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The effect of pH on the oxidative polymerization of aniline and the morphology and properties of products

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Abstract. The synthesis and properties of the most popular and widely used electrically conducting polymer, polyaniline, are considered. The proposed mechanisms of the molecular synthesis and self-assembly of macromolecules occurring during the polymerization agree with the large body of experimental data. The reaction medium acidity is demonstrated to affect the mechanism of aniline oxidative polymerization and the formation of different types of supramolecular structures, namely, nanoglobules, nanofibres, nanotubes and microspheres. The bibliography includes 250 references.

I. Introduction

Polyaniline (PANI) pertains to the class of conducting polymers the history of which dates back to 1977 when electrically conducting polyacetylene was synthesized. Due to the presence of the extended system of conjugated bonds, these polymers exhibited properties typical of semiconductors.[1] The Nobel Prize in Chemistry of 2000 was awarded jointly to A Heeger, A MacDiarmid and H Shirakawa for the discovery and development of conducting polymers. Polyaniline has captured attention of scientists and engineers due to the following unique complex of properties: the redox activity, the wide variation range of electronic conductivity, the presence of ionic conductivity.[2] Due to its high thermal and chemical stability and the low prime cost, PANI was the first among conducting polymers to be used in practice. It was applied in energy-saving devices, for shielding electromagnetic radiation and as a corrosion inhibitor for ferrous and non-ferrous metals, served as the active component in chemical sensors and also was put through clinical trials and as a potentially catalytically active material.[1 – 5] In the past decade, the interest in PANI steadily increased and the PANI application field widened. This is evident from the increasing number of scientific publications (Fig. 1) and registered patents with the keyword 'polyaniline'.

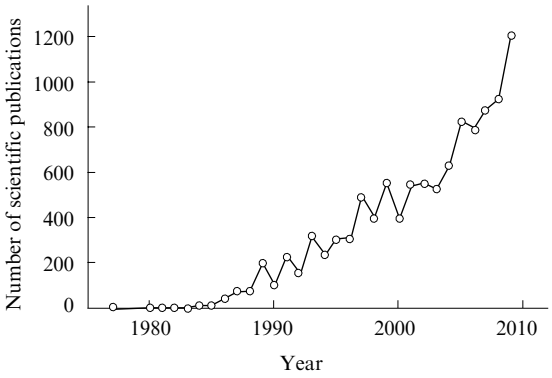


Figure 1. Dynamics of the increase in the number of scientific publications on the subject 'polyaniline' according to the database SCOPUS.

The PANI history in Russia has deep roots. In 1840, J Fritzsche, a German chemist who worked in Russia, described in detail the procedure of synthesis of a dark-

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green powder, the aniline oxidation product.† Most likely, this was polyaniline and thus the first polymer synthesized in laboratory. According to the Internet database Web of Science, in the past 15 years the Russian scientists published more than 450 scientific studies on polyaniline. These publications were devoted to the PANI synthesis,[6–15] the fundamental investigations into its structure[16–18] and the mechanism of charge transport in this polymer[19,20] as well as to the development of miscellaneous composite materials,[21–24] materials for catalysis,[25,26] sensors[27–29] and proton-conducting and gas-separating membranes.[30–33]

During the past 10 years, the authors of the present review also studied the molecular reactions of aniline oxidation,[34–39] the processes of self-organization throughout the polymer synthesis,[38,40–45] the PANI interaction with different types of templates,[46–52] and synthesized PANI-based nanostructured composite materials.[53–68]

II. Polyaniline structure and properties

Studies on the molecular structure of conducting polyaniline have shown that the structure of its chains was highly regular. Aniline monomer units were coupled in the 'head-to-tail' manner; thus, PANI contained regularly alternating benzene rings and nitrogen-containing groups. Moreover, virtually all monomer units were *para*-coupled.[69] Such an organization of macromolecules allowed a continuous conjugation system to be formed, thus providing the high conductivity level and, in certain cases, even metallic properties.[4]

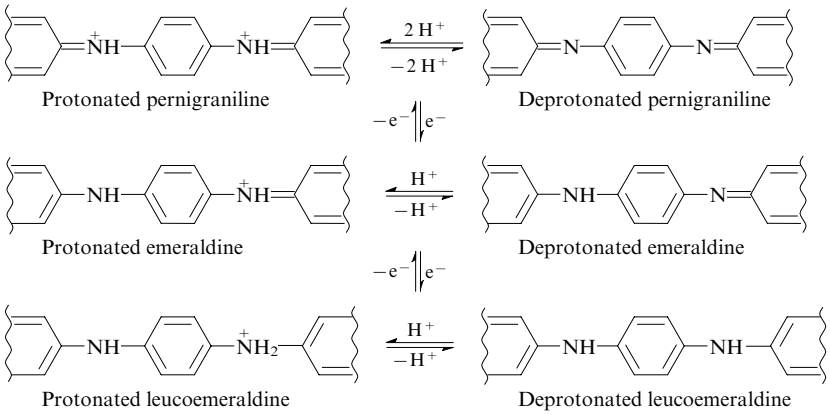
Polyaniline can exist is different oxidation states,[70] *i.e.*, contain different numbers of oxidized nitrogen atoms in its backbone (Scheme 1).[71] The polymer is characterized by the following oxidation states: the reduced form, namely, leucoemeraldine, containing non-oxidized nitrogen atoms; the intermediate oxidation state, emeraldine in which every second nitrogen atom is oxidized; and the highest degree of oxidation, pernigraniline with fully oxidized nitrogen atoms. Each PANI oxidation state exists in two forms, namely, protonated and deprotonated.[72] Oxidized nitrogen atoms are protonated more easily than the non-oxidized atoms,[4,73] because protonation leads to their stabilization as radical cations or the so-called positive polarons.[70] The latter serve as charge carriers so that PANI in its protonated form acquires the p-type electronic conduction. Usually, the conductivity of the protonated emeraldine polymeric form is 1–10 S cm^{-1} and can exceed the conductivity of leucoemeraldine and deprotonated emeraldine by 10 orders of magnitude.[4]

Under the term 'polyaniline', the protonated emeraldine polymeric form is usually understood, which can directly be prepared by synthesis. However, this is also often applied not only to the polymer with the regular structure but also to very different oxidation products of aniline. The properties of these materials can largely differ. Thus some samples demonstrated the conductivity of several tens and even hundreds of S cm^{-1} whereas the specific conductivity of other samples did not exceed 10^{-10} S cm^{-1} (Refs 74 and 75). The optical absorption of highly conducting samples covered the whole range of visible and the near IR spectra,[76] whereas the low-conducting materials absorbed in the range below 500 nm. The molecular mass (MM) of products could vary from several hundred to several hundred thousand Dalton, which affects the mechanical properties of the material.[77]

The aniline oxidation products were obtained in the form of various supramolecular structures, their morphology was extremely diversified. The polymer chains could form one-dimensional structures, namely, rods, nanofibres and nanotubes,[78–80] planar two-dimensional particles, *e.g.*, the so-called 'micromats',[81] ribbons, nanobelts and nanoplates,[82–86] and three-dimensional objects such as the globular structure typical of polymers, microspheres, nanospheres and hollow microspheres.[87–89] Furthermore, more complicated hierarchical formations were observed such as flowers, urchins, branches, corals.[82,89–91] In line with the development of nanotechnology,[1] the active studies of organized supramolecular structures of organic semiconductors were aimed at the development of materials to be used in molecular electronics, solar cells and sensors and also in the field of catalysis and polymeric nanolithography.[92] As a rule, the nanoscale structured objects exhibit the unique surface properties and the high mobility of charge carriers.[76] As a consequence, the development of methods of targeted synthesis of materials with the desired properties and the particular supramolecular structure became extremely challenging.

† This study was published in German in the Scientific Bulletin of the St Petersburg Imperial Academy of Sciences [J Fritzche. Ueber das Anilin, ein neues Zersetzungsproduct des Indigo. *Bulletin Scientifique publié par L'Academie Impériale des Sciences de Saint-Petersbourg. Tome VII* (*No. 12*), No. 156 (1840)]. At present, this publication is available at the St Petersburg Public Library.

Scheme 1



III. Polyaniline synthesis

The wide diversity of aniline oxidation products with different properties and supramolecular structures were directly formed in the course of a one-step synthesis. The assembly of polymer chains was initiated by an oxidant added to an acidified aniline solution. With the correctly chosen [oxidant] : [monomer] ([Ox] : [An]) molar concenrations, the polymer is obtained in the emeraldine form used most often in practice.[4, 93] The synthesis is carried out in the presence of inorganic, organic and polymeric acids that protonate PANI (this process is also termed doping).[7, 9, 13, 94, 95] However, the mechanism of polymerization and formation of supramolecular structures remains obscure so far. All the types of supramolecular structures listed above rather than being the target products were obtained accidentally when developing the methods of the polymer synthesis.

Polyaniline samples with different properties and supramolecular structures can be obtained by varying the conditions of synthesis.[96, 97] Smooth variation of the polymer properties and morphology following the transformation of one supramolecular structure to another was described in several publications.[78, 88, 98–104] However, the mechanism of these transformations and the underlying factors remain unclear. In some studies, such transformations were associated with the changes in the [monomer] : [acid] ratio or in their absolute magnitudes,[91] in other studies, the nature of the acid anion was considered as the main factor.[105] Some scientists explained the changes in oxidation products by the variation of the oxidant concentration[90] and the temperature factor.[106] Thus when analyzing the factors responsible for the formation of supramolecular structures, the well recognized and highly esteemed explorer of polyaniline M Wan, whose team was the first to synthesize PANI nanotubes, concluded that the situation 'is strongly affected by the nature of dopant and reaction conditions including the concentration of dopant, oxidant and monomer as well as the molar ratio of oxidant and dopant to aniline monomer even reaction temperature and stirring conditions'.[82, 88]

Such a diversity of synthesis parameters that affect the properties of the final product baffles experimentalists and explains why the phrase of MacDiarmid 'there are as many different types of PANI as there are people who synthesize it' has become polular.[107] In this situation, studying the mechanism of PANI synthesis became a challenge.

1. Modern concepts on the mechanism of aniline polymerization

Aniline forms macromolecules in the course of oxidative polymerization. This reaction can formally be presented as a covalent coupling of monomer molecules as the result of elimination of two hydrogen atoms. This polymerization type is characteristic of various classes of compounds, namely, aromatic amines, phenols, arenethiols, aromatic hydrocarbons and heterocycles.[108] Polymerization may be carried out by electrochemical or chemical methods with different oxidants. Most often, strong oxidants with the oxidation potentials exceeding 1.0 V on the standard hydrogen electrode scale (persulfates, dichromates, cerium(IV) salts, *etc.*) are employed. This is associated with the fact that the onset of the propagation of the polymer chains in acidic media requires overcoming the energy barrier corresponding to the oxidation potential of 1.1 V.[4] Once the chains have begun their propagation, the oxidation potential of polymerization products decreased to 0.8–0.7 V. Under certain conditions, conducting PANI could be synthesized in the presence of weaker oxidants, for example, silver or iron(III) salts, vanadium(V) oxide, *etc.* The synthesis of PANI starts under homogeneous conditions; however, the polymerization becomes a heterogeneous process even in the initial step. In the chain propagation step, the reaction is also heterogeneous,[109] because PANI is insoluble in either water or organic solvents. This polymerization type is called the precipitation polymerization because the polymer is formed as a precipitate.

a. The chain mechanism of polymerization

The polymerization of aniline pertains to the class of chain reactions,[110] *i.e.*, its monomer units are 'being added' one after another on a polymer chain that bears an active terminal group. Y Wei[111] singled out the polymerization of aniline into a special type of reactivation chain process. The chain growth involves the repeated acts of activation–deactivation of the polymeric structure

$$M_n \xrightarrow[\text{activation}]{\text{Ox}} M_n^* \xrightarrow[\text{deactivation}]{\text{An}} M_{n+1},$$

M is the monomer unit, M* is the active form, An is aniline.

The dormant polymer chain (M_n) is activated by an oxidant (to form M_n^*), then it adds an aniline molecule to yield a new dormant chain of higher molecular mass (M_{n+1}).

b. The active site of the polymerization

The question on the nature of the terminal active group responsible for the polymerization of aniline was disputed for a long time.[112] This was assumed to be the nitrenium cation[113–115] or the radical cation.[116, 117] Studies on the aniline oxidation in the presence of 'traps' for both types of structures showed that alkyl-substituted phenols (2,6-di-*tert*-butyl-4-methylphenol) and electron-enriched alkenes (2,3-dimethoxybuta-1,3-diene) inhibited the polymerization by acting as scavengers of the radical cations. At the same time, PANI readily formed in the presence of electron-enriched arenes (1,3- and 1,4-dimethoxybenzene) well known as the 'traps' of nitrenium cations. This proved that the oxidation of aniline proceeds *via* a radical cation site.[3]

The activated terminal group of the chain was generated by the oxidant. In the initial step, it is the monomer that is oxidized; however, upon formation of oligomers, these are terminal amino groups of the oligomer (polymer) that were oxidized because they had lower oxidation potential.[118] It was shown that in the course of polymerization, the propagating polymer chain oscillated between the highest and intermediate oxidation states, *i.e.*, pernigraniline and emeraldine.[116] Thus, the polymer chain performed the function of a mediator in the monomer oxidation.[116, 119, 120] The active site formed at the end of the chain attacked the monomer molecule. This attack was directed at a hydrogen atom in the aromatic ring and resulted in its displacement by a polymer fragment. This reaction pertains to the electrophilic substitution, because the active site is the electrophilic agent. The chain propagates due to the addition of new monomer units.[121, 122]

c. Polymer chain structure

It is surprising that in acidic media the oxidation afforded high-molecular and strictly regular polymer chains. Aniline

monomer units were coupled in the 'head-to-tail' mode and had exclusively the *para*-structure.[69, 121, 122] The formation of so regular chains is not typical of the closest analogues of aniline (phenols, arenethiols), which also underwent oxidative polymerization according to the electrophilic substitution mechanism.[118] Phenols and arenethiols formed relatively low-molecular products, their polymer chains are represented by random sets of monomer units of different structures.[108] Polyaniline contains a small amount (< 2%) of phenazine fragments as the 'foreign' units. Their appearance is explained by the intermolecular coupling processes that occurred in the post-polymerization period.[80, 123]

d. Kinetic features of polymerization

Studying aniline polymerization in acidic media has shown that the oxidation proceeded non-monotonically.[119, 124] It started with a slow process (induction period) during which the aniline oligomers formed; the structure of the latter is still little studied. The induction period is followed by a rapid exothermic step of the polymer chain propagation. The following kinetic dependence was proposed to describe the two-step process:[109]

$$-\frac{d[An]}{dt} = k_1[An][Ox] + k_2\sigma[An]P,$$

where [An] is the molar concentration of aniline, [Ox] is the molar concentration of the oxidant, k_1 is the rate constant of the initial step (induction period) of polymerization, k_2 is the rate constant for the polymer chain propagation, σ is the surface factor, P is the surface of the reaction medium interface.

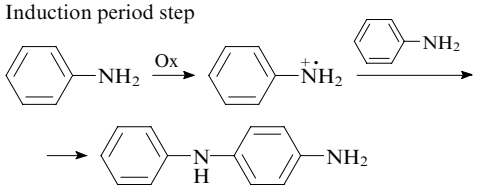
Both the first and, presumably, the second steps are the first-order reactions with respect to the monomer.[125] For the initial step, the reaction order with respect to the oxidant was also the first. In the propagation step, the monomer was oxidized by the oxidized pernigraniline form of PANI rather than by the original oxidant.[119] Polyaniline was insoluble and the reaction was heterogeneous; hence, the parameter P and the factor σ were introduced into the equation in order to characterize the interface on which the reaction proceeded. The rate constant for the chain propagation (k_2) was three orders of magnitude higher than the rate constant for the initial step of polymerization (k_1). In other words, the formation of the polymer led to impressive acceleration of oxidative polymerization.[14, 109, 126, 127] The acceleration was also observed upon the introduction of PANI 'seeds' into the reaction medium. Such autocatalysis has not been explained so far.[109] The polymerization rate was sensitive to the presence of different inert and insoluble materials in the reaction medium, for example, alumina,[109] silica gel, carbon, cellulose, synthetic polymers, *etc*.[39, 44, 56, 61, 62] The effect was stronger for materials with the greater surface area (P).[11] The mechanism of this effect is still unclear and the surface factor (σ) is very difficult to estimate experimentally.

The strong effect of the medium acidity exerted on the polymerization rate was revealed.[13, 15, 17, 128–134] This effect was different at different pH. Under conditions of high acidity (for pH < 1), direct proportionality between the molar concentration of the strong acid and k_2 was observed. At the same time, the increased acidity had a little effect on the rate constant of the initial step; however, the induction period substantially shortened with the decrease in pH.

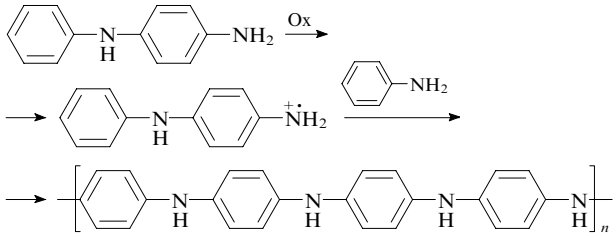
e. Molecular mechanism

At present, the only mechanism proposed for the description of molecular processes of the oxidative polymerization of aniline was the Wei scheme.[114, 135]

Induction period step



Polymer chain propagation step



Presumably, in the induction period, aniline radical cations formed,[6] which was followed by their recombination by the electrophilic substitution mechanism to afford a dimer, namely, *N*-phenylphenylene-1,4-diamine (*p*-semidine).[114] The subsequent propagation step was assumed to be similar to the electrophilic substitution process where the oxidized terminal amino group of an oligomer (polymer) attacked the *para*-position in the monomer. It was assumed that the reaction involved the monomer in its most reactive non-protonated form.[136] The oxidation rate-limiting step was considered to be either the formation of aniline radical cations [114] or their dimerization.[116] The experimental observation that the introduction of small amounts of the aniline dimer (*p*-semidine) sharply accelerated polymerization can be considered as a substantiation of the proposed mechanism. The rationale was that the introduction of *p*-semidine eliminated the limiting step so that the polymerization began with the rapid step of chain propagation.

Wei's scheme did not contradict formally the data on the structure of PANI polymer chains, because it postulated the growth of a regular polymer with *para*-substituted monomer units. However, it failed to explain why it is the *para*-coupled monomer units that should be reproduced during the growth. In the electrophilic substitution reaction of the protons in the benzene ring containing an electron-donating substituent (amino group), the attack by the electrophilic agent should be directed to both *para*- and *ortho*-positions of the ring.[137] Hence, a polymer of a mixed *ortho* and *para*-structure should be formed. It is this pattern that is observed in the oxidative polymerization of phenols and arenethiols containing an electron-donating substituent. At the same time, high-molecular-mass PANI was shown to consist of over 98% of *para*-coupled monomer units.[69]

The Wei mechanism has also other drawbacks.

1. It ignores the effect of the reaction medium acidity on polymerization; the mechanism as a whole contradicts the experimental data [109] on the effect of acidity on the poly-

merization rate. In this scheme, the polymerization rate decreased rather than increased with the increase in acidity due to the lower content of the major reactant, the non-protonated aniline form.

2. The scheme fails to explain the following changes in the oxidation potential in the course of polymerization: its increase to 1.1 V followed by its drop to 0.7–0.8 V in the chain propagation step.

3. No explanation was given for the great difference in the rate constants of the first and second steps.[109] At the same time, both reactions are associated with the identical processes of nucleophilic substitution and afforded similar structures.

4. The scheme is not consistent with the experimental observation that homogeneous polymerization transformed into a heterogeneous process as early as during the induction period, because the putative initial-step intermediates, linear aniline oligomers, are well soluble in acidic aqueous media. The effect of different types of surfaces on the polymerization kinetics remains so far unclear as well as the phenomenon of autocatalysis.

5. No species with unpaired spins (aniline radical cations) that according to the Wei scheme should be accumulated during the induction period were detected in the initial polymerization step. The radical cation sites appeared only with the onset of the propagation step.[108]

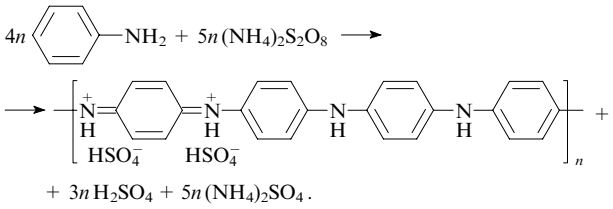
As a rule, discussions on the oxidative polymerization of aniline state that the Wei scheme is inconsistent and the molecular mechanism of this process remains obscure so far.[136]

Carrying on development of the concepts of PANI synthesis, the authors of the present review proposed a molecular mechanism of oxidative polymerization of aniline. This mechanism is based on the experimental data[69, 108, 109, 111, 114, 118] described above and proved to be consistent with the latter. In addition to the existing concepts, this mechanism takes into account the effect of the medium acidity on the state and reactivity of polymerization intermediates. Naturally, as for the majority of chemical reactions, the oxidation of aniline depends on the concentration factors and the temperature. However, their effects is not that pronounced as that of the principal factors. Presumably, the principal factors that determine the course of this process are the reaction medium acidity and the oxidant potential. To eliminate the effect of the oxidation potential out, we consider the polymerization induced by a strong oxidant (persulfate), which is capable of oxidizing all intermediate reaction products. Under these conditions, the pH of the medium is the main factor that determines the mechanism of aniline oxidation and the nature of polymerization products.

IV. Aniline oxidation in media of different acidity

1. The effect of pH

In the oxidation of aniline, coupling of the monomer units occurs according to the electrophilic substitution mechanism. The oxidized terminal imino structure is substituted for a proton in the benzene ring of the monomer.[137–139] In this reaction, protons are liberated and the medium acidity moniotonically increases.[108] This is typical of all oxidative polymerization processes that proceed by the electrophilic substitution mechanism. The overall reaction of aniline with the oxidant [in our case, ammonium peroxydisulfate (persulfate)] with liberation of sulfuric acid can be described by the following equation:



Both the initial pH value and the rate of pH variation (drift) depend on many factors that are the subject of this discussion. These include the initial concentrations of the monomer and the oxidant, the presence of alkalis, acids or buffering agents in the reaction medium the degree of conversion of the monomer to the polymer, *etc*. Thus for the initial aniline and persulfate concentrations of 0.4 mol litre^{-1} and 0.5 mol litre^{-1}, respectively, and upon the complete monomer-to-polymer conversion, the reaction medium pH varied from 9 to 1, *i.e*., the reaction that has started in an alkaline medium ends under the conditions of acid-promoted polymerization.

The pH factor plays a very important role in the polymerization, because aniline and its polymerization products are organic bases. They comprise different types of the nitrogen-containing groups that exhibit different basicities and react with acids at characteristic pH values to form salts. Aniline is the strongest base with the protonation constant (pK) $\sim$ 4.6 (Ref. 140). In alkaline and weakly acidic media, aniline exists as a neutral structure, whereas in acidic media, it is protonated, *i.e*., acquires a positive charge.

In addition to the monomer, the reaction involves various polymeric (oligomeric) chains. They contain oxidized nitrogen atoms, which are protonated at pH $\sim$ 2.5 (Refs 4, 141–143). During the protonation of the amino groups, PANI is transformed into its acidic pernigraniline form.[143] As a result, the overall polymer structure is covered with a system of delocalized positive charges (polarons) and transformed into a polycation (see the first line in Scheme 1).[144, 145] This transformation changes in principle the mechanism of aniline oxidation.

Other nitrogen-containing fragments, *i.e*., the non-oxidized disubstituted amino groups and the nitrogen atoms of the phenazine units, can be protonated only at very low pH values usually unattainable under synthesis conditions. It is extremely important to consider that the reactivities of neutral and protonated molecules substantially differ, the latter being far less reactive,[146, 147] which cannot but affect the aniline oxidation when polymerization proceeds at different pH values.

Thus the oxidative polymerization of aniline is a complex process accompanied by permanent changes in the synthesis conditions. What is important is the pH value at which the process begins and the nitrogen-containing groups (either protonated or non-protonated) that are involved. However, of no less importance is how quickly the pH drifts and at which pH values the polymerization comes to end. The reaction often coveres the pH ranges where nitrogen-containing fragments in different degrees of protonation dominate. The transition from one pH region to another can be accompanied by the changeover of the polymerization mechanism. This can result in the changes in the molecular structure of chains and, hence, in the proper-

ties of products and also lead to transformations in the PANI supramolecular structure.

2. Methods for studying the processes of the oxidation of aniline

Analysis of the reaction parameters in the course of the synthesis is among the most informative methods for the studies on the mechanisms of chemical reactions. In the case of the polymerization of aniline, the concentration of products can be traced by gas chromatography,[119] ^{1}H NMR spectroscopy,[145] UV-visible and near-IR absorption spectroscopy.[71, 148, 149] A procedure for *in situ* monitoring of the polymerization of aniline was developed where FTIR spectroscopy was applied following the deposition of a drop of the reaction mixture on a ZnSe crystal.[95] The EPR method made it possible to observe the appearance of stable paramagnetic species [33, 138] and the changes in the oxidation potential of reaction products were followed by electrochemical methods.[116, 119, 143] Each method provided important information and helps understanding of the process as the whole.

In our studies, pH of the reaction medium and the temperature of the polymerization mixture were monitored in the course of the synthesis. The oxidation of aniline is an exothermic process and can easily be followed by temperature changes. The temperature dependence provides information on the intensity of the oxidation processes in individual steps of the synthesis, thus supplementing the results of pH measurements. The interpretation of results involved the use of additional data obtained by the *in situ* analysis of oxidation with the use of spectral and potentiometric methods [35, 36, 45, 71, 115, 116] as well as the data [138] on the formation of paramagnetic sites.

Experiments were carried out in order to elucidate the kinetics of oxidation of aniline in different pH regions. We used a strong oxidant (ammonium peroxydisulfate), which has the oxidation potential of 2.0 V and is capable of oxidizing all intermediates of the PANI synthesis. The reaction proceeded under ambient conditions. It was initiated by instantaneous mixing of the reactant solutions and proceeded without stirring. The kinetic data were supplemented by information on the properties and the morphology of the reaction products. These were isolated by filtration, dried in air at room temperature and then analyzed by conductometry, spectroscopy, gel permeation chromatography and electron microscopy.

3. Oxidation of aniline at different initial pH values

In the first series of experiments, the oxidative polymerization of aniline (0.2 mol litre^{-1}) was carried out with the stoichiometric amount of ammonium persulfate (0.25 mol litre^{-1}), which provided the complete monomer-to-polymer conversion. Polymerization was started in the media of different acidity, namely, 1) in 0.2 M ammonia solution (pH 10); 2) in water (pH 6); 3) in 0.4 M acetic acid (pH 4.5), 4) in 0.1 M sulfuric acid (pH 2). Monitoring of temperature and pH is shown in Fig. 2. It is evident that both parameters change synchronously. The decrease in pH corresponded to the exothermic steps: the sharper increase in the temperature corresponded to the more pronounced decrease in the pH. This also suggested that thermal effects were due to the processes of oxidation and proton liberation.

General features of the aniline oxidation processes can be formulated as follows.

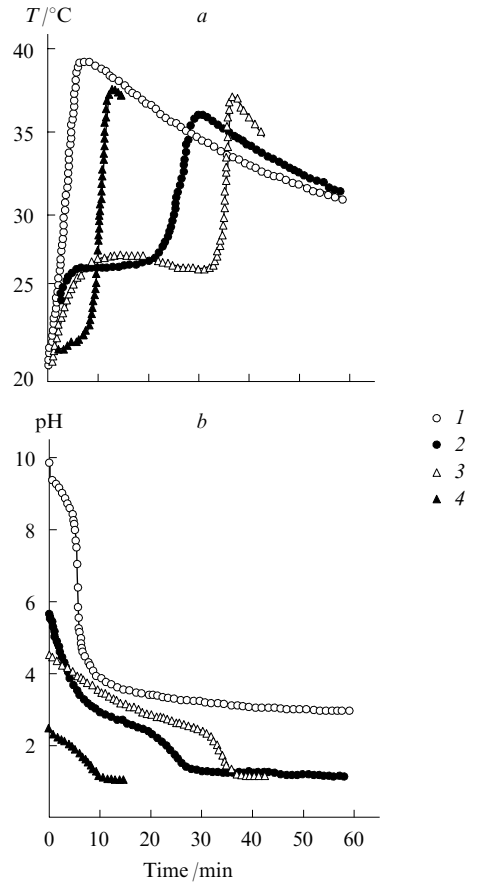


Figure 2. Changes in the temperature (*a*) and pH of the medium (*b*) in the course of the oxidation of aniline (0.2 mol litre^{-1}) initiated by ammonium persulfate (0.25 mol litre^{-1}) at different initial acidities;[41] (*1*) in 0.2 M $NH_3 \cdot H_2O$; *2*, in water; (*3*) in 0.4 M acetic acid; (*4*) in 0.1 M H_2SO_4.

1. The initial rate of the oxidation of aniline increases with the increase in the pH of the medium. In sulfuric acid (pH 2), it was close to zero (the oxidation induction period).

2. The oxidation processes in which the pH dependence did not pass through pH $\sim$ 2.5 are characterized by a single temperature wave of oxidation. These processes include the oxidation in ammonia, which began at pH 10 and ended at pH > 3, and the reaction in sulfuric acid, which proceeded at pH < 2.2.

3. The oxidation processes that occurred in a pH region including pH $\sim$ 2.5 had two temperature waves. These processes include the reactions in water and acetic acid, which stared at pH 6 and 4.5, respectively, and ended at pH 1.

4. The first oxidation wave fell in the range with pH > 3 and resembled the monotonic process of the oxidation of aniline in ammonia. The range 2.5 < pH < 3 is characterized by the abrupt deceleration of the oxidation processes. However, with the attainment of pH 2.5, the exothermic reaction regained its vigour and the oxidative polymerization was concluded by the second temperature wave. The character of pH variations in the second wave was identical to that typical of polymerization in sulfuric acid.

5. The pH decrease in water proceeded much faster than in acetic acid because this weak acid served as the buffer.

4. Oxidation of aniline at different monomer : oxidant ratios

In the second series of experiments, the oxidation of aniline (0.2 mol litre^{-1}) was carried out in 0.4 M acetic acid at different [Ox] : [An] molar ratios. The ammonium persulfate concentration was varied from 0.25 to 0.025 mol litre^{-1}. At the low oxidant concentrations, the monomer was oxidized incompletely. In all the experiments, polymerization started at pH 4.5 and continued up to the complete consumption of the oxidant. Figure 3 shows the temperature and pH dependences obtained in this series of experiments. It is evident that the higher oxidant concentration, the lower the final pH, which is associated with the more complete monomer-to-polymer conversion and, correspondingly, the larger amount of liberated protons.

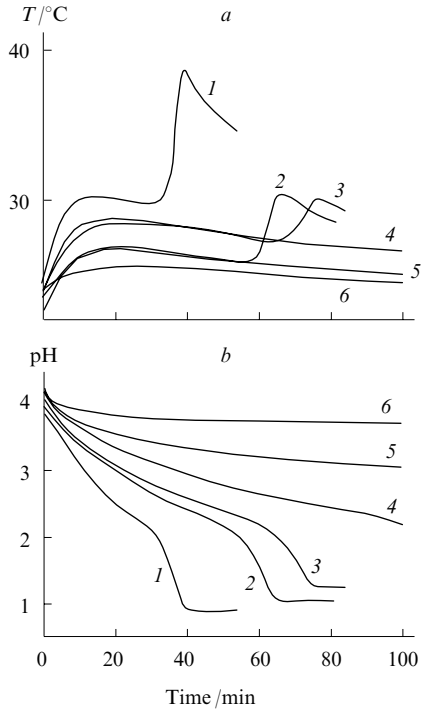


Figure 3. Changes in the temperature (*a*) and pH of the medium (*b*) in the course of the polymerization of aniline (0.25 mol litre^{-1}) in 0.4 M acetic acid under the action of different amounts of ammonium persulfate.[40]
[Ox] : [An] = 1.25 (*1*), 1.0 (*2*), 0.75 (*3*), 0.5 (*4*), 0.25 (*5*), 0.1 (*6*).

The second experimental series produced the relationships similar to those of the first series. For the oxidation at low [Ox] : [An] ratios (0.025, 0.5, 0.25), no acidity drift below pH 3 was observed. In this pH region, as for the oxidation of aniline in ammonia, the reaction proceeded monotonically and the single temperature wave was observed. For high [Ox] : [An] ratios (1.25, 1.0, 0.75), the final pH of the medium was < 2.0. Moreover, the processes demonstrated two temperature oxidation waves. As in the first series, in the range $2.5 < \text{pH} < 3$, the reaction proceeded extremely slowly. The second exothermic wave began once the reaction medium pH reached 2.5.

As follows from the data presented, irrespective of which reaction parameter was varied (pH of the medium or the [Ox] : [An] ratio), the process had the similar character if proceeded in the same pH region. Judging from the sharp change in the oxidation character in a point with pH 2.5, different molecular mechanisms of the synthesis were realized in the pH ranges above and below this point.

5. Properties and morphology of the aniline oxidation products

In the first experimental series, the synthesis proceeded up to the 100% conversion of the monomer to the polymer (Table 1). For polymerization in ammonia ($3 < \text{pH} \leqslant 10$), the oxidation products represented aniline oligomers with the weight-average molecular mass (M_w) of 4000 and polydispersity (M_w/M_n) of 1.3. The conductivity of the material

Table 1. Properties of oxidation products of aniline (0.2 mol litre^{-1}) with ammonium persulfate (0.25 mol litre^{-1}) for different acidity of the medium.

Product properties	Synthesis conditions			
	$NH_3 \cdot H_2O$ (0.2 M) (see [a])	water (see [b])	acetic acid (0.4 M) (see [c])	H_2SO_4 (0.1 M) (see [d])
Conductivity /S cm^{-1}				
protonated form	$< 10^{-10}$	0.055	0.036	3.7
deprotonated form	—	6.0×10^{-8}	7.9×10^{-9}	1.1×10^{-9}
Protonated form density /g cm^{-3}	—	1.35	1.338	1.402
Molecular mass (M_w)	4.090	—	32 200	39 400
Polydispersity (M_w/M_n)	1.3	—	19.0	13.1
Morphology	microspheres	plates, nanotubes	nanotubes	granules

[a] pH 9.5 → 3.0, [b] pH 5.7 → 1.1, [c] pH 4.5 → 1.1, [d] pH 2.2 → 1.0.

in the completely doped state did not exceed 10^{-10} S cm^{-1}. The electronic spectrum of oligomers (Fig. 4) contained no polaron charge transfer band typical of the emeraldine polymer form with a continuous conjugation system. Studies on the morphology of the oxidation products showed that the microsphere structure dominated, *i.e.*, the oligomers formed spherical particles with the diameter from 500 nm to 2 μm (Fig. 5).

The aniline oxidation products synthesized in the presence of sulfuric acid ($1 < \text{pH} < 2.2$) represented the polymer with $M_w \approx 40\,000$ and $M_w/M_n = 13.1$. The material was characterized by an absorption band at 618 nm typical of deprotonated emeraldine (see Fig. 4) and the conductivity of the protonated emeraldine form of 3.7 S cm^{-1}. The polymer had the globular structure typical of PANI with globules measuring from 100 to 200 nm (Fig. 6).

The oxidation products obtained in acetic acid and water exhibited characteristics intermediate between those of aniline oligomers and high-molecular PANI. As compared with PANI synthesized in sulfuric acid, the molecular masses of the products were lower and their polydispersities were higher; their conductivities were two orders of magnitude lower and the band corresponding to polaron charge transfer was less intense and shifted to the short-wavelength range. These characteristics suggested that PANI synthesized in the intermediate pH range $1 < \text{pH} < 6$ represented a mixture of oligomers and polymer.

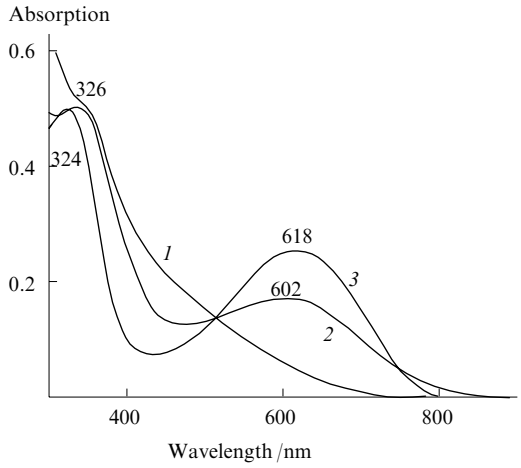


Figure 4. Electronic absorption spectra of the oxidation products of aniline (0.2 mol litre^{-1}) initiated by ammonium persulfate (0.25 mol litre^{-1}) recorded in media with different acidities;[84]
(*1*) in 0.2 M $NH_3 \cdot H_2O$; (*2*) in 0.4 M AcOH; (*3*) in 0.1 M H_2SO_4.
Oxidation products are deprotonated and dissolved in *N*-methylpyrrolidone. Absorption peaks of the corresponding bands are given in nanometres.

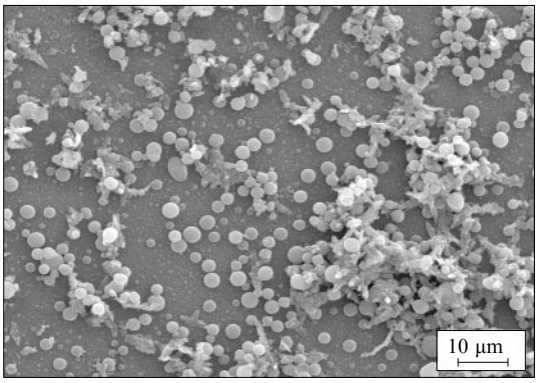


Figure 5. Oxidation products of aniline (0.2 mol litre^{-1}) with ammonium persulfate (0.25 mol litre^{-1}) in 0.2 M aqueous ammonia.[38]
From here on, microimages obtained by a scanning electron microscope are shown unless otherwise specified.

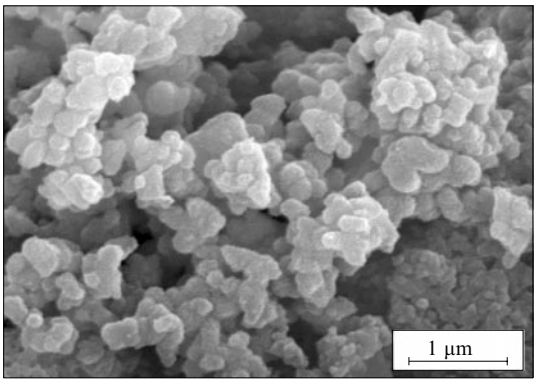


Figure 6. The globular structure of polyaniline synthesized by oxidation of aniline (0.2 mol litre^{-1}) with ammonium persulfate (0.25 mol litre^{-1}) in 0.1 M sulfuric acid.[38]

Table 2. Properties of oxidation products of aniline (0.2 mol litre^{-1}) with different amounts of ammonium persulfate in 0.4 M acetic acid.

Product properties	[Ox] : [An] (pH_{fin}) [a]				
	0.25 (4.0)	0.5 (3.3)	0.75 (2.5)	1.0 (1.2)	1.25 (1.1)
Conductivity of protonated form /S cm^{-1}	$< 10^{-10}$	2.4×10^{-10}	–	0.036	0.095
Density of protonated form /g cm^{-3}	–	1.307	–	1.338	1.465
Molecular mass (M_w)	3600	< 1000	23 600	17 600	44 600
Polydispersity (M_w/M_n)	3.8	16.4	11.1	9.4	10.6
Morphology	amorphous	two-dimensional formations	nanotube inclusions	nanotubes	nanotubes

[a] pH_{fin} is the final pH; the initial pH_{in} = 4.5.

In the second series of experiments (Table 2), the relationships typical of the first series were reproduced. If the polymerization was completed at pH > 2.5 ([Ox] : [An] = 0.025, 0.5, 0.25), it produced non-conducting aniline oligomers without continuous conjugation systems. At the same time, if the synthesis was completed at pH < 2.5, the products comprised high-molecular PANI in addition to oligomers, and the extent of conjugation and, hence, the conductivity were higher.

The morphology of PANI synthesized in the intermediate pH range 1 < pH < 4 that included two temperature waves was characterized by the presence of one-dimensional structures, namely, nanotubes and nanofibres. The one-dimensional structures began to appear in synthetic products at pH ~ 2.5. The appearance of nanofibres and nanotubes accompanied the transition from oligomeric products to polymeric ones. As the pH drifted to acidic values, the length of tubular fragments increased together with the fraction of one-dimensional structures. For PANI synthesized in acetic acid in the pH range 1 < pH < 4.5, the one-dimensional structures prevailed (Fig. 7). However, further decrease in pH increased the globular precipitate fraction. Polyaniline synthesized in water also contained fibres and tubes with the outer diameter of 150 – 200 nm; in addition to tubes, the PANI precipitate contained the so-called 'plates' (Fig. 8) and the globules measuring up to several hundred nanometres.

A comparative study of oligomers and conducting PANI carried out by electronic and IR spectroscopy, NMR spectroscopy and elemental analysis has shown that in contrast to the polymer, low-molecular products had irregular structures.[36, 37, 41, 84] Most probably, this was due to the formation of dissimilar units and also to the secondary processes of oxidation and hydrolysis that occurred in parallel with the chain propagation. In addition to different molecular structures and properties, the products also had basically different morphology. However, no direct correlation between the conductivity, the molecular mass and the type of supramolecular structure could be found. Depend-

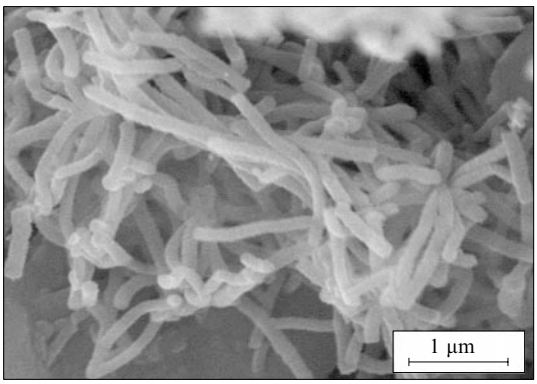


Figure 7. One-dimensional morphology of the oxidation product of aniline (0.2 mol litre^{-1}) with ammonium persulfate (0.25 mol litre^{-1}) in 0.4 M acetic acid.[84]

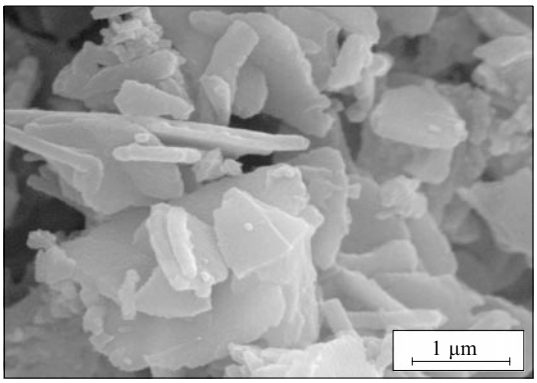


Figure 8. Two-dimensional structures shaped as plates with the thickness of ~200 nm obtained in the polymerization of aniline (0.2 mol litre^{-1}) initiated by ammonium persulfate (0.25 mol litre^{-1}) in water (our data).

ing on the syntheis conditions, the oligomers could represent microspheres, one- or two-dimensional formations, whereas the high-molecular PANI could have either the one-dimensional structure of nanofibres and nanotubes or the three-dimensional structure of globules.

The results presented above demonstrated that pH is an extremely important factor capable of inducing deep changes in the polymerization process, the morphology and the properties of the aniline oxidation products. However, the effect of pH was not always so obvious. It was often masked by other parameters of the synthesis. The changes in the overall concentrations of reactants and their ratios, the presence of additives could perform the dual function. They exerted the standard effect of reaction acceleration or deceleration and, simultaneously, could change the reaction medium pH. Thus aniline increased the pH being an organic base. The increase in the monomer concentration was equivalent to solution alkalization. By adding the monomer to the solution, it was possible to elevate the pH up to 9. Addition of acids and acidic salts decreased the pH. The [monomer]:[acid] ratio and the nature of the acid used were also important parameters. Weak acids exhibited the buffer effect suppressing the pH variations during the synthesis. The oxidant concentration could affect the pH thus controlling the degree of conversion and the number of liberated protons. The range of pH variations during the synthesis was much wider in concentrated solutions as compared with dilute solutions.[150] It should be borne in mind that the pH factor masked by the action of multiple diverse parameters could have the decisive effect on the oxidation of aniline.

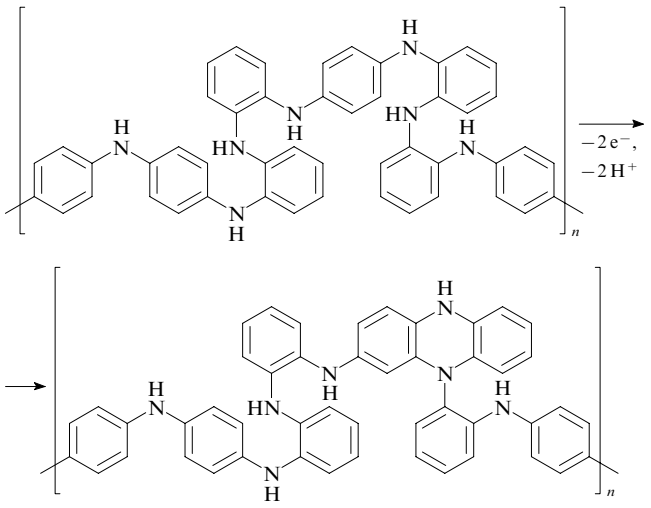
V. Molecular mechanism of aniline oxidation at different pH of the medium

The results considered in the previous section demonstrated the existence of two pH regions in which the oxidation of aniline occurred in different fashion. At pH > 2.5, the reaction gives oligomers without polyconjugation and with low conductivity. At pH < 2.5, high-molecular PANI with a high degree of conjugation are formed and the conductivity of products is much higher. It is evident that different properties can be attributed to the structures of the polymer chains (irregular in oligomers and regular in polymer). Thus, at a characteristic pH of the medium, the synthesis was observed to abruptly 'switch' from the mixed irregular addition of monomer units to the mechanism of regular polymerization.

1. Formation of oligomers with units of irregular structure

As mentioned above, in the course of the oxidative polymerization of aniline the attachment of the monomer units occurs by the mechanism of electrophilic substitution. The oxidized terminal imino group substitutes a hydrogen atom in the benzene ring of the monomer.[129, 130] The monomer units are linked in a 'head-to-tail' fashion. However, even where this type of coupling is strictly reproduced, a high probability exists that the resulting chains would contain dissimilar monomer units. The substitution can produce *ortho*-, *para*- and *meta*-isomers. A similar set of monomer units was formed in the oxidative polymerization of phenols and arenethiols, the closest analogues of aromatic amines.[108] The content of dissimilar units in the polymers can be different. The probability of the formation of *meta*-structures is very low, because aniline, like phenol, has an electron-donating substituent in the aromatic ring, which induces the excess negative charge on the *ortho*- and *para*-carbon atoms in the ring and directs the attack of the electrophilic agent to the *ortho*- or *para*-positions.[137] Thus, polyaniline should contain the *ortho*- and *para*-coupled monomer units, where the *ortho*-units prevailed due to the presence of two *ortho*-positions.[146]

Apparently, in the pH range >2.5, the oxidation of aniline did occur by this mechanism to form chains of mixed irregular structure. In parallel with the chain propagation, the secondary reactions could occur in the oligomeric chain.[116] Monomer units with the *ortho*-structure have a low oxidation potential and can be oxidized further to close the phenazine rings.[151, 152] These reactions can be of both the intramolecular type such as the oxidation of *o*-phenylenediamine[152] and the intermolecular type with involvement of the monomer. Thus, the oligomers can contain phenazine rings in addition to the linear *ortho*- and *para*-substituted monomer units.[133]



The more complicated irregular structure of oligomers becomes obvious if we compare their IR and Raman spectra with those of high-molecular PANI. The presence of phenazine units in aniline oligomers was confirmed by the data from IR spectroscopy,[153] UV-Vis spectroscopy,[154, 155] NMR spectroscopy[130] and also electrochemical methods.[113, 156]

Oligomers of irregular structure lack the continuous conjugation system and should have low conductivity (this agrees with the data listed in Tables 1 and 2). We call this mechanism of the oxidation of aniline 'oligomerization'.

2. The features of the oligomerization of aniline depending on pH

At pH > 5, all nitrogen-containing groups (the NH_2 group of the monomer, the oxidized terminal imino groups and the inner NH groups) involved in the oxidative polymerization are deprotonated. Neutral nitrogen-containing structures have the low oxidation potential ($\sim$0.4 V) and their oxidation should proceed at a high rate. According to Fig. 2, this is encountered in the oxidation in ammonia and in the initial step of oxidation in water. In a series of experiments where the pH decreased, the rate of the initial step decreased. The initial step of oxidation in acetic acid (pH $\sim$ 4) proceeded much more slowly. This is associated with the first step of protonation of nitrogen-containing structures involved in polymerization.

At pH < 4.6, the monomer is largely protonated;[140] however, the oxidized imino groups of the polymer chains remain deprotonated. This brings about unbalance between the oxidation processes involving the chain and the monomer. According to the general principles of redox processes of organic compounds, the electron transfer steps must occur independently of the mass transfer steps including the processes of restructuring of the bulky organic molecule, *i.e.*, the electron transfer should proceed preferentially between the fragments of the similar structure. In the particular case of aniline oxidation, the deprotonated chains are involved in a redox reaction with the deprotonated monomer, but the electron exchange between the protonated monomer form and the deprotonated chain is forbidden.[157, 158]

According to Figs 2 and 3, in the pH range 2.5 < pH < 4, where the monomer is largely protonated but the polymeric chain is not protonated yet, the oxidation rate decreased. The reaction proceeds slowly being limited by the supply of the neutral monomer through a step of its deprotonation.[158] The sharp deceleration of the oxidation processes in the pH range 2.5 < pH < 4 was observed in all kinetic dependences and is associated with the deficiency of the main reactant, *i.e.*, neutral aniline. For polymerization in acetic acid, the step of slow oxidation was the exceptionally long due to the buffer nature of acetic acid, which prevented the further decrease in pH and the transition to the next step of oxidation.

How do the pH changes affect the oligomerization products? Oligomers obtained at pH > 4 included several tens of monomer units (see Tables 1 and 2). The relatively low degree of polymerization is explained by the close rate constants for the first and subsequent additions of the monomer and also by the possibility of formation of terminal phenazine structures. Aromatic phenazine units have the high oxidation potential and their formation at the chain end inhibited their further propagation. The slowing down of oxidation, which is caused by a decrease in pH, and the resulting deficiency of neutral molecules bring about changes in the oligomer size and composition. The rate of monomer addition, *i.e.*, of the chain propagation, decreases and the rate of intramolecular cyclization increases.[159, 160] This must result in the formation of short and for the most part cyclic molecules. Indeed, according to Table 2, even at pH $\sim$ 3, the chains become shorter (MM below 1000). In the electronic spectra of the products, a broad absorption band was observed in the vicinity of 500 nm, which corresponded to the n$-\pi^*$-transition in substituted phenazines;[161] the IR spectra demonstrated a set of bands at 1208, 1108 and 1144 cm^{-1}, also typical of cyclic phenazine structures.[84]

3. Synthesis of polymer chains with the regular structure

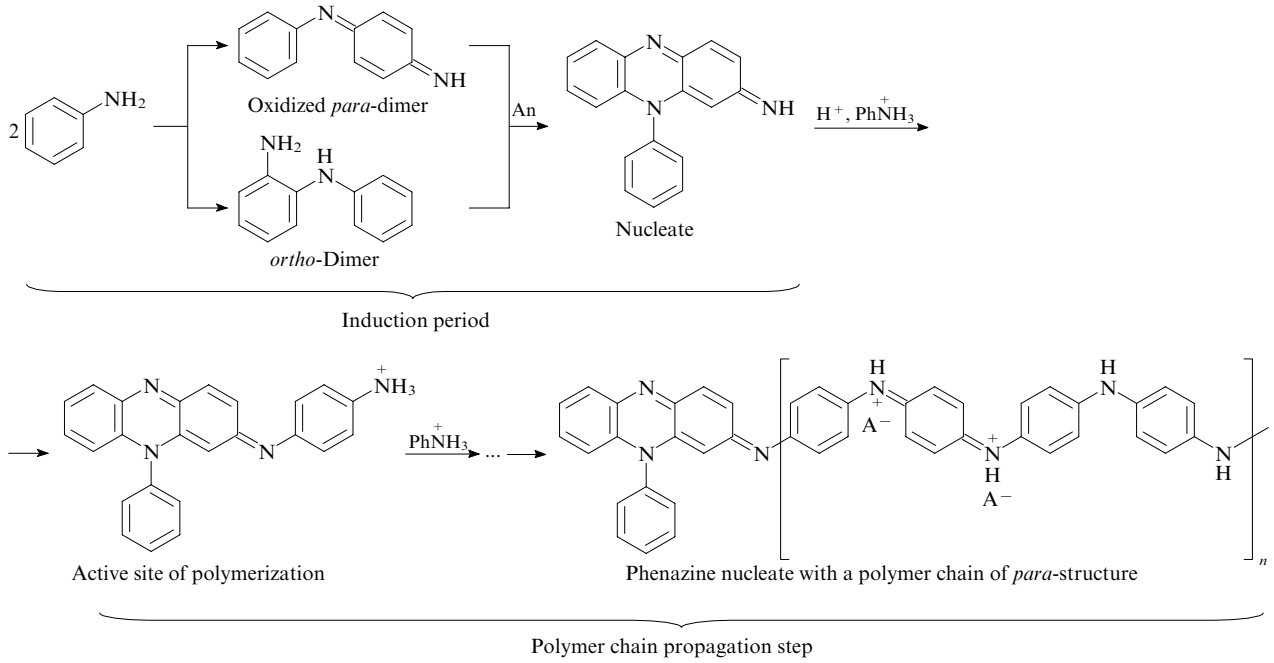
The propagation of polymer chains with the regular structure becomes possible in the next step of protonation. Spectral studies have shown that at pH < 2.5 the imino groups in the polymeric (oligomeric) chains are protonated.[141] The interaction with the acid stabilizes the radical cationic state of the oxidized nitrogen atoms as indicated by the appearance of a stable EPR signal.[138] A positive charge appeared on the nitrogen atoms, which results in substantial changes in the reaction system. In all kinetic dependences, the point pH 2.5 marked the onset of a new exothermic oxidation step (see Figs 2 and 3). The oxidation rate increased by several orders of magnitude and, in place of oligomers, high-molecular chains with the regular polyconjugated structure grow.

a. Formation of the nucleates of polymeric chain propagation

However, in those cases where the pH of the reaction medium is < 2.5 (*i.e.*, with both types of reaction groups in the protonated state), the propagation of regular chains did not start with the interaction of two monomer units. The chain propagation step is always preceded by an induction period during which the slow formation of aniline oligomers takes place.

The presence of the induction period could not be explained in terms of the Wei scheme as the formation and accumulation of aniline radical cations followed by their slow recombination to afford a dimer, namely, *p*-semidine. The absence of an EPR signal suggests that no stable paramagnetic centres form in this step. On the other hand, it was shown[84] that the IR spectra of the initial-step products were identical to those of oligomers recorded at the high pH and containing a set of bands typical of

Scheme 2



phenazines. Moreover, the electronic spectra of initial oligomers were identical to those of phenazine derivatives.[154, 162] During the induction period, the oxidation potential of products increased from 0.6 to 1.05 V,[163–167] and cyclic voltammograms, too, demonstrated peaks typical of phenazine fragments.[113] It was shown[157] that initial oligomers, like phenazine derivatives, had the low conductivity; moreover, mass spectrometric studies[160] identified them with the low-molecular compounds corresponding to aniline di- and trimers.

Considered together, all these factors suggest that in the initial step of the oxidation of aniline, the formation and accumulation of oligomers of the phenazine type occur. It can be assumed that at any, even low, pH values, the process follows the mechanism of 'oligomerization' (Scheme 2). Under the conditions of high acidity, the reaction proceeds very slowly and involves trace amounts of the neutral non-protonated monomer. Due to the higher probability of *ortho*-coupling and the high cyclization rate of *ortho*-dimers, the structures of the phenazine type are mainly formed. As a result of formation of an aromatic ring, the oxidation potential of products increased to 1.05 V so that their further propagation by the 'oligomerization' mechanism is inhibited.[119, 165]

Apparently, at pH < 2.5, in the slow initial step of polymerization (in the induction period), the accumulation of single-type trimers shown in Scheme 2 took place. These trimers with the well-developed conjugation system nucleate future polymer chains and play an important role in both the synthesis of polymer chains and the formation of supramolecular structures.

b. The chain propagation step

The chain propagation starts with the addition of a monomer unit to the phenazine nucleate. This is the limiting step of the overall process, its energy barrier corresponds to the potential of 1.05 V.[156, 166] With the beginning of imino group protonation (pH < 2.5), the prohibition for the redox reactions between the monomer and the nucleate imino group is eliminated. If during the induction period the neutral non-protonated monomer form[136] present in an extremely low concentration is oxidized, then the oxidation of the dominant protonated monomer form becomes possible. Both species transformed into the protonated state and can readily be involved in the electron transfer.

Like oligomerization, the oxidation proceeds by the electrophilic substitution mechanism. However, the complexity of the first act of addition is explained by the fact that the interaction occurs between two electron-deficient molecules, namely, the phenazine nucleate containing the oxidized, protonated imino group and the positively charged monomer molecule. It is most likely that the role the phenazine nucleate as a bulky molecule with the well-developed conjugation system played in the addition of the first monomer unit is very important. The aromatic phenazine structure is capable of lowering down the energy barrier for the interaction of two species bearing charges of the same sign. The nucleate contains a non-protonated aromatic ring. In the instant of the monomer addition, the excess positive charge of the nucleate can be delocalized over the cyclic aromatic structure. This explains why even in acidic media with pH < 2.5, the chain propagation is always preceded by the induction period. The propagation reaction could not start with small molecules containing insufficiently developed conjugation systems, *e.g.*, with a reaction between the oxidized and non-oxidized forms of the protonated monomer. For the propagation to begin, a bulky conjugated molecule, *i.e.*, the phenazine nucleate, is required.

The addition of monomer units elongates the conjugation system and facilitates the further chain growth. This is why after the growth has started, the oxidation potential decreases to 0.7–0.8 V.[116, 168] However, the common system of conjugation could only be realized if the monomer unit was added in the *para*-position. The formation of units with other structures destroys the conjugation system and makes impossible the charge delocalization. Thus, the protonation of imino groups in the polymeric chain changes the mechanism of oxidative polymerization. In contrast to a deprotonated chain for which the reactions of *ortho*- and

para-substitution are equivalent as regards the energy, for its protonated analogue the *para*-structure is energetically advantageous. In this case only, for a linear chain, the π-conjugation and the delocalization of the charge of imino groups becomes possible; this is accompanied by a decrease in the oxidation potential.[38, 40, 165] For this reason, in the acidic medium the *para*-substitution is virtually the only way of attachment of the monomer units. A polymer with the strictly regular structure and a high conjugation level forms. The conductivity of PANI reaches several tens S cm^{-1}. The chain size also increased from ten to several hundred monomer units, because at pH < 2.5 the chain propagation reaction becomes energetically advantageous as compared with the formation of new nucleation centres.

Concluding the section on molecular processes in the synthesis of PANI, it should be mentioned that the most significant changes in the parameters of synthesis and in the properties of oxidative polymerization products are associated with the pH effect. According to the protonation constants of nitrogen-containing groups involved in the polymerization, the oxidation process can be divided into the following three regions (Fig. 9):

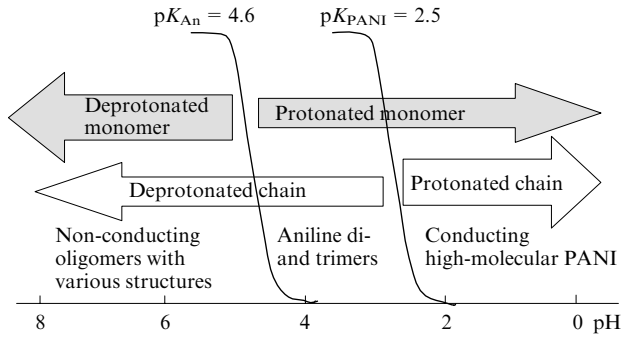


Figure 9. Dependence of the aniline oxidation process on the protonation constants of the monomer (pK_{An}) and the chain imino groups (pK_{PANI}).

1) pH > 4; all types of nitrogen-containing groups are deprotonated and the oxidation proceeds in the same fashion as the synthesis of typical polymers-dielectrics (*e.g.*, polyphenols[108]) to afford irregular chains with the molecular mass up to 10 000;

2) 2.5 < pH < 4; the monomer is protonated in contrast to the backbone imino groups; an unbalance of redox processes is observed, which results in the slow formation of di- and trimers with the cyclic structure;

3) pH < 2.5; the backbone imino groups, like the monomer, are protonated and this recovers the balance of electron exchange between the chain and the monomer; however, prohibition is imposed on all other types of chain propagation except for *para*-substitution; this leads to the growth of regular conjugated chains with the high molecular mass.

Thus, the regular structure that underlies the unique PANI properties is formed at pH < 2.5 as a result of protonation of imino groups in the polymeric chain.

A concept that the protonated monomer form is oxidized in the chain propagation step makes it possible to explain the phenomena of shortening of the induction period and the increase in the reaction rate.[109] This is associated with the acceleration of protonation of the nucleate imino group and the increase in the concentration of the reactive protonated monomer form. The low aniline oxidation rate in the initial step in acidic media is due to the necessity of oxidizing the neutral molecules the concentration of which is very low at pH < 2.5.

The introduced concept of a cyclic intermediate with the phenazine structure explains the following non-monotonic changes in the oxidation potential in the course of the reaction: its increase throughout the induction period due to the formation of an aromatic ring with the high oxidation potential and its subsequent drop during the propagation of a polyconjugated chain.

In Sections VI – VIII, it will be shown that the described molecular mechanism makes it possible to explain the following peculiarities of the oxidative polymerization of aniline:

1) the transition from the homogeneous reaction mechanism to heterogeneous one, observed in the induction period;

2) the effect of different types of surfaces on the polymerization kinetics;

3) the effect of *p*-semidine and phenylenediamine isomers on the kinetics of the polymerization of aniline;

4) the phenomenon of autocatalysis.

Finally, the molecular mechanism is the clue to understanding the PANI self-organization processes in the course of synthesis and the formation of all known types of supramolecular structures.

VI. Supramolecular structures of polyaniline

1. Types of supramolecular structures

The vigorous interest in supramolecular PANI structures dates back to 2004 when this polymer was synthesized in the form of nanotubes and nanofibres.[78, 79] These forms represented one-dimensional PANI objects with the diameter from several tens to several hundred micrometres. The tube diameter could vary from several nanometres to one hundred nanometres (Fig. 10). The earlier known globular structure of PANI did not attract much attention of scientists, although the synthesized specimens represented

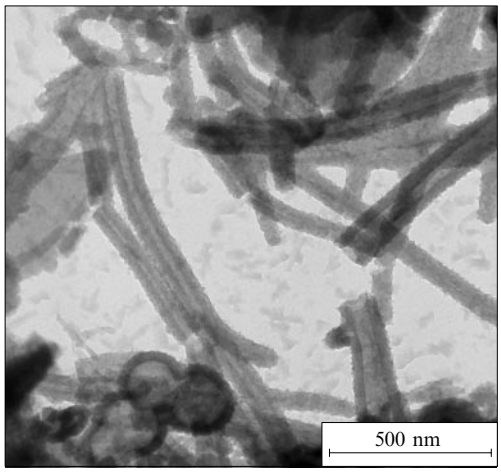


Figure 10. Polyaniline nanotubes and nanofibres in the presence of nanospheres.[38]
The microimage was obtained by the transmission electron microscopy method.

strictly spherical globules with a narrow size distribution (see Fig. 6). This morphology suggested that throughout the synthesis, the self-assembly occurred (in place of the trivial agglomeration of insoluble polymers). The specific sorption processes occurring throughout the PANI synthesis is also evidenced by the formation of thin uniform polymeric films on surfaces in contact with the polymerization medium.[165–173] This phenomenon was explained by the sorption of aniline oligomers on these surfaces followed by the heterogeneous propagation of polymer chains, this time on the surface. It has been shown earlier that under synthesis conditions both the monomer and the oxidant are soluble and are not adsorbed on the solid phase.[174] The sorption was expected to be of the ionic nature, because the protonated nitrogen-containing oligomers are positively charged. However, the formation of PANI films was observed not only on negatively charged surfaces but virtually on every surface.[175–177] The adhesion of films to different supports was amazingly strong.[174,178] The structures of sorbed oligomers remain unclear.

Recently, numerous types of supramolecular structures of PANI have been obtained. Their synthesis and potentialities are discussed in several reviews.[88,179–185] Those with one-dimensional, two-dimensional planar and three-dimensional spherical morphology belong to the main types. Their combination and more complicated organization give rise to the vast diversity of structures. Different hierarchical formations are built of fibres coming from the common centre or axis.[186] One-dimensional structures can be packed in bundles[105] or form a sort of networks or dendrimers (Fig. 11).[187] PANI fibres can also form two-dimensional structures called 'micromats'.[81] These are rhomboid particles, 'weaved' to produce mats of several layers of fibres coming from the vertex of the rhombus and crossing at right angle (Fig. 12). Among three-dimensional structures, microspheres and hollow microspheres should be mentioned (see Figs 5, 10).[188–191] Their outer diameters fall in the range from a half of micrometre to several micrometres and the thickness of their walls varied from nano- to submicrometre sizes. Moreover, nanospheres with the diameter of several tens and several hundred nanometers have been prepared (see Fig. 12). The spheres can serve as the centres of fibre growth or, conversely, the fibres can grow inside the spheres. Under certain synthesis conditions, one or another structural type dominates thus virtually determining the morphology of the polymer as a whole.

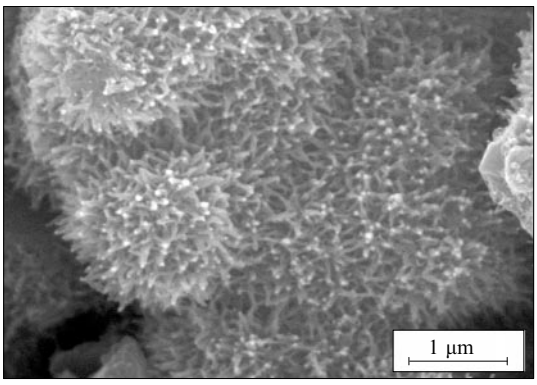


Figure 11. Hierarchical nanostructure of polyaniline.[187]

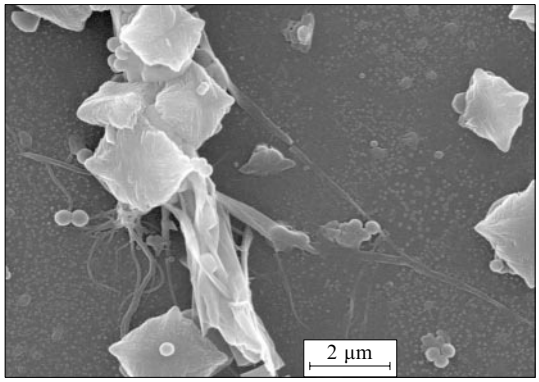


Figure 12. The structure of two-dimensional polyaniline, 'micromats', in the presence of nanospheres.[169]

2. Studies of the mechanism of polyaniline organization in the course of synthesis

All supramolecular structures were discovered accidentally when refining the methods of PANI synthesis. At present, the pathways to the synthesis of all main types of the polymer structures are known, but the mechanisms of their formation remain unclear. All supramolecular structures are formed in the course of the synthesis and the synthesis conditions exert the decisive effect on this process. Although the morphology is very sensitive to the polymerization conditions, it proved to be reproducible when the experimental conditions are strictly obeyed. Smooth transition from one structural type to another with the changes in the synthesis parameters is described in many publications.[38,88,169] The size characteristics of different structural types (film thickness, size of colloidal particles, radii of globules, radial sizes of fibres and tubes) were shown to increase as the temperature was reduced, the monomer concentration increased and the extent of the monomer conversion increased.[192–194] Moreover, the sizes of different supramolecular structures obtained in one synthesis coincide.[195] Thus the radii of colloidal particles and the thickness of films obtained in the same reaction vessel were equal. This suggests the common nature of all types of supramolecular structures and the common mechanism of their formation.

The first studies devoted to the elucidation of the mechanism of synthesis of nanotubes related their formation to the presence of a certain structured template, *i.e.*, a matrix on which oligomers first adsorbed and then grew to PANI, which emerged in the polymerization medium.[196–198]

Presumably, this template could represent salts or micelles formed by aniline with an organic acid used as the dopant.[199,200] It was also assumed that aniline can form one-dimensional micelles with ammonium persulfate,[143,155] which in turn induced the synthesis of one-dimensional structures. However, it was shown that PANI could form fibres and nanotubes with many other oxidants (not only with ammonium persulfate)[131] for which the formation of micelles could hardly be assumed. Considering the PANI growth on a template, the polymerization of aniline on the template surface under the conditions of formation of a thin uniform film indeed reproduced the template structure. Thus polymerization of aniline in the presence of liquid crystals,[167] nanosized inorganic particles,[201,202] polymer

networks[203] or salt agglomerates formed by aniline and the dopant could result in the aniline growth on the template surface to reproduce the template structure.[204] However, neither the micelles formed by the monomer with the dopant nor, particularly, the micelles with the one-dimensional structure and the size matching the nanotube inner hollow were observed experimentally.

Recent studies convincingly demonstrated that PANI could form organized supramolecular structures not only in the presence of a structured template. The majority of scientists accepted that the self-organization is the intrinsic property of PANI.[131,143,155,181,205–208] One-dimensional PANI structures were observed to form under the action of different oxidants in dilute aqueous media containing only the monomer or the monomer weakly acidified with an inorganic acid in which neither salt agglomerates nor micelles could form.

At present, many methods of synthesizing one-dimensional PANI structures that employ various experimental procedures are known (of which a great deal have their own names). These are the polymerization at the interface of immiscible solvents[180,202,209] one of which contains the monomer and the other contains the oxidant[207] (polymerization on the interface); the synthesis in aqueous media diluted with water-soluble organic compounds, for instance, with lower alcohols,[210] or in very dilute aqueous media (dilution method); polymerization in water[131,210] in the presence of weak organic acids (soft template method)[197] and also at low concentrations of strong inorganic acids;[186,211] the electrochemical polymerization under potentiodynamic conditions[212] (potential cycling method), the use of oxidants with potentials lower than that of persulfates ($\leqslant 1$ V),[79,213–215] *etc*. The authors of different methods give different rationale to the formation of one-dimensional structures. Although the methods leading to the formation of organized particles tend to increase in number, the mechanism of self-organization of polymeric chains during the synthesis has not been elucidated so far.

We believe that the mechanism of formation of supramolecular PANI structures has a common origin irrespective of whether thin PANI films or stable colloids, or particles with the one-, two- or three-dimensional structures are formed. The mechanism could be a logical extension of molecular reactions of this synthesis and help to explain the formation of particles with a given morphology under different experimental conditions. Below we consider a mechanism of self-organization of PANI macromolecules in the course of the synthesis that will explain the formation of all types of supramolecular structures from a common standpoint. The molecular mechanism of oxidative polymerization of aniline described in Section V served as the basis of this mechanism of formation of supramolecular structures.

VII. Mechanism of polyaniline self-organization during the synthesis

1. Sorption and association of phenazine nucleates in the induction period

With few exceptions, the polymerization of aniline started under homogeneous conditions, because in acidic aqueous media both the monomer and the oxidant form true solutions. However, as demonstrated experimentally, the reaction became heterogeneous even in the early step.[109,165] In the induction period, the accumulation of phenazine oligomers, *i.e*., nucleates of future polymeric chains, occurred. Under the usual polymerization conditions (pH $\geqslant$ 0), the phenazine heterocycle does not react with the acid and is not protonated.[216] It is well-known that non-protonated phenazine structures are hydrophobic and poorly soluble. They can strongly adsorb on different surfaces or form agglomerates due to the $\pi-\pi$-electron interaction.[38,152]

Nucleation of the main morphological types (films, colloidal particles, coated particles[139,156,217–220]) can be represented as follows (Fig. 13). Even in the induction period, the phenazine nucleates form templates for the future supramolecular structures. Their adsorption on the support or on stabilizer determines the formation of PANI films or colloidal particles. As a result of association of phenazine oligomers with one another, nuclei of the PANI precipitate form. The adsorption and association can proceed both randomly and regularly. The random processes lead to the formation of irregular particles, the nuclei of PANI globules. However, it is the processes of regular assembling of phenazine heterocycles that proved to be the most energetically favourable. Phenazines are planar aromatic structures pertaining to discotics. They can stack one flat molecule on another to form either one-dimensional 'columns' or two-dimensional planar precursors. The intermolecular coupling into columns occurs due to the $\pi-\pi$-electron interaction of the aromatic rings.[38,169]

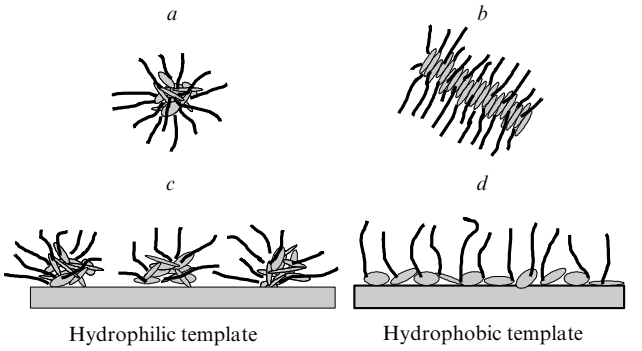


Figure 13. Formation of polyaniline precipitate particles shaped as globules (*a*) and one-dimensional structures (*b*); propagation of PANI chains on hydrophilic (*c*) and hydrophobic (*d*) supports.

The formation of organized intermediates is typical not of all oligomers, but only of cyclic di- and trimers obtained at pH < 4. The regular self-assembly is favoured by the presence of single-type phenazine nucleates and the absence of bulky substituents. The primary structures built of regularly assembled nucleates served as the basis for the preparation of one-dimensional fibres and tubes and two-dimensional PANI structures. The *in situ* formation of PANI films on various supports, colloidal particles and PANI nanoparticles as such with different morphologies including fibres and nanotubes was surveyed in detail.[38,169]

2. Self-organization during the polymer chain propagation

In the propagation step, the growth of high-molecular chains from the phenazine nucleates begins. In contrast to the phenazine heterocycle, the propagating chains are protonated and hence hydrophilic. Hydrophilic polymer chains propagate from the nucleation centres into the aqueous

phase; hence, PANI particles have most probably the radial organization. In globules, the chains are arranged along the radii, whereas in one-dimensional structures they are arranged perpendicularly to the particle axis (see Fig. 13).[38, 169] Planar two-dimensional structures (plates, ribbons) and films can be assembled in a brush-like chain ordering.[221] During the propagation, the chains are associated with one another due to hydrogen bonding, which additionally stabilizes the supramolecular structure.[38, 169] Supramolecular PANI structures were shown to be very stable,[222] they are not destroyed during the polymer carbonization[223] and are apparently soluble only in *N*-methylpyrrolidone. Presumably, it is the high binding energy of the initial phenazine heterocycles and the interchain interaction that are the reasons for the poor processability of PANI.

Conducting polyaniline in the form of highly organized particles that consist of chains with the high degree of conjugation can be synthesized only in the pH range $0 \leqslant pH < 2.5$, because only here the following conditions required for the synthesis of a conducting material are realized: the growth of chains with the regular *para*-structure, which provided the interchain electron mobility, and the self-assembling of chains into particles, which is necessary for the interchain conduction.

The assembly of phenazine nucleates plays the key role in the self-organization processes. However, in strongly acidic media (in H_2SO_4, $\geqslant 2$ mol litre^{-1}), the phenazine nitrogen atoms are in their protonated state, which exerts a negative effect, because the solubility of phenazine nucleates is increased and consequently the polymer self-organization level is reduced. At high concentrations of strong acids, the synthesis of PANI becomes altogether problematic, because the polymer yield and its conductivity and the degree of organization decrease.[224]

3. The heterogeneous nature of the polymer chain propagation

The growth of PANI, like apparently the growth of other conducting polymers, differs from that of high-molecular dielectrics. This polymer can serve as a model of the fractal growth of biological objects. Its propagation resembles the growth of nano- and submicroparticles rather than individual macromolecules. This is possible because PANI exhibits both the electronic[4, 225] and ionic[226–228] conduction. The redox-active polymer mediates the aniline oxidation.[109, 229, 230] A PANI particle is oxidized by the oxidant and then, in turn, oxidizes the monomer and attaches the latter. The positive polaron that appeared upon oxidation can easily be delocalized over the polymer particle and stabilized by a mobile anion of the acid. The monomer oxidation can occur in a site different from the site of the chain - oxidant interaction. The PANI particle is involved in the redox interaction as a whole.[38, 224, 228, 231, 232] This increases the probability of the process by a large factor and is one of the factors favouring the acceleration of polymerization, *i.e.*, the autocatalysis.

4. Structure – property relationships

The heterogeneous mechanism of the PANI growth, which includes the *in situ* organization of the polymer chains, enables the synthesis of organized particles. In turn, the high degree of organization determines the high mobility of electrons within a particle. For a globular polymer with polymer chains packed along the radii, the degree of chain organization and hence the conductivity is high in the central part of the particle and decreases to its periphery due to the increase in the number of organization defects. The electron transfer between PANI particles is the most hindered process. Hence, this determines the conductivity of the material as a whole. A polymer with such a structure should consist of highly conductive regions surrounded by zones with low conductivity.

It is this pattern that is observed in studies of the electrodynamic and magnetic properties of PANI. The heterogeneous mechanism of polymer propagation in the form of individual organized particles fits completely the 'islands' model proposed for describing the properties of this material.[144, 233] The model represents PANI as conducting 'islands' embedded in the non-conducting matrix. Apparently, it is the central parts of the globules grown from phenazine agglomerates that served as the 'islands'. It was shown experimentally that the conductivity of PANI increased after exposure of the polymer to certain organic solvents capable of solvating chains as well as to aqueous acidic media.[234] This is associated with the fact that PANI particles swell, which improves the contacts at the interfaces. In aqueous acidic solutions, the processes of proton transport can also considerably contribute to the conductivity.[228]

VIII. Growth of particles with different morphologies

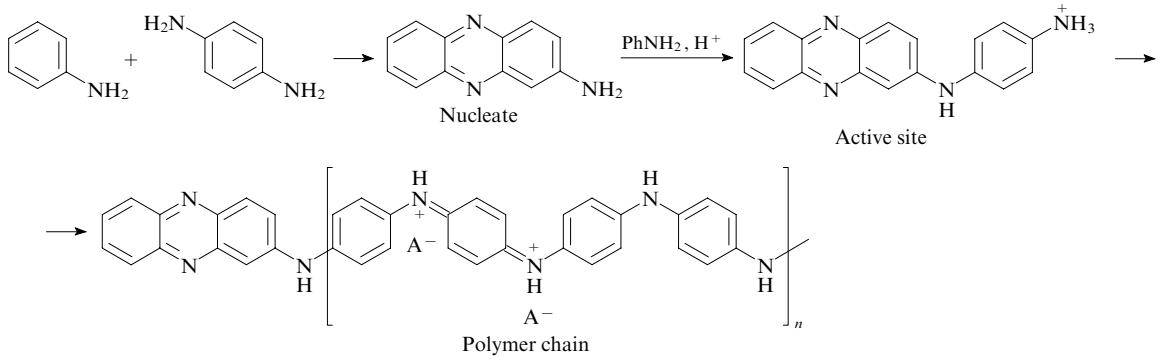
The formation of particles with different supramolecular structures was predetermined by the synthesis conditions. In the present Section, we shall consider the general principles of the effect of polymerization conditions on the PANI morphology and analyze the particular cases of the formation of supramolecular structures described in Sections IV and VI.

1. General mechanism of the effect of the synthesis conditions on the morphology

According to the proposed mechanism of self-organization, the form of the polymer particles is predetermined by the structure of agglomerates of the phenazine nucleates. Hence, the PANI morphology must be defined by the processes of phenazine nucleate assembly during the initial polymerization period. It is well known that the assembly of similar molecules can result in the formation of regular structures. It can be assumed that the deficiency of similar nucleates leads to the formation of random agglomerates, which determine the formation of globular polymer particles. In contrast, when nucleates of one type are accumulated, the probability of formation of regular PANI structures where the phenazine heterocycles form stacks is high. These nucleates initiate the growth of one-dimensional or planar two-dimensional structures.

The conditions of regular assembly are implemented in the case of the accumulation of similar aniline di- and trimers with the phenazine structure, while the phenazine coupling reactions, for example, when chains begin to grow by the mechanisms of oligomerization or polymerization, are hindered. Such a situation is encountered under different experimental conditions. However, as a rule, this is characterized by a common feature, *viz.*, by the presence of a long induction period. As mentioned above, in the induction period, phenazine nucleates are formed; hence, a long induction period should favour their accumulation and organization. The conditions of the oxidative polymeriza-

Scheme 3



tion of aniline characterized by the presence of a durable induction period are listed below. Note that, as a rule, these conditions correspond to one of the methods of synthesis of one-dimensional structures known in the literature.[38]

1. The polymerization in aqueous acidic media with low ($\leqslant$0.02 mol litre^{-1}) reactant (an oxidant and the monomer) concentrations, the dilution method. In addition, the oxidant : monomer molar ratio >1 and the single-step instantaneous mixing of reactants, *i.e.*, fast mixing procedure,[155, 208] favours the formation of one-dimensional structures. This procedure enables the more active production of the phenazine nucleates.

2. The use of oxidants with the low potential ($\leqslant$1 V) in place of persulfates[79, 187, 213–215] or the electrochemical synthesis carried out under the conditions providing a low potential, which include the potentiodynamic method of synthesis, *i.e.*, the cyclic potential technique.[211] The low oxidation potentials ensure the generation of nucleates, but hinder further chain growth from them in the acidic medium.

3. Synthesis under conditions of low initial pH and relatively high reactant concentrations (the order of magnitude is several tenth of mol litre^{-1}). The reaction can proceed in the aqueous medium in the presence of weak acids (the soft template method)[196, 197, 235–238] or at the low concentrations of strong acids[205, 206] as well as at the high concentration of the reactants (aniline and persulfate) in the absence of acids.[153] The prerequisite for the formation of one-dimensional structures was that the reaction coordinate covered the pH range 4 > pH > 2.5 where only the accumulation of nucleates occurs and the phenazine-initiated growth reactions are inhibited.

4. Polymerization in mixed water–organic solvents[119, 216, 239, 240] and at the interface between the poorly miscible aqueous and organic phases, *i.e.*, the interface polymerization.[206, 207, 241, 242] Under these conditions, the protonation of amino structures is suppressed even in the presence of strong acids due to the lower permittivity of the mixed solvent as compared with water.[137] Hence, as in the previous case, the reaction falls in the range 4 > pH > 2.5 corresponding to the nucleate accumulation.

In all the cases, the low ionic strength of the solution favours the formation of one-dimensional structures (at the high ionic strength, phenazines are salted out from the solution);[216, 243, 244] the reduction of the polymerization temperature is also beneficial.[203, 240, 245] All the discussed conditions for the synthesis of one-dimensional structures ensure prolonged processes due to the long induction periods of polymerization. The effect of the synthesis conditions on the PANI morphology is described in several publications.[38, 169]

The only exception is the well-known synthesis of PANI fibres based on the addition of the following *para*-arylenediamines that mimic the PANI monomer unit: *p*-semidine[205, 246] and *p*-phenylenediamine.[126, 135, 216, 247] In this case, the formation of one-dimensional structures is accompanied by the shortening of the induction period rather than by its extension. The mechanism of this process is probably as follows. Aromatic diamines take part in the limiting step of the polymerization, *i.e.*, in the growth of the polymer chain. Their oxidation potential is lower than that of aniline and they are oxidized preferentially. Their reactions with the aniline molecule even in the dimerization step afford the phenazine nucleates capable of inducing growth of a regular conjugated chain. This leads to considerable reduction of the induction period (Scheme 3).

On the other hand, the formation of a great number of similar phenazine structures forces their regular assembly. In this case, the acceleration of polymerization is accompanied by the increase in the content of PANI nanofibres. It is significant that the addition of *ortho*-isomers of the same diamines affected neither the acceleration nor the morphology. In contrast, the addition of *meta*-isomers caused the sharp deceleration of polymerization due to the extension of the induction period. The latter was associated with the formation of 'defective' nucleates incapable of continuing the propagation of the conjugated chains.[38] After the exhaustion of *meta*-phenylenediamine due to its conversion to 'defective' oligomers, the polymerization of aniline is resumed.

2. Selected syntheses of miscellaneous supramolecular structures

Let us consider the peculiarities of the formation of different types of supramolecular structures by the example of syntheses described in Section IV. Recall that in all the cases, the polymerization was carried out at the high initial concentration of aniline (0.2 mol litre^{-1}) at 25 °C under the action of a strong oxidant (ammonium persulfate) with the oxidation potential of 2.01 V. All listed initial parameters remained unchanged from one experiment to another; the only parameter that changed was pH of the medium. Thus, the transformation of one morphological type to another could be followed as a function of a single factor, the reaction medium acidity.

a. Microspheres

When the oxidation was carried out in 0.2 M aqueous ammonia, PANI mainly consisted of spherical particles of

micron-scale sizes (see Fig. 5). The formation of microspheres is determined by the emulsion mechanism of polymerization of aniline. At pH 10, aniline is in the non-protonated form and hence poorly soluble. It exists as droplets in the reaction medium. Under the action of persulfate, the primary aniline oligomers partly sulfonated by a strong oxidizing agent are formed. Such molecules behaved as surfactants and could stabilize aniline droplets to form a microemulsion with sufficiently narrow particle size distribution. The oxidation proceeded mainly on the surfaces of droplets, they were covered with a layer of oligomers but could contain the non-consumed monomer in their internal region. In this way, hollow spheres are formed (see Fig. 10).

b. Two-dimensional structures

When the oxidation proceeded in acetic acid (the initial pH value is 4.5), the monomer is for the most part protonated and soluble. Oligomerization started under homogeneous conditions. At low oxidant concentrations (0.02 mol litre^{-1}), pH decreased only to 4 by the end of synthesis and the oxidation products represented shapeless micrometre-sized agglomerates (Fig. 14). These oligomers contained up to ten monomer units with the irregular structure. Upon precipitation, they formed shapeless agglomerates. At the same time, the tenfold increase in the oxidant concentration led to changes in the morphology of products synthesized in the same pH range ($3.5 < pH < 4.5$). The aniline polymerization products ([aniline] = 0.2 mol litre^{-1}) in 0.4 M acetic acid under the action of persulfate (0.25 mol litre^{-1}) isolated in the intermediate step of synthesis contained the planar two-dimensional structures rather than shapeless agglomerates (Fig. 15). Such morphology is explained by the intensification of oxidation processes. As a result, the content of phenazine fragments in oligomers, the oligomer length, the degree of uniformity of the molecules as well as their trend towards regular organization increased. Short oligomers with the high concentration of phenazine fragments formed two-dimensional structures.

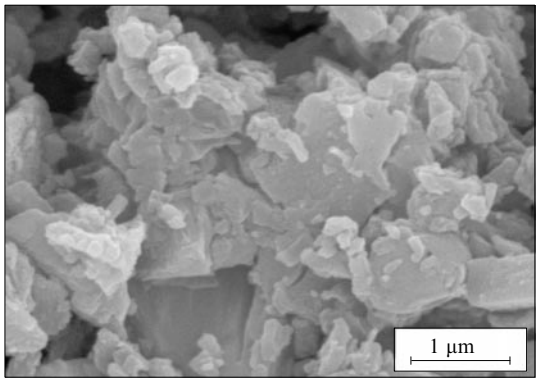


Figure 14. Amorphous agglomerates of aniline oligomers synthesized upon oxidation of aniline (0.2 mol litre^{-1}) under deficiency of ammonium persulfate (0.05 mol litre^{-1}) (our data).
Complete conversion at pH ~ 3.5.

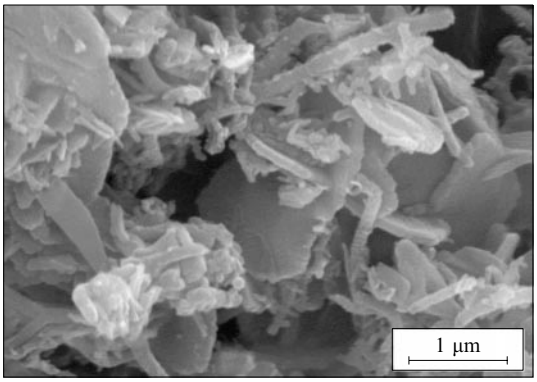


Figure 15. Oxidation products of aniline (0.2 mol litre^{-1}) with ammonium persulfate (0.25 mol litre^{-1}) isolated in the intermediate step of polymerization at pH ~3.5.[40]

c. One-dimensional structures

Nanofibres and nanotubes are formed among the polymerization products when the reaction started in a weakly acidic medium and then covers the pH range $2.5 < pH < 4$ (Ref. 84) (see Figs 7, 10). One-dimensional structures appear in the polymerization medium at $pH < 3$.[129] As pH drifts towards higher acidity, the one-dimensional fragments elongate and their diameter increases; the portion of one-dimensional structures in the polymerization products increases as well. We explain the presence of one-dimensional structures in the polymerization products by the fact that the reaction proceeds in a pH range where the chain propagation processes are hindered and similar phenazine nucleates are accumulated. The formation of phenazine columnar nucleates (see Fig. 13) is sufficient for the growth of a fibre. For a nanotube to form, the presence of an initial template that determines the internal diameter is necessary. Its role could be played by various nanosized objects.[248] However, most often the role of the template was played by PANI oligomers formed at pH ~ 3. It is most probable that these represented needle-shaped crystalline 'columns' of phenazine nucleates tens of nanometers in diameter formed in this period. It is shown [40] that no nanotubes formed if the PANI oligomers were removed from the polymerization medium at pH 3.

In the propagation step at $pH < 2.5$, the tube walls grew and the tube became longer.[129, 249] The one-dimensional structures grew like organic crystals.[250] It can be shown that in the propagation step, the elongation of fibres and tubes occurred as a result of formation of new phenazine nucleates directly at their ends. This process is energetically more favourable than the formation of new nucleation centres in the solution bulk.[38] For polymerization in acetic acid, the ratio of one-dimensional structures is higher than in water. This agreed with the duration of the period of phenazine nucleate accumulation, *i.e.*, this period is twice longer in acetic acid (see Fig. 2).

d. Globules

The polymerization that started at $pH < 2.5$ in the presence of a strong oxidant and high concentrations of reactants produced the globules of high-conducting high-molecular PANI (see Fig. 6). The induction period of polymerization in sulfuric acid is several times shorter as compared with acetic acid. The rapid growth of polymer chains from the phenazine nucleates is the main reason for the impossibility of their assembly into planar or one-dimensional primary structures so that random agglomeration prevailed. The globules had a sufficiently narrow size distribution. This is

associated with the fact that after the beginning of propagation, the oxidation potential of the system decreased. The supply of new nucleation centres that should proceed through a high-energy route is hindered. The radial sizes of globules are determined by the PANI chain length.

The results presented above demonstrate the effect of the pH factor on the morphology of oligomers and high-molecular-mass PANI. Under similar synthesis conditions, by varying only the reaction medium acidity, it is possible to obtain different types of supramolecular structures from three-dimensional globules and spheres to one-dimensional fibres and tubes. The type of supramolecular structures is determined by the size and the structure of aniline oligomers as well as by conditions of their assembly. These correlate with the presence and duration of the induction period. In alkaline and weakly acidic media, in the absence of the induction period, the oligomers of various structures containing 10–20 units formed and later assembled into either spheres growing on aniline droplets or amorphous agglomerates. For pH 2.5–4, in the induction period, the short cyclic oligomers formed. For a longer induction period where the chain growth from nucleates is hindered, the latter formed primary structures of one- and two-dimensional morphology. With the onset of the propagation step at pH 2.5, the formation of organized PANI structures began. At the same time, a short induction period typical of the low pH values and the rapid chain growth from phenazine nucleates leads to the formation of globules.

IX. Conclusion

Polyaniline is a multifunctional nanostructured material. It is often called the 'smart' polymer. The area of practical application of PANI and PANI-based composite materials steadily increases, including the rapidly developing field of nanotechnology. The latter field is associated with the development of methods for the controlled polymerization. Such methods of PANI synthesis aimed at the manufacture of materials with the desired properties and supramolecular structures may become the powerful tools for the preparation of new nanostructured materials and devices on their basis.

The main obstacle to the development of methods of controlled synthesis can be the insufficiently developed concepts of the mechanisms of the oxidative polymerization of aniline and self-assembly of its supramolecular structures. The mechanism shown in this review is an attempt to explain the whole body of so-far accumulated experimental data on the PANI synthesis from the unified standpoint. This concerned both the molecular processes of polymerization and also the self-assembling into different supramolecular structures, which accompanied the chain propagation. The factors that determine the formation of non-conducting oligomers with miscellaneous structures at low acidity and the propagation of regular *para*-coupled polymeric chains with the high conductivity under the conditions of high acidity were revealed. Based on the principles of molecular synthesis, a mechanism of self-assembly of polymer chains into one-, two- and three-dimensional structures is proposed. The acidity of the medium is considered to be the most important parameter of this synthesis that had the crucial effect on both the molecular and supramolecular polymer structures.

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