J. G., Sun, Y., Weis, H. and Epstein, A. J., *Synth. Met.*, 1991, **41–43,** 621–626.
39. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *Polymer*, 1993, **34,** 1330–1332.
40. Gospodinova, N., Terlemezyan, L., Mokreva, P. and Kossev, K., *Polymer*, 1993, **34,** 2434–2437.
41. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *Polymer*, 1993, **34,** 2438–2439.
42. Gospodinova, N., Terlemezyan, L., Mokreva, P. and Tadjer, A., *Polymer*, 1996, **37,** 4431–4433.
43. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *Polymer*, 1995, **36,** 3585–3587.
44. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *Polymer*, 1994, **35,** 3102–3106.
45. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *Polym. Int.*, 1996, **41,** 79–84.
46. Gospodinova, N., Mokreva, P. and Terlemezyan, L., *J. Chem. Soc., Chem. Commun.*, 1992, 923–924.
47. Stejskal, J., Kratochvil, P., Gospodinova, N., Terlemezyan, L. and Mokreva, P., *Polymer*, 1992, **33,** 4857–4858.
48. Gospodinova, N., Terlemezyan, L., Mokreva, P., Stejskal, J. and Kratochvil, P., *Eur. Polym. J.*, 1993, **29,** 1305–1309.
49. Stejskal, J., Kratochvil, P., Gospodinova, N., Terlemezyan, L. and Mokreva, P., *Polym. Int.*, 1993, **32,** 401–405.
50. Sreitwieser, E., *Teoria moleculiarnih orbit*. Moscow, 1995.
51. Willstatten, R. and Moore, C. W., *Berichte*, 1907, **40,** 2665.
52. Cao, Y., Li, S., Xue, Z. and Guo, D., *Synth. Met.*, 1986, **16,** 305–315.
53. Wawzonek, S. and McIntyre, T. W., *J. Electrochem. Soc.*, 1967, **114,** 1025–1029.
54. Cushman, R. J., McManus, P. M. and Yang, S. Ch., *J. Electroanal. Chem.*, 1986, **291,** 335–346.
55. Takehara, Z., Kanamura, K. and Yonezawa, S., *J. Electrochem. Soc.*, 1989, **136,** 2767–2768.
56. Lapkowski, M. and Fryczkowski, R., *Pol. J. Chem.*, 1994, **68,** 1597–1602.
57. Pasquali, M., Pistoia, G. and Rosati, R., *J. Adv. Mater. Optics Electron.*, 1992, **1,** 263–270.
58. Yamada, K., Teshima, K., Kobayashi, N. and Hirohashi, R., *J. Electroanal. Chem.*, 1995, **394,** 71–79.
59. Pron, A., Genoud, F., Menardo, C. and Nechtschein, M., *Synth. Met.*, 1988, **24,** 193–201.
60. Cui, C. Q., Ong, L. H., Tan, T. C. and Lee, J. Y., *Electrochim. Acta*, 1993, **38,** 1395–1404.
61. Pud, A. A., *Synth. Met.*, 1994, **66,** 1–18.
62. Syed, A. A. and Dinesan, M., *Talanta*, 1991, **38,** 815–834.
63. Masters, J. G., Sun, Y., MacDiarmid, A. G. and Epstein, A. J., *Synth. Met.*, 1991, **41–43,** 715–718.
64. Kalaji, M., Nyholm, L. and Peter, L. M., *J. Electroanal. Chem.*, 1992, **325,** 269–284.
65. Yuki, M., Kalaji, M., Nyholm, L. and Peter, L. M., *Synth. Met.*, 1993, **55–57,** 1515–1520.
66. Nyholm, L. and Peter, L. M., *Synth. Met.*, 1993, **55–57,** 1509–1514.
67. Nyholm, L. and Peter, L. M., *J. Chem. Soc. Faraday Trans.*, 1994, **90,** 149–154.
68. Odin, C. and Nechtschein, M., *Synth. Met.*, 1991, **41–43,** 2943–2946.
69. Odin, C., Nechtschein, M. and Hapiot, P., *Synth. Met.*, 1992, **47,** 329–350.
70. Andrieux, C. P., Audebert, P., Hapiot, P., Nechtschein, M. and Odin, C., *J. Electroanal. Chem.*, 1991, **305,** 153–162.
71. Aoki, K. and Kawase, M. J., *Electroanal. Chem.*, 1994, **377,** 125–129.
72. Aoki, K., Cao, J. and Hoshino, Y., *Electrochim. Acta*, 1994, **39,** 2291–2297.
73. Pistoia, G., *Adv. Mater.*, 1994, **6,** 57–59.
74. Koziel, K. and Lapkowski, M., *Synth. Met.*, 1993, **55–57,** 1011–1016.
75. Koziel, K. and Lapkowski, M., *Synth. Met.*, 1993, **55–57,** 1005–1010.
76. Jelle, B. P., Hagen, G., Hesjevik, S. M. and Odegard, R., *Electrochim. Acta*, 1993, **38,** 1643–1647.
77. Watanabe, A., Mori, K., Iwasaki, Y., Nakamura, Y. and Niizuma, S., *Macromolecules*, 1987, **20,** 1793–1796.
78. Rodrigues, M. A., De Paoli, M. and Mastragostino, M., *Electrochim. Acta*, 1991, **36,** 2143–2146.

79. Bernard, M. C., Cordova-Torresi, S. and Hugot-Le Goff, A., *Solar Energy Materials and Solar Cells*, 1992, **25,** 225–240.
80. Klavetter, F. L. and Cao, Y., *Synth. Met.*, 1993, **55–57,** 989–992.
81. Orata, D., Matheka, A. and Munge, B., *Macromol. Chem. Phys.*, 1994, **195,** 3003–3013.
82. Agbor, N. E., Petty, M. C., Monkman, A. P. and Harris, M., *Synth. Met.*, 1993, **55–57,** 3789–3792.
83. Goldenberg, L. M., Petty, M. C. and Monkman, A. P., *J. Electrochem. Soc.*, 1994, **141,** 1573–1576.
84. Kenwright, A. M., Feast, W. J., Adams, P., Milton, A. J., Monkman, A. P. and Say, B. J., *Polymer*, 1992, **33,** 4292–4298.
85. Maeda, Y., Katsuta, A., Nagasaki, K. and Kamiyama, M., *J. Electrochem. Soc.*, 1995, **142,** 2261–2265.
86. Kang, E. T., Neoh, K. G. and Tan, K. L., *Surface and Interface Analysis*, 1993, **20,** 833–840. and references therein.
87. Pasquali, M., Pistoia, G. and Rosati, R., *Synth. Met.*, 1993, **58,** 1–15.
88. Focke, W. W., Wnek, G. E. and Wei, Y., *J. Phys. Chem.*, 1987, **91,** 5813–5818.
89. Kang, E. T., Neoh, K. G. and Tan, K. L., *Adv. Polym. Sci.*, 1993, **106,** 136–190. and references therein.
90. Pekmez, N., Pekmez, K. and Yildiz, A., *J. Electroanal. Chem.*, 1994, **370,** 223–229.
91. Hirao, T., Higuchi, M., Ikeda, I. and Ohshiro, Y., *J. Chem. Soc., Chem. Commun.*, 1993, 194–195.
92. Yoneyama, H., Takahashi, N. and Kuwabata, S., *J. Chem. Soc., Chem. Commun.*, 1992, 716–717.
93. Hsu, C.-H., Peacock, P. M., Flippen, R. B., Manohar, S. K. and MacDiarmid, A. G., *Synth. Met.*, 1993, **60,** 233–237.
94. Ohira, M., Sakai, T., Takeuchi, M., Kobayashi, Y. and Tsuji, M., *Synth. Met.*, 1987, **18,** 347–352.
95. McCoy, Ch. H., Lorkovic, I. M. and Wrighton, M. S., *J. Am. Chem. Soc.*, 1995, **117,** 6934–6943.
96. Chiang, J. and MacDiarmid, A. G., *Synth. Met.*, 1986, **13,** 193–205.
97. Bernard, M. C. and Hugot-Le Goff, A., *Surface and Interface Analysis*, 1992, **19,** 27–32.
98. Neoh, K. G., Kang, E. T. and Tan, K. L., *Polymer*, 1992, **33,** 2292–2298.
99. Neoh, K. G., Kang, E. T. and Tan, K. L., *Polym. Degrad. Stab.*, 1994, **45,** 77–81.
100. Kang, E. T., Neoh, K. G. and Tan, K. L., *Synth. Met.*, 1995, **68,** 141–144.
101. Angelopoulos, M., Ray, A. and MacDiarmid, A. G., *Synth. Met.*, 1987, **21,** 21–23.
102. Travers, J. P. and Nechtschein, M., *Synth. Met.*, 1987, **21,** 135–141.
103. Travers, J. P., Menardo, C., Nechtschein, M., Manohar, S. K. and MacDiarmid, A. G., *Mat. Res. Soc. Symp. Proc.*, 1990, **173,** 335–340.
104. Diaz Calleja, R. and Matveeva, E. S., *J. Phys.*, 1993, **3,** 1569–1572.
105. Colomban, Ph., Gruger, A., Novak, A. and Règis, A., *J. Mol. Struct.*, 1994, **317,** 261–271.
106. Gruger, A., Novak, A., Règis, A. and Colomban, Ph., *J. Mol. Struct.*, 1994, **328,** 153–167.
107. Colomban, Ph., Folch, S., Gruger, A., Règis, A. and Michel, D., *C.R. Acad. Sci. Paris*, 1996, **322 série IIb,** 63–70.
108. Shacklette, L. W. and Han, C. C., *Mat. Res. Soc. Symp. Proc.*, 1994, **328,** 157–166.
109. Shacklette, L. W., *Synth. Met.*, 1994, **65,** 123–130.
110. Matveeva, E. S., Diaz Calleja, R. and Sanchez-Martinez, E., *Synth. Met.*, 1994, **67,** 207–210.
111. Diaz Calleja, R., Matveeva, E. S. and Parkhutik, V. P., *J. Non-Cryst. Solids*, 1995, **180,** 260–265.
112. Matveeva, E. S., Diaz Calleja, R. and Parkhutik, V. P., *Synth. Met.*, 1995, **72,** 105–110.
113. Passiniemi, P., *Synth. Met.*, 1995, **69,** 685–686.
114. Pereira, E. C., Londo, E. and Bulhols, L. O. S, *J. Mol. Struct.*, 1995, **335,** 141–147.
115. Bahceci, S., Toppare, L. and Yurtsever, E., *Synth. Met.*, 1994, **68,** 57–60.
116. Gruger, A., Règis, A. and Colomban, Ph., *C.R. Acad. Sci. Paris*, 1995, **321 série IIb,** 191–197.
117. Colomban, Ph., Gruger, A. and Règis, A., *C.R. Acad. Sci. Paris*, 1995, **321 série IIb,** 247–254.
118. Engert, Ch., Umapathy, S., Kiefer, W. and Hamaguchi, H., *Chem. Phys. Lett.*, 1994, **218,** 87–92.
119. Masters, J. G., Ginder, J. M., MacDiarmid, A. G. and Epstein, A. J., *J. Chem. Phys.*, 1992, **96,** 4768–4778.
120. Tsubakihara, H., Okamura, H., Okada, K. and Sakamoto, A., *Kobunshi Ronbunshu*, 1994, **51,** 565–567.

121. Tsubakihara, H., Okamura, H., Yosimura, H., Hayashi, K., Okada, K. and Sakamoto, A., *Kobunshi Ronbunshu*, 1994, **51,** 759–763.
122. MacDiarmid, A. G., Yang, L. S., Huang, W. S. and Humphrey, B. D., *Synth. Met.*, 1987, **18,** 393–398.
123. Somasiri, N. L. D. and MacDiarmid, A. G., *J. Appl. Electrochem.*, 1988, **18,** 92–95.
124. Koga, K., Yamasaki, S., Narimatsu, K. and Takayanagi, M., *Polym. J.*, 1989, **9,** 733–738.
125. Desilvestro, J., Scheifele, W. and Haas, O., *J. Electrochem. Soc.*, 1992, **139,** 2727–2736.
126. Ueda, F., Mukai, K., Harada, I., Nakajima, T. and Kawagoe, T., *Macromolecules*, 1990, **23,** 4925–4928.
127. Mu, S. L., Ye, J. H. and Wang, Y. H., *J. Power Sources*, 1993, **45,** 153.
128. Yang, L. S., Shan, Z. Q., Hou, P. M., Chen, W. H. and Liu, L., *J. Power Sources*, 1993, **44,** 499–503.
129. Geskin, V. and Nechtschein, M., *Synth. Met.*, 1993, **55–57,** 1533–1538.
130. Osaka, T., Momma, T., Shiota, K. and Nakamura, S., *Denki Kagaki*, 1993, **61,** 1361–1365.
131. Sotomura, T., Uemachi, H., Miyamoto, Y., Kaminaga, A. and Oyama, N., *Denki Kagaku*, 1993, **61,** 1366–1372.
132. Sotomura, T., Uemachi, H., Takeyama, K., Naoi, K. and Oyama, N., *Electrochim. Acta*, 1992, **37,** 1851–1854.
133. Kaminaga, A., Tatsuma, T., Sotomura, T. and Oyama, N., *J. Electrochem. Soc.*, 1995, **142,** L47–L49.
134. Geniès, E. M. and Picart, S., *Synth. Met.*, 1995, **69,** 165–166.
135. Oyama, N., Tatsuma, T., Sato, T. and Sotomura, T., *Nature*, 1995, **373,** 598–600.
136. Tatsuma, T., Sotomura, T., Sato, T., Buttry, D. A. and Oyama, N., *J. Electrochem. Soc.*, 1995, **142,** L82–L84.
137. Troch-Nagels, G., Winand, R., Weymeersch, A. and Benard, L., *J. Appl. Electrochem.*, 1992, **22,** 756–764.
138. Wessling, B., *Adv. Mater.*, 1994, **6,** 225–228.
139. Lu, W.-K., Elsenbaumer, R. L. and Wessling, B., *Synth. Met.*, 1995, **71,** 2163–2166.
140. Jelle, B. P., Hagen, G., Hesjevik, S. M. and Odegard, R., *Mat. Sci. Eng.*, 1992, **B13,** 239–241.
141. Jelle, B. P., Hagen, G., Sungle, S. and Obegard, R., *Synth. Met.*, 1993, **54,** 315–320.
142. Morita, M., *Macromol. Chem. Phys.*, 1994, **195,** 609–620.
143. Morita, M., *J. Appl. Polym. Sci.*, 1994, **52,** 711–719.
144. Jelle, B. P. and Hagen, G., *J. Electrochem. Soc.*, 1993, **140,** 3560–3564.
145. Yano, J. and Kitani, A., *Synth. Met.*, 1995, **69,** 117–118.
146. Barbero, C., Miras, M. C., Koetz, R. and Haas, O., *Synth. Met.*, 1993, **55–57,** 1539–1544.
147. Barbero, C., Koetz, R., Kalaji, M., Nyholm, L. and Peter, L. M., *Synth. Met.*, 1993, **55–57,** 1545–1551.
148. Bidan, G. and Ehui, B., *J. Chem. Soc., Chem. Commun.*, 1989, 1568–1570.
149. Doblhofer, K. and Armstrong, R. D., *Electrochim. Acta*, 1988, **33,** 453–460.
150. Zhong, C. and Doblhofer, K., *Electrochim. Acta*, 1990, **35,** 1971–1975.
151. Miras, M. C., Barbeto, C., Koetz, R. and Haas, O., *J. Electroanal. Chem.*, 1994, **369,** 193–197.
152. Nagaoka, T., Fujimoto, M., Nakao, H., Kakuno, K., Yano, J. and Ogura, K., *J. Electroanal. Chem.*, 1994, **364,** 179–188.
153. Nagaoka, T., Kakuno, K., Fujimoto, M., Nakao, H., Yano, J. and Ogura, K., *J. Electroanal. Chem.*, 1994, **368,** 315–317.
154. Syed, A. A. and Dinesan, M. K., *Synth. Met.*, 1990, **36,** 209–215.
155. Syed, A. A. and Dinesan, M. K., *Analyst*, 1992, **117,** 61–66.
156. Teasdale, P. R. and Wallace, G. G., *Polym. Int.*, 1994, **35,** 197–205.
157. Tsamouras, D., Dalas, E., Sakkopoulocos, S. and Vitoratos, E., *Appl. Surface Sci.*, 1993, **65–66,** 388–393.
158. Mu, S. L. and Xia, C. F., *Synth. Met.*, 1993, **59,** 243–247.
159. Yuan, R. K., Liu, Y. X., Yuan, H., Wang, Y. B., Zheng, X. Q., Xu, J. and Shen, X. C., *Synth. Met.*, 1993, **55–57,** 4087–4092.
160. Dalas, E., Sakkopoulocos, S., Vitoratos, E., Maroulis, G. and Kobotiatis, L., *J. Mater. Sci.*, 1993, **28,** 5456–5460.

161. Yang, Y., Westerweele, E., Zhang, C., Smith, P. and Heeger, A. J., *J. Appl. Phys.*, 1995, **77,** 694–698.
162. Yang, Y. and Heeger, A. J., *Appl. Phys. Lett.*, 1994, **64,** 1245–1247.
163. Yang, Y. and Heeger, A. J., *Mol. Cryst. Liq. Cryst.*, 1994, **256,** 537–542.
164. Gustafsson, G., Treacy, G. M., Gao, Y., Klavetter, F., Colaneri, N. and Heeger, A. J., *Synth. Met.*, 1993, **55–57,** 4123–4127.
165. Bsiesy, A., Nicolau, Y. F., Ermolieff, A., Muller, F. and Gaspard, F., *Thin Solid Films*, 1995, **255,** 43–48.
166. Parkhutik, V. P., Diaz Calleja, R., Matveeva, E. S. and Martinez-Duart, J. M., *Synth. Met.*, 1994, **67,** 111–114.
167. Matveeva, E. S., Parkhutik, V. P., Diaz Calleja, R. and Martinez-Duart, J. M., *J. Luminescence*, 1993, **57,** 175–180.
168. Onoda, M. and Yoshino, K., *Jpn. J. Appl. Phys.*, 1995, **34,** L260–L263.
169. Yoneyama, H., *Adv. Mater.*, 1993, **5,** 394–396.
170. Kuwabata, S., Takahashi, N., Hirao, S. and Yoneyama, H., *Chem. Mater.*, 1993, **5,** 437–441.
171. Kuwabata, S., Kishimoto, A. and Yoneyama, H., *J. Electroanal. Chem.*, 1994, **377,** 261–268.
172. Ruizhitzky, E., *Adv. Mater.*, 1993, **5,** 334–336.
173. Liu, Y. J., Degroot, D. C., Schindler, J. L., Kannewurf, C. R. and Kanatzidis, M. G., *Adv. Mater.*, 1993, **5,** 369–371.
174. Liu, Y. J., Degroot, D. C., Schindler, J. L., Kannewurf, C. R. and Kanadzids, M. C., *J. Chem. Soc., Chem. Commun.*, 1993, 593–596.
175. Pokhodenko, V. D., Koshechko, V. G. and Krylov, V. A., *J. Power Sources*, 1993, **45,** 1–5.
176. Kanatzidis, M. G., Tonge, L. M., Marx, T. J., Marcy, H. O. and Kannerwurf, C. R., *J. Am. Chem. Soc.*, 1987, **109,** 3797–3799.
177. Kanatzidis, M. G., Wu, C.-C., Marcy, H. O. and Kannerwurf, C. R., *J. Am. Chem. Soc.*, 1989, **111,** 4139–4141.
178. Pokhodenko, V. D. and Krylov, V. A., *Synth. Met.*, 1991, **41–43,** 533.
179. Epstein, A. J. and MacDiarmid, A., *Synth. Met.*, 1995, **69,** 179–182. and references therein.
180. Joo, J., Oh, E. J., Min, G., Epstein, A. J. and MacDiarmid, A., *Synth. Met.*, 1995, **69,** 251–254.
181. Epstein, A. J., Joo, J., Kohlman, R. S., Du, G., MacDiarmid, A., Oh, E. J., Min, Y., Tsukamoto, J., Kaneko, H. and Pouget, J. P., *Synth. Met.*, 1994, **65,** 149–157.
182. Trivedi, D. C. and Dhawan, S. K., *Synth. Met.*, 1993, **59,** 267–272.
183. Huang, J.-Ch., *Adv. Polym. Technol.*, 1995, **14,** 137–150.
184. Joo, J. and Epstein, A. J., *Appl. Phys. Lett.*, 1994, **65,** 2278–2280.
185. Colaneri, N. F. and Shacklette, L. W., *IEEE Transactions on Instrumentation and Measurements*, 1992, **41,** 291–297.
186. Hourquebie, P. and Olmedo, L., *Synth. Met.*, 1994, **65,** 19–26.
187. Olmedo, L., Hourquebie, P. and Jousse, F., *Synth. Met.*, 1995, **69,** 205–208.
188. Matsue, T., *Trends Anal. Chem.*, 1993, **12,** 100–108.
189. Fabrizio, M., Furlanetto, F., Mengoli, G., Musiani, M. M. and Paolicci, F., *J. Electroanal. Chem.*, 1992, **323,** 197–212.
190. Cooper, J. C. and Hall, E. A. M., *Electroanalysis*, 1993, **5,** 385–389.
191. Sukeerthi, S. and Contractor, A. Q., *Indian J. Chem.*, 1994, **33A,** 565–571.
192. Kanclerz, K., Koziel, K., Suchecka, A., Strojek, J. W., Lapkowski, M., Niedzielski, C. and Szeja, W., *Pol. J. Chem.*, 1995, **69,** 316–319.
193. Kaneto, K., Kaneko, M., Min, Y. and MacDiarmid, A. G., *Synth. Met.*, 1995, **71,** 2211–2212.
194. Kaneto, K., Kaneko, M. and Takashima, W., *Jpn. J. Appl. Phys.*, 1995, **34,** L837–L840.
195. Takashima, W., Fukui, M., Kaneko, M. and Kaneto, K., *Jpn. J. Appl. Phys.*, 1995, **34,** 3786–3789.
196. Huang, W. S., Angelopoulos, M., White, J. R. and Park, J. M., *Mol. Cryst. Liq. Cryst.*, 1990, **189,** 227–235.
197. Kang, E. T., Ting, Y. P., Neoh, K. G. and Tan, K. L., *Synth. Met.*, 1995, **69,** 477–478.
198. Ting, Y. P., Neoh, K. G., Kang, E. T. and Tan, K. L., *J. Chem. Tech. Biotech.*, 1994, **59,** 31–37.
199. Hasik, M., Turek, W., Stochmal, E., Lapkowski, M. and Pron, A., *J. Catalysis*, 1994, **147,** 544–551.
200. Lapkowski, M., Turek, W., Barth, M. and Lefrant, S., *Synth. Met.*, 1995, **69,** 127–128.
201. Laborde, H., Léger, J.-M. and Lamy, C., *J. Appl. Electrochem.*, 1994, **24,** 219–226.

202. Sviridov, D. V. and Kulak, A. I., *Solar Energy Materials and Solar Cells*, 1995, **39,** 49–53.
203. Coplin, K. A., Leng, J. M., Mccall, R. P., Epstein, A. J., Manohar, S. K., Sun, Y. and MacDiarmid, A. G., *Synth. Met.*, 1993, **55–57,** 7–14.
204. McCall, R. P., Ginder, J. M., Leng, J. M., Coplin, K. A., Ye, H. J., Epstein, A. J., Asturias, G. E., Manohar, S. K., Masters, J. G., Scherr, E. M., Sun, Y. and MacDiarmid, A. G., *Synth. Met.*, 1991, **41–43,** 1329–1332. and references therein.
205. Leng, J. M., McCall, R. P., Cromack, K. R., Ginder, J. M., Ye, H. J., Sun, Y., Manohar, S. K., MacDiarmid, A. G. and Epstein, A. J., *Phys. Rev. Lett.*, 1992, **68,** 1184–1187.
206. Epstein, A. J., Blatchford, J. W., Kim, K., Lin, L.-B., Gustafson, T. L., Coplin, K. A. and MacDiarmid, A. G., *Mol. Cryst. Liq. Cryst.*, 1994, **256,** 399–406. and references therein.
207. Chen, W.-Ch., Jenekhe, S. A., Meth, J. S. and Vanherzeele, H., *J. Polym. Sci.*, 1994, **32,** 195–200.
208. Osaheni, J. A., Jenekhe, S. A., Vanherzeele, H., Meth, J. S., Sun, Y. and MacDiarmid, A. G., *J. Phys. Chem.*, 1992, **96,** 2830–2836.
209. Anderson, M. R., Mattes, B. R., Reiss, H. and Kaner, R. B., *Science*, 1991, **252,** 1412–1415.
210. Kuwabata, S. and Martin, Ch., *J. Membrane Sci.*, 1994, **91,** 1–12.
211. Ghosh, S. and Kalpagam, V., *Indian J. Chem.*, 1992, **31,** 338–341.
212. Schmidt, V. M., Tegtmeyer, D. and Heitbaum, J., *Adv. Mater.*, 1992, **4,** 428–431.
213. Ohtani, A., Abe, M., Ezoe, M., Doi, T., Miyata, T. and Miyke, A., *Synth. Met.*, 1993, **55–57,** 3696–3701.
214. Schoch, K. F. Jr., Byers, W. A. and Buckley, L. J., *Synth. Met.*, 1995, **72,** 13–23.
215. Kulkarni, V. G., Campbell, J. C. and Mathew, W. R., *Synth. Met.*, 1993, **57,** 3780–3785.
216. Roth, S. and Graupner, W., *Synth. Met.*, 1993, **55–57,** 3623–3631.
217. Holland, E. R. and Monkman, A. P., *Synth. Met.*, 1995, **74,** 75–79.
218. Kohlman, R. S., Min, Y., MacDiarmid, A. and Epstein, A. J., *Synth. Met.*, 1995, **69,** 211–212.
219. Hwang, H. Y., Lee, S. W., Kim, I. W. and Lee, H., *Synth. Met.*, 1995, **69,** 225–226.
220. Petrov, D. V., Gomes, A. S., de Araujo, Cid B., de Souza, J. M., de Azevedo, W. M., de Melo, J. V. and Diniz, F. B., *Optics Lett.*, 1995, **20,** 554–556.
221. Gao, Y., Colaneri, N., Heeger, A. J. and Smith, P., *Appl. Phys. Lett.*, 1994, **65,** 2001–2003