polymer review

Properties of electronically conductive polyaniline: a comparison between well-known literature data and some recent experimental findings

Frank Lux*
Department of Materials Science, Polymer Physics, Technical University of Berlin, Englische Strasse 20, D-10587 Berlin, Germany
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This paper deals with the synthesis and properties of the electronically conductive polymer polyaniline. Firstly, the *accepted* properties of polyaniline are reviewed. Secondly, the problems of this electronically conductive material with respect to the mechanism of its synthesis, the oxidation state of the individual molecules, the nature of the crystalline arrangement in differently prepared grades and the nature of the charge carriers are discussed. The most important result in this paper is a totally new reaction mechanism for the synthesis of polyaniline, being the most detailed and comprehensive mechanism published to date.

(Keywords: polyaniline; reaction mechanism; catalytic action of acid)

INTRODUCTION

General remarks

This paper deals with the synthesis and properties of chemically prepared polyaniline (PANI). Those with some knowledge of PANI might worry about the gain of reviewing the properties of this quite well-established material. However, it will be shown in the following paragraphs that some aspects of PANI are far from being fully understood and a complete understanding of this electronically conductive polymer needs a critical comparison between the huge amount of scientific papers on the subject (starting with the very old ones from the beginning of the century) and recent experimental findings. Furthermore, in doing so, it might be very easy to establish an understanding of the chemical and physical properties of PANI simply by a straightforward comparison of all the available data. But let us start with some facts about the synthesis and properties of PANI.

Properties of polyaniline according to the literature

Electronically conductive PANI is the simple 1,4-coupling product of monomeric aniline molecules. This coupling reaction is dominating in acidic media at pH 0–1. If the reaction is carried out in less acidic media, the appearance of more or less branched phenylenequinoneimines (which are not electronically conductive) becomes more and more important[1,2]. The appearance of the phenylenequinoneimines is naturally accompanied by a decrease in the yield of 1,4-coupled aniline chains. The coupling reaction is usually initiated through the use of ammonium persulfate, which is known to be a very strong oxidizing agent (oxidation potential $E_{ox} = 2$ eV). The reaction product consists of a powder, its colour depending strongly on the details of the reaction[3,4] (e.g. influential factors are the size of the reaction flask, stirrer speed and reaction temperature). Potential by-products of the reaction are *p*-benzoquinone (*Figure 1*) and the very toxic cancer-causing agent benzidine (*Figure 2*).

The molecular weight of as-prepared polyaniline is not well defined. On the one hand, MacDiarmid *et al.*[5] have observed the molecular weights $M_w = 64\,000$ and $M_n = 25\,000$ for PANI in the course of their gel permeation investigations. On the other hand, Adams *et al.*[4] have estimated an M_n value of only 2500–6000 for a PANI grade, prepared under similar conditions to those used by MacDiarmid *et al.*, by use of the end-group technique. The discrepancy in the estimates is accounted for by Adams *et al.* as the result of the problem of effectively disrupting the strong intermolecular interactions when dissolving undoped PANI in its standard solvent, 1-methyl-2-pyrrolidinone (NMP).

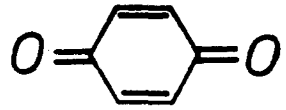
Figure 1 Structure of *p*-benzoquinone

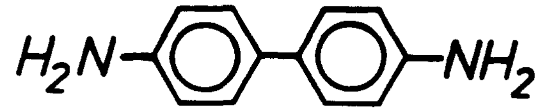
Figure 2 Structure of benzidine

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* Present address: University of Bristol, School of Chemistry, c/o Professor Brian Vincent, Cantock's Close, Bristol BS8 1TS, UK

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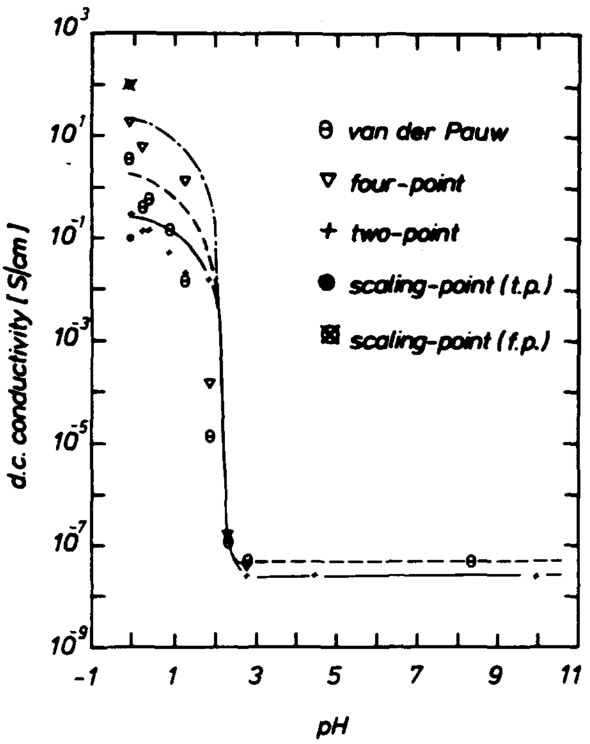


Figure 3 Dependence of the d.c. conductivity of PANI–H_2SO_4 samples (compressed pellets) on pH (t.p. = two-point measurement; f.p. = four-point measurement). The S-shaped lines in the plot are not based on the individual conductivity–pH pairs, but rather indicate the general trend of the conductivity when changing the pH value (results of Lux[6])

Figure 3 shows what is necessary to achieve the electronically conductive or doped state of PANI powders. The plots display the dependence of the direct current (d.c.) conductivity of PANI (measured on compressed pellets and using different experimental arrangements) on its pH value (designated as its inner acidity by De Surville *et al.*[7]). It is seen in this figure that it is necessary to keep the pH value of the PANI powder after synthesis in the range 0 to 2–3 (with the d.c. conductivity, depending on the exact pH value, in the range 10^{-2} to $10\,\mathrm{S\,cm^{-1}}$). If the pH value is increased above the critical value of 2–3, the PANI powder becomes insulating with a typical d.c. conductivity in the range 10^{-10} to $10^{-7}\,\mathrm{S\,cm^{-1}}$. A very undesirable feature of this way of making PANI powders electronically conductive is that the resulting acid-doped material is totally insoluble in all known organic solvents.

The temperature dependence of the d.c. conductivity of PANI shows that most of the currently synthesized PANI grades are somewhat away from the metal-to-insulator transition, i.e. the conduction process is dominated by some sort of hopping conduction (see *Figure 4*).

The underlying hopping mechanism has not been cleared up until now. Undoubtedly, the hopping process involves a mechanism having a $T^{-1/2}$ temperature dependence (see *Figure 5*). However, the assignment of this temperature dependence of the d.c. conductivity to the responsible hopping mechanism is not straightforward. Three mechanisms, i.e. the one-dimensional variable range hopping, the three-dimensional variable range hopping with coulombic interactions between the conduction electrons and Sheng's charging energy limited tunnelling model, could account for the observed temperature behaviour. To find out which mechanism is valid in one case or the other, it is necessary to perform detailed field-dependent d.c. conductivity and thermopower measurements. A good example of the difficulty in interpreting the results of such measurements is given by the work of Epstein *et al.*[8–10]. The earlier reports of this group favoured Sheng's charging energy limited tunnelling model as the underlying hopping process[8]. On the other hand, the more recent publications of Epstein *et al.*[9,10] give evidence for the one-dimensional variable range hopping model.

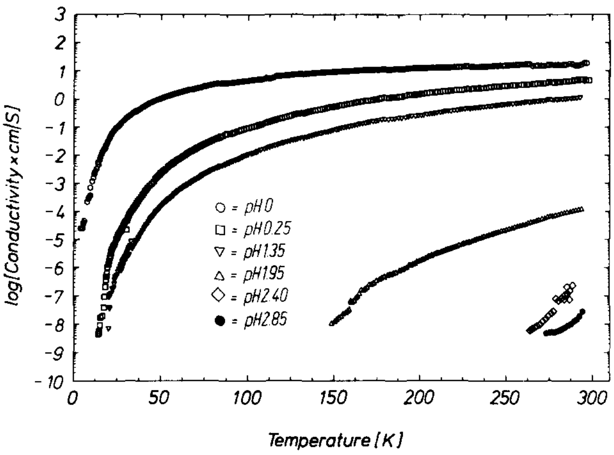


Figure 4 Temperature dependence of the d.c. conductivity of PANI–H_2SO_4 samples of different pH, i.e. doping level (results of Lux[6])

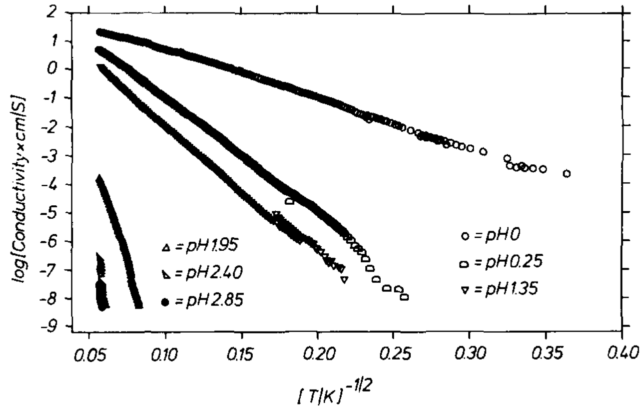


Figure 5 D.c. conductivity of PANI–H_2SO_4 samples plotted *versus* $T^{-1/2}$ (results of Lux[6])

An important feature of undoped PANI is its solubility in NMP[3]. This offers the possibility of producing stable, free-standing films and fibres of PANI, and composite materials if a conventional polymer is dissolved in the same solution. Moreover, pure PANI films and fibres offer the opportunity of checking the influence of the orientation of the individual molecules on the conduction properties of the materials. Indeed, a large increase in the conductivity (along the stretching direction) has been observed upon stretching PANI films by a factor of three or four[11]. Unfortunately, the high boiling point of NMP represents a serious drawback to this way of overcoming the unprocessability of PANI.

Another standard solvent for PANI, but in the undoped and doped states, is concentrated sulfuric acid.

Like NMP, such solutions offer the opportunity of producing films and fibres of PANI, with improved mechanical and conduction properties if a stretching treatment is applied in the course of the preparation and/or composite materials with other polymers, like poly(*p*-phenyleneterephthalamide) (PPTA), are produced[12].

The low solubility of doped PANI in the more conventional organic solvents is quite a difficult problem to solve. Nevertheless, only recently the group of Heeger and Smith at the University of California at Santa Barbara has claimed that the use of camphor sulfonic acid (CSA) and dodecyl benzenesulfonic acid (DBSA) renders doped polyaniline soluble in *m*-cresol and *o*-xylene, respectively[13,14]. According to these authors, such solutions allow the preparation of pure and composite films having d.c. conductivities of up to 450 S cm^{-1}. However, a word of caution must be said with respect to the findings of Heeger *et al.* According to the findings of other groups[15,16], it is not possible to get a soluble product on treating undoped PANI with DBSA. Furthermore, *m*-cresol is suspected to be a cancer-causing substance (at least in Germany), thus counting out this route for obtaining soluble, doped PANI on a large scale immediately.

Purely physical questions with respect to PANI concern the nature of the charge carriers, the way in which these carriers effect the conductivity and the nature of the intermolecular arrangement and its effect on the conduction properties of the materials.

With respect to the charge carriers in PANI, there is quite a large difference in opinion in the scientific world. Whereas Nechtschein *et al.*[17] have observed spinless bipolarons as the responsible carriers in most of their samples, Epstein, MacDiarmid and their coworkers[8,9] strongly favour spin-carrying polarons for the intramolecular charge transport process. Furthermore, some other groups[18–21] recall the possibility of polaron–bipolaron transformations.

Figure 6 shows what happens to a PANI grade having a totally reduced structure at pH values $\geqslant 10$, i.e. the leucoemeraldine oxidation state (see *Figure 10*), when it undergoes an acidification process. The top row displays what is called the leucoemeraldine oxidation state in terms of the assignment made by Green and Woodhead[22]. Note that the description of the repeat unit of PANI as an octameric sequence is the best choice because it allows a straightforward distinction between all five boundary oxidation states (see later). The second row shows that the leucoemeraldine structure of the individual molecules is changed via a protoemeraldine and/or emeraldine structure (see *Figure 10*) if the pH value of the PANI powder is lowered to values between 2 and 5. It is seen that the change in the oxidation state of the individual molecules is accompanied by the appearance of diimine units on the backbones of the PANI chains. If one lowers the pH value of the PANI powder even further, i.e. below pH 2, the PANI chains become protonated or oxidized. To compensate the positive charges from the protons attached to the nitrogen atoms, counterions (hydrogen sulfate ions in this case) are absorbed by the PANI chains. The protonation step is accompanied by the occurrence of radical cations or polarons (rows three and five) and/or divalent cations or bipolarons (rows four and six). The transformation of polarons into bipolarons and *vice versa* is seen when going from row three to row four and from row five to row six, respectively. Furthermore, rows five and six indicate the possibility for the appearance of protonated nitrogen atoms on the backbones of the PANI chains. These latter species have sometimes been proposed to occur in the doping step[23,24]. Note that a change in the oxidation state of the individual PANI chains on lowering the pH value of the powder, as shown in *Figure 6*, has also been reported to take place when the undoped material has an overoxidized structure, i.e. a nigraniline and/or pernigraniline structure[25,26].

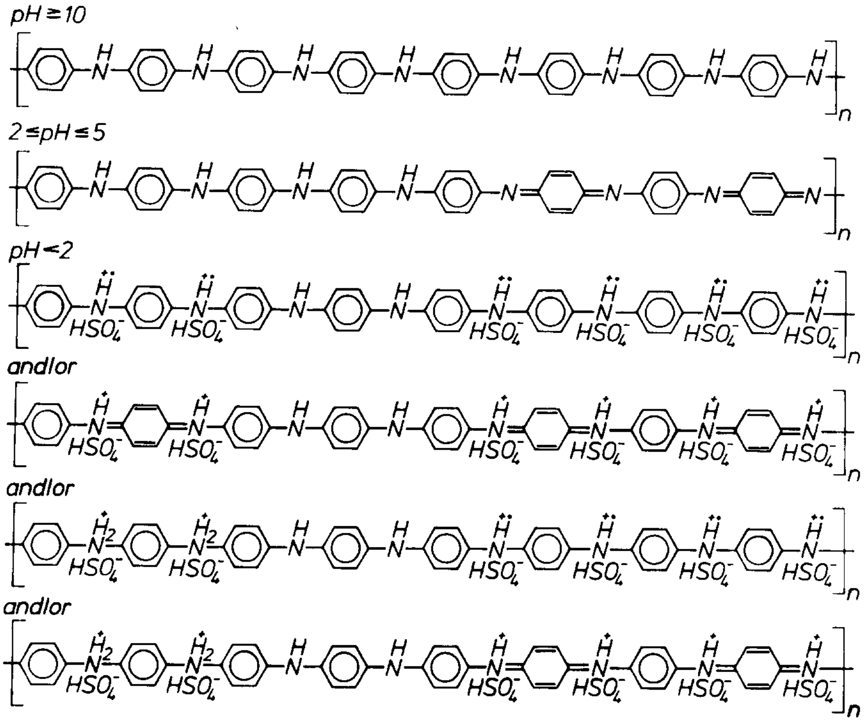


Figure 6 Polaron/bipolaron formation and their transformation in sulfuric acid doped polyaniline (results of Lux[6])

The mechanism by which the existing polarons and/or bipolarons effect the conductivity is still not clear. The simple idea that these heavy carriers (the mass of a polaron lies somewhere in the region of six to 30 times the electron mass[27]) should be able to move along the individual chains like free electrons and, even more, be able to hop from one chain to a neighbouring one or across the grain boundaries of macroscopic PANI crumbs seems rather unreasonable. On the other hand, the possibility that the lower mobility of the polarons/bipolarons might have some influence on a conduction mechanism involving free electrons or holes hopping from one fixed polaron/bipolaron to another cannot be discounted. Note that the latter mechanism necessarily involves a timely confined transformation of a polaron into a bipolaron and *vice versa.*

The importance of a better intermolecular arrangement, i.e. a higher level of crystallinity in the PANI samples, for obtaining a higher conductivity has become a well-accepted factor all around the world recently, and this idea is not restricted to PANI but involves most of the more prominent electronically conductive polymers. The observation that the conductivity of PANI films and fibres can be increased upon stretching is direct evidence for the importance of a good intermolecular arrangement (the latter being detectable with the aid of X-ray diffraction studies).

The arrangement of PANI molecules within the crystalline parts of powders, films and fibres and the total amount of the crystalline phase in the samples under investigation have been treated in several studies by Pouget *et al.*[28,29]. These authors found two readily discernible arrangements, i.e. the emeraldine base 1/emeraldine salt 1 (EB1/ES1) and emeraldine base 2/emeraldine salt 2 (EB2/ES2) systems, respectively. Both crystalline arrangements belong to the orthorhombic system. The difference between them is found in the packing of the chains and the counterions within the individual cells[28]. X-ray diffraction patterns of both crystalline arrangements are shown in *Figure 7.* It is necessary to point out that Pouget *et al.* claim that all the observable crystalline structures in differently prepared PANI samples can be accounted for by the EB1/ES1 and EB2/ES2 crystalline arrangements. Furthermore, it is important to stress the following statements of Pouget *et al.* concerning the EB1/ES1 and EB2/ES2 systems.

1. The undoped ES1 salt has in every case an almost completely amorphous structure. On the other hand, ES1 itself shows in every case a semicrystalline structure.
2. Doped and undoped ES2 salts can show either a totally amorphous structure or a semicrystalline one, depending on the details of the preparation.
3. If the ES2 salt has a semicrystalline structure and undergoes an undoping process, a totally amorphous material results in every case.

Finally, some words should be addressed to the thermal/environmental stability of PANI. It is well accepted that PANI is a member of the family of the more environmentally stable electronically conductive polymers. Nevertheless, it undergoes a certain amount of degradation if exposed to heat and/or the environment. The observable changes in mass and conductivity are caused by the uptake/loss of water, the loss of dopant molecules, different chemical reactions between the PANI chains themselves or with dopant molecules, or by more complex reactions between the doped material and the substances absorbed during the environmental and/or thermal exposure.

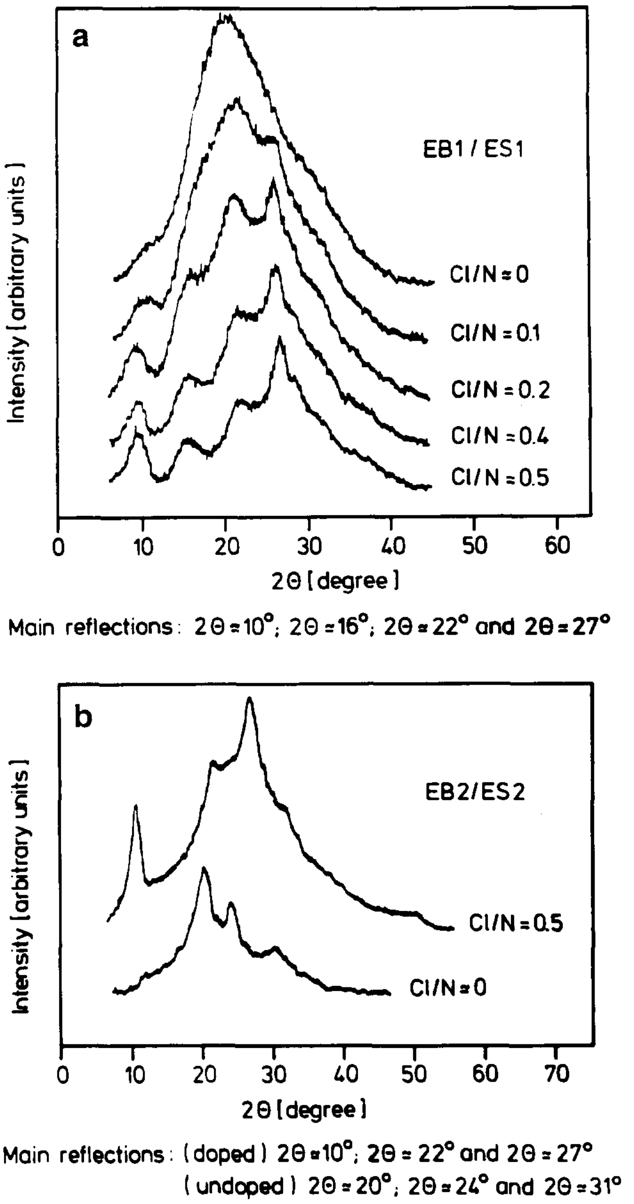


Figure 7 X-ray diffraction patterns of the (a) EB1/ES1 and (b) EB2/ES2 systems of acid-doped PANI according to Pouget *et al.*[28]

Examples of the observable changes in mass are given in *Figures 8* and *9* for undoped and sulfuric acid doped PANI samples, respectively. Whereas the loss in mass in the undoped material is caused by some sort of impurity (resulting from incomplete purification after synthesis), the change in mass in the doped sample mainly results from the loss of water that was absorbed by the powder in the doping step[30]. Note that a more comprehensive discussion of the thermal degradation of PANI has been published by Traore *et al.*[31].

DISCUSSION

General remarks

Having summarized some of the accepted properties of PANI above, it is now time to turn to the unsolved

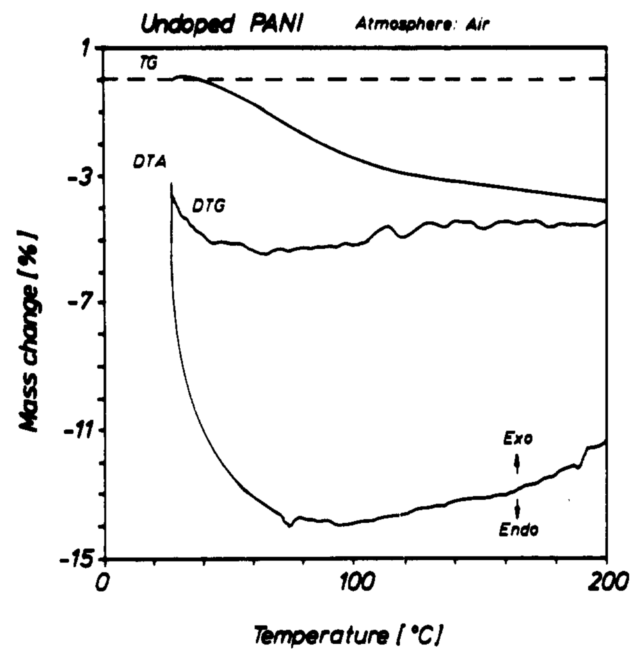


Figure 8 Mass change of undoped PANI in the temperature interval room temperature to 200°C (TG = thermogravimetric curve; DTG = first derivative of the TG curve; DTA = differential thermoanalytic curve; measurements in air with a heating rate of 4 K min^{-1}; results of Lux[6])

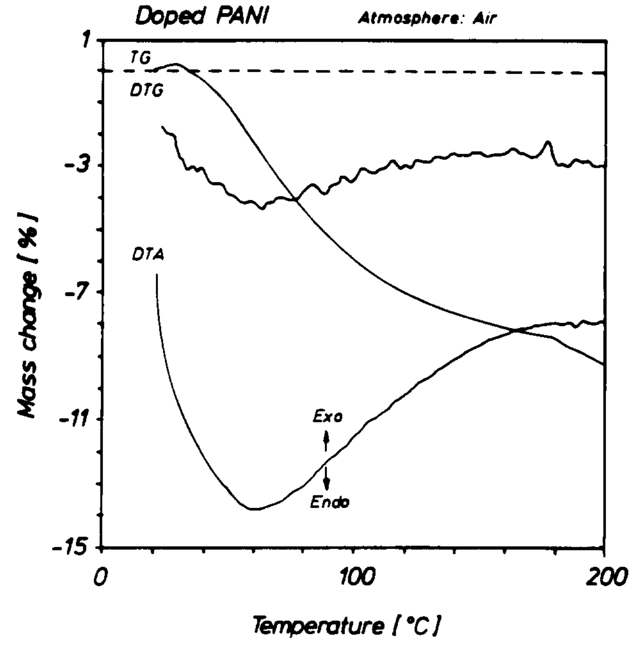


Figure 9 Mass change of sulfuric acid doped PANI in the temperature interval room temperature to 200°C (results of Lux[6])

problems concerning this electronically conductive polymer. These include (from the chemical standpoint) the identification of the reaction mechanism of the PANI synthesis and the oxidation state of the PANI molecules, and (from the physical standpoint) the elucidation of the nature of the charge carriers and the crystalline structures in differently prepared PANI samples. The following discussion will be focused mainly upon the recent work of Lux[6], who showed how easy the interpretation of experimental results might be if one does not restrict the discussion to a comparison of the experimental data with its own list of publications in the area (or a certain amount of the available literature) but includes the whole information available about the subject. With respect to the reaction mechanism for PANI, the discussion will bear to some extent a descriptive character. However, recognizing the quite poor picture that still exists regarding the reaction mechanism for PANI, this way of treating the complex matter of the PANI synthesis should enable the reader to follow easily the individual reaction steps.

Problems concerning the chemical aspects

Reaction mechanism for polyaniline. The most obvious problem with respect to PANI is related to the colour of the as-synthesized powder, and this is the basis for the questions about how the polymerization of aniline to form oligomers and/or polymers proceeds and what the by-products of the reaction are.

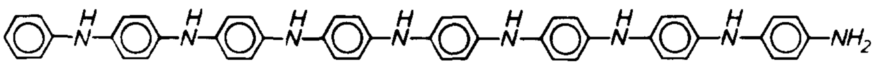
As has already been mentioned above, the usual polymerization route to polyaniline, as it has been carried out in different laboratories[32–35], has not yielded PANI powders of the same colour in every case. Most often, colours ranging from violet to deep blue for undoped powders have been reported. Besides that, the occurrence of purple-red undoped powders has also been reported. As the colour of the undoped powder should be characteristic of the oxidation state of the individual chains, differences in the oxidation state are to be expected between PANI powders of different colours. Despite this obvious relation between the colour and the oxidation state of PANI, most of the groups, having produced differently coloured PANI samples, have claimed that they produced PANI in the emeraldine oxidation state.

Figure 10 shows the structures and some of the physicochemical properties of aniline octamers according to Green and Woodhead[22]. It has already been mentioned that the description of the repeat units of aniline polymers in terms of these octamers is desirable because it offers the advantage that the intermediate structures between the leucoemeraldine and emeraldine structures, i.e. the protoemeraldine oxidation state, and between the emeraldine and pernigraniline structures, i.e. the nigraniline structure, can be easily defined. Furthermore, even these five boundary oxidation states are sometimes not sufficient to describe all the possible structures (i.e. oxidation states) of polymeric aniline molecules, because the normal situation encountered is a complicated mixture of the structures shown in *Figure 10* (see later). Indeed, the latter fact has already been highlighted by Green and Woodhead in their papers[22,36].

According to *Figure 10*, the emeraldine oxidation state is to be expected if the undoped powders are violet-blue and the acid-doped ones are emeraldine green. On the same basis, a purple-red undoped PANI grade should have the highest degree of oxidation possible for PANI, i.e. the pernigraniline oxidation state.

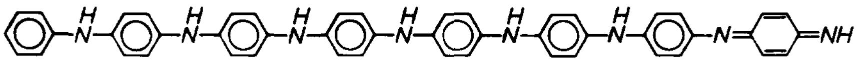
Confronted with these facts, one immediately wonders about the differences in the propagation of the polymerization that are responsible for the differences in the oxidation state, and this was exactly the point Lux reached after having started his experiments with aniline. During the different polymerization experiments the standard PANI grade was pale brown when undoped (indicative of the existence of the leucoemeraldine oxidation state, according to *Figure 10*) and deep blue

Leucoemeraldine:



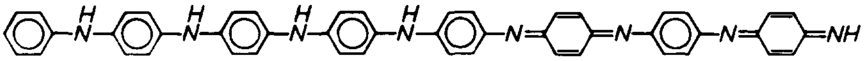
Pale-brown, amorphous substance, probably white when pure. Nearly insoluble in all solvents, including 80 per cent acetic acid. High melting point. On exposure to air in the damp state is slowly oxidised to protoemeraldine, more rapidly when warm.

Protoemeraldine (monoquinonoid stage):



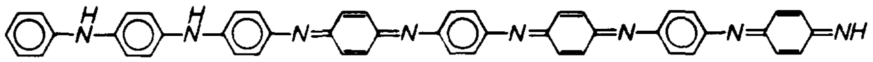
Violet substance, forming yellowish-green salts. Soluble in 80 per cent acetic acid with a grass-green colour.

Emeraldine (diquinonoid stage):



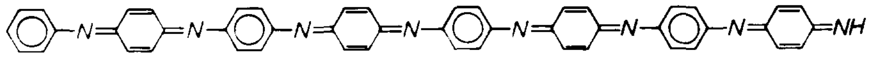
Violet-blue substance, forming green salts. Soluble in 80 per cent acetic acid and in 60 per cent formic acid with a pure green colour. Dissolves in pyridine with a bright blue colour. Dissolves in pure concentrated sulphuric acid with a purplish-brown colour, and on dilution with water gives a bright green precipitate. The salts are stable, but the base is slowly oxidised by air to nigraniline base.

Nigraniline (triquinonoid stage):



Dark blue substance, forming blue salts. Soluble in 80 per cent acetic acid and in 60 per cent formic acid with a pure blue colour, which on heating becomes green through reduction to emeraldine. Dissolves in pyridine with a bright blue colour. Dissolves in concentrated sulphuric acid with a violet colour, and on dilution with water gives a bright green precipitate of emeraldine sulphate. The base is stable, but the salts are very unstable.

Pernigraniline (tetraquinonoid stage):



Purple substance, forming purple salts. Soluble in 80 per cent acetic acid with a violet colour. Both the base and its salts are very unstable, quickly undergoing degradation to the lower quinonoid stages with simultaneous production of decomposition products.

Figure 10 Structures and some physicochemical properties of aniline octamers according to Green and Woodhead[22]

when doped. Besides, the powders, prepared under variable conditions, were most often blue when undoped and green to blue when doped (both indicative of an emeraldine and/or a nigraniline oxidation state). The results of Lux's polymerization experiments, from the standpoints of the conductivity and the yield of the PANI powder, are shown in *Figures 11–13*. As can be seen in these figures, huge differences are observed in the yields of the PANI powders prepared under different conditions. Less drastic differences are seen in the d.c. conductivities of the powders, except for the powder prepared in 5 M sulfuric acid. However, the latter fact probably results from the poor quality of the pellet used for the conductivity measurement. Other interesting observations, not included in *Figures 11–13*, were as follows.

1. The polymerization reaction at −13°C was completely suppressed, i.e. the total amount of the ammonium persulfate solution could be added to the reaction vessel without any sign of reaction. However, the polymerization reaction starts immediately (it is nearly explosive) when the temperature is increased to −10°C. A similar observation has been made by Wei *et al.*[37]. These authors did not observe an induction period before the start of the polymerization, because they added the whole amount of the ammonium persulfate solution at once to the acidic aniline solution.
2. The amount of *p*-benzoquinone produced during the reaction increased with the molarity of the acidic reaction medium. Note that *p*-benzoquinone can be simply identified by its characteristic smell[36].
3. The polymerization reaction did not start immediately after the first drops of the ammonium persulfate solution had been added to the reaction flask, i.e. there is an induction period before the polymerization reaction starts. Similar observations have been made by other groups[38–41].
4. An increase in the reaction temperature of typically 8°C was observed after only a few minutes after the reaction has started (duration of the temperature increase ca. 15 min). Such an unusual increase in the reaction temperature is indicative of some sort of autoacceleration process taking place in the polymerization vessel. Again, similar observations have already been made[38–46].

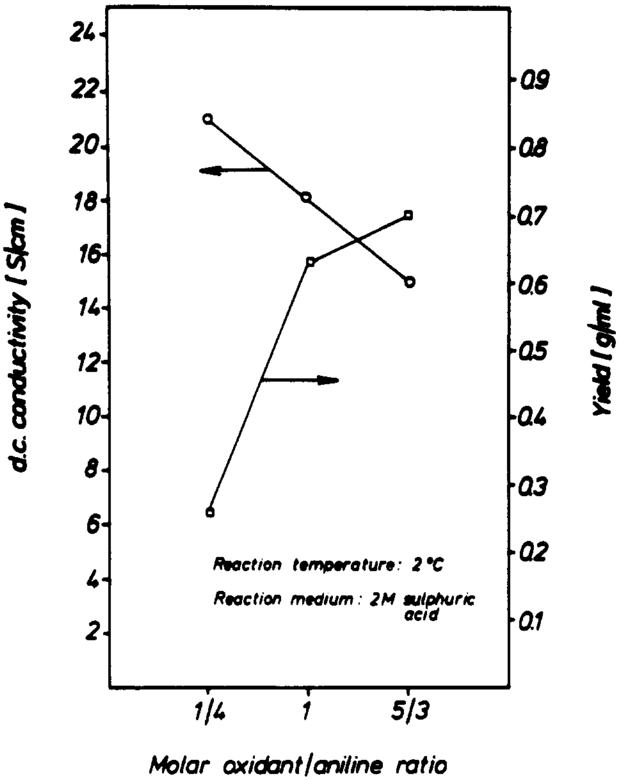


Figure 11 Dependence of the polyaniline yield and d.c. conductivity on the molar oxidant-to-aniline ratio. Note that the yield is given as mass of powder (g)/volume of aniline (ml), because the powder was not washed to the absolutely pure state after the synthesis (results of Lux[6])

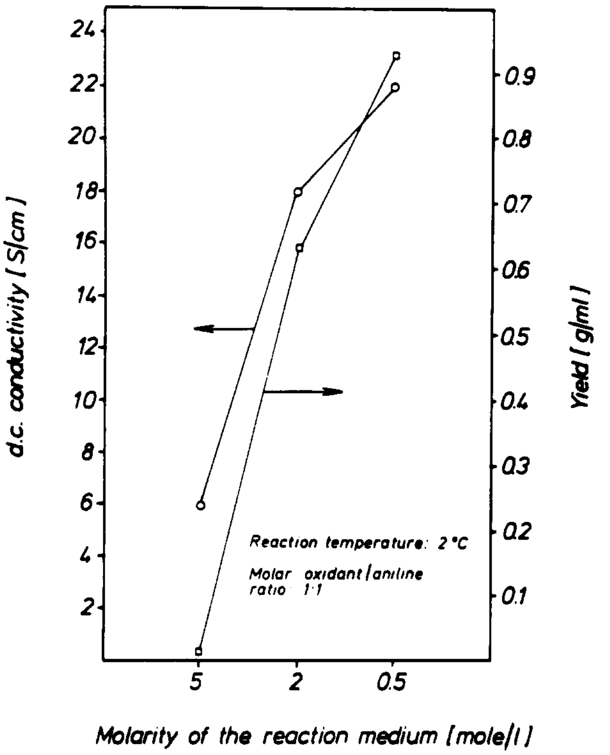


Figure 12 Dependence of the polyaniline yield and d.c. conductivity on the acidity of the reaction medium (results of Lux[6])

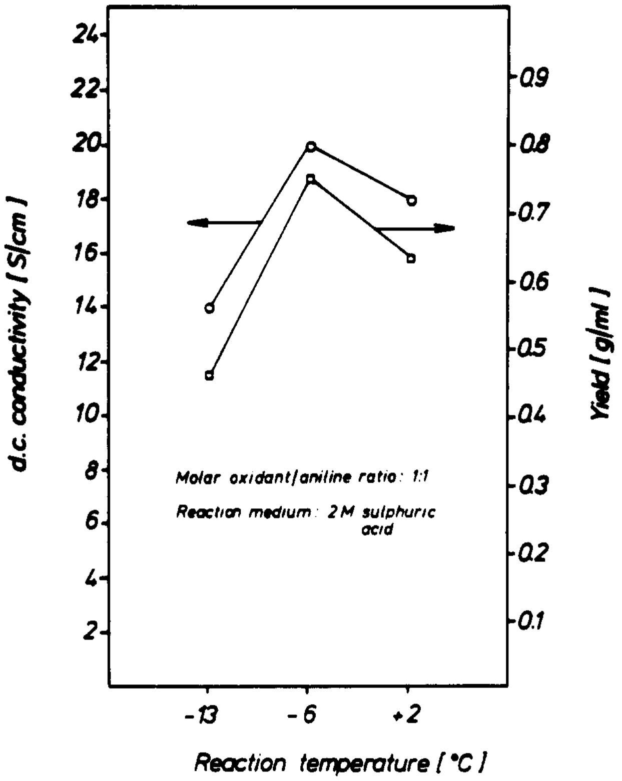


Figure 13 Dependence of the polyaniline yield and d.c. conductivity on the reaction temperature (results of Lux[6])

Turning back to the reaction mechanism of the polyaniline synthesis, it is interesting to note that no comprehensive picture is to be found in the literature, even though the synthesis of polyaniline under various conditions has been carried out for more than 130 years (starting with the synthesis by Letheby[47]). Moreover, even the suppliers of commercial grades of PANI (i.e. Neste Oy, Finland and Allied Signal, USA) are not sure about the mechanism of the synthesis. This is especially true for the question if the cancer-causing substance benzidine is produced somewhere in the course of the PANI synthesis. So, the toxicological tests on the PANI grade supplied by Neste Oy are based on animal experiments rather than on chemical analyses. An equivalent treatment is to be expected for the Versicon^{R} grade from Allied Signal.

Before continuing the discussion about the reaction mechanism for the formation of PANI, some words should be addressed to the general problem of combining the results from electrochemical and chemical experiments to establish a reaction mechanism for the whole coupling reaction. Undoubtedly, most of the information concerning the formation of PANI has been gathered with the aid of electrochemical studies. Consequently, most of the above-mentioned investigations are purely electrochemical studies. On the other hand, chemical investigations concerning the kinetics of PANI formation are so scarce that it is impossible to construct a straightforward picture from these results alone. To overcome the latter problem, it is usual to assume that both the electrochemical and the chemical synthesis take the same course, and for this reason it is allowed to combine the results of studies in both areas. Of course, this has also been done in this paper. However, one should bear in mind that the conditions of the electrochemical syntheses might be totally different from those of the chemical syntheses, simply because the spatial situation in front of the working electrodes is quite different from the spatial situation encountered in chemical experiments. So, electrochemical experiments might allow more different coupling reactions between the neutral aniline species, the intermediate products and the resulting aniline oligomers and polymers, especially if the experiments are carried out in the higher concentration regime of aniline and when using higher anodic oxidation potentials. Some indications in this direction have already been published in the literature[20,38–40,42,43,45].

On the other hand, what is known about the propagation of the synthesis of PANI? To answer this question, it is worth having a look at the rather old work of Willstätter and coworkers[1,2,48–50] and various others[19,20,51], as well as the more recent investigations[37–40,42–46,52–56]. As has already been mentioned, PANI is the 1,4-oxidation product of aniline. This coupling occurs because the amine group of the aniline molecule bears the highest reactivity under the conditions of the usual PANI synthesis[48,55]. Assuming the 1,4-coupling of aniline molecules, it is easy to deduce that potential dimers are *p*-aminodiphenylamine (ADPA, *Figure 14*), *trans*-azobenzene (*Figure 15*) and benzidine (*Figure 2*). However, the question remains as to which ions and/or radical ions and/or radicals are the intermediates forming the dimers (and potentially the higher oligomers and polymers). To address this point, let us start with the mixing process of aniline and the acidic reaction medium. According to Breitenbach and Heckner[52–54] and Dunsch[55], this process involves the occurrence of a protonated aniline species, i.e. the anilinium cation (*Figure 16*), depending on the pH value of the reaction medium. The lower the pH value, the larger is the fraction of protonated aniline. Moreover, Breitenbach and Heckner found that the start of the coupling reaction of aniline molecules is only possible if the respective molecules are non-protonated. Note that this might be the obvious explanation for the very low yield of PANI which Lux observed for the preparation in 5 M sulfuric acid (see *Figure 12*). The pH value of this reaction medium was somewhere below 0, and all the aniline molecules within the reaction flask were protonated and could not undergo the desired coupling reaction. Rather, some side-reactions took place, leading (among others) to a pronounced production of *p*-benzoquinone. The next point to be considered is the oxidation of the unprotonated aniline molecule by the peroxide. We need to know if the oxidation step is a mono-oxidation process leading to a monovalent cation, i.e. the anilinium radical cation (*Figure 17*), or if it is possible to oxidize the aniline directly to the divalent state, i.e. the anilinium dication (*Figure 18*). Breitenbach and Heckner[53,54] have found a solution to this problem. It appears that the oxidation leads to the monovalent cation, because the oxidation to the divalent state is not possible when using an oxidizing agent with an oxidation potential of 2 eV. Moreover, their results suggested that the oxidation step is followed by abstraction of a proton from the nitrogen atom by more basic molecules like water or unprotonated aniline, resulting in the appearance of the anilinium radical 1 (*Figure 19*). The anilinium radical 1 should then be able to undergo another oxidative attack, leading to another monovalent cation carrying two free electrons at the nitrogen atom (cation **II** in *Scheme 1*). The latter species finally can undergo a coupling reaction with free aniline molecules, having a rearranged electronic structure (resonance structure) according to *Scheme 1*, to form the aniline dimers *p*-aminodiphenylamine and benzidine. Note, that cation **IIa** in *Scheme 1* is produced by a rearrangement of the electronic structure of cation **II**.

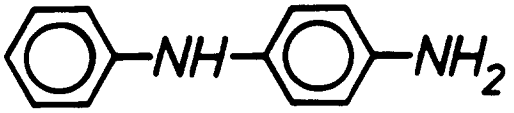


Figure 14 Structure of *p*-aminodiphenylamine

Figure 15 Structure of *trans*-azobenzene

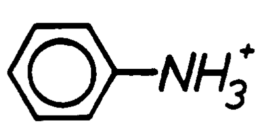


Figure 16 Structure of the anilinium cation

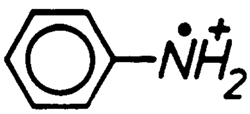


Figure 17 Structure of the mono-oxidized aniline molecule, i.e. the anilinium radical cation

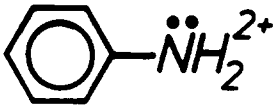


Figure 18 Structure of the doubly oxidized aniline molecule, i.e. the anilinium dication

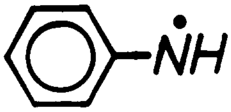
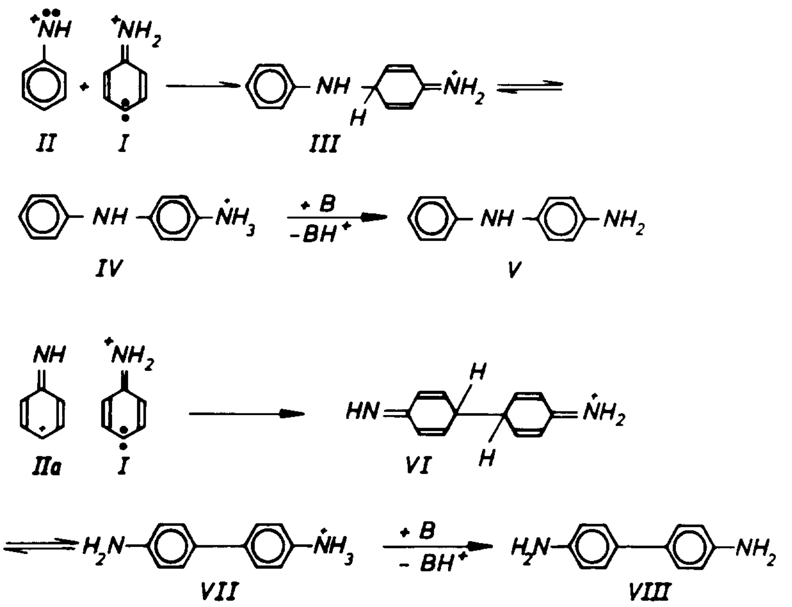


Figure 19 Structure of the anilinium radical 1

Although the findings of Breitenbach and Heckner seem very reasonable with respect to the possible oxidation of aniline by the peroxide or at the working electrodes in electrochemical syntheses, the assumption that the resulting cation **II** will react with some sort of reorganized free aniline molecule is not acceptable, because the authors could not give any reasonable explanation for the factors forcing the aniline molecule to rearrange its electronic structure. Nevertheless, Wei *et al.*[37] have adopted this dimerization step for the establishment of a rough reaction scheme for the synthesis of PANI. The argument given by Wei *et al.* for doing so stems from a result obtained by Genies and Lapkowski[38]. The latter authors claimed in their paper that they had found evidence for the appearance of cation **II**, because this species was the only reasonable explanation for some new peaks occurring in the current–voltage diagrams and visible spectra taken



Scheme 1 Formation of the aniline dimers *p*-aminodiphenylamine and benzidine according to Breitenbach and Heckner[52-54]

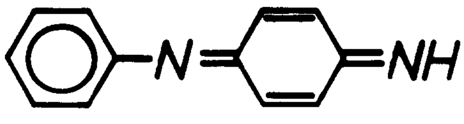


Figure 20 Structure of the oxidized form of *p*-aminodiphenylamine, i.e. *N*-phenyl-1,4-benzoquinonediimine

during the polymerizations. However, as was shown by Kitani *et al.*[45,46] and Gospodinova *et al.*[57,58], the new peaks in the spectra of Genies and Lapkowski can also be explained by the appearance of the oxidized form of *p*-aminodiphenylamine, i.e. *N*-phenyl-1,4-benzoquinonediimine (PBQI, *Figure 20*), and by assuming the existence of a certain fraction of chemical crosslinks between the growing PANI chains. Indeed, the latter aspect has been adopted by Genies and Lapkowski in a subsequent paper[20].

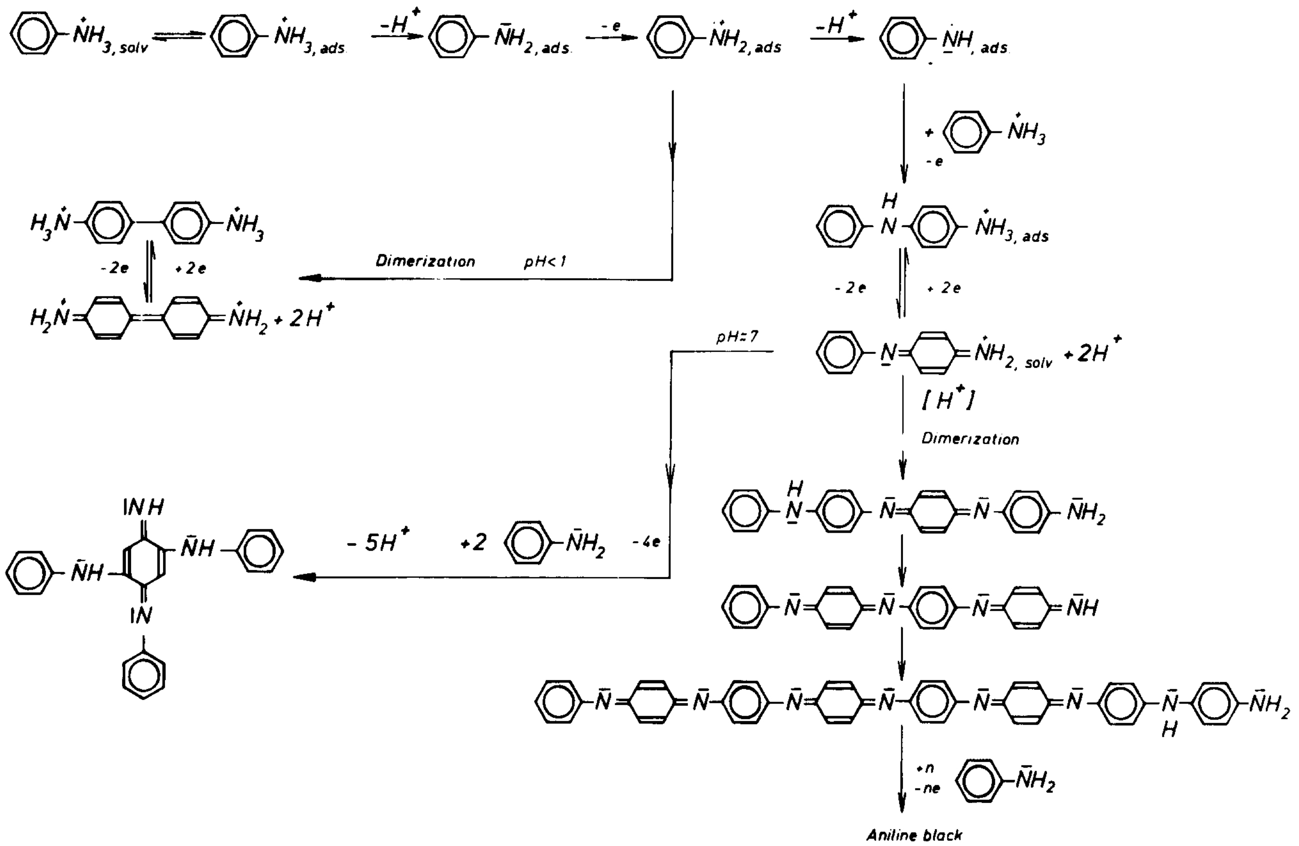
Dunsch[55] has avoided the assumption concerning the rearrangement of the electronic structure of aniline molecules by postulating that it is not the doubly oxidized cation **II** of Breitenbach and Heckner which undergoes a coupling reaction with aniline, but rather the anilinium radical 1 (*Figure 19*) that does so. Moreover, he assumed that the anilinium radical does not react with free aniline molecules, but with existing protonated anilinium cations (see *Figure 16* and *Scheme 2*). Furthermore, Dunsch has proposed that the production of benzidine in the course of the reaction starts only if mono-oxidized aniline (*Figure 17*) is not able to lose its proton (see *Scheme 2*). Note that the latter reaction needs the rearrangement of the electronic structure of the anilinium radical cation.

Obviously, the start of the polymerization reaction according to Dunsch is more reasonable than the scheme proposed by Breitenbach and Heckner. However, it is still in disagreement with some of the observations Lux made during his experiments. It has already been said that an induction period is observed before the polymerization of aniline starts. This would not be the case if, as proposed by Dunsch, the anilinium radicals in the reaction solution underwent a coupling reaction with anilinium cations. Furthermore, Dunsch claimed (see *Scheme 2*) that tetramers, higher oligomers and polymers, respectively, are simply formed by the dimerization of aniline dimers, tetramers and so on. This opinion of Dunsch contradicts Lux's observations, made in the course of polymerization experiments using *p*-aminodiphenylamine as the starting substance. The experiments showed (in agreement with the results of other groups[37,45,56]) that the reactions differ totally from those observed in the experiments with pure aniline. The characteristics of these experiments were as follows.

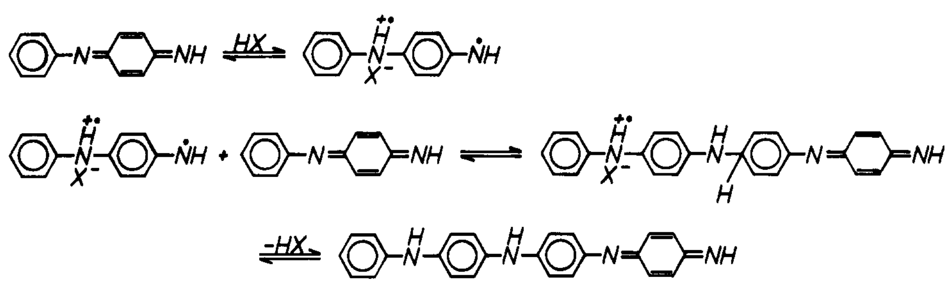
1. There was no autocatalytic reaction phase, i.e. no temperature increases in the course of the reactions.
2. Only very low molecular weight oligomers were produced in these experiments, because the resulting undoped powders were completely soluble in *N*,*N*-dimethylformamide (DMF) and methanol and also soluble to a considerable extent (ca. 40%) in benzene. Polyaniline produced from aniline was only slightly soluble in methanol and DMF and not soluble in benzene. According to Wei *et al.*[37], the solubility of PANI oligomers in benzene is indicative of the existence of (only) aniline dimers and tetramers. Furthermore, the resulting powders also showed a considerably lower d.c. conductivity when doped, i.e. 10^{-2} S cm^{-1}. This result stands in excellent agreement with that of Kitani *et al.*[56].

As a consequence of the above discussion about the first steps of the aniline polymerization, i.e. the dimerization reaction, Lux adopted the first four steps of the scheme of Dunsch for his reaction scheme for the synthesis of PANI. Note that on this basis the production of the cancer-causing substance benzidine is quite certain.

Now it is time to consider the conversion of the desired aniline dimer *p*-aminodiphenylamine into higher oligomers, and maybe even polymers. It is a widely accepted fact (based on different experimental evidence) that ADPA is more easily oxidized than aniline itself.



Scheme 2 Formation of aniline oligomers and polymers according to Dunsch[55]



Scheme 3 Dimerization reaction of PBQI to form the blue imine of Willstätter, as deduced from the original papers of Willstätter *et al.*[48–50] by Lux[6]

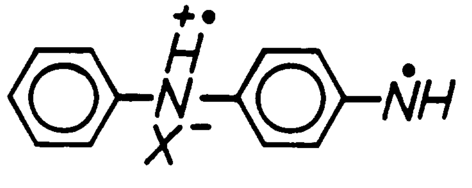


Figure 21 Structure of the protonated *p*-aminodiphenylamine radical

Furthermore, this continues to the higher oligomers, in that they are more accessible to oxidation than the corresponding oligomeric forerunners. However, this feature of ADPA and the higher oligomers is not the only key to understanding the polymerization behaviour of aniline and the different oxidation states of powders prepared under nearly identical conditions. Another important aspect is the fact that the oxidized form of ADPA, i.e. PBQI, is susceptible to dimerization if it is stored in an acidic medium of a sufficient pH, without the need for an oxidizing agent. This observation was first made by Willstätter and coworkers[48–50]. They concluded that the behaviour of PBQI is in favour of a catalytic reaction, caused by the acid used in the experiments. Lux has proposed the process in *Scheme 3* for this catalytic reaction. According to this scheme, the occurrence of a protonated ADPA radical (*Figure 21*) is to be expected in the course of the dimerization. Part of this species is identical to the anilinium radical proposed by Breitenbach and Heckner, and Dunsch.

In fact, if one carefully studies the other investigations concerning the reaction mechanism of PANI formation[25,40,41,43,45,46,51,56–58], one will find that aniline oligomers bearing one or more imine units on their backbones are prominent species in forming radical ions of the types shown in *Figure 21* and *Scheme 3* for the protonated ADPA molecule. Green and Wolff[51] observed 'a strong oxidative action of nigraniline (resembling that of lead superoxide, i.e. PbO_2, with $E_{ox} = 1.5$ eV) in acidic media'. Tzou and Gregory[41] (presumably not knowing the work of Green and Wolff) postulated exactly this property for nigraniline molecules to account for the observation of the autoacceleration phase in their syntheses. Gospodinova *et al.*[57,58] and others[21] have found that polyaniline formation can be terminated by simply increasing the pH value of the reaction medium from the acidic regime to the alkaline regime, probably indicative of the neutralization of the oligomeric and polymeric radicals or radical ions through the separation of the acidic catalyst. Furthermore, Gospodinova *et al.*[58] observed the acidification of the reaction medium during their experiments in aqueous solutions, caused by the release of protons from originally reduced aniline oligomers (especially from ADPA), which is responsible for the appearance of higher oligomeric and/or polymeric aniline molecules if the process is able to establish pH values below ca. 2. Kitani *et al.*[45,46,56] found that the electrochemical polymerization of aniline is possible at oxidation potentials between 0.55 and 0.8 eV if the working electrodes are seeded with a PANI film. Note that the oxidation potential of pure aniline is ca. 1 eV. They concluded that the existing PANI films must be able to incorporate neutral aniline by some means. Assuming again an oligomeric and/or polymeric radical ion existing at the surface of the working electrodes, the observations of Kitani *et al.* are easily explained. The occurrence of the radical ions at the working electrodes allows a chemical oxidation step to take place, leading to the oxidation of the arriving anilinium cations and/or deprotonated aniline molecules and the incorporation of the resulting species into the already existing PANI films. With respect to the synthesis of PANI, evidence for the appearance of doped PANI material on the working electrodes in electrochemical syntheses has been published by Schultze *et al.*[40,43]. The authors observed microscopically the existence of 'green nuclei of PANI', i.e. doped polyaniline, in what they called 'the first stage of the polymerization reaction'. Furthermore, Schultze *et al.*[43] were able to show by the use of pulsed potentiostatic methods that an increased number of such nuclei leads to the faster occurrence of the autocatalytic phases of the polymerization (designated by Schultze *et al.* as 'the second stage of the polymerization reaction').

Adopting the catalytic action of the acidic reaction medium for the polymerization of PANI directly from aniline, one has to propose a reasonable species able to couple with dimeric, trimeric and higher oligomeric radicals or radical cations. As already mentioned above, the easiest assumption is the idea that these species attack anilinium cations or unprotonated aniline molecules. However, this would only offer a reasonable explanation for the polymerization after the dimerization step is finished. This fact becomes clear when comparing the results of Tzou and Gregory[41] with those of Lux. *Figure 22* shows the course of the polymerization reaction (i.e. the variation of the aniline concentration with time) in hypochloric acid according to Tzou and Gregory. It is seen in *Figure 22* that the polymerization reaction starts sooner when the reaction medium is more acidic. This result stands in sharp contrast to Lux's result, according to which the polymerization is suppressed by the more acidic reaction media (see *Figure 12*). One reasonable explanation for the behaviours observed by Tzou and Gregory and by Lux is the idea of two species being responsible for the start of the polymerization. As a consequence, the polymerization starts after the shortest induction period if both species are formed at the same time. Moreover, it is not too difficult to find a species able to react with anilinium radicals (*Figure 21*), protonated ADPA radical cations and higher oligomeric radical cations. As has already been proposed by Breitenbach and Heckner[53,54], the anilinium radicals might undergo a rearrangement of their electronic structure. The result of the rearrangement is another anilinium radical bearing the free electron at the 1-position of the benzene ring and having a saturated nitrogen atom (*Figure 23*).

Something should now be said about the possibilities for the production of *p*-benzoquinone. Willstätter and Dorogi[49] investigated the production of *p*-benzoquinone directly from aniline. Unfortunately, they were not able to establish a detailed reaction scheme. Therefore, they only stated that it is produced via aminophenol (*Figure 24*) as a reaction intermediate. With respect to the considerations of Willstätter and Dorogi, the reaction scheme proposed by Lux includes the same inexact route from aniline to *p*-benzoquinone. On the other hand, there

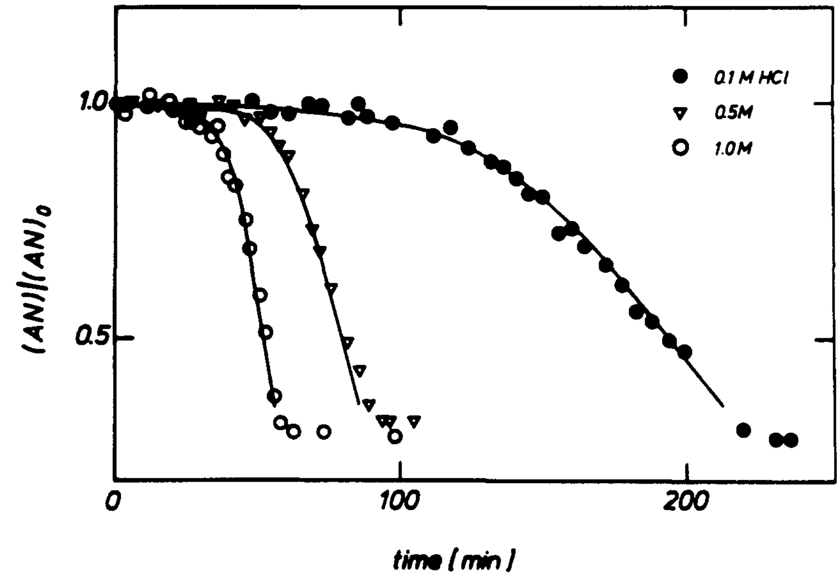


Figure 22 Variation of the aniline concentration in the reaction flask during the polymerization of aniline according to Tzou and Gregory[41] ((AN) = current aniline concentration: $(AN)_0$ = starting concentration of aniline)

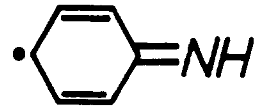


Figure 23 Structure of the anilinium radical 2

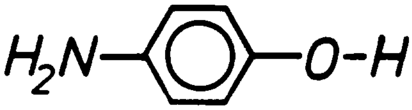


Figure 24 Structure of aminophenol

is also the chance to produce *p*-benzoquinone after the coupling of aniline has started. This was shown by Green and Woodhead[36] in the course of their studies aimed at the production of aniline oligomers from ADPA. The authors detected the smell of *p*-benzoquinone at the end of the experiments. So, because no aniline was present in the reaction beaker, some sort of oxidative degradation had to take place involving either ADPA or higher oligomers prepared from ADPA. To account for the observation of Green and Woodhead, Lux's reaction mechanism also includes this route for the production of *p*-benzoquinone.

In summary, Lux's reaction scheme for the synthesis of aniline oligomers and polymers from aniline and ADPA is shown in *Scheme 4*.

The first eight steps involve the establishment of the anilinium radicals, two possibilities for the appearance of benzidine, the production of *p*-benzoquinone from aniline (or, more precisely, from the protonated aniline molecule), the possible reactions between the anilinium radicals themselves or with each other, and finally the oxidation of ADPA by the peroxide to form PBQI.

Step 9 is the most important one, because it shows that the catalytic action of the acidic reaction medium accelerates the coupling of aniline (or, more precisely, anilinium radical 2) with existing dimers and higher oligomers (step 9b). Thus, it can (in combination with step 7) account for the observation of the autocatalytic reaction phase some minutes after the start of the polymerization. Moreover, step 9b also supplies a reasonable explanation for the different oxidation states in PANI powders prepared under similar conditions. To understand this, let us look at the intermediate **9b,m**. This molecule bears one diimine unit on its backbone. As has been stated by Koch and Heitz[59] in the course of their investigations concerning the reaction mechanism giving poly(*p*-phenylene sulfide), such a diimine unit might be delocalized along the backbone of the molecule. On the other hand, the diimine sequence might undergo protonation to form radicals of the type **9b,r1** and **9b,r2**. It is clear that there should be some sort of equilibrium between both reactions and that it strongly depends on the conditions of the experiment. Thus, if the conditions are more in favour of a high mobility of the diimine sequence, one might expect the possibility of another oxidative attack by the peroxide to form a second diimine unit on the backbone of the aniline oligomer. This then gives a higher overall oxidation level for the resulting oligomers and polymers.

Although the appearance of protonated imine sequences at the ends of the growing PANI chains is very important for reaching high molecular weights, the protonated character of the chain ends (and the already established PANI molecules) might also be responsible for a decrease in the reaction rate if the molecules become even longer. According to Baughman *et al.*[21], the delocalization of the protonated imine sequences along the molecules increases rapidly with increasing chain length, thus establishing a more homogeneous distribution of the charges and free electrons on the chains and making the whole arrangement chemically less reactive. This conclusion might provide a very convenient explanation for the observed limitation in the molecular weight of PANI obtained from the usual polymerization experiments and also for the limited lengths of the aniline polymers (oligomers) obtained from experiments using the aniline dimer ADPA as the starting reagent. Furthermore, it is possible to explain the high molecular weights of PANI grades synthesized via the emulsion polymerization route of Österholm *et al.*[60]. Since the polymerization reaction is carried out only in a small fraction of the volume of the reaction beaker, the reactive intermediates are in close contact with each other, and therefore the growing step of the polymerization reaction (step 9b in *Scheme 4*) dominates over the termination reaction (according to Baughman *et al.*[21]).

Steps 10–12 in *Scheme 4* show some reactions proposed to take place in the course of the polyaniline synthesis using ADPA as the starting substance. Note that the intermediates have been termed 'Willstätter's imines', because this author first found them in the course of the dimerization of PBQI. Most importantly, the reaction steps describe the formation of *p*-benzoquinone via the degradation of aniline oligomers and polymers.

Oxidation state of polyaniline molecules. This section includes some of Lux's results concerning the oxidation state of his standard PANI powder. These results are included to highlight the complex situation that exists with respect to the true oxidation state of a certain PANI grade. It will become evident in this section that even the description of the repeat units of PANI molecules in terms of the octameric sequences shown in *Figure 10* is sometimes inadequate to account for the many oxidation states of PANI structures.

Figure 4 shows what happens to the leucoemeraldine structure of PANI powder when lowering the inner acidity of the powder, i.e. the leucoemeraldine structure is altered via the emeraldine structure and finally undergoes protonation and/or oxidation to form the emeraldine salt. Such a change can be followed by N(1s) X-ray photoelectron spectroscopy (XPS) investigations conducted on differently doped powders, as shown in *Figure 25* for Lux's standard PANI powder. The observed peaks can easily be assigned to nitrogen atoms with imine bonds ($E_b = 398.1$ eV), nitrogen atoms with amine bonds ($E_b = 399.3$ eV) and nitrogen atoms that are oxidized or protonated ($E_b > 400.5$ eV). However, it is also seen in *Figure 25* that the totally undoped PANI grade (pH 10) still contains a certain proportion of diimine units. Nearly the same information is obtained from *FT*i.r. investigations carried out on undoped and sulfuric acid doped PANI films. *Figures 26* and *27* show the results of such investigations. It is apparent in both spectra that while the undoped PANI film should have an oxidation state between the emeraldine and leucoemeraldine oxidation states, the doped PANI film has the typical

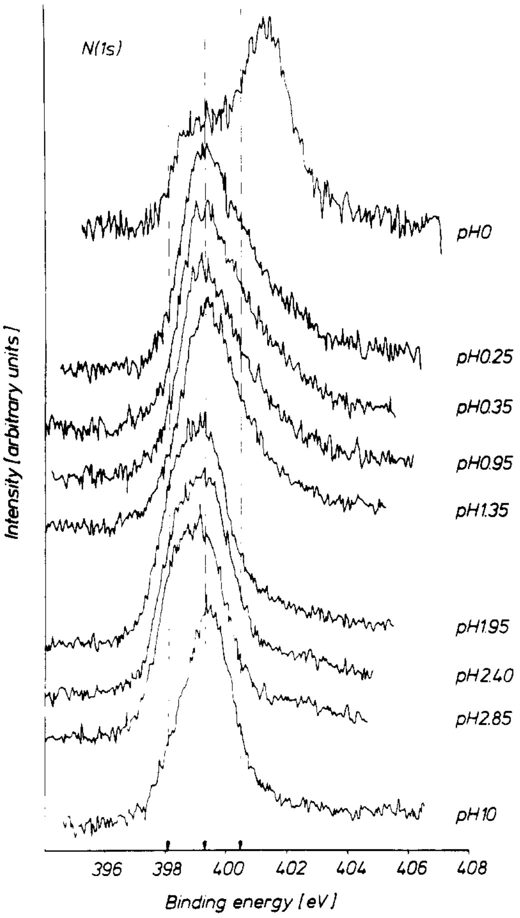


Figure 25 XPS N(1s) spectra of PANI powders having different pH values (results of Lux[6])

emeraldine salt spectrum[61]. Note that these conclusions can be drawn with the aid of the bands at 1510 cm^{-1} and 1587 cm^{-1}, which are characteristic of the stretching vibrations of nitrogen atoms in aromatic and diimine units, respectively. It has already been published in many papers that these bands are of equal strength in the emeraldine oxidation state of PANI[61,62]. Consequently, Lux's undoped, standard PANI grade must have a lower overall oxidation state. However, it cannot be in the protoemeraldine oxidation state because the undoped powder is pale brown, which contradicts the assignment given by Green and Woodhead (see above; accordingly, protoemeraldine should be violet).

The identification of the exact oxidation state is possible with the aid of a quantitative analysis of the XPS spectra, as has already been described by Kang and coworkers in several papers[34,62–66]. The result of such an analysis on the standard PANI grade is an imine-to-amine ratio of ca. 1:2. In other words, because the imine units can only exist in diimine sequences in a strictly 1,4-coupled aniline chain, this means that every PBQI group is accompanied by two ADPA groups*, describing a hexameric structure of 1,4-coupled aniline molecules.

Obviously, such a structure is just in between the protoemeraldine and emeraldine structures, which have imine-to-amine ratios of 1:4 and 1:1, respectively. However, what is the reason for the pale-brown (leucoemeraldine) colour of the undoped material? The answer to this question might be found by doubling the hexameric structure, giving a dodecameric sequence (*Figure 28*). The resulting sequence is depicted in *Figure 28* in the manner already used in *Figure 10* for the aniline octamers. The comparison of the dodecameric sequence with that in *Figure 10* shows that the former can also be understood as a sequence of one leucoemeraldine and a half pernigraniline chain, the colour being (or lying) predominantly on the white-coloured side of the leucoemeraldine structure. Thus, the pale-brown colour of the undoped powder might be a mixture of the purple-red colour of the pernigraniline sequences and the white colour of pure leucoemeraldine.

Problems concerning the physical properties

Crystalline structures of PANI powders. As stated earlier, the results of Pouget *et al.*[28,29] concerning the crystalline structures of semicrystalline PANI grades are in favour of only two possible crystalline arrangements of the undoped materials and the salts. However, this might not be the whole truth, because it will be shown in this section that the crystalline structures of powders precipitated from concentrated sulfuric acid have different

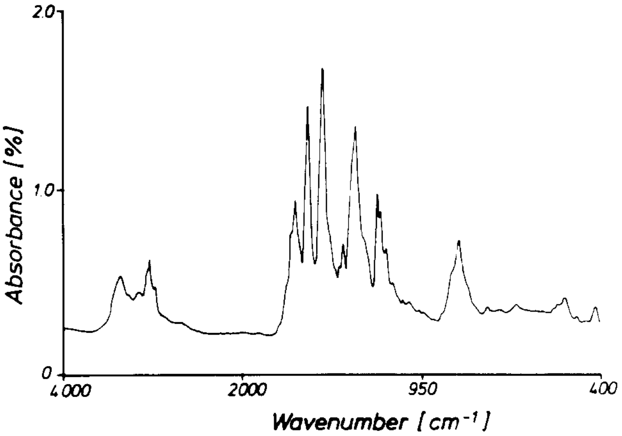


Figure 26 *FT*i.r. spectrum of an undoped PANI film prepared from a solution in NMP (results of Lux[6])

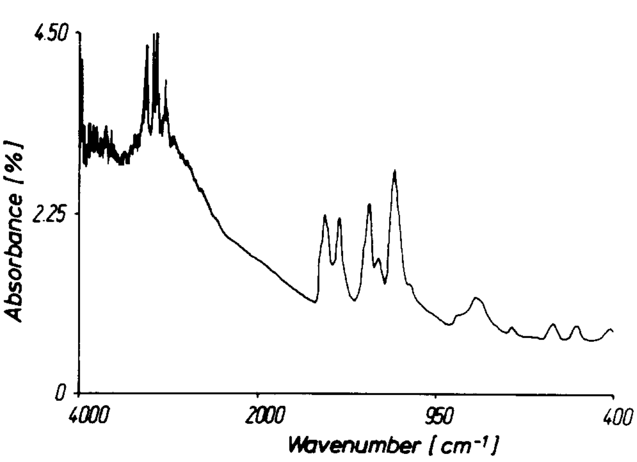


Figure 27 *FT*i.r. spectrum of a sulfuric acid doped PANI film prepared from a solution in NMP (results of Lux[6])

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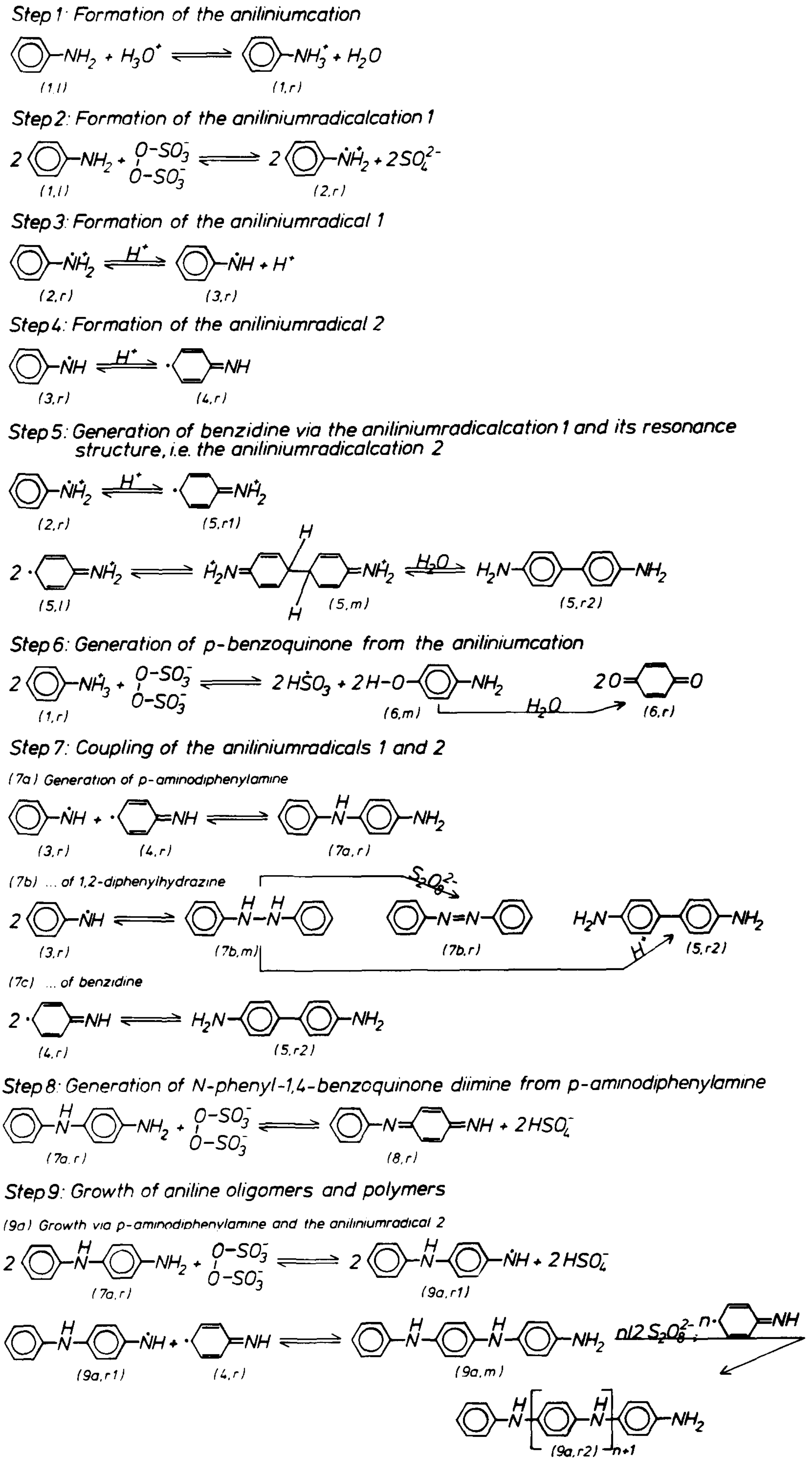
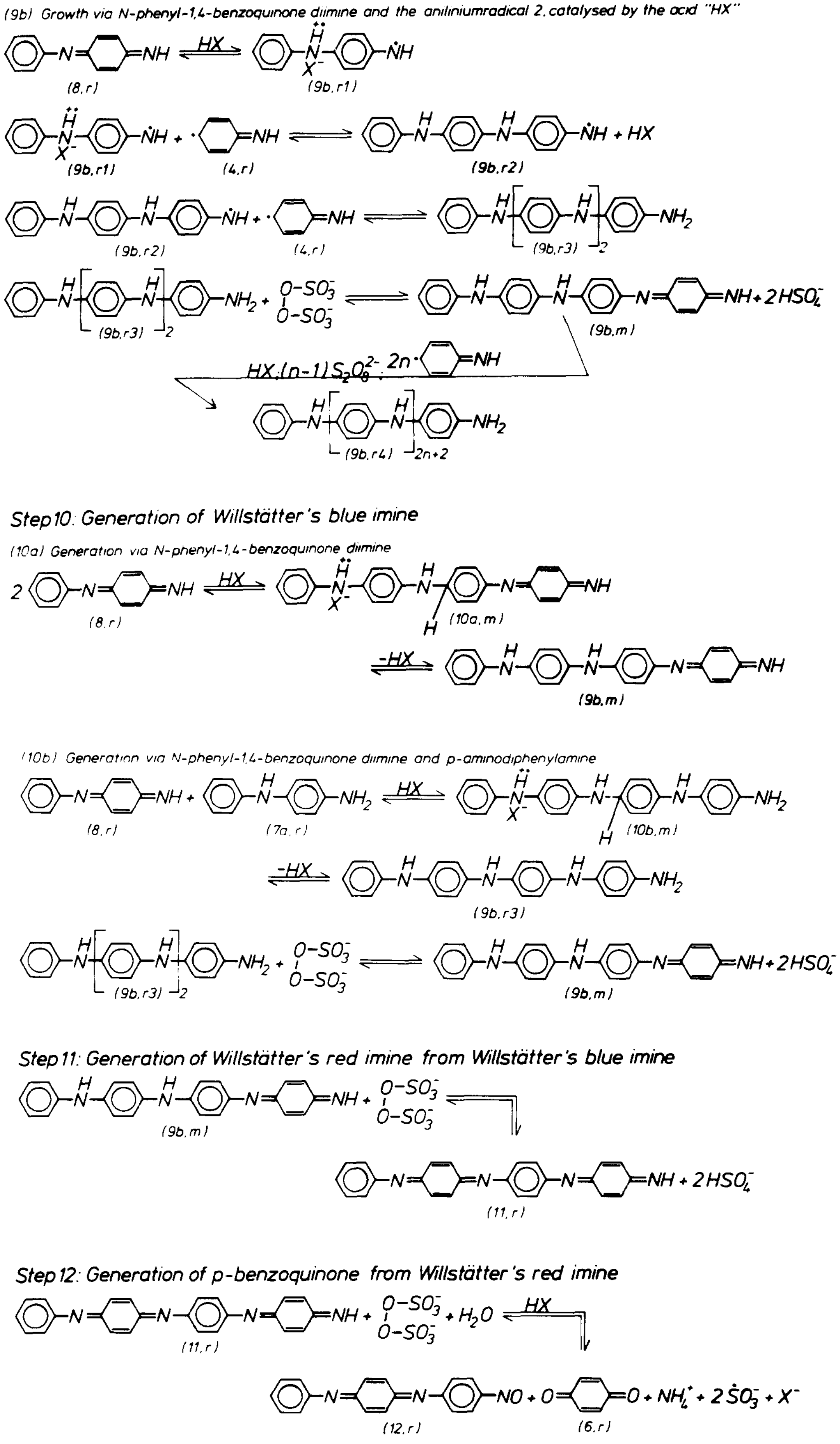
*Note that these ADPA and PBQI units each have a hydrogen deficiency of two compared with the ordinary ADPA and PBQI molecules



Scheme 4 Reaction mechanism for the chemical oxidation of aniline and *p*-aminodiphenylamine in acidic media according to Lux[6]



Scheme 4 *Continued*

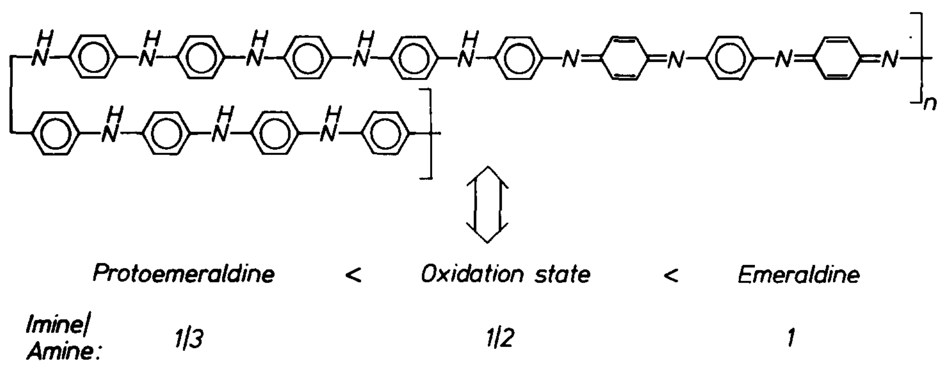


Figure 28 Dodecameric sequence of aniline molecules for the description of the true oxidation state of Lux's[6] standard PANI powder

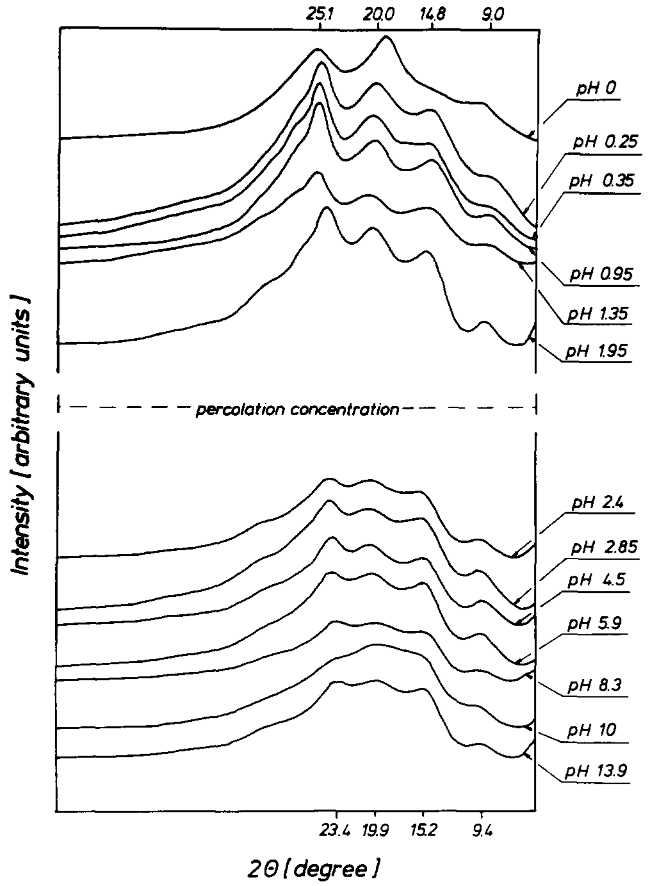


Figure 29 X-ray diffraction patterns of PANI powders immediately after synthesis in 2 M H_2SO_4. Note that the powders have been equilibrated with acidic solutions of different pH values, and the individual tracings are not scaled to each other (results of Lux[6]). pH 0 sample precipitated from concentrated sulfuric acid into water

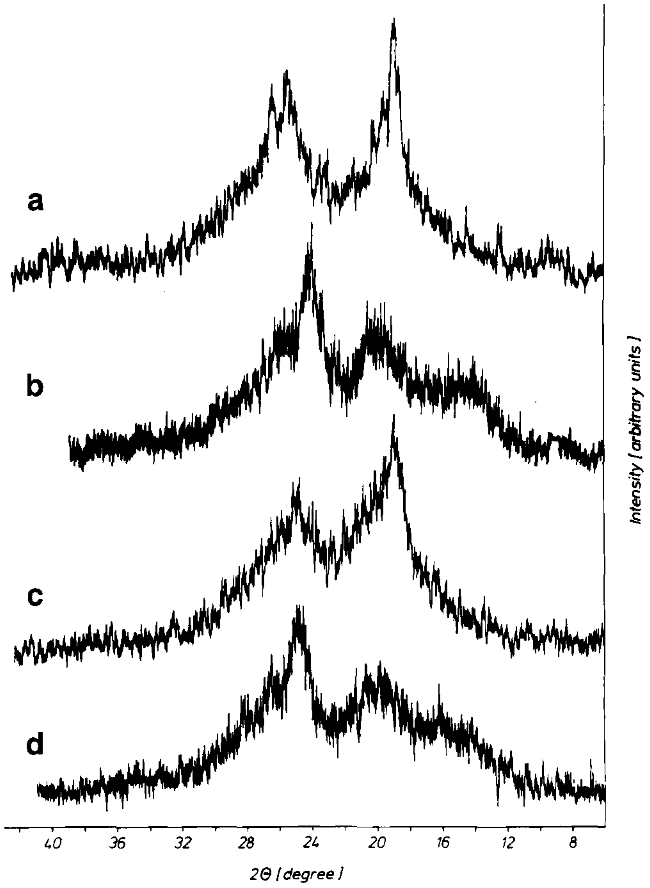


Figure 30 Comparison of the X-ray diffraction patterns of PANI powders (a, c) precipitated from concentrated sulfuric acid and (b, d) obtained directly from the reaction flask (results of Lux[6])

features. *Figures 29* and *30* show X-ray diffraction patterns of PANI powders taken from the reaction flask (and doped to different extents) and precipitated from concentrated sulfuric acid, respectively. It is clearly visible in both figures that the PANI powders show EB1/ES1 crystal features only if the powder is not precipitated from concentrated sulfuric acid. On precipitation of sulfuric acid dissolved PANI powder into a different acidic medium, a totally different crystal structure becomes visible, resembling that of highly oriented PANI (see *Figure 31*). The latter structure has been assigned by MacDiarmid *et al.*[67] to be a special case of the EB2/ES2 system. However, the crystalline structure in the precipitated PANI powders cannot have any correlation to the EB2/ES2 system because the undoped powder still has a semicrystalline structure (see *Figure 32*), which is in total contrast to the statements of Pouget *et al.*[28,29] (see earlier).

An alternative explanation for the crystalline structure of PANI powders precipitated from concentrated sulfuric acid can be deduced by a comparison of their X-ray diffraction patterns (in the undoped and doped states) with those of undoped and doped aniline octamers prepared from ADPA. The X-ray diffraction patterns of

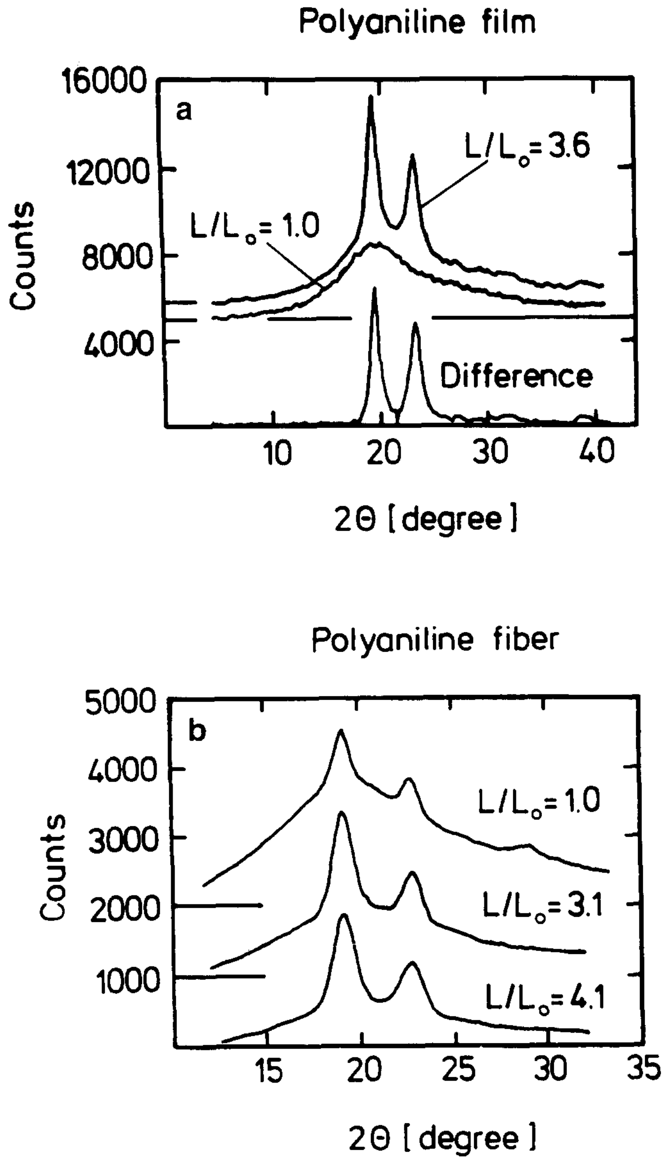


Figure 31 X-ray (*h*,*k*,0) scans of stretched and unstretched PANI films (a) and fibres (b) according to MacDiarmid *et al.*[67]

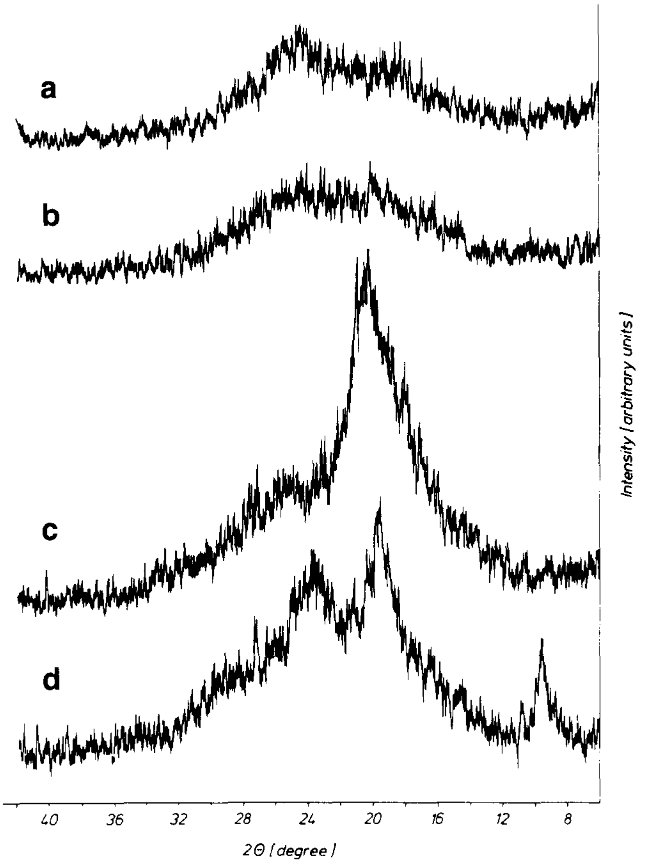


Figure 32 X-ray diffraction patterns of undoped PANI precipitated from concentrated sulfuric acid (d) and undoped aniline octamers prepared from ADPA (c). Note that (a) and (b) show diffraction patterns obtained for CF_3COOH-doped and H_2SO_4-doped PANI films prepared from solutions in NMP, and the individual tracings are not scaled to each other (results of Lux[6])

these powders are shown in *Figures 32* and *33*, respectively. It is evident from the comparison that a close correlation exists between the crystalline arrangements in both powder systems, suggesting that the crystalline structure in the precipitated powders is exactly that observed in the case of the octamers. If this correlation is right, it suggests that the precipitated powders show the crystalline structure of what might be called 'the homologous row of perfectly 1,4-coupled aniline molecules'. Consequently, there would be a need to establish the details of this true crystalline arrangement of perfectly 1,4-coupled aniline oligomers and polymers. Indeed, some recent investigations by Lux *et al.*[68] have supported the correlation between the crystalline arrangements in powders of aniline oligomers and polymers.

Charge carriers in PANI powders. This final section includes some of the results which Lux obtained with respect to the charge carriers in PANI powders. It has already been stated that opinion is somewhat divided, in that some favour polarons as the charge carriers in PANI, while others favour spinless bipolarons. Obviously, the democratic way to handle the problem is to find out that a combination of polarons and bipolarons establishes the conducting properties of the material. Indeed, Lux has found some evidence for this point of view, although it seems, at first glance, that polarons can account for the conduction process alone.

Figure 34 shows the results of electron spin resonance (e.s.r.) measurements on doped PANI powders. It can be seen that different sorts of spin-carrying species are present in the undoped material. However, as the powder becomes more and more conductive, the e.s.r. signal is shifted to higher fields and becomes a single peak, indicative of the presence of only one mobile spin carrier.

The same conclusion can be drawn from *Figures 35* and *36*. These diagrams show respectively the dependence of the spin concentration and the linewidth of the e.s.r. signal on the pH value of the PANI powder and temperature. It is easily deduced that the number and mobility of the spin-carrying species increases as the powder becomes more and more doped.

A different argument for the existence of spin-carrying polarons as the responsible charge carriers is obtained from SQUID measurements on PANI powders having different pH values. The results of such measurements are shown in *Figures 37* and *38*. *Figure 37*, showing the original data from the measurements, again indicates the presence of different spin-carrying species in the less-

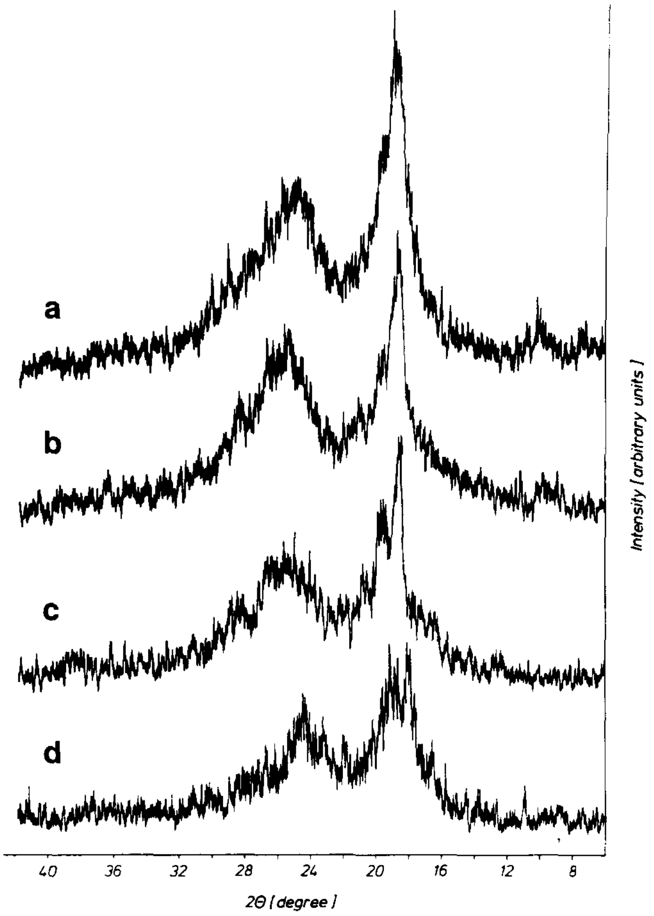


Figure 33 X-ray diffraction patterns of doped PANI precipitated from concentrated sulfuric acid (b–d) and doped aniline octamers prepared from ADPA (a). Note that the individual tracings are not scaled to each other (results of Lux[6])

doped samples. This fact becomes even more clear in the manipulations of the original data, shown in *Figure 38*. Furthermore, it can be deduced from the curves that the magnetic susceptibility of the doped samples (at pH 1.35, 0.25 and 0) contains a temperature-independent part originating from the non-paired spins in the conduction band, i.e. the Pauli part of the paramagnetic susceptibility. Moreover, these results are in close agreement with the findings of Ginder[61] and Fite *et al.*[69]. *Figure 39* shows a combined plot of the data of Ginder and Lux. It can be seen that no differences exist between these studies.

However, there are also results to be found in Lux's studies that at least suggest the possibility for some sort of polaron–bipolaron transformation. Firstly, *Figure 38* shows some sort of interaction between different spin carriers below ca. 120 K. Secondly, even more straightforward are the results concerning the temperature dependence of the linewidth of the e.s.r. signal in the X-band (*Figure 40*). It can be seen in *Figure 40* that some sort of interaction between the spin carriers gives rise to an increase in the linewidth at ca. 200 K in the doped samples (pH 1.35 and 0.25).

Finally, a result of Krinichnyi *et al.*[19] should be mentioned. They found in the course of a more comprehensive e.s.r. study in the W band that the number of spins in the more-doped samples, i.e. below pH values of ca. 1.5, is nearly constant. This is, of course, the strongest evidence for polaron–bipolaron transformations,

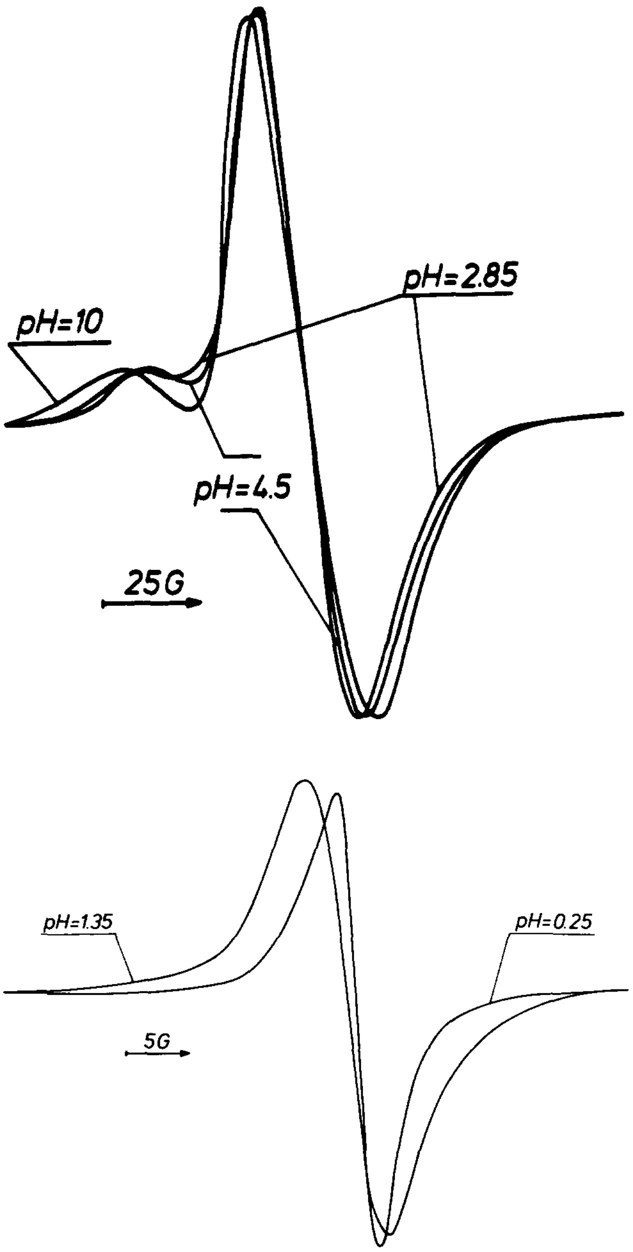


Figure 34 E.s.r. signals of differently doped PANI samples taken in the W band. Note that the individual signals are not scaled to each other (results of Lux[6])

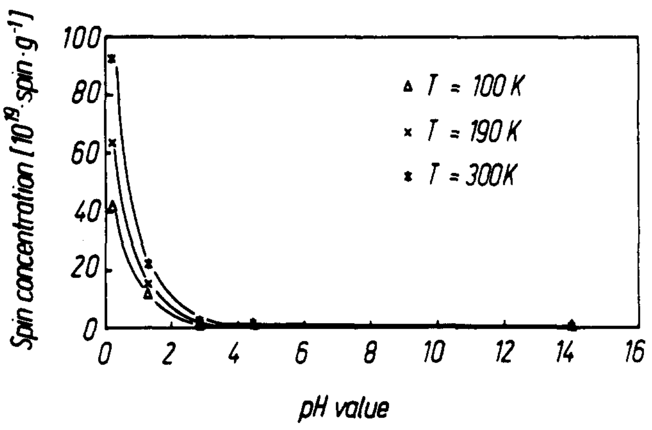


Figure 35 Variation of the spin concentration in differently doped PANI samples with pH; additional parameter: temperature (results of Lux[6])

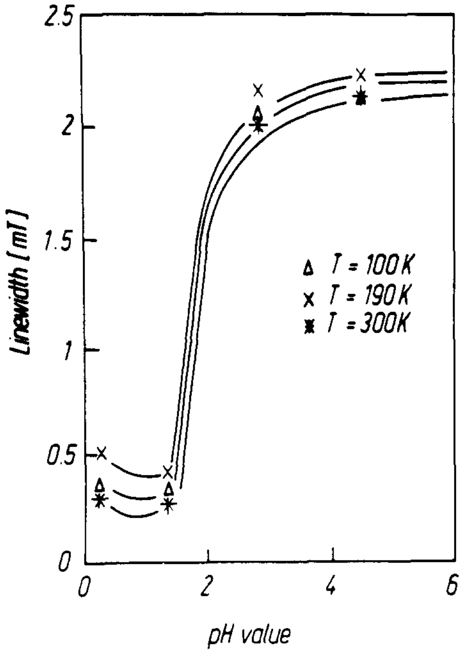


Figure 36 Variation with temperature and pH of the e.s.r. linewidth in the X band for differently doped PANI samples (results of Lux[6])

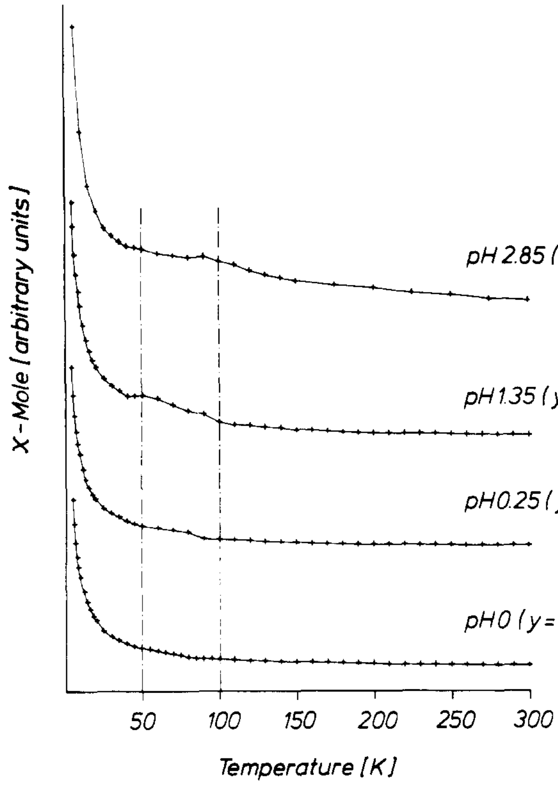


Figure 37 Variation of the SQUID response of differently doped PANI powders with temperature. Note that the individual curves are not scaled to each other (results of Lux[6])

because the d.c. conductivity still increases by a factor of 50–100 in this pH range. One might argue that the increase in the conductivity is caused by a higher mobility of the polarons, thus increasing the amount of 'σ' ($\sigma = \mu n e$, where n is the number of charge carriers, μ is the mobility of a single charge carrier and e is the charge on a single charge carrier). However, there should only be minor changes in the mobility of the polarons, too, because the crystallinity of the doped samples, i.e. the measure of the order in the microstructure of the samples, does not change very much below pH values of 1.5 (see *Figure 29*).

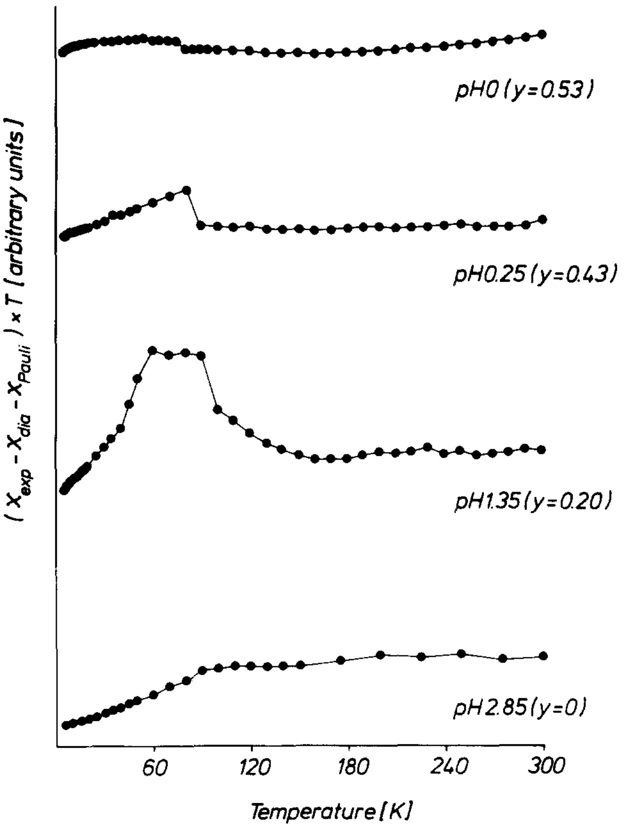


Figure 38 Curie part of the paramagnetic susceptibility multiplied by the temperature for differently doped PANI powders as a function of temperature. Note that the individual curves are not scaled to each other (results of Lux[6])

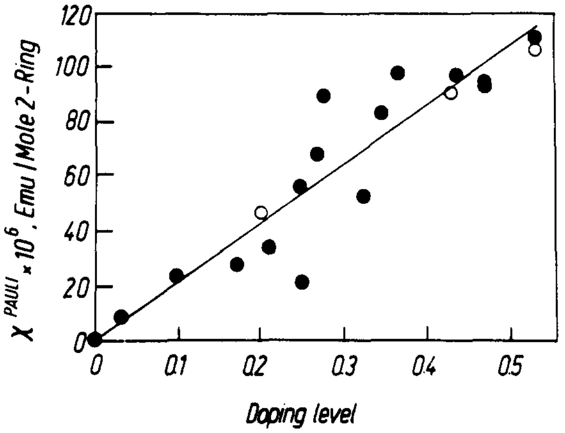


Figure 39 Pauli spin susceptibility measured by (●) Ginder[61] and (○) Lux[6] as a function of the doping level of the PANI powders. Note that the data were taken at room temperature

CONCLUSION

In summary, this review has shown that polyaniline, as an electronically conductive material, still offers many interesting problems to be solved before it can be recognized as a well-characterized material ready for introduction to the commercial market.

Further studies are especially necessary concerning the reaction mechanism leading to PANI, because in the current environmentally sensitive times it is a necessity to be sure that no toxic and/or cancer-causing products appear in the course of the synthesis. One might argue that the amounts of benzidine produced in scientific experiments have so far been too small for any kind of detection, and therefore one can be sure that it is not produced at all. However, this is nothing more than speculation, because everyone knows that scientific experiments are usually carried out in the very low concentration regimes of both aniline and the oxidant. Consequently, if one thinks about what might go on in a technical, i.e. large scale, synthesis, it appears very quickly to the mind that such synthetic conditions are tailor-made for the appearance of many side-reactions, including the benzidine synthesis. In fact, indications for what can happen in a large scale PANI synthesis have already been gathered in some scientific investigations (e.g. the occurrence of crosslinks, *ortho* couplings, overoxidation and oxidative degradation)[20,38–40,42,43,45]. On the other hand, one might promise to be able to wash out all the by-products of the synthesis afterwards and therefore avoid the problem of harmful by-products. However, this possibility is also accompanied by the problem of the disposal/destruction of the undesired by-products.

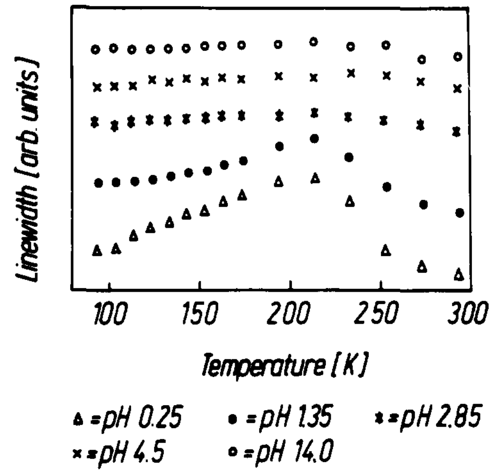


Figure 40 Variation with temperature of the e.s.r. linewidth in the X-band for differently doped PANI powders. Note that the individual plots are not scaled to each other (results of Lux[6])

The reaction mechanism proposed by Lux for the chemical synthesis of PANI oligomers and polymers from aniline and ADPA puts some emphasis on the possibility of the production of benzidine under conditions more appropriate for obtaining large amounts of PANI, i.e. synthesis in an acidic reaction medium with a pH value below 0.8. It has been shown that no matter what the reaction intermediates forming the aniline dimers are, the appearance of benzidine in the course of the reaction is very likely. Changing the acidity of the reaction medium to higher pH values in order to avoid the appearance of benzidine would make no sense, because less acidic reaction media will bring about an increase in other by-products (i.e. branched phenylenequinonediimines and other possibly hazardous substances), and thus result in a lower yield of PANI[1,2].

Besides the toxicological aspects of the PANI synthesis, Lux's reaction mechanism is the first to highlight the importance of the catalytic action of the acidic reaction medium for obtaining 1,4-coupled aniline oligomers and polymers. It is noteworthy that all the investigations conducted into the PANI synthesis in the past have failed to realize this important aspect of the PANI polymerization.

The most important aspect of Lux's reaction mechanism is its ability to explain both the autocatalytic reaction phase in the course of the polymerization and the differences in the oxidation states of similarly prepared PANI grades, simply through the ability of the acid used as the reaction medium to intervene in the reaction, i.e. to protonate the diimine-carrying reaction intermediates.

On the other hand, it is beyond all doubt that Lux's reaction mechanism can only represent a boundary mechanism with emphasis on a radical-initiated polymerization mechanism for PANI, i.e. it includes aspects which have to be considered in more detail or have to be completed by other steps. Most obviously, this is true for the real mechanism for the production of *p*-benzoquinone. Furthermore, experimental evidence for the appearance of the anilinium radicals forming the dimers and taking part in the autoacceleration reaction

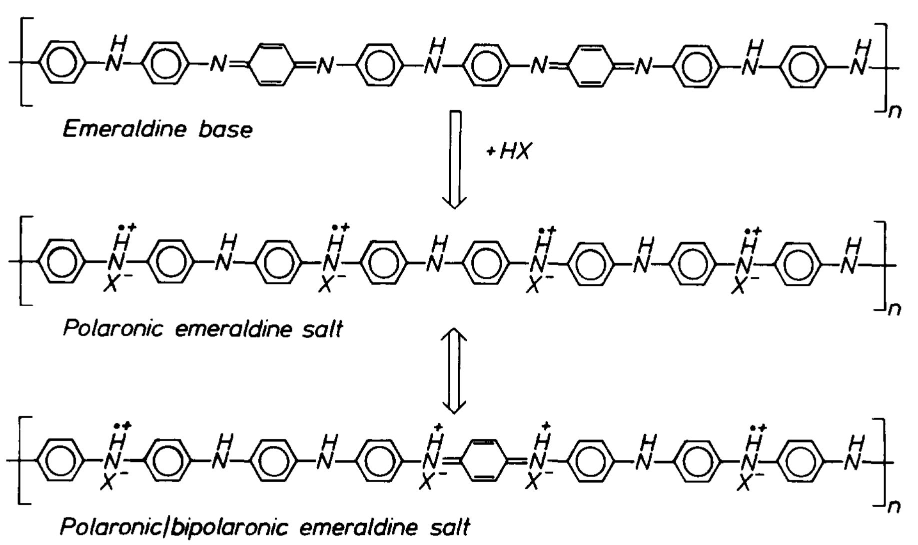


Figure 41 Possible polaron–bipolaron transformation for aniline oligomers and polymers in the emeraldine oxidation state

has to be given. As has been stated above, it is quite certain that at least anilinium radical 1 (*Scheme 4*) occurs somewhere in the polymerization. However, as this species should be very short-lived[70], it is very difficult to establish evidence for its participation in any coupling step. Another serious problem in Lux's reaction mechanism, and probably also in every other mechanism that has been proposed to date, is the fact that the polymerization of aniline is a heterogeneous reaction, i.e. after reaching the *tetrameric stage* the product molecules become insoluble in the acidic reaction medium and undergo precipitation. Afterwards, the production of larger molecules can only be accomplished via a boundary phase reaction at the solid–liquid interphase. Consequently, one probably encounters a much more complicated situation than is described by the pure solution mechanism in *Scheme 4*.

Besides the discussion of a new reaction mechanism for the synthesis of PANI, this paper has demonstrated that the crystalline arrangements in semicrystalline PANI grades are far from being understood. In particular, the crystalline arrangements in PANI powders precipitated from concentrated sulfuric acid cannot be explained by the EB1/ES1 and EB2/ES2 arrangements originally proposed by Pouget *et al.*[28,29], and need further detailed investigations.

Finally, the results concerning the charge carriers in PANI powders suggest that a combination of polarons and bipolarons is responsible for the electronically conductive properties of the material. In fact, when looking at the idealized structure of what is called 'the polaronic emeraldine salt' (i.e. molecules consisting of two ADPA and two PBQI units*, with the imine nitrogens of the PBQI units being protonated and separated by one aromatic nitrogen atom), one has only to imagine a mismatch of the strict alternating arrangement of aromatic and protonated imine nitrogens to meet with a structure capable of giving both polarons and bipolarons (see *Figure 41*). Not surprisingly, even the defenders of the polaron concept[71] have recently adopted the coexistence of polarons and bipolarons under certain conditions.

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*These ADPA and PBQI units each lack two hydrogen atoms compared with ordinary ADPA and PBQI

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