RADICAL INTERMEDIATES IN ELECTROCHEMICAL POLYMER-FORMING REACTIONS

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The role of organic radicals in the formation of functional polymers, in particular intrinsically conducting polymers, is reviewed. New results recently obtained with *in situ* spectroscopic methods illustrating the influence of the molecular structure of monomers (aniline and substituted anilines) on the behaviour of radical intermediates are presented. The stabilising influence of substituents at various positions of the aniline molecule is evaluated and compared based on conceivable structures of reaction intermediates.

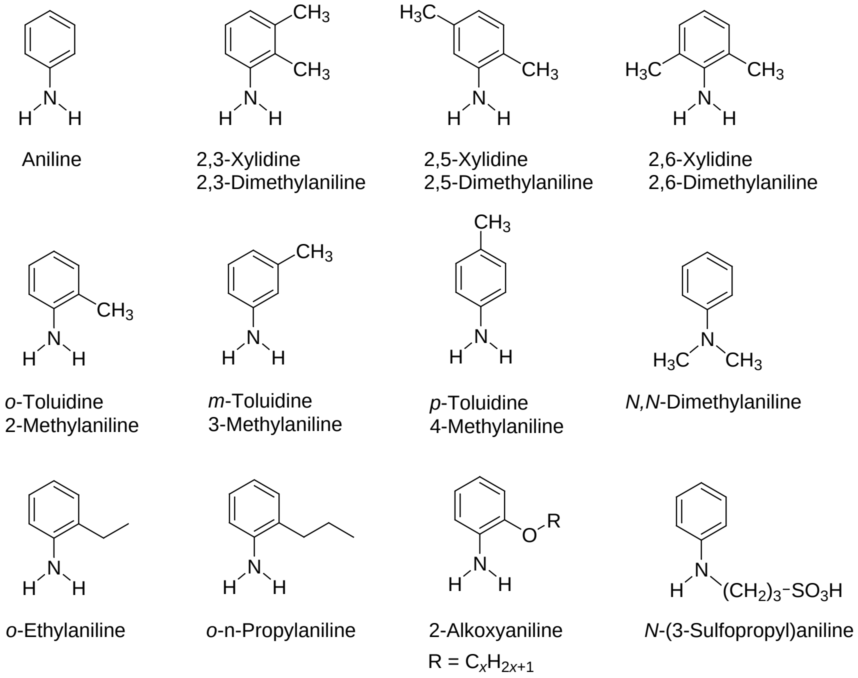
Key words: Electrochemistry; Conducting polymers; Polyaniline; Intermediates; Spectroelectrochemistry; Radicals.

Radicals formed by electroreduction or electrooxidation of organic molecules including dimers and oligomers of the parent molecule play a central role in numerous electrochemical processes involving molecules being converted in electrochemical reactions at electrodes as well as organic monolayers and electrode-modifying films attached to an electrode surface. In the case of heteroatom carrying monomers like aniline and numerous substituted anilines (for a selection of the molecules treated in this report see Fig. 1) radicals are observed during oxidation of these molecules. Their further reaction results in many cases in the formation of oligomers or polymers (*e.g.* polyaniline PANI). The electrochemically induced changes of these newly formed species again involve radicals. Finally, during the interaction of these oligomers or polymers with their environment (species from the solution or gas phase) again in many cases radicals present in the polymer system participate.

This report focuses on the role played by radicals in the initial process of oligomerisation. The other aspects briefly outlined before have been the subject of numerous reports and reviews (see *e.g.* ref.[1]). An overview with particular attention to results pertaining to these species as obtained with *in situ* spectroelectrochemical methods has been provided elsewhere[2]. After an introductory section wherein results reported so far are reviewed new data from the authors laboratory are reported and discussed with particular attention to the reviewed results and conclusions.

Polyaniline is a very prominent and intensely investigated member of the family of intrinsically conducting polymers. These materials are a fairly recent, new class of materials combining typical properties of metals and synthetic polymers. They do this in a way so fascinating that they are sometimes called “synthetic metals”.

Polyaniline has attracted special attention presumably for at least two reasons: It can be prepared easily both by chemical and electrochemical oxidation processes and it shows a particular sensitivity to the proton activity of its environment because of the nitrogen atoms which are not part of the aromatic ring systems. This interest has resulted in an overwhelming number of original reports and a considerable collection of reviews[3–8].



Aniline

2,3-Xylidine
2,3-Dimethylaniline

2,5-Xylidine
2,5-Dimethylaniline

2,6-Xylidine
2,6-Dimethylaniline

o-Toluidine
2-Methylaniline

m-Toluidine
3-Methylaniline

p-Toluidine
4-Methylaniline

N,N-Dimethylaniline

o-Ethylaniline

o-n-Propylaniline

2-Alkoxyaniline
R = C_xH_{2x+1}

N-(3-Sulfopropyl)aniline

FIG. 1
Aniline and substituted anilines investigated in the work treated in this report

The formation of PANI and the polymers of substituted anilines can be attained by chemical oxidation or electrooxidation. The mechanism and the kinetics of PANI formation have been the subject of numerous investigations devoted to the identification of the steps of the electrooxidation and electropolymerisation processes and the identity of intermediates. This knowledge gains additional importance when relationships between the mechanism of polymerisation and possible reaction pathways and properties of the polymer product are sought. Figure 2 depicts a very general pathway of aniline oxidation and the formation of first oligomers. The initial step seems to be in all cases the adsorption of the monomer from the electrolyte solution on the electrode surface. This is a necessary prerequisite for the consecutive charge transfer during the electrooxidation step. Investigations of the adsorption of aniline or related compounds are scanty; they have been reviewed elsewhere[9].

According to Dunsch[10] the anilinium cation is deprotonated on the electrode surface before undergoing the first oxidation step. This conclusion was based on electrochemical measurements with a rotating-disc electrode. Considering simple electrostatic arguments, adsorption of the neutral aniline should be favoured as compared with the adsorption of the positively charged anilinium cation. Direct evidence from spectroscopic measurements of this process is lacking so far. It seems to be noteworthy, that results of spectroscopic measurements often used in support of a proposed reaction pathway should be considered with care. Virtually all spectroscopic methods will yield results primarily in support of the species which can be detected most easily with the employed experimental method or which is the most stable one. Unfortunately, this reaction intermediate is not necessarily the reaction intermediate in the main reaction pathway; in the worst case it is actually a byproduct formed which does not participate in the main reaction path at all[11].

In most reports dealing with electropolymerisation of aniline and its derivatives, formation of a cation radical or another intermediate in the initial stage of the process is assumed[12]. A basic reaction mechanism of the anodic oxidation of anilines, leading to head-to-tail, head-to-head and tail-to-tail dimers, as well as to polymer products with the participation of electrogenerated cation radicals, was proposed in early works[13–17].

Direct proof of the radical nature of the reaction intermediate proposed in the reaction scheme can be expected from *in situ* measurements with electrochemical electron spin resonance spectroscopy ECESR. So far all experimental attempts with aniline in aqueous solution with an electrochemical cell described previously[18,19] and based on the design by Allendoerfer *et al.*[20], as described elsewhere in detail[21], have failed. Always a single line spectrum has been observed. This indicates the presence of highly delocalised spins attributed to radical cations formed on the polymer chain. Investigations of

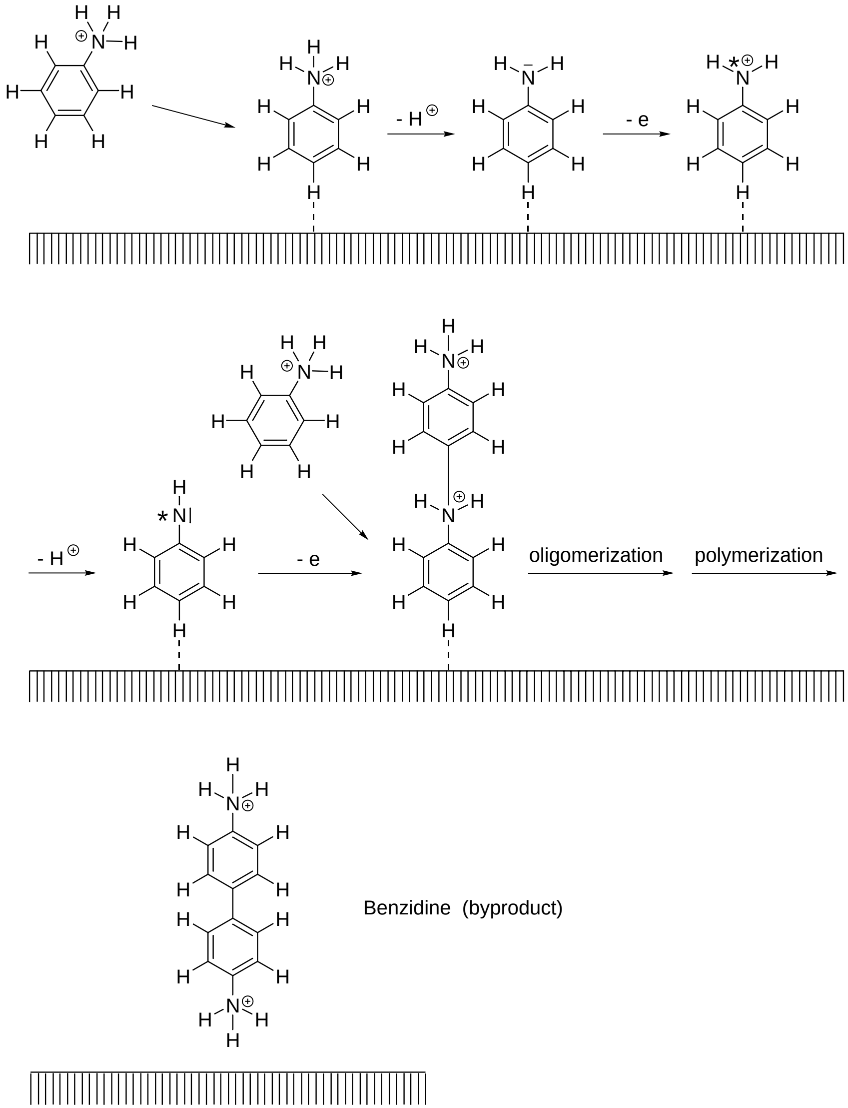


FIG. 2
General reaction mechanism for polyaniline formation

the change in the ESR signal amplitude during electropolymerisation have revealed interactions between the cations formed on the polymer and the monomer in solution[22]. The latter fact is the main difference as compared with the numerous ESR studies reviewed in detail below. The major result is the observation that after stopping electrolysis at a highly positive electrode potential, the ESR intensity rapidly increases again. This is caused by the conversion of spinless systems in the film into spin-carrying radical cations. As this was observed only in the presence of aniline molecules in the solution phase their participation (perhaps by chemical oxidation of solution phase monomers by the positive charges on the film) seems to be effective. This result fits with observations reported by Pekmez *et al.*[23]. In their report the interaction of protonated sites on the polyaniline in particular in its pernigraniline form (which essentially does not contain free spins) with aniline monomer units resulting in their oxidation with a concomitant loss of pernigraniline sites is stated.

The absence of an ESR signal caused by a monomeric radical cation can be explained readily when considering the reactivity of the aniline radical cation. According to Neugebauer *et al.* this radical is highly reactive, its ESR spectrum could be recorded only in a flow apparatus under fairly extreme conditions[24]. The failure to observe an ECESR spectrum with the hyperfine splitting indicative of a molecular (not an oligomeric) unit with an unpaired electron can be explained by various arguments, which are all related to the high reactivity. The detection limit of ESR spectroscopy is very low, consequently the absence of the ESR spectrum implies an extremely low stationary radical concentration (if any). This argument has to be considered with care, because the use of the ECESR cell drastically rises the detection limit. Upon substitution of the aniline molecule the situation changes considerably. With *N*,*N*-dimethylaniline the ESR spectrum displayed in Fig. 3 could be recorded[25]. Results similar with respect to the stabilising influence of *N*-substitution at the nitrogen atom of aniline were obtained during chemical oxidation of various *N*-substituted anilines by Yatsimirskii *et al.*[26]. Further substitution was used by Male and Allendoerfer. They observed a complete ECESR spectrum of *p*-aminodiphenylamine[27]. A highly substituted aniline (2,6-di-*tert*-butylaniline) was investigated by Speiser *et al.*[28]; their results imply again a radical cation as the oxidation product. Reduction of a radical cation further supporting its radicalic nature was observed for 2,6-di-*tert*-butyl-4-phenylaniline by Kvarnström *et al.*[29,30]. No polymerisation was observed. Yang *et al.* investigated the ESR and UV-VIS absorption of diphenyl-1,4-phenylenediamine and tetraanilinobenzene in the electrode potential range between the first and the second oxidation current wave[31]. The fairly broad, yet extremely poorly resolved ESR spectra seem to indicate the presence of some hyperfine splitting, which may be taken as indication of the presence of radical species. Optical absorptions observed for both monomers as a function of electrode potential were taken as support for this conclusion. In an electrolyte solution of aniline in acidified dimethyl sulfoxide polymerisation after the initial electrooxidation does not occur. In this solution Petr and Dunsch[32] have found using ECESR the indamine radical cation. Its presence can be seen as proof of the aniline radical cation intermediate proposed by many authors, as reviewed above, when considering this indamine radical cation as part of a reaction sequence assuming the occurrence of the aniline radical cation as a precondition. Hambitzer and Stassen reported the detection of soluble products of aniline electrooxidation by using electrochemical thermospray mass spectrometry[33–36]. Certain features of their mass spectra were used as arguments in favour of the presence of a radical species.

Less direct evidence of a reaction intermediate and its radical nature can be obtained with *in situ* UV-VIS spectroscopy with optically transparent electrodes. Aromatic radicals and their derivatives are generally coloured because electronic transitions not possible in the educt molecule cause the observed optical absorption. Unfortunately, other conceivable reaction intermediates, in particular dimers and small oligomers conceivably being

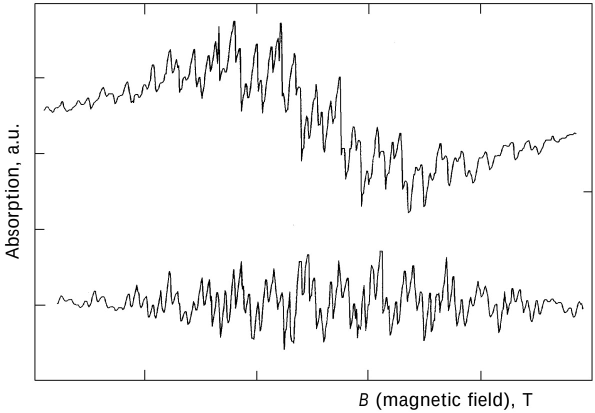


FIG. 3

Top: Electron spin resonance spectrum of the chemically formed *N*,*N*-dimethylaniline radical cation in concentrated nitric acid; 9.41 GHz, 79 mW, modulation 0.65 G, sweep 2 min, T = 10 °C. Bottom: Calculated spectrum: coupling constants a_{N} = 7.75 G, $a_{\mathrm{CH_3}}$ = 8.54 G, $a_{\mathrm{H},ortho}$ = 3.71 G, $a_{\mathrm{H},meta}$ = 0.95 G, $a_{\mathrm{H},para}$ = 6.9 G (based on data taken from ref.[25])

present in their oxidised state as part of the reaction sequence, will also show colouration. So far attempts to record UV-VIS spectra of an oxidised reaction intermediate of aniline under conditions where its oxidation takes place have failed. Kemp *et al.* have used a fast scan UV-VIS spectrometer in an attempt to detect intermediates in the oxidation of various *N*-substituted anilines with limited success only[37]. Radicals of substituted alkylanilines were identified, whereas unsubstituted aniline did not yield a signal attributable to a radical intermediate. With a combination of *in situ* UV-VIS and infrared spectroscopy Zimmermann *et al.*[38] have studied the initially formed product in an acidic electrolyte solution containing aniline on an electrode deposited on an ATR element for infrared spectroscopy and at a platinum grid electrode for *in situ* UV-VIS spectroscopy in the transmission mode. The obtained spectra did not imply a monomeric reaction intermediate. Instead it was concluded, that *N*-phenylbenzoquinonediimine is formed in its fully oxidised state. It was only suggested, that this dimer must have been formed from two monomer molecules by way of a radical-monomer substitution reaction. This species is reduced during a subsequent electrode potential scan in a two-electron reduction. In a comproportionation reaction with its fully oxidised form radical dimers are formed, which finally form a tetramer. UV-VIS data obtained with this system as well as data obtained with *p*-aminodiphenylamine support this conclusion. Leger *et al.* presented a detailed study of *o*-toluidine electropolymerisation with fast scan UV-VIS differential reflectance spectroscopy at a gold electrode[39]. These authors obtained UV-VIS spectra in the first potential scan different from those of the resulting polymer itself, indicating intermediate species as a precursor of the polymer. Genies and Lapkowski used fast scan visible spectroscopy during electrolysis of aniline and found a short-lived intermediate created before the formation of polyaniline in an eutectic of $NH_4F \cdot 2.3HF$ (refs[40,41]). They proposed this intermediate to be the nitrenium cation ($Ph\text{-}NH^+$). This electrolyte system was assumed to be less prone to degradation by overoxidation of the polymer during its formation[42]. Somewhat later, Genies *et al.* claimed the formation of the nitrenium cation to proceed during electropolymerisation of azobenzene in the same medium, as studied by fast scan UV-VIS spectroelectrochemistry[43]. Shim *et al.*[44] observed a transient absorbance band at $\lambda = 430$ nm during electrooxidation of aniline and ascribed it to an intermediate species, probably the nitrenium cation based on the reports by Genies and Lapkowski. Once formed, the nitrenium cation leads to all three possible dimers, *i.e.* head-to-tail, tail-to-tail and head-to-head coupling products, which are capable of growing into polyaniline in the presence of aniline. Later, Johnson and Park again observed a spectral band at λ = 440 nm, which is prominent in early stages of aniline electrooxidation, and believed the nascent products to be the cation radical of aniline or a product formed before the radical undergoes a dimerisation reaction[45]. de Santana *et al.* have used *in situ* resonance Raman spectroscopy to investigate oxidation products of diphenylamine[46]. Various diphenylbenzidine species including radical ones, but no polymer or oligomer, were found.

In this paper data pertaining to the effect of the substitution on the reactivity of the monomer are reported and discussed in more detail. The electrooxidation of a selection of *N*-alkyl substituted (*N*-ethyl- and *N,N*-dimethylsulfopropyl) and ring substituted (*o*-, *m*-, *p*-methyl-, *o*-ethylaniline) derivatives was investigated. Results are reported here.

EXPERIMENTAL

Analytical grade aniline (Riedel-de-Haen), *o*-toluidine, *m*-toluidine, *p*-toluidine, *o*-ethylaniline, *N,N*-dimethylaniline (Merck) and *N*-ethylaniline (Lancaster) were used as received. *N*-(3-sulfopropyl)aniline (NSPA) was synthesised as previously described[47]. Electrolyte solutions were prepared from ultrapure water (Seralpur Pro 90C) and 0.5 M sulfuric acid (Merck) for all experiments if not stated otherwise.

UV-VIS spectra were recorded with a Shimadzu model UV-2101 PC spectrometer. Spectroelectrochemical experiments were done in a 1 cm path length quartz cuvette as an electrochemical cell fitted with a transparent indium-doped tin oxide coated (ITO) glass working electrode with a specific surface resistance of 10–20 Ω/square installed perpendicular to the light beam. A platinum wire served as counter electrode. A relative hydrogen electrode filled with 0.5 M H_2SO_4 solution served as reference connected with a salt bridge. All potential values given below refer to this relative hydrogen electrode. Before experiments, ITO glass working electrodes were degreased with acetone and rinsed with an excess of water. In the reference channel of the spectrometer a quartz cuvette containing an identical glass electrode without polymer coating was inserted. All spectra reported are background-corrected. A Wenking model LB 81 M potentiostat was used in the spectroelectrochemical experiments. For further details see ref.[48].

For cyclic voltammetry (CV) a personal computer equipped with an ADDA-converter and custom designed software were connected to a custom built potentiostat.

RESULTS AND DISCUSSION

With *N*-ethylaniline (NEA) well defined absorbance peaks of an intermediate and of an end product were observed after an anodic potential step (Fig. 4). Two absorbance bands are located at λ = 450 and 725 nm. Both bands grow in intensity during electrolysis. At lower concentrations of NEA, the absorbance band located at λ = 450 nm, grows at a higher rate, than that observed at λ = 725 nm (Fig. 4, middle). At low concentrations of NEA, only a band at λ = 450 nm can be detected after a few minutes of electrolysis.

After interruption of electrolysis, the absorbance band at λ = 450 nm diminishes in intensity, whereas the intensity of the band at λ = 725 nm in-

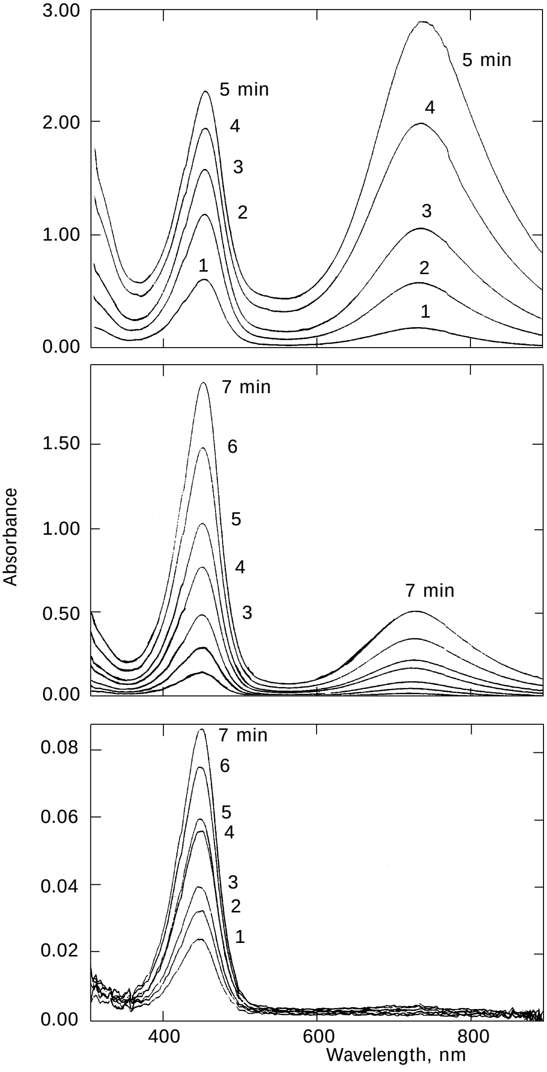


FIG. 4
UV-VIS spectra of an ITO electrode after time intervals (as indicated, in minutes) after a potential step to E_{RHE} = +1.2 V in solutions containing 100 mmol/l (top), 20 mmol/l (middle) or 1 mmol/l (bottom) of *N*-ethylaniline (for further experimental details see ref.[48])

creases simultaneously. Figure 5 (top) shows an increase of both absorbance bands during electrolysis performed for up to 7 min at E_{RHE} = +1.2 V. Immediately after interruption of electrolysis, spectra were recorded in time intervals of a few minutes. Figure 5 (bottom) shows a decrease in the intensity of the band at λ = 450 nm proceeding after interruption of electrolysis simultaneously with an increase in absorbance in the red region.

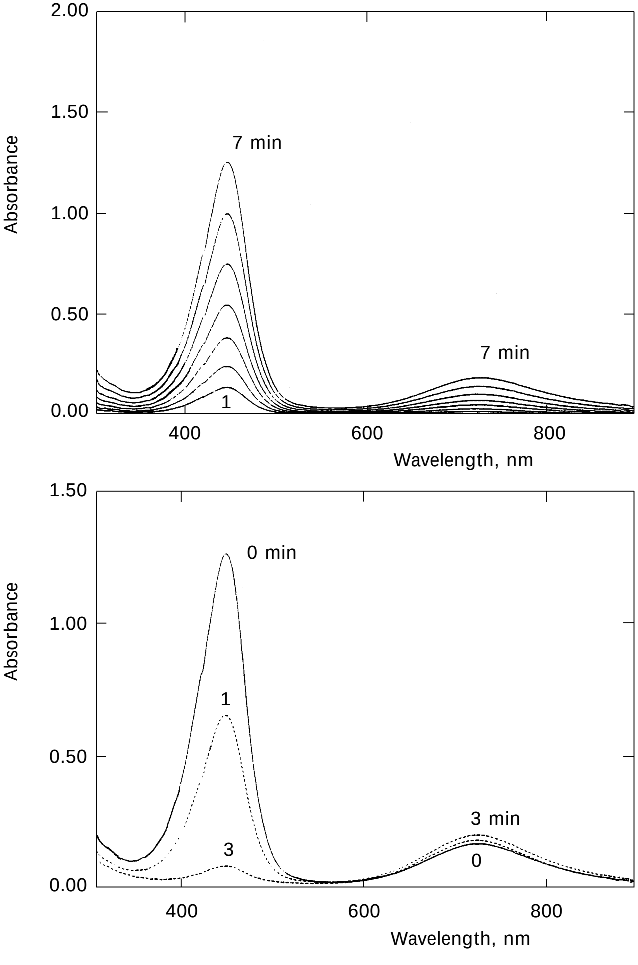


FIG. 5
Top: UV-VIS spectra obtained in intervals ranging from 1 to 7 min after a potential step to E_{RHE} = +1.2 V in solutions containing 10 mM *N*-ethylaniline. Bottom: spectra obtained after 0, 1 and 3 min after interruption of electrolysis done initially for 7 min

Figure 6 shows absorbance transients recorded at λ = 450 nm in NEA solutions of different concentrations, ranging from 0.5 to 50 mmol/l. After stepping to E_{RHE} = +1.2 V, an almost linear increase in absorbance proceeds at a rate depending on the concentration of NEA. After interruption of electrolysis a decrease in absorbance is observed. The rate of decrease depends on the concentration of NEA being greater for more concentrated solutions. This indicates that the decay of intermediate concentration proceeds due to the reaction of the intermediate with unreacted NEA, rather than due to recombination of intermediates themselves, because in the latter case, the decay rate should be independent of the concentration of NEA in solution.

As with *N*-methylaniline[49], no polymer film was formed on ITO glass electrodes during electrolysis of NEA solution. Accordingly, all spectra are caused by solution phase species including the end product of electrooxidation. For *N*-methylaniline, well adherent polymer films may be obtained by electropolymerisation on platinum electrodes, in contrast to ITO glass electrodes[50]. For NEA, the deposition of a polymer film by electrooxidation at a graphite electrode was reported[51] yielding an electrochemically active polymer layer, showing $E_{1/2,\mathrm{SCE}}$ = 0.37 V in a perchlorate solution of pH 1.0.

Based on the evidence reviewed in the introductory section, the spectral absorption assigned to a reaction intermediate may also be caused by a chemical reaction between unreacted monomers and dications formed by

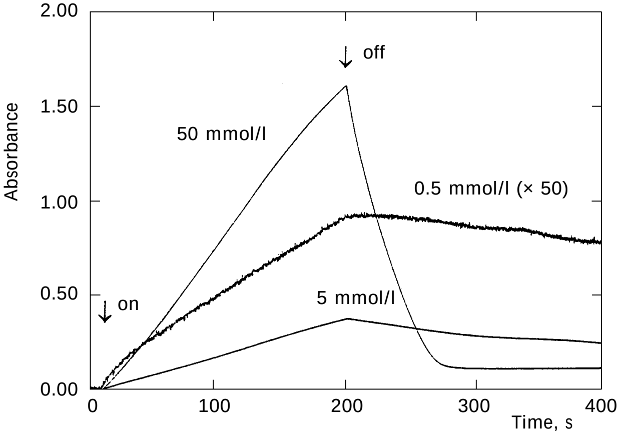


FIG. 6
Absorbance–time profiles recorded at λ = 450 nm, obtained after a potential step to E_{RHE} = +1.2 V, and after interruption of electrolysis (as indicated by the arrows (on and off) in solutions containing *N*-ethylaniline in different concentrations

oxidation of the end product. In this case the absorption at $\lambda = 725$ nm should decrease after switching off the polymerisation potential (see Fig. 5) with a corresponding increase in the absorption at $\lambda = 450$ nm. This was not observed in the results reported here.

With *N*,*N*-dimethylaniline (Fig. 7), a slightly different situation was encountered. The formation of an electrogenerated intermediate (see the figure) as well as its consumption after interruption of electrolysis (not shown here) were observed. A UV-VIS absorption at longer wavelengths indicative

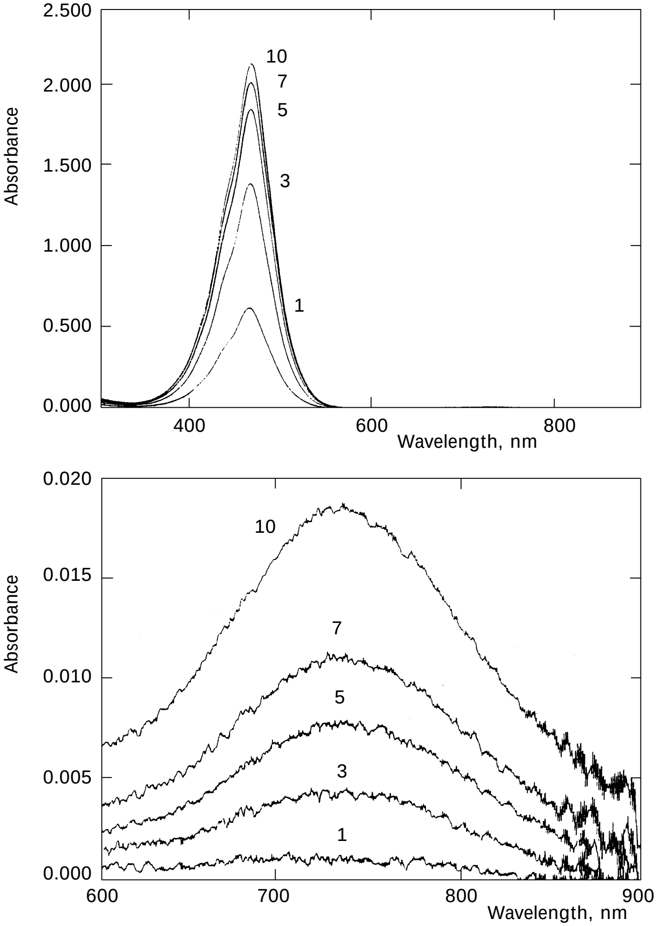


FIG. 7

Top: UV-VIS spectra obtained after different time intervals (as indicated, in minutes) after a potential step to $E_{RHE} = +1.2$ V in a solution, containing 100 mM *N*,*N*-dimethylaniline. Bottom: magnification of the long-wavelength part of spectra of an oligomeric end product was observed only as a very weak band around λ = 740 nm. This can be interpreted in terms of a preferred C–C (tail-to-tail) coupling, leading to a benzidine type end product which is not detectable in the investigated spectral range. Only a minor fraction of polymer is formed (see also ref.[52]).

Better defined absorbance transients are observed for *o*-toluidine (OT). Figure 8 shows absorbance transients recorded at λ = 450 nm (for the inter-

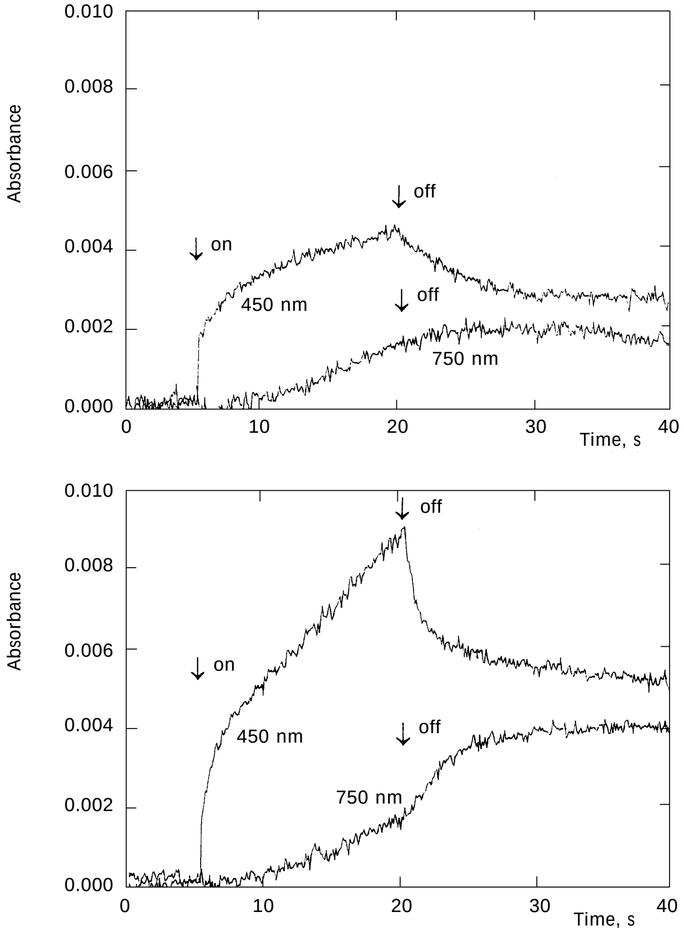


FIG. 8
Absorbance–time profiles recorded at λ = 450 nm and λ = 750 nm (as indicated), obtained after a potential step to E_{RHE} = +1.2 V, and after interruption of electrolysis (as indicated by the arrows) in solutions containing 20 mmol/l (top) or 100 mmol/l (bottom) of *o*-toluidine

mediate) and at λ = 750 nm (for the end product) for two concentrations of OT obtained after anodic potential steps. In both cases, a growth of absorbance after the anodic step was found. The increase of the growth rate corresponds to an increase of the concentration of OT similar to the case of NEA (Fig. 4). After a fast initial drop in the absorbance at λ = 450 nm after interruption of electrolysis finally a constant value is reached (Fig. 8, bottom). When measured at λ = 750 nm the absorbance begins to grow after a time delay of a few seconds. After interruption of electrolysis the absorbance at λ = 750 nm continues to grow, reaching a constant value (Fig. 8). Both the growth rate of the absorbance at λ = 750 nm after interruption of electrolysis and its end value achieved after *ca* 20 s are higher for higher amounts of the intermediate formed in the preceding anodic oxidation, especially at higher concentrations of OT. This confirms, that the intermediate observed at λ = 450 nm is converted spontaneously into the end product, which absorbs at λ = 750 nm. The stabilising effect of the alkyl substituent is discussed below in more detail.

As can be seen in Fig. 8 an initially very fast increase in absorbance at λ = 450 nm occurs after the potential step. Subsequently the absorbance grows at a nearly constant rate. This fast initial increase proceeds up to a nearly constant absorbance value of *ca* 0.002, independent of the OT concentration. It may be assumed, that this initial fast increase corresponds to electrooxidation of the OT layer adsorbed on the ITO glass electrode surface. In this case the independence of the slope of the fast initial increase of OT concentration shows, that even at the lowest concentration studied (10 mmol/l), presumably the entire electrode surface is covered with an adsorbed layer of OT prior to start of electrolysis.

An even more stabilising effect on the intermediate has the introduction of ionogenic groups into the aniline molecule. These groups (*e.g.* sulfonic acid groups) may act as proton sources for doping of the nitrogen atoms. Consequently these polymers are called “self-doping” or “self-acid-doping” (refs[53–56]). A direct UV-VIS spectroelectrochemical observation of an intermediate present during the anodic oxidation is possible in case of *N*-(3-sulfopropyl)aniline (NSPA), an aniline derivative containing a sulfoalkyl group at the nitrogen atom[57]. The relatively high stability of the intermediate enables the time-dependent spectral observation of the intermediate on a multisecond time scale. Figure 9 shows a set of UV-VIS spectra recorded with solutions of various concentrations of NSPA (for details see ref.[58]). The absorption band found at low wavelengths was assigned to a reaction intermediate, whereas the band at high wavelength was attributed to the polymeric reaction product. The time dependent absorption of both bands as

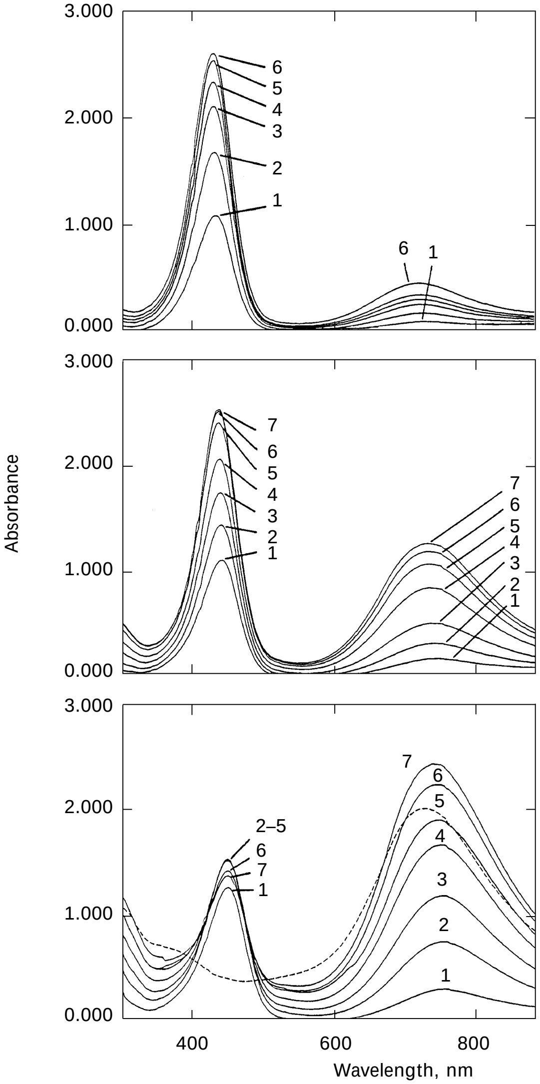


FIG. 9
UV-VIS spectra obtained at different time intervals (as indicated, in minutes) after applying an electrode potential of E_{RHE} = +1.1 V in solutions containing NSPA in various concentrations (0.01 mol/l (top), 0.03 mol/l (middle) and 0.05 mol/l (bottom), as indicated). Dashed line in bottom part shows a spectrum obtained 3 min after interruption of an electrolysis performed for 7 min (for further details see ref.[59])

displayed in Fig. 10 shows the typical shape indicative of a reaction intermediate observed with the band around λ = 445 nm. At low concentration of the monomer consumption of the formed intermediate is faster than formation because of the depletion of the monomer in the electrochemical double layer and slow diffusion. A subsequent chemical reaction of this intermediate, leading to a soluble oligomer or polymer product, was concluded. In the case of NSPA no polymer is formed, accordingly the observed spectrum is solely caused by soluble species. These spectroscopic data do not prove the radicalic nature of the species causing this absorption. The

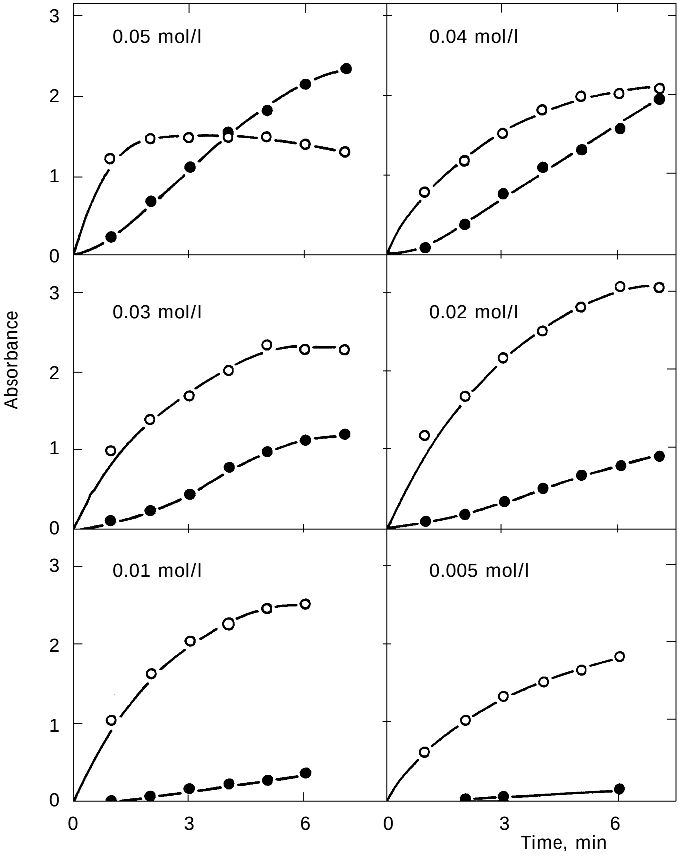


FIG. 10
Time dependence of the absorbance at λ = 453 nm (hollow circles) and λ = 745 nm (full circles) after stepping the electrode potential to E_{RHE} = +1.1 V in solutions containing NSPA in a concentration range of 0.005 to 0.05 mol/l (as indicated) (for further details see ref.[56])

question for the chemical identity of the reaction intermediate should be answered based on a consideration of conceivable reaction pathways of the initially formed radical cation as depicted in Fig. 11 for the case of *N*-ethylaniline. At the anode potential used, all anilines should be quickly oxidised to their radical cations. In the next following step, according to previous work[43,59–61], either a deprotonation of the radical cation to the neutral radical with a subsequent one electron oxidation, or a direct one-electron oxidation of the cation radical to a corresponding dication with a subsequent deprotonation should proceed, yielding an intermediate nitrenium cation. Thus an oxidation square scheme as presented in Fig. 11 can be derived.

The final product of this interconversion is a nitrenium cation analogous to the intermediate in aniline electrooxidation[43,59,60]. In the case of NSPA a radical cation is particularly likely as a reaction intermediate because of a possible stabilisation by the negative charge located on the sulfo group. Definite proof may be available by using ECESR spectroscopy. Because the previously proposed assignment of bands in the spectral region around λ = 440 nm to non-radical species is based mostly on the absence of an ESR signal this experiment will be particularly helpful in case of the system investigated here. The high stability of the proposed intermediate assumed here should enable detection with ECESR. In case of previous studies the lifetimes of assumed intermediates may have been too short leading to ambiguous results, but no definitive proof; *i.e.* the absence of an ESR signal is no proof of a non-radical nature of an intermediate.

Further help in interpretation of experimental evidence as obtained with the different methods mentioned so far may be expected from theoretical considerations, in particular from calculations of UV-VIS spectra of the radical and the nitrenium cation. A comparison of experimental data and

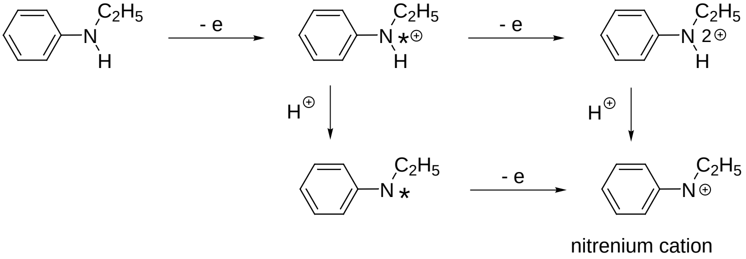


FIG. 11
Pathways indicating the initial steps of aniline oxidation and deprotonation

modelling should enable the assignment of electronic absorption bands in the UV-VIS spectra to one of the possible intermediates. The values of λ_{max} of the absorption band assigned to the intermediate reported so far indicate at least a relationship between the type and degree of substitution and the energy of the electronic transition. Confusion with the absorption bands observed with oxidised polymers in their polaron state is impossible, as the corresponding values differ considerably (Table I). The positions of the bands assigned here only tentatively to the intermediate are in good agreement with those reported by Speiser *et al.* for a series of radicals of substituted anilines[28].

At sufficiently high positive electrode potentials, all investigated aniline derivatives undergo electrooxidation, yielding intermediates. In the following chemical reaction step, these intermediates react with molecules of the substrate in the solution phase. Alternatively, further oxidation of the initial monomer may occur resulting in a dication (see Fig. 11). The fastest chemical reaction proceeds with unsubstituted aniline, whereas its derivatives with alkyl groups substituted at the ring react somewhat slower. The slowest chemical reaction proceeds with *N*-alkylaniline derivatives. This conclusion is again in agreement with the implications of ECESR measurements as reported so far.

As already indicated, stability and reactivity of the reaction intermediate(s) and the reactivity of the monomer are closely related. In a comparative study the influence of various substituents on the reactivity of substituted anilines was investigated[62–65]. The slow film formation enabled the detection of two oxidation steps in cyclic voltammograms before the redox processes of the polymer film became the major cause of the Faradaic currents. A typical example is shown in Figs 12 and 13.

TABLE I
Absorption maxima in UV-VIS spectra of monomers, intermediates and polymers of substituted anilines. Data taken from refs[48,62]

Monomer	$\lambda_{interm.}$, nm	$\lambda_{polym.}$, nm
N-Methylaniline	443	410
N,*N*-Dimethylaniline	465	–
N-Ethylaniline	450	400
p-*o*-Toluidine	490–520	410
N-Benzylaniline	460	–

With a gold electrode the first oxidation wave is obvious. Even in the first negative going scan a cathodic wave at E_{RHE} = 0.6 V is evident indicative of a reduction process. This wave increases during subsequent cycles. Because

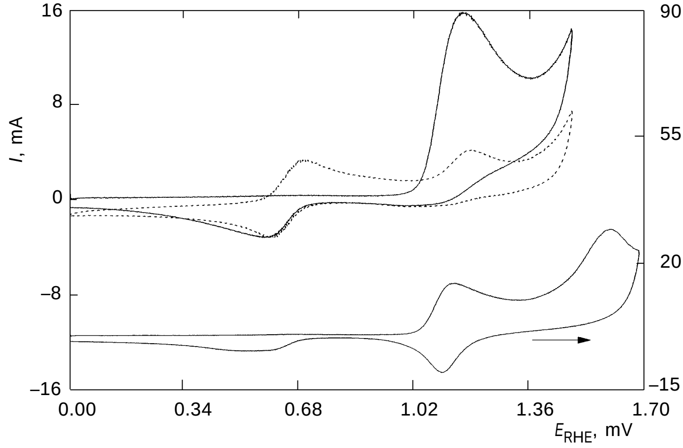


FIG. 12
Cyclic voltammogram (first (——) and tenth (- - - -) cycle) of a gold electrode in contact with a solution of 0.01 M 2,5-xylidine + 1 M $HClO_4$, dE/dt = 1 V/s, nitrogen saturated. CV of first cycle with more positive potential limit below

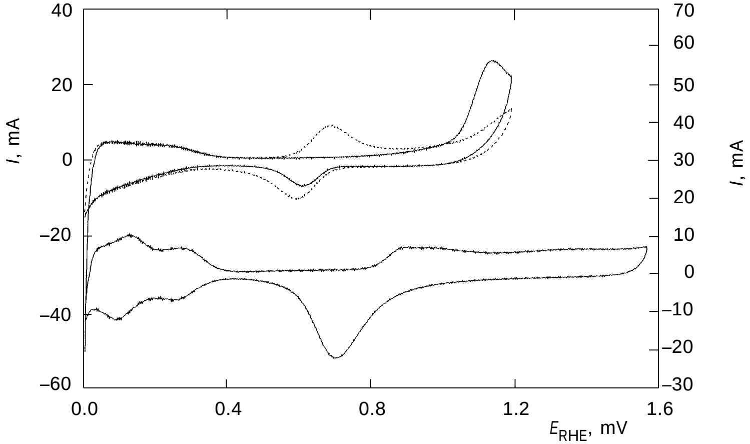


FIG. 13
Cyclic voltammogram (first (——) and tenth (- - - -) cycle) of a platinum electrode in contact with a solution of 0.01 M 2,5-xylidine + 1 M $HClO_4$, dE/dt = 1 V/s, nitrogen saturated. CV with supporting electrolyte solution only shown for comparison below

the position does not change considerably as a function of cycle number, it seems safe to assign this wave to the reduction of oligomers or polymers. The appearance and increasing height of a corresponding wave in the second and in further cycles support this assignment. A cathodic wave indicative of the reduction of the initial oxidation product cannot be observed. This implies that the subsequent reaction of the first reaction intermediate is considerably faster than a conceivable electroreduction of the intermediate. Upon shifting the anodic potential limit, a weak anodic wave is visible. This may be taken as a sign of a subsequent oxidation of the product of the first electron transfer. Since the negative going scan does not show any significant change, it may be assumed, that the product of the reaction of the species formed in the second oxidation process is basically the same as the one formed by the species of the first oxidation step. Some confusion may be caused by the well defined oxidation wave observable at around E_{RHE} = 1.57 V found only when the positive scan limit is moved to values of about E_{RHE} = 1.7 V. The appearance of this wave is accompanied by a cathodic wave around E_{RHE} = 1.1 V. The former current peak is caused by the gold oxide formation, the latter by the corresponding layer reduction as evidenced by comparison with a CV obtained in the supporting electrolyte solution.

Further support of this assignment can be obtained from CVs measured with a platinum electrode. The cathodic wave around E_{RHE} = 1.1 V is absent with platinum, confirming the assignment presented above. The cathodic wave caused by the reduction of the polymer film is seen at about the same electrode potential as observed with the gold electrode.

The observed appearance of two current waves at very low scan rates reported by Probst[62] can be seen as evidence of two consecutive electron transfers supporting the proposed reaction sequence. Electrode potentials of the first and, if available, the second oxidation peak are listed in Table II.

Introduction of two ring substituents reduces the energy needed for the initial oxidation step by about 120 mV as compared with the parent compound. A single alkyl substituent reduces the energy by about 60 mV. This has been attributed to a positive inductive effect of alkyl substituents[66–68]; elsewhere this has been called electron-donating effect[65]. This effect causes an increase in the electron density on the aromatic ring system by inductive displacement of the bonding electrons. The positive charge on the intermediate is stabilised. An analogue can be seen in the σ-complex assumed as an intermediate state in the electrophilic substitution of aromatic compounds (Fig. 14). Alkyl groups also stabilise this state. Because formation of the intermediate is the rate determining step (otherwise, detection of the

TABLE II
Oxidation potentials E_1, E_2 and E_{ox} of aniline and substituted anilines in solutions of 1 M $HClO_4$ + 10 mM monomer in water, data taken from cyclic voltammograms with a scan rate of dE/dt = 10 mV s^{-1} (refs[63,64,65])

Monomer	Acronym	$E_{1,RHE}$, mV	$E_{2,RHE}$, mV	$E_{ox,SCE}$, V (ref.[65])
Aniline	PANI	1 134	–	1.03
2,3-Xylidine	P23X	1 031	1 168	–
2,5-Xylidine	P25X	1 021	1 202	0.81
2,6-Xylidine	P26X	1 043	1 187	–
o-Toluidine	PoTl	1 080	–	0.88
m-Toluidine	PmTl	1 085	–	–
o-Ethylaniline	PEtA	1 081	–	–
o-n-Propylaniline	PPrA	1 055	–	–
N-Methylaniline	PNMA	1 170	–	–
N-Ethylaniline	PNEA	1 085	–	–
2-Methoxyaniline[a]	MOA	–	–	0.75
2-Aminobenzyl alcohol	ABA	–	–	1.01
2-Methoxy-5-methylaniline	MOMA	–	–	0.75
2-Methyl-5-methoxyaniline	MMOA	–	–	0.87
2,5-Dimethoxyaniline	DMOA	–	–	0.67

[a] *o*-Anisidine.

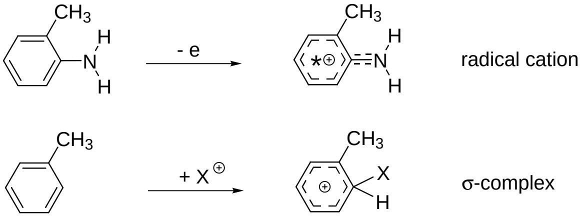


FIG. 14
Comparison of electronic structure and charge distribution in a radical cation and a σ-complex formed during electrophilic substitution

radical with ECESR should pose no problem) this accelerates the overall reaction. The second oxidation takes place at electrode potentials about 160 mV more positive, the position of the substituents is of only minor importance. The potential window thus given may correspond to the range

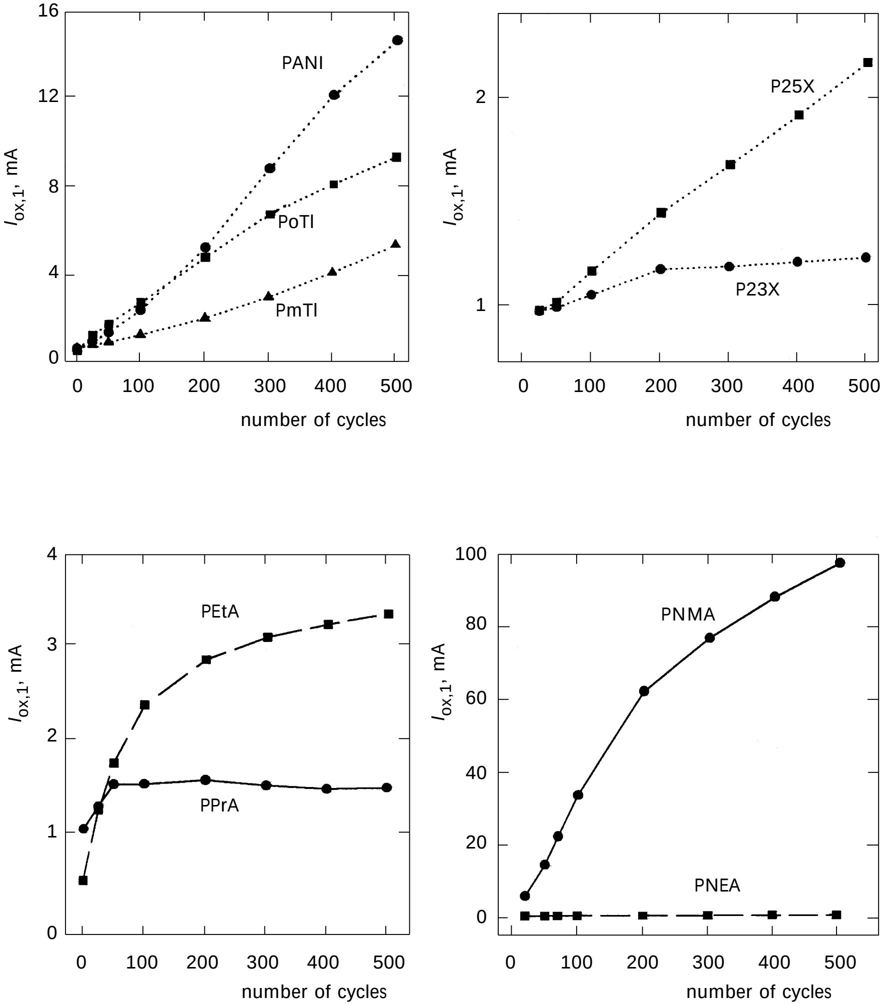


FIG. 15

Anodic peak current of first oxidation peak of polymers as recorded during polymer deposition of various polymers (for acronyms see text and Table I) in aqueous solution with pH 0 and $E_{\text{anodic limit,RHE}}$ = 1 000 mV wherein the initial oxidation product, perhaps the primary radical cation, exists. Kinetic and mechanistic investigations in particular of the initial reaction step of these compounds with spectroscopic methods as outlined above have not been reported so far.

The reaction intermediate formed during the first electron transfer step or in a subsequent second electron transfer (see Fig. 11) may undergo further reactions. Based on the evidence obtained with UV-VIS spectroscopy it reacts with solution phase species (radical substitution reaction). The formed dimer or oligomer is oxidised again. Because of the extended molecular structure of the latter species the electrode potential necessary to effect this is lower as in the case of the monomer; consequently oxidation of di- and oligomers is actually preferred as compared to oxidation of the monomer. Repeated reactions of this type finally result in oligo- and polymers. A very simple estimate of the rate of polymer formation can be obtained by plotting the peak current in the CV obtained during polymerisation as a function of cycle number. Figure 15 shows a set of results for the selected anilines investigated here. Except for PNMA, the rating of the investigated compounds is similar to the one found with UV-VIS spectroscopy (see above). Alkyl substitution of the ring decreases the rate somewhat, whereas *N*-substitution results in considerably lower rates of polymer formation. This may be seen as an argument for the assumption, that radical cation formation (irrespective whether from the monomer or an oligomer) is the rate determining step. Further investigations elucidating the peculiar behaviour of PNMA and providing results with more compounds are necessary.

CONCLUSIONS

Based on spectroscopic evidence obtained with *in situ* UV-VIS spectroelectrochemistry of a transient reaction intermediate formed during the electrooxidation of substituted anilines a relative rating of the stability of this intermediate and its possible position in an electrooxidation and – subsequently – polymerisation sequence is deduced. Unsubstituted aniline shows the lowest stability, *i.e.* its intermediate is converted with the highest rate. Ring-substituted anilines react somewhat slower, whereas *N*-substituted anilines show the lowest rate of further reaction.

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