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Oxidative Polymerization of Aniline: Molecular Synthesis of Polyaniline and the Formation of Supramolecular Structures

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1. Introduction

The growing interest in nanostructured conducting polymers is caused by expanding area of their practical application. Conducting polymers can be used in new electronic devices (transistors, displays, sensors, energy-storage and memory cells), materials for shielding electromagnetic irradiation, polymer nanolithography, inhibition of corrosion, membrane constructing, catalysis and medicine. Miniaturization of devices, increasing their efficiency and lowering cost prices require development of new materials. The studies of polyaniline (PANI) and other conducting polymers (polyacetylene, polythiophene, polypyrrole, poly-*p*-(phenylenevinylene) have shown that they possess semiconducting properties. These polymers can exist in different oxidation states and, in common with inorganic semiconductors, respond to external influences by changing some characteristics (conductivity, color, density, magnetic properties, hydrophilicity or hydrophobicity, permeability to gases and liquids). Therefore, conducting polymers (which are sometimes called “smart polymers”) may serve as an alternative to inorganic semiconductors (Trivedi, 1997). In 2000, the scientists who have discovered and studied conducting polymers were awarded Nobel Prize in chemistry.

Due to its high stability and unique complex of properties, PANI was the first among conducting polymers to be used in practice as an antistatic coating, electrode material for batteries and condensers, as a corrosion inhibitor and detecting material for sensors. Polyaniline possesses controlled conductivity within the $10^{-10} - 10^1 \text{ S}\cdot\text{cm}^{-1}$ range combined with ionic and proton conductivity, redox activity, electro- and solvatochromism, non-linear optical properties and paramagnetism. In addition, the polymer is nontoxic, stable in aggressive chemical environments, has high thermal stability and low manufacturing cost.

PANI properties are determined by the regular structure of polymer chains. The polymer consists almost entirely of *para*-substituted monomer units coupled in the “head-to-tail” manner. The formation of organized supramolecular structures is also of great importance. Both these factors are responsible for the existence of elongated polyconjugated system and high conductivity of macroscopic sample (Skotheim & Reynolds, 2007).

A great number of publications are devoted to the synthesis and study of nanostructured PANI forms (Zhang & Wang, 2006; Stejskal et al. 2010; Wan, 2009; Tran et al. 2009). As a rule, nanostructured materials possess high homogeneity, unique surface properties and high charge carrier mobility. Due to the development of nanotechnology, organized supramolecular structures are considered, first of all, as materials for molecular electronics. Nanostructured forms of PANI show a striking diversity. The polymer chains can form one-dimensional structures (nanofibers, nanorods and nanotubes), planar two-dimensional objects (e.g., the so-called, ribbons, nanobelts and nanoplates) and three-dimensional particles (microspheres, nanospheres and granules). These main architectural elements may serve as a base for more complicated hierarchical formations such as flowers, urchins, branches, corals, “micromats”, complex geometric figures.

Polyaniline is synthesized by oxidative polymerization of aniline (Higashimura & Kobayashi, 2004). All the above-listed supramolecular structures are also formed in the process of oxidative polymerization. PANI synthesis includes two interrelated processes. In the course of polymerization, monomer undergoes a chain reaction with the formation of regular macromolecules, and growing chains are simultaneously organized into complex supramolecular structures. As a result, conducting polymer containing stable supramolecular structures with various morphologies is formed. Most of these structures cannot be dissolved or melted without destruction of polymer chains and changing properties of the polymer. Therefore, synthesis is the only unique instrument allowing us to control structure of polymer chains and obtain nanostructured forms of the conducting polymer and its composites with other materials. In this connection, it is very important to develop methods of controlled synthesis of PANI giving polymers with predetermined properties and supramolecular structure. Experimentalists should have the capability of making deliberate choice of aniline polymerization parameters based on understanding the molecular mechanism of chain assembly and self-organization.

The present publication is devoted to developing concepts of mechanism of PANI synthesis and ways of formation of supramolecular structures. The authors attempt to answer the following fundamental questions:

- What is responsible for regular assembly of PANI chains during oxidative polymerization of aniline?
- Which synthesis parameters and why have the most pronounced influence on properties and morphology of polymerization products?
- In which manner is the assembly of all the types of PANI supramolecular structures realized and how does this process correlate with molecular stages of the synthesis?

- What are the experimental conditions for obtaining the main types of supramolecular structures: one-, two- and three-dimensional ones?
- How are supramolecular PANI particles organized and in which manner is the macroscopic structure of conducting polymer (possessing the properties of disorganized metal) formed?

First we should give a brief description of conducting PANI, structure of polymer chains, forms and properties of the polymer.

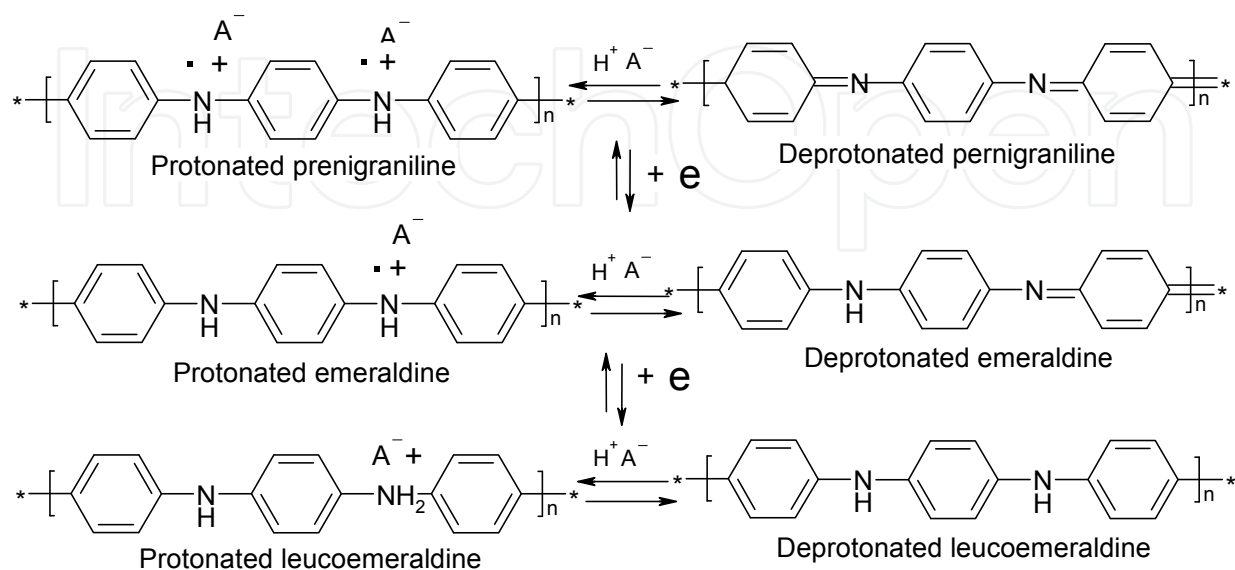
2. Polyaniline: Structure, forms and their properties

The chains of conducting PANI have ordered structure; they contain regularly alternating phenyl rings and nitrogen-containing groups. This structure provides for polyconjugation: polymer chain forms a zigzag lying in one plane, and π -electron clouds overlap above and below this plane. The lone electron pair of nitrogen performs the same function as π -electrons and assures polyconjugation. Polyconjugated system is a transport path providing charge carrier mobility. It is formed as a result of strictly regular assembly of monomer units. The chain of conducting PANI contains more than 95% of *para*-substituted aniline fragments linked in a "head-to-tail" configuration (Hagiwara et al. 1987). Defects in this regular structure arising during copolymerization of aniline with other monomers or after introduction of aniline units with another configuration (*ortho*- or *meta*-substituted fragments) lead to dramatic decrease in conductivity.

Charge carriers are formed in polymer during its oxidation. Nitrogen atoms of PANI serve as oxidation centers. During oxidation, i.e., removal of electron, positive polaron is generated in the chain; it deforms chain structure considerably. Content of oxidized nitrogen atoms in the polymer can change from zero (in its reduced form, leucoemeraldine) to nearly one (in the fully oxidized state, pernigraniline), see Scheme 1. The most stable form of PANI is emeraldine, in which every second nitrogen atom is oxidized, and polymer chain contains equal number of oxidized and reduced units. In the absence of external potential, the fully reduced and fully oxidized forms of the polymer simultaneously transform into this oxidation state. In the case of leucoemeraldine, the transformation into emeraldine takes place at the expense of slow oxidation of amino groups by air oxygen. This reaction is reversible. Pernigraniline also tends to lower its oxidation state and turn into emeraldine. When the degree of oxidation of PANI exceeds 0.7, the polymer becomes unstable, and irreversible transformations of macromolecules begin. Crosslinking and intrachain oxidative cyclization are the most common processes. Destruction of chains and formation of quinones accelerated in the presence of electron donor agents are also possible.

In all the conducting polymers, charge carriers are formed under the action of oxidizing or reducing agent. Charge carriers are located in the main chain and compensated by counterions. Removal of counterion results in changes in the oxidation state of polymer and disappearance of polaron. PANI demonstrates a special feature: removal of counterion does not necessary changes oxidation state of polymer chain. After withdrawal of counterion, the

benzene ring adjacent to nitrogen atom “accepts” a fraction of positive charge. With that, benzoid structure is transformed into quinoid one, the ring leaves polyconjugation plane, and, therefore, conductivity of the chain is disturbed. Although the oxidation state remains unchanged, PANI loses its conductivity due to decrease in polyconjugation chain length.



Scheme 1. Polyaniiline forms

The best charge stabilizing agents for PANI are strong acids. Acids are sometimes called “doping agents”, because they “introduce” charge carriers into polymer chain and impart conductivity to the polymer. However, this term is not correct, since acid molecule does not create positive polaron, and only stabilizes the polaron generated during oxidation. Another term, “protonation”, does not adequately describe interaction between PANI and acid either. It was introduced from ammonia and amine chemistry. Protonation of amines by acids means binding a non-oxidized nitrogen atom with proton, with the formed ammonium cation being stabilized by acid anion. The interaction between acid and oxidized nitrogen atom differs from that between acid and neutral nitrogen. As was shown, PANI polarons are stabilized rather by acid anion than by proton. At the same time, proton remains relatively free (Colomban & Tomkinson, 1997), thus providing high proton conductivity of PANI (which is absent in ammonia salts and protonated amines). However, in this paper we will use the common term “protonation” to describe interaction between acids and nitrogen-containing polymer structures.

Among conducting polymers, PANI possesses the greatest number of revealed and characterized forms with different properties (Skotheim & Reynolds, 2007). Due to interaction with acids, each of three protonated states has a corresponding deprotonated form with low conductivity. Thus, polymer can exist in a minimum of six forms differing in both degree of oxidation and protonation state (Scheme 1). PANI is a unique polymer, since its conducting forms (emeraldine and pernigraniline) can be transformed into non-conducting states in two different ways. The first approach consists in introducing electrons into PANI and reduction of nitrogen atoms; the second method is removal of polaron-

stabilizing acid which leads to transformation of polymer chain structure and disappearance of polyconjugation. In other words, we can destroy charge carriers or their “paths”. In both cases, polymer conductivity decreases by eight or ten orders of magnitude.

Conductivity, optical, magnetic and other properties of PANI may change depending on its oxidation state and degree of protonation. The reduced polymer which does not contain charge carriers possesses a conductivity of $10^{-8} - 10^{-10} \text{ S}\cdot\text{cm}^{-1}$; it is weakly colored and diamagnetic. As oxidation of protonated PANI proceeds within the potential window of 0 to +1 V (*versus* the reference hydrogen electrode (RHE)), concentration of polarons in the polymer increases. At the same time, electrical and ionic conductivity, intensity of its absorption bands in the visible and near IR regions also increase, and the polymer becomes paramagnetic. The highest electric conductivity is inherent to the most stable PANI form – emeraldine. Under usual conditions in solid state, emeraldine has an electronic conductivity of 10^0 to $10^1 \text{ S}\cdot\text{cm}^{-1}$. However, samples with conductivity of the order of $10^2 \text{ S}\cdot\text{cm}^{-1}$ were obtained. The charge carrier mobility in the highly conductive emeraldine ranges from 10^{-3} to $10^{-1} \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ (Harima et al., 2001). Protonated emeraldine also possesses the highest proton conductivity (up to $10^{-2} \text{ S}\cdot\text{cm}^{-1}$). Thus, oxidized and protonated PANI demonstrates a mixed electron and proton conductivity (Colomban & Tomkinson, 1997). When the degree of oxidation exceeds a certain optimum value, PANI conductivity lowers. Conductivity of protonated pernigraniline is less than $10^{-2} \text{ S}\cdot\text{cm}^{-1}$. The absorption band of polaron in pernigraniline form is shifted to shorter wavelength as compared with that of emeraldine, indicating considerably higher localization of polaron.

Deprotonation of PANI is performed by neutralization of acid with the aid of base. Acid molecules are bound with PANI main chain at the expense of reversible ionic interactions. While protonation-deprotonation cycles continue, the acid is alternately absorbed and expelled from the polymer matrix until the new equilibrium between changed medium and modified polymer is established. Deprotonation may lower emeraldine conductivity by 10 orders of magnitude. Polymer becomes dielectric, its paramagnetism and density decrease, polaron absorption band becomes less intense and shifts to the short-wavelength region. Since these changes are reversible, reprotonation (i.e., PANI-acid interaction following deprotonation) leads to recovery of conductivity and attendant properties of the polymer (Skotheim & Reynolds, 2007).

3. Oxidative polymerization

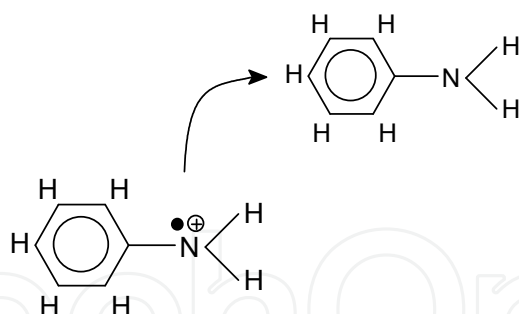
In a vast majority of cases, PANI is synthesized by oxidative polymerization of aniline. Other methods, e.g., polycondensation of aniline derivatives with reactive functional groups ($\text{Y-An-X} = (-\text{An})_n + \text{XY}$), are used very seldom. Oxidative polymerization is used for the synthesis of polymeric (oligomeric) products from various classes of monomers (aromatic amines, phenols, thiophenols, aromatic hydrocarbons and heterocycles (Higashimura & Kobayashi, 2004)). The monomers used in oxidative polymerization are characterized by pronounced electron donor properties and high oxidation tendency. These properties, in particular, are inherent to aromatic amines, phenols and thiophenols or sulphur- and

nitrogen-containing heterocycles due to the presence of electron donor substituent in benzene or heterocyclic ring. Oxidation of monomer takes place under the action of inorganic (or organic) oxidizing agent or the applied potential. During this process, cation or cation radical sites are generated in monomer (polymer) molecule, thus initiating polymer growth.

Technically, oxidative polymerization may be considered as formation of covalent bond between monomer molecules at the expense of abstracting two protons. There are many types of linkage between monomer units. For example, in the case of aniline, "head-to-head", "tail-to-tail" and "head-to-tail" configurations are possible. In addition, in the last two cases chain assembly may occur due to substitution in phenyl ring with the formation of *ortho*-, *para*- and *meta*- monomer units. Thus, oxidative polymerization yields chains with a wide variety of monomer unit structures.

3.1. The chain mechanism of aniline polymerization

Oxidative polymerization is often considered as a kind of polycondensation, since chain growth is accompanied by the formation of low-molecular products. However, it is not always true. The formation of chain may proceed in two ways. The first one is recombination of cation radical oxidation sites. In this case, polymer growth process is classed as polycondensation, since fragments of any length may recombine. The second way of chain growth belongs to electrophilic substitution; in the case of aniline, oxidized nitrogen-containing structure attacks phenyl ring of another aniline molecule and substitutes one proton of the ring.



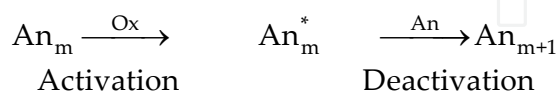
Scheme 2. Electrophilic substitution reaction

Both the ring and nitrogen-containing structure lose one proton; after that, monomer units bind with each other, and the chain becomes longer.

In the case of electrophilic substitution, both variants (polycondensation and chain-growth processes) are possible. To determine the type of addition, we should measure molecular mass of the polymer throughout the reaction. In the course of polycondensation, fragments with any molecular mass can react with each other; therefore, average molecular mass of the product increases slowly, monomer is rapidly transformed into low molecular weight oligomers coexisting with the high molecular weight fraction up to high conversion. Different molecular weight distribution is observed during chain-growth processes. In the

course of chain-growth polymerization, monomer units are sequentially added to the polymer chain bearing active end group. Here, during oxidation monomer coexists with high molecular weight fraction of the product, and the content of low molecular weight oligomers is minimal. Oxidative polymerization of several monomers containing heteroatoms (including aniline) was found to proceed according to the chain-growth mechanism.

Y. Wei (Wei, 2001) singled out the polymerization of aniline into a special type of reactivation chain process. The chain growth involves repeated acts of activation/deactivation of the polymeric structure:



The dormant polymer chain (An_m) is activated by an oxidant (to form An_m^*), then it adds aniline molecule to yield a new dormant chain of higher molecular mass (An_{m+1}). In contrast with other types of chain-growth polymerization (e.g., radical process, where oxidant takes part only in the formation of initial radical), oxidative polymerization requires large amounts of oxidizing agent. Here, oxidant is spent in every step of monomer addition, and molar concentration of oxidant should be comparable with monomer concentration. Oxidant “works” throughout the polymerization and takes part in redox interactions until the last monomer molecule is added to polymer chain.

3.2. Chain growth according to electrophilic substitution mechanism

The process occurring during the formation of polyconjugated PANI chains belongs to electrophilic substitution reactions, since the attacking species is oxidized and acts as an electrophilic agent. Let us consider the most probable structure of monomer unit during electrophilic substitution process. Due to the presence of electron donor (heteroatom) in the monomer, this heteroatom will most likely be oxidized, and monomer units will be linked in the “head-to-tail” fashion. However, even when this type of linkage is repeated, PANI structure may be heterogeneous. Monomer units with *ortho*-, *para*- and *meta*-structure may be formed as a result of attacks of the electrophilic agent directed to different atoms of phenyl ring. Contents of different types of units in the polymer should vary. The probability of the formation of *meta*-structures is low, since aniline possesses electron donor substituent in its phenyl ring. Donor substituent creates excess negative charge on *ortho*- and *para*- carbon atoms of phenyl ring, and electrophilic attack is thus directed to *ortho*- and *para*-atoms. Therefore, according to the existing theory of organic reactions, in the case of aniline oxidation, the most probable monomer structures are *ortho*- and *para*-units linked in the “head-to-tail” fashion. The *ortho*-units should prevail, since phenyl ring contains two vacant *ortho*-positions (Cram & Hammond, 1964). The probability of the formation of other structures also exists, and we should expect the formation of irregular PANI chains.

Thus, from general theoretical considerations, the formation of regular PANI structure containing only *para*-substituted monomer units linked in the “head-to-tail” mode cannot be explained.

3.3. The active site of polymerization

The question of the nature of the terminal active group (active site) responsible for the polymerization of aniline was disputed for a long time (Percec V and Hill, 1996). This was assumed to be nitrenium cation or radical cation. 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) inhibit the polymerization by acting as scavengers of radical cations. At the same time, PANI is readily formed in the presence of electron-enriched arenes (1,3- and 1,4-dimethoxybenzene) well known as “traps” of nitrenium cations. This fact proves that oxidation of aniline proceeds via a radical cation site (Ding at al., 1999).

The activated terminal group of the chain is generated by an 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 are oxidized because they have lower oxidation potential. In the course of polymerization, the polymer chain performs the function of a mediator in the oxidation of monomer. It oscillates between the highest and intermediate oxidation states, i.e., pernigraniline and emeraldine. The active site formed at the end of the chain attacks the monomer molecule. This attack is directed at a hydrogen atom in the aromatic ring and results in replacing hydrogen by a polymeric fragment. The chain propagates due to the addition of new monomer units.

3.4. Oxidizing agents

Polymerization of aniline and synthesis of its conducting polymer may be performed by electrochemical or chemical methods. During electrochemical synthesis of PANI, electrode potential is increased (if only once) so that it exceeds +1.05 V (RHE) (Yang et al. 2007). A wide range of oxidants is used in the chemical synthesis of PANI. As a rule, compounds with high oxidation potentials exceeding +1.0 V (persulfates, dichromates, cerium (IV) salts, aurates etc.) are employed. This is associated with the fact that the onset of the propagation of the polymer chains in acidic media requires overcoming energy barrier corresponding to an oxidation potential of +1.05 V. Once the propagation starts, the oxidation potential of the reaction decreases. In the chemical synthesis of polyaniline, persulfates (having an oxidation potential of +2.01 V) are used most widely. However, experiments showed that aniline is also oxidized under the action of weak oxidants with a potential close to +1 V or even lower (Sapurina & Stejskal, 2012). Such agents can oxidize aniline not only in basic and neutral media, but also, strange as it may seem, in acidic media where potential barrier of oxidation is high. However, the use of weak oxidants causes some problems because it does not necessary lead to the formation of conducting products.

3.5. Kinetic features of polymerization

Studies of aniline polymerization in acidic aqueous media (where conducting PANI is formed) have shown that the oxidation of monomer proceeds non-monotonically. It starts with a slow process ("induction period"); during this period, aniline oligomers are formed. The induction period is followed by the rapid exothermic step of polymer chain propagation. The following kinetic dependences were suggested for description of this two-step process (Tzou & Gregory, 1992):

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

where

[An] is the molar concentration of aniline;

[Ox] is the molar concentration of the oxidant;

P is the surface of the reaction medium interface;

σ is the surface factor;

k_1 is the rate constant for the initial step (induction period) of polymerization;

k_2 is the rate constant for the polymer chain propagation.

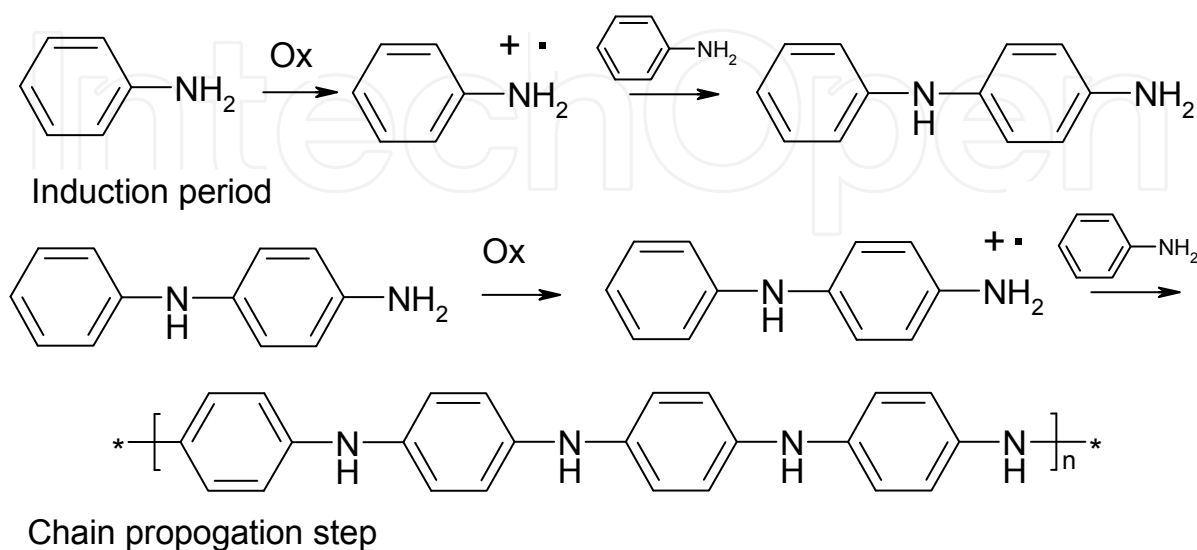
Both the first and, presumably, the second steps are first-order reactions with respect to monomer. For the initial step, the reaction order with respect to the oxidant is also the first one. In the propagation step, monomer is oxidized with pernigraniline form of PANI rather than with the original oxidant. Polyaniline is insoluble, and the reaction is heterogeneous; hence, the P parameter and the σ factor are introduced into the equation in order to characterize the interface on which the reaction proceeds. The rate constant for the chain propagation (k_2) is 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 leads to impressive acceleration of oxidative polymerization. Similar acceleration was also observed upon the introduction of PANI "seeds" into the reaction medium. This process is called "autoacceleration" (Tzou & Gregory, 1992).

Polymerization rate is sensitive to the presence of different inert and insoluble materials in the reaction medium, for example, alumina oxide, silica gel, carbon, cellulose, synthetic polymers, etc. (Stejskal & Sapurina, 2005). This effect is stronger for materials with greater surface areas (P). The strong effect of the medium acidity exerted on the polymerization rate was revealed. This dependence is complex in nature and varies with the pH range. Under conditions of high acidity (for $\text{pH} < 1$), direct proportionality between molar concentration of the strong acid and k_2 was observed. At the same time, the increased acidity has a little effect on the rate constant of the initial step; however, the induction period shortens substantially with decreasing pH.

3.6. Modern concepts of the mechanism of aniline polymerization

Presently, electrochemical and chemical synthesis of conducting PANI by oxidative polymerization is usually described by the following scheme (Scheme 3) (Wei et al., 1989). It

involves: 1) oxidation of nitrogen atom of monomer followed by oxidation of end nitrogen atom of oligomer and polymer; 2) addition of monomer in the “nitrogen-carbon” fashion as a result of chain reaction (electrophilic substitution of proton in aromatic ring of monomer by oxidized polymer fragment).



Scheme 3. Aniline oxidative polymerization

Presumably, in the induction period, aniline radical cations are formed; this process is followed by their recombination (according to the electrophilic substitution mechanism) to afford a dimer, namely, N-phenylphenylene-1,4-diamine (*p*-semidine). The subsequent propagation step is assumed to be similar to the electrophilic substitution process where the oxidized terminal amino group of oligomer (polymer) attacks *para*-position in monomer. It is assumed that the reaction involves monomer in its most reactive deprotonated form. The oxidation rate-limiting step is considered to be either the formation of aniline radical cations or their dimerization. The experimental observation that the introduction of small amounts of the aniline dimer (*p*-semidine) sharply accelerates polymerization can be considered as a substantiation of the proposed mechanism. The rationale is that the introduction of *p*-semidine (intermediate formed in the initial limiting step) eliminates this limiting process so that the polymerization begins with the rapid step of chain propagation.

The presented scheme of PANI synthesis is practically similar to the general mechanism of oxidative polymerization suggested in the 1950s for phenol polymerization and, subsequently, for a vast majority of monomers (Higashimura & Kobayashi, 2004). However, PANI synthesis seems anomalous compared with reactions of synthesis of dielectric polymers. Polyphenyleneoxides obtained by oxidation of phenols in aqueous basic or organic media are comparatively low molecular weight products with molecular masses of 20 000 - 30 000. The structure of polyphenyleneoxide monomer units is heterogeneous. The polymer contains units linked in a “tail-to-tail”, “head-to-head”, “head-to-tail” fashion; both *ortho*- and *para*-substituted aromatic rings are present. Polyphenyleneoxides with “head-to-tail” chains and high content of *para*-substituted monomer units possess better mechanical

properties, higher degree of crystallinity and chemical stability than irregular polymers. To increase degree of homogeneity of polymer structure, oxidative polymerization of phenol should be carried out under special conditions: 1) use of "soft" organic oxidants (peroxidases or laccase in combination with peroxides or oxygen); 2) use of monomers with blocked *ortho*-positions (2,6-dialkylsubstituted phenols); 3) low concentrations of reactants and low temperatures. Only in this case it is possible to obtain more regular polyphenylene oxide containing a large amount of *para*-substituted units. However, polymers with high molecular weight still cannot be synthesized (Higashimura & Kobayashi, 2004).

By contrast, oxidative polymerization of aniline in acidic medium yields polymers with strictly regular structure. The studies of molecular structure of PANI chains by Raman, ESR, electron and X-ray photoelectron spectroscopy, chromatography and chemical analysis have shown that the polymer contains 95-98% of *para*-substituted monomer units linked in the "head-to-tail" fashion (Trivedi, 1997). Polyaniline contains only a small amount of "foreign" units (phenazine rings). The appearance of these rings is explained by chain branching and intermolecular crosslinking occurring during synthesis or after termination (do Nascimento, 2006). It is surprising that the synthesis of this highly regular polymer can be initiated by a wide range of oxidizing agents (from persulfates possessing high oxidation potential of +2.01 V to iron (III) with a potential of + 0.7 V). There is no need to use aniline with blocked *ortho*-positions. Moreover, polymerization occurs at a high rate; and neither high concentrations of reactants nor high temperatures lead to the formation of irregular chains. The high selectivity of oxidative polymerization of two other heterocyclic monomers (thiophene and pyrrole) should be noted; their polymers (polythiophene and polypyrrole) are also conductive. The peculiar features of synthesis of these polymers have much in common with PANI synthesis.

However, within the framework of the existing concepts of oxidative polymerization of aniline (Scheme 3), we cannot explain several important features of PANI synthesis.

1. It is unclear why oxidative polymerization of aniline is highly selective, and only *para*-structure of monomer unit is repeated during chain propagation.
2. No explanation is given for the non-monotonic course of oxidation and the great difference between rate constants of the first and second steps, although the scheme represents them as reactions of the same type leading to the formation of similar structures.
3. The scheme fails to explain the following changes in the oxidation potential in the course of polymerization: its increase up to +1.05 V followed by its drop down to +0.7 V - 0.8 V in the chain propagation step.
4. The pH of reaction medium having a great influence on polymerization is not taken into account.
5. The scheme does not explain "autoacceleration", i.e., heterogeneous process of chain growth, and influence of different types of surfaces on polymerization kinetics.

As a rule, in discussion of oxidative polymerization of aniline, it is stated that the existing concepts are controversial, and molecular mechanism of the process is still unclear. In what follows the authors will attempt to explain anomalies of aniline polymerization and, in the first place, the reasons for high selectivity of this process in acidic medium.

4. Influence of pH on aniline polymerization, properties of products and their supramolecular structure

Oxidative polymerization of aniline can occur within a very wide interval of acidity (from 1M base solution to 2M sulfuric acid solution), i.e. in the pH range 14 to -1. However, it is known from the experiment that oxidation products formed in different pH intervals possess radically different properties. Polymerization in basic, neutral and weakly acidic media gives brown powder with low conductivity. The synthesis in highly acidic medium yields highly conductive PANI, since only under these conditions conducting dark-green emeraldine can be obtained. Depending on pH of reaction media, the conductivity of protonated products of aniline oxidation may vary from 10^{-10} to 10^2 S·cm⁻¹. Cyclic voltammograms may contain from one to four pairs of waves; optical and magnetic properties of material may also vary. Oxidation products either dissolve in different organic solvents or are insoluble at all. However, all these materials obtained by aniline oxidation and demonstrating various properties are called "polyaniline". This general name creates considerable difficulties during comparison of experimental results, particularly, in discussion of PANI applications (Stejskal et al. 2010).

The composition and structure of non-conducting materials obtained at high pH are little studied. However, they have many potential applications in development of membranes for gas separation and pervaporation, as antioxidants, in catalysis, sensor devices and treatment of heavy metal-contaminated runoff water. In addition, some products synthesized in neutral and weakly acidic media demonstrate very complex and interesting supramolecular structure, and are of great scientific interest (Stejskal & Trchova 2012).

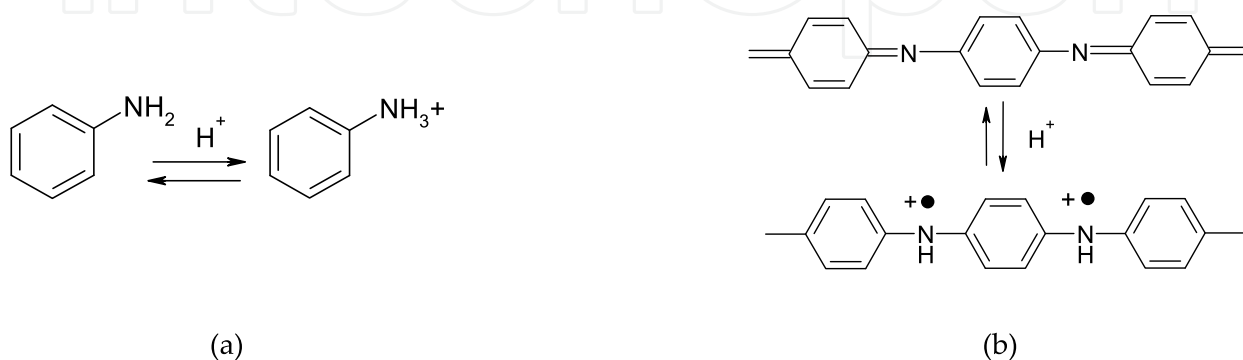
Let us consider the effect of pH on aniline polymerization, properties of products and their supramolecular structure.

4.1. Acid-base properties of aniline and poly (oligo) aniline

Aniline, its oligomers and polymers are organic bases taking part in acid-base equilibria, and their properties depend on pH. They include different types of nitrogen-containing structures which are protonated at different pH values. Aniline is the strongest base. At low ionic strength, i.e., at low concentrations of aniline in distilled water, the protonation constant of aniline takes on a value of ~ 4.6 (Lide & Frederikse, 1995). Increasing ionic strength in the presence of electrolytes leads to equilibrium shifts towards lower pK values. Thus, in solutions of salts with concentrations of 0.1 - 0.9 mol·L⁻¹, protonation constant of aniline takes on a value of ~ 3.5 . According to these data, at pH>3.5 aniline exists mainly as a neutral molecule, and at pH<3.5 it is protonated and acquires positive charge.

Polymeric (oligomeric) PANI chains include two types of nitrogen-containing structures: disubstituted amino groups (where nitrogen atom is not oxidized) and imino groups with oxidized nitrogen. Disubstituted amino groups can be protonated only at very low pH which are not used in the synthesis. As a rule, leucoemeraldine consisting of amino groups is not protonated. PANI in higher oxidation states contains imino groups which are

protonated at higher pH values. However, protonation constant of imino group depends on the content of these groups in polymer. With increasing concentration of ionogenic groups, polymer basicity decreases. While imino groups of emeraldine can be protonated by acids of medium strength, during oxidation and increasing number of imino groups, multiple interactions between positive charges within the chain arise, and the protonation ability of imino groups decreases. In contrast with emeraldine ($pK=3-4$), pernigraniline is protonated at $pH < 2.5$ (Trivedi, 1997). In the course of protonation of imino groups, PANI is transferred into protonated emeraldine or protonated pernigraniline form. As a result, the whole polymer chain becomes covered with a net of positive charges and turns into polycation.



Scheme 4. Protonation of aniline a) and polyaniline chain b)

It should be taken into account that oxidation potentials and, therefore, reactivity of neutral and protonated molecules differ considerably. Deprotonated nitrogen-containing structures have low oxidation potential and oxidize readily. Neutral, uncharged aniline molecule easily gives away electron and can be oxidized even at +0.3 V. Protonation results in the appearance of excess positive charge on nitrogen atom that hinders oxidation. Consequently, oxidation potential of nitrogen-containing structure increases up to more than +1.0 V (Li et al., 2002).

It should be also kept in mind that in the course of oxidation protons are released, and pH is being constantly lowered. The rate of pH change depends on many factors: the presence of alkali, acids or buffering agents in the reaction medium, intensity of oxidation processes, conversion degree etc. For example, in water for the initial aniline and persulfate concentrations of 0.4 and 0.8 mol·L⁻¹, respectively, and upon the complete monomer-to-polymer conversion, pH of reaction medium varies from 9 to 1, i.e., the reaction that has started in an alkaline medium ends under the conditions of acid-promoted polymerization (Stejskal et al. 2010).

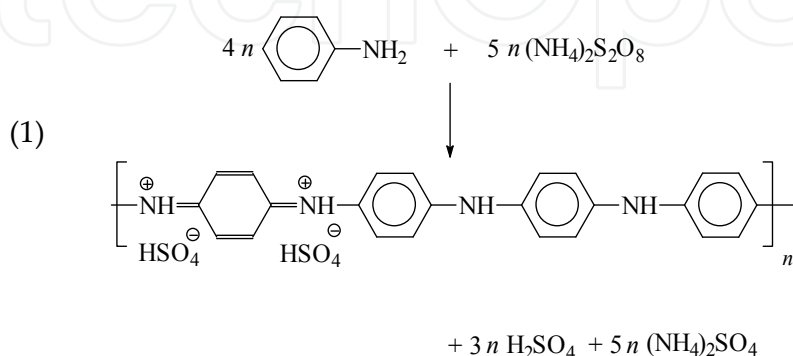
Thus, the oxidative polymerization of aniline is a complex dynamic process accompanied by permanent changes in synthesis conditions. What is important is the pH value at which the process begins, and the nitrogen-containing groups (either protonated or non-protonated) that are involved. However, of no less importance is how quickly the pH drifts and at which pH values the polymerization comes to an end. The reaction often covers the pH ranges where nitrogen-containing fragments in different degrees of protonation dominate. As will be shown later, the transition from one pH region to another can be accompanied by some

changes in kinetic parameters of the process. This can result in changing molecular structure of chains and, hence, varying properties of products, and also lead to transformations in PANI supramolecular structure. Now we will illustrate these points by aniline polymerization processes occurring in media with different pH (Konyushenko et al. 2010; Sapurina & Stejskal, 2010)

4.2. The influence of pH on aniline polymerization carried out under the action of strong oxidizing agents

In this section, two series of experiments are discussed demonstrating kinetics of aniline oxidation within various pH intervals. Acidity of reaction medium and temperature of polymerization mixture were monitored in the course of the synthesis. Every elementary reaction of monomer unit addition in the process of electrophilic substitution is accompanied by release of two protons; therefore, change of pH throughout the synthesis can serve as an objective characteristic of the process. Oxidation of aniline is an exothermic process and can easily be followed by temperature changes. The temperature dependence provides information on the intensity of 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 in the *in situ* analysis of oxidation with the use of spectral and potentiometric methods, as well as the data 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 persulfate), which has an oxidation potential of 2.01 V and is capable of oxidizing all intermediates of PANI synthesis. The reaction shown by Scheme 5 proceeded under ambient conditions. It was initiated by instantaneous mixing of 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.



Scheme 5. Oxidation of aniline with ammonium persulfate.

4.2.1. Oxidation of aniline at different initial pH values

In the first series of experiments, oxidative polymerization of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) was carried out using the stoichiometric amount of ammonium persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$), 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 ($\text{pH}=10$); 2) in water ($\text{pH}=6$); 3) in 0.4 M acetic acid ($\text{pH}=4.5$), 4) in 0.2 M sulfuric acid ($\text{pH}=2$). The results of monitoring of temperature and pH are shown in Fig. 1 a,b.

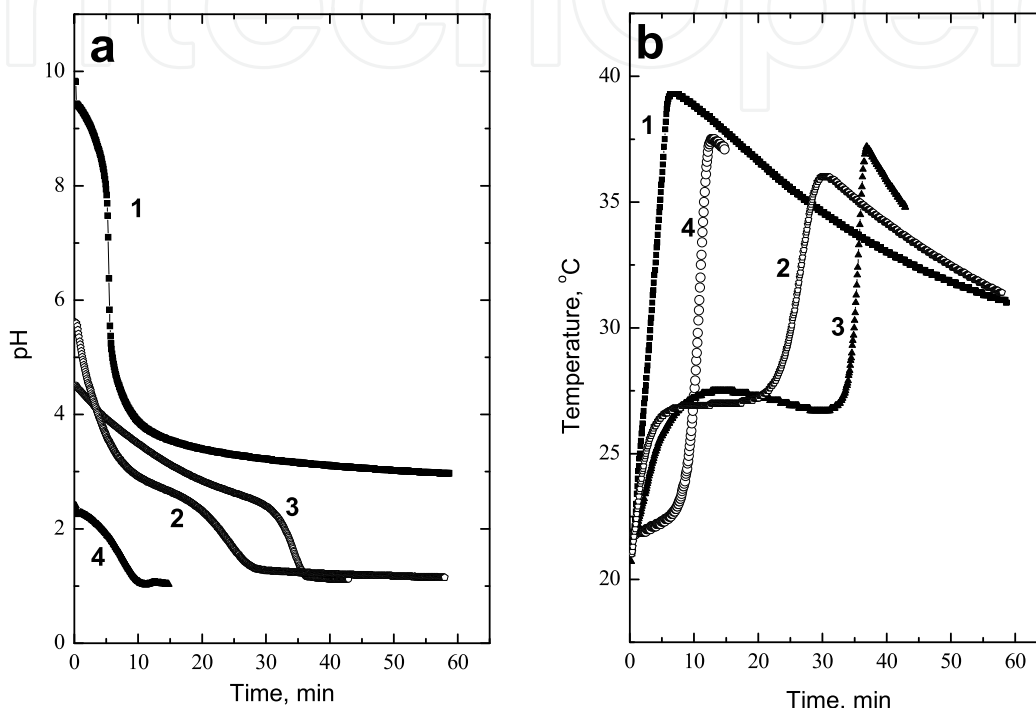


Figure 1. Changes in the temperature (a) and pH (b) of the medium in the course of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) oxidation initiated by ammonium persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$) at different initial acidities; (1) in 0.2 M $\text{NH}_3\cdot\text{H}_2\text{O}$; (2) in water; (3) in 0.4 M acetic acid; (4) in 0.1 M H_2SO_4 .

It is evident that both parameters change synchronously. The decrease in pH corresponds to the exothermic steps: the sharper increase in temperature corresponds to the more pronounced decrease in pH. This also suggests that thermal effects are due to the processes of oxidation and proton liberation

The general features of aniline oxidation processes can be formulated as follows.

1. The initial rate of aniline oxidation increases with increase in the initial pH of the medium. It can be seen from slopes of temperature and pH dependences in the initial stage. With increasing acidity, initial oxidation rate decreases. In sulfuric acid ($\text{pH}=2$), it is close to zero (the so-called "oxidation induction period").
2. The oxidation processes in which the pH dependence does not pass through $\text{pH}\sim 2.5$ are characterized by a single temperature wave of oxidation. These processes include the oxidation in ammonia, which begins at $\text{pH}=10$ and ends at $\text{pH}>3$, and the reaction in sulfuric acid, which proceeds at $\text{pH}<2.2$.

3. The oxidation processes that occur in the pH region including pH~2.5 have two temperature waves. These processes include the reactions in water and acetic acid, which start at pH=6 and pH=4.5, respectively, and end at pH=1.
4. The first oxidation wave falls in the range with pH>3 and resembles the monotonic process of oxidation of aniline in ammonia. The range 2.5<pH<3.5 is characterized by the abrupt deceleration of the oxidation processes. However, with the attainment of pH 2.5, the exothermic reaction regains its vigor, and oxidative polymerization is concluded by the second temperature wave. The character of pH variations in the second wave is identical to that typical of polymerization in sulfuric acid.
5. The pH decrease in water proceeds much faster than in acetic acid because this weak acid serves as a buffer and binds protons released in the course of polymerization.

4.2.2. Oxidation of aniline at different monomer: oxidant ratios

In the second series of experiments, oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) was carried out in 0.4 M acetic acid at different [Ox] : [An] molar ratios. The ammonium persulfate concentration was varied from 0.25 (stoichiometric amount) to $0.025 \text{ mol}\cdot\text{L}^{-1}$ (Fig.2). At low concentrations of oxidant, monomer is not completely oxidized. In all the experiments, polymerization started at pH=4.5 and continued up to the complete consumption of the oxidant. Figure 2 shows the temperature and pH dependences obtained in this series of experiments. It is evident that the higher the oxidant concentration, the lower the final pH; this fact is associated with the more complete monomer-to-polymer conversion and, correspondingly, the presence of a larger amount of liberated protons.

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 well as in the case of oxidation of aniline in ammonia, the reaction proceeds monotonically and the single temperature wave is observed. For high [Ox] : [An] ratios (0.75, 1.0, 1.25), the final pH of the medium is less than 2.5. Moreover, the processes demonstrate two temperature oxidation waves. As well as in the first series, in the range 2.5<pH<3, the reaction proceeds extremely slowly. The second exothermic wave begins once the reaction medium pH reaches 2.5.

As follows from the data presented, irrespective of which reaction parameter was varied (initial pH of the medium or the [Ox] : [An] ratio), the processes have similar character if proceed 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 are realized in the pH ranges above and below this point.

4.3. Properties and morphology of products of aniline oxidation

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<pH<10), the oxidation products are aniline oligomers with a weight-average molecular mass (M_w) of 4000 and polydispersity (M_w/M_n) of 1.3. Conductivity of the material in the completely

protonated state does not exceed $10^{-10} \text{ S}\cdot\text{cm}^{-1}$. The electronic spectrum of oligomers (Fig. 3) contains 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 diameters ranging from 500 nm to 2 μm (Fig. 4a).

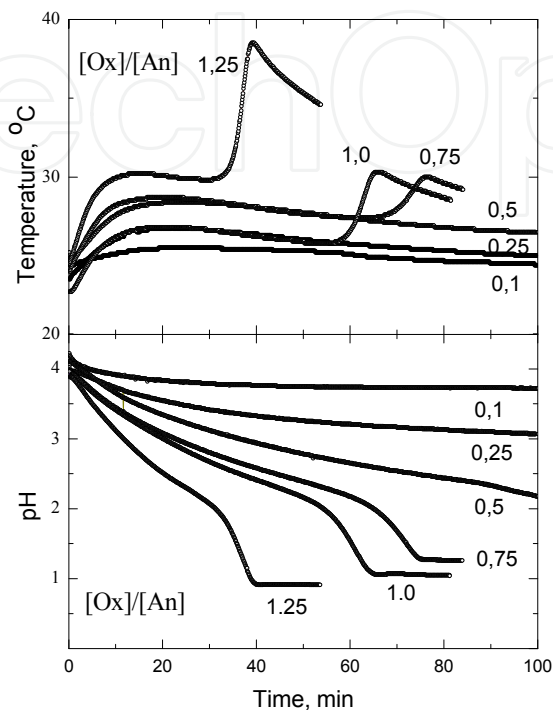


Figure 2. Changes in the temperature (a) and pH (b) of the medium in the course of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) polymerization in 0.4 M acetic acid under the action of different amounts of ammonium persulfate. The ratios of molar concentrations of oxidant and aniline are denoted by numbers. $[\text{Ox}] : [\text{An}] = 1.25$ (1), 1.0 (2), 0.75 (3), 0.5 (4), 0.25 (5), 0.1 (6).

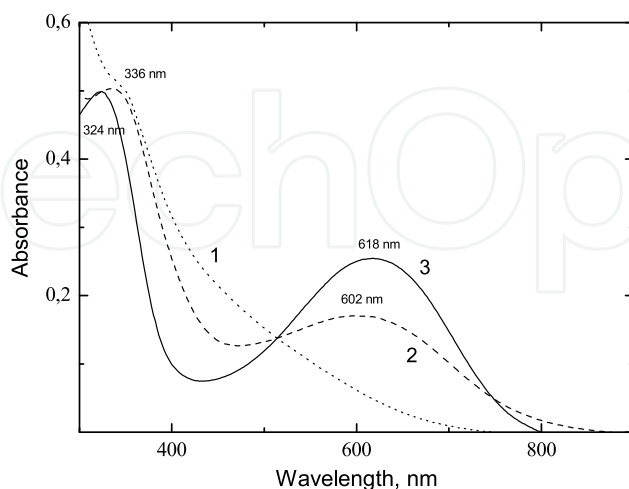


Figure 3. Electronic absorption spectra of the products of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) oxidation initiated by ammonium persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$) taken in media with different acidities; (1) in $0.2 \text{ M NH}_3\cdot\text{H}_2\text{O}$; (2) in 0.4 M acetic acid; (3) in $0.1 \text{ M H}_2\text{SO}_4$. Oxidation products are deprotonated and dissolved in N-methylpyrrolidone. Wavelengths of absorption peaks are given in nanometers.

Properties of products	NH ₃ ·H ₂ O (0.2 M)	Water	Acetic acid (0.4 M)	H ₂ SO ₄ (0.1 M)
Initial pH	9.5	5.7	4.5	2.4
End pH	3.0	1.1	1.1	1.0
Conductivity of protonated form (S·cm ⁻¹)	<10 ⁻¹⁰	0.055	0.036	3.7
Conductivity of deprotonated form (S·cm ⁻¹)	—	6.0×10 ⁻⁸	7.9 ×10 ⁻⁹	1.1×10 ⁻⁹
Density of protonated form (g·cm ⁻³)	—	1.35	1.338	1.402
Molecular mass M _w	4.090	-	32200	39400
Polydispersity, M _w /M _n	1.3	-	19.0	13.1
Morphology	Microspheres	Plates, nanotubes	Nanotubes	Granules

Table 1. Properties of products of aniline oxidation (0.2 mol·L⁻¹) with ammonium persulfate (0.25 mol·L⁻¹) at various pH values.

The aniline oxidation product synthesized in the presence of sulfuric acid (1<pH<2.2) is the polymer with M_w ~ 40 000 and M_w/M_n=13.1. The material demonstrates an absorption band at 618 nm typical of deprotonated emeraldine (Fig. 3) and the conductivity of the protonated emeraldine form (3.7 S·cm⁻¹). The polymer has a globular structure typical of PANI with globules measuring from 100 to 200 nm (Fig. 4d).

The oxidation products obtained in acetic acid and water exhibited characteristics intermediate between those of aniline oligomers and high molecular weight PANI. As compared with PANI synthesized in sulfuric acid, 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, as well as broadening of MWD of polymerization products suggested that PANI synthesized in the intermediate pH range (1<pH<6) is a mixture of oligomers and polymer.

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

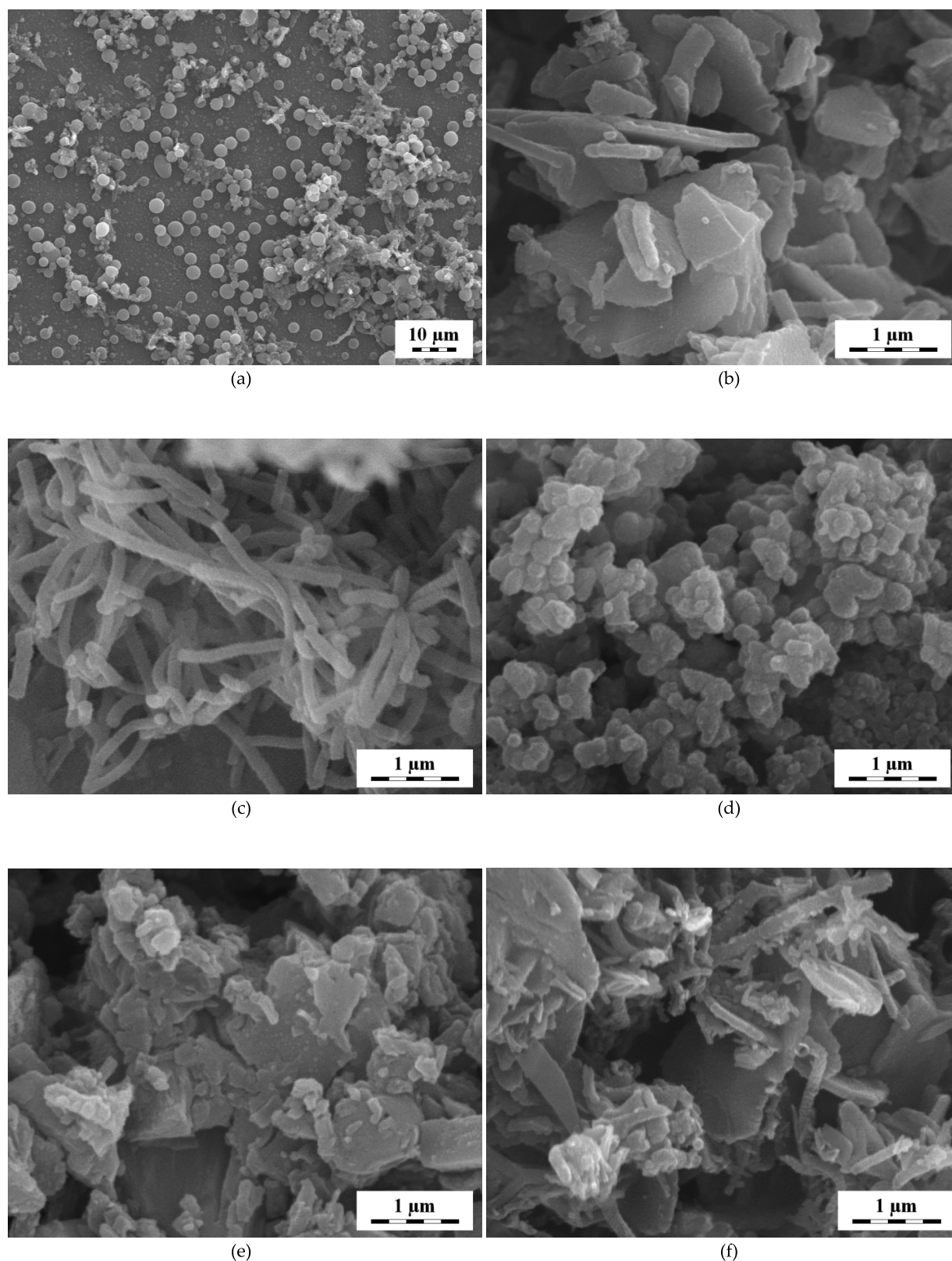


Figure 4. Scanning electron microscopy. Products of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) oxidation with ammonium persulfate in different experimental conditions: a) in aqueous ammonia (microspheres); b) in water (two-dimensional structures – “plates”); c) in 0.4 M acetic acid (nanotubes); d) in sulfuric acid (globular PANI morphology). e) Amorphous agglomerates of aniline oligomers synthesized upon oxidation of

aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) under deficiency of ammonium persulfate ($0.05 \text{ mol}\cdot\text{L}^{-1}$) at $\text{pH}>3.5$. f) Products of aniline oxidation ($0.2 \text{ mol}\cdot\text{L}^{-1}$) in 0.4 M acetic acid with ammonium persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$) isolated in the intermediate step of polymerization at $\text{pH} \sim 2.5$ -3.

The morphology of PANI synthesized in the intermediate pH range ($1<\text{pH}<4.5$) that includes two temperature waves is characterized by transition from amorphous to organized morphologies (Fig 4e and 4f) and the presence of one-dimensional structures, namely, nanotubes and nanofibers. The one-dimensional structures begin to appear in products at $\text{pH}\sim 2.5$. The appearance of nanofibers and nanotubes accompanies the transition from oligomeric products to polymeric ones. As the pH drifts to acidic values, the length of tubular fragments increases together with the fraction of one-dimensional structures. For PANI synthesized in acetic acid in the pH range $1<\text{pH}<4.5$, the one-dimensional structures prevail (Fig.4c). However, further decrease in pH increases the granular precipitate fraction. Polyaniline synthesized in water also contains fibers and tubes with an outer diameter of $150 \pm 200 \text{ nm}$; in addition to tubes, PANI precipitate contains the so-called "plates" (Fig.4b) and the granules measuring up to several hundred nanometers.

[Ox]/[An]	0.25	0.5	0.75	1.0	1.25
End pH	4.0	3.3	2.5	1.2	1.1
Conductivity of protonated form ($\text{S}\cdot\text{cm}^{-1}$)	$<10^{-10}$	2.4×10^{-10}	-	0.036	0.095
Density of protonated form ($\text{g}\cdot\text{cm}^{-3}$)	-	1.307	-	1,338	1.465
Molecular mass M_w	3600	2100	23600	17600	44600
Polydispersity, M_w/M_n	3.8	16.4	11.1	9.4	10.6
Morphology	Amorphous	Two-dimensional	Inclusions of nanotubes	Nanotubes	

Table 2. Properties of products of aniline oxidation ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with different amounts of ammonium persulfate in 0.4 M acetic acid. The initial pH is 4.5.

Transition from one pH range into another leads to changes in molecular structures of chains and properties of products accompanied by transformation of supramolecular structure of PANI. During oxidation at $\text{pH}<2.5$, high molecular weight polyaniline with developed polyconjugation system and high conductivity is formed. By contrast, at higher pH, PANI oligomers are obtained. Oligomers have low conductivity and, judging by spectral characteristics, there is no polyconjugation. If the reaction proceeds within both pH ranges, the mixture of oligomeric and polymeric products is obtained. In various pH intervals morphology of products also varies. However, there is no direct correlation between conductivity, molecular mass and type of supramolecular structure. Depending on

synthesis conditions, oligomers may exist in the form of microspheres or two-dimensional formations, and high molecular weight PANI may have one-dimensional (nanofibers or nanotubes) or three-dimensional structure (granules).

4.4. pH of reaction medium as a critical factor in aniline oxidation

The literature contains a vast amount of information concerning influence of various parameters of synthesis on properties and morphology of products obtained in aniline oxidation. There are many publications (Wan, 2009; Liu & Zhang, 2009; Venancio et al., 2006) demonstrating that changes in concentrations of monomer, oxidizing agent and their ratio, nature and concentration of acids which protonate PANI, or other additives have a significant effect on polymerization process, properties and morphology of products. However, authors do not take into account that this effect is not always obvious; usually it is indirect and carried out via changes in pH of the reaction medium. There are many examples of indirect influence of pH masked by other synthesis parameters. Thus, aniline and its polymers, being organic bases, increase pH. The increase in monomer concentration is equivalent to alkalization of the solution. Addition of acids and acidic salts decreases pH. The [monomer] : [acid] ratio and the nature of the acid used (its strength and buffering properties) are also important parameters. Weak acids exhibit the buffer effect suppressing the pH change during the synthesis.

The pattern of pH changes occurring during the reaction may be altered by certain factors one would think independent of pH. Thus, changes in [oxidant] : [monomer] ratio have an effect on pH, determine conversion degree and a number of released protons. The dilution of reaction medium also influences this pattern, because the range of pH changes in concentrated solutions is much wider than in diluted ones, and, as a result, the reaction may pass to another pH interval. The presence of organic phase immiscible with aqueous medium is also a striking example of such factor. This is the so-called aniline polymerization at the interface between two immiscible media; monomer is dissolved in organic phase, and oxidizing agent is present in water. The mechanism of "interface" polymerization and the factors leading to the formation of one-dimensional structures in this system are actively discussed in the literature. It was shown (Li et al., 2011) that characteristics of aniline oxidation, as well as properties and morphology of products, depend on pH and correspond to the profile of change of water phase pH.

Frequently, effects of various factors in oxidative polymerization of aniline mask the one factor which has a critical influence on the mechanism of synthesis. In polymerization with strong oxidant, it is the pH factor that is masked by a large number of various parameters of the reaction (Konyushenko et al. 2006a; Stejskal et al. 2006; Sapurina & Stejskal, 2010). Considerable changes in polymerization process, properties and morphology of products occur when the acidity falls within pH intervals coinciding with protonation constants of reactants (monomer and growing polymer chain). At the same time, if the experiment is carried out within the same acidity interval, changes in these parameters (concentrations of

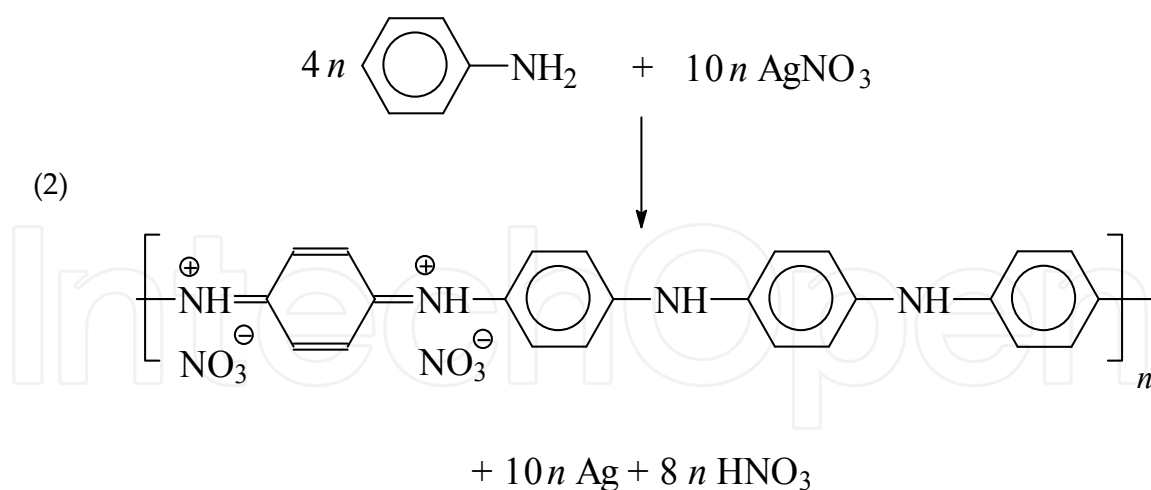
reactants and/or nature of additives) do not lead to dramatic changes in properties of products. Thus, at $\text{pH} \leq 2.5$, polymerization always yields emeraldine with characteristic electronic spectrum (absorption band at wavelengths higher than 800 nm) and high conductivity ($\geq 10^{-1} \text{ S}\cdot\text{cm}^{-1}$). By contrast, products of aniline oxidation at $\text{pH} > 2.5$ definitely have low conductivity which can be raised neither by protonation nor by redox reactions. All these facts indicate that products obtained at $\text{pH} < 2.5$ and $\text{pH} > 2.5$ have fundamentally different molecular structure.

5. The influence of oxidation potential on the process of aniline oxidation, properties and morphology of products

Oxidation potential of nitrogen-containing structures, including aniline, increases with increasing acidity of the medium, due to protonation of nitrogen atom. The potential increases non-monotonically. In the pH range corresponding to protonation constant, oxidation potential changes discontinuously, in accordance with the pattern of change in concentration of protonated and deprotonated forms of reactants. Deprotonated form of aniline existing in alkaline and neutral media is oxidized at low potential (+0.3 V). In acidic media, start of polymer chain propagation requires overcoming the energy barrier corresponding to an oxidation potential of +1.05 V (Li et al 2002). Therefore, oxidants with potentials lower than 1.05 V capable of oxidizing aniline in alkaline and neutral media should not initiate polymerization at low pH. However, experiments have shown that oxidation of aniline in acidic media can be performed and leads to the formation of polyconjugated PANI. Such oxidants as FeCl_3 (+0.77 V), V_2O_5 , (+0.98 V), AgNO_3 (+0.8 V), MnO_2 (+1.2 V), KIO_3 (+1.1 V), Pd^{+2} (+0.89 V), Au^{+3} (+1V) (Sapurina & Stejskal, 2012), possessing potential close to 1 or even lower, may oxidize aniline not only in alkaline or neutral media, but, strange as it may seem, in acidic media with high potential barrier of oxidation.

5.1. Oxidation of aniline under the action of a weak oxidant (silver nitrate)

In this section, we will discuss oxidation of aniline under the action of a weak oxidizing agent – silver nitrate AgNO_3 with a potential of +0.80 V (which is much lower than potential barrier of aniline oxidation in acidic media) (Sapurina & Stejskal, 2012). Oxidation was carried out at different pH values; the initial pH values of reaction medium were 11, 6 and 2.5. Thus, oxidation proceeded within three pH ranges where both the monomer and growing chains are deprotonated and have low oxidation potential or are present in protonated state with high oxidation potential. To aid the visualization, oxidation of aniline with AgNO_3 is compared with oxidation under the action of persulfate under similar conditions. In the course of oxidation, silver cation is reduced to give metallic silver. Silver forms composites with polymeric products; this composite was analyzed by electron microscopy, spectroscopy, conductometry, gel-permeating chromatography and thermogravimetry. The content of reduced silver in products was determined by thermogravimetry; this allowed us to control the participation of AgNO_3 in the reaction of aniline oxidation.



5.2. The oxidation process and properties of products

5.2.1. Oxidation at $\text{pH} > 3.5$

At $\text{pH} > 3.5$ both monomer and polymer chain are deprotonated. Only deprotonated nitrogen-containing structures with low oxidation potential take part in the reaction. As well as in the case of persulfate and AgNO_3 , oxidation starts at once and proceeds monotonically with high rate. Fig. 5a shows aniline oxidation profiles for both oxidants in 0.5 M ammonia solution. At an initial aniline concentration of $0.2 \text{ mol}\cdot\text{L}^{-1}$ and $[\text{Ox}]_0/[\text{An}] = 2.5$, reactions are completed within several minutes. Silver mirror is formed on the walls of the reaction vessel in the course of oxidation of aniline with AgNO_3 . In the case of persulfate, the initial pH of 10.0 lowers down to 8.9 by the end of the reaction. When AgNO_3 was used, the interval of pH change was 10.8 – 9.3. This fact indicates that both monomer and polymer chain remain deprotonated throughout the process.

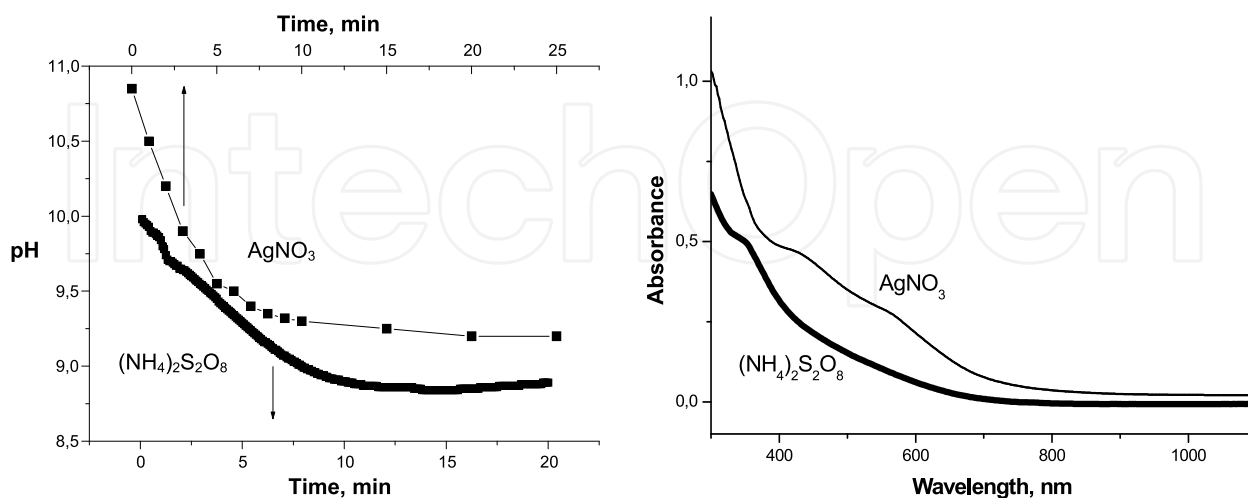


Figure 5. (a) Change of pH in the course of aniline oxidation under the action of ammonium persulfate and silver nitrate in 0.5 M aqueous ammonia. (b) Electronic spectra of products is lost of aniline oxidation with ammonium persulfate and silver nitrate; samples are dissolved in N-methylpyrrolidone.

Yields of oxidation products and their properties are given in Tables 1,3,4 . In the spectra of products obtained during oxidation of aniline with both oxidants, absorption bands lie in the wavelength region below 600 nm (Fig. 5b); this fact indicates the absence of polyconjugation in these samples. Conductivity of the products synthesized using persulfate does not exceed 10^{-10} S·cm⁻¹. The material obtained in the reaction with AgNO₃ is a composite containing 75 wt% of metallic silver. Its density is almost four times higher than that of PANI. Electric conductivity of this composite is 3300 – 5030 S·cm⁻¹ (Table 4). Oxidation of aniline with both persulfate and AgNO₃ yields mainly amorphous products (Fig.6 a, b). Silver is present as particles with dimensions ranging 50-200 nm.

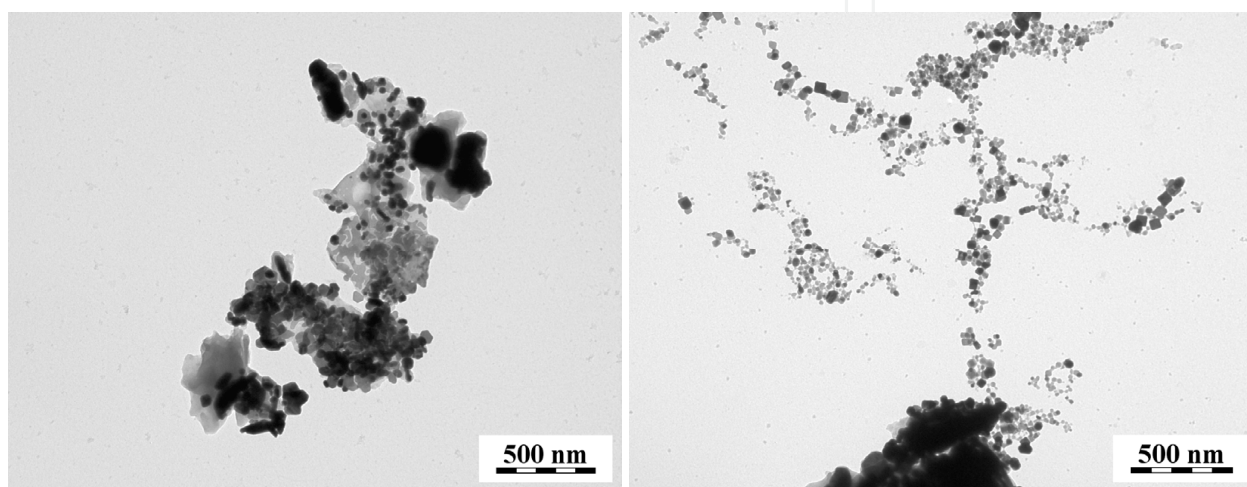


Figure 6. Products of aniline (0.2 mol·L⁻¹) oxidation by AgNO₃ in 0.5 M aqueous ammonia. Scanning electron microscopy

5.2.2. Oxidation at $3.5 > \text{pH} > 2.5$

Oxidation of aniline at higher pH was studied in solutions of carboxylic acids. For example, in the solution of acetic acid (0.4 M) containing 0.2 mol·L⁻¹ of aniline and 0.25 mol·L⁻¹ of persulfate (or 0.5 mol·L⁻¹ of silver nitrate), the initial pH values are 4.5 and 5.7, respectively. The considerable part of aniline is protonated, but imino groups of the chain are still in deprotonated state. Fig. 7a shows pH profiles of oxidation of aniline with both oxidizing agents. It can be seen that within the $3.5 > \text{pH} > 2.5$ region, oxidation is dramatically decelerated. This pH range lies between two stages of more intense oxidation with more sharp decrease in pH.

When persulfate is used, the stage of slow oxidation drift within the $3.5 > \text{pH} > 2.5$ range is completed after 30 min and culminates in vigorous exothermic reaction accompanied by intensive release of protons and decrease in pH. In the case of AgNO₃, at the same initial concentrations of reactants, oxidation drags on for hundreds of hours. In fourteen days, conversion of aniline oxidation in acetic acid reaches 30%, and pH decreases down to 3.5 (due to abstraction of protons). Then oxidation continues and somewhat accelerates.

The yield of aniline oxidation in the 2.5-3.5 pH range is very low. As was previously shown, in the case of persulfate, the products are non-conducting oligomers with low molecular masses (Table 2). In the case of AgNO_3 , homogeneous dark brown powder was isolated; its density is $3.28 \text{ g}\cdot\text{cm}^{-3}$, and conductivity is $4350\text{-}7160 \text{ S}\cdot\text{cm}^{-1}$ (Table 3, 4). As well as after oxidation in 0.5 M ammonia solution, the obtained product contains metallic silver. The electronic spectrum of organic fraction of the product extracted with N-methylpyrrolidone is similar to the spectrum shown in Fig. 5b. This fact evidences that oxidation of aniline with AgNO_3 to 30% conversion gives products with low degree of polyconjugation.

Supramolecular structure of products of aniline oxidation in the pH range 2.5 to 3.5 differs from the structure of products obtained in alkaline medium. In the case of oxidation with persulfate, these are planar formations with dimensions of the order of microns and thickness of up to 100 nm and "sticks" with a diameter of up to 200 nm (Fig. 4f). In the case of oxidation of aniline with silver nitrate, two-dimensional morphology also prevails. The significant part of the material consists of planar disks with a diameter of several microns; sticks and thread-like formations are also observed. Transmission microscopy allows us to reveal localization of metallic silver. Silver in the form of dark stripes covers planar and one-dimensional objects or forms spherical nanoparticles with a diameter of the order of 10 nm which then turn into larger agglomerates (Fig. 8).

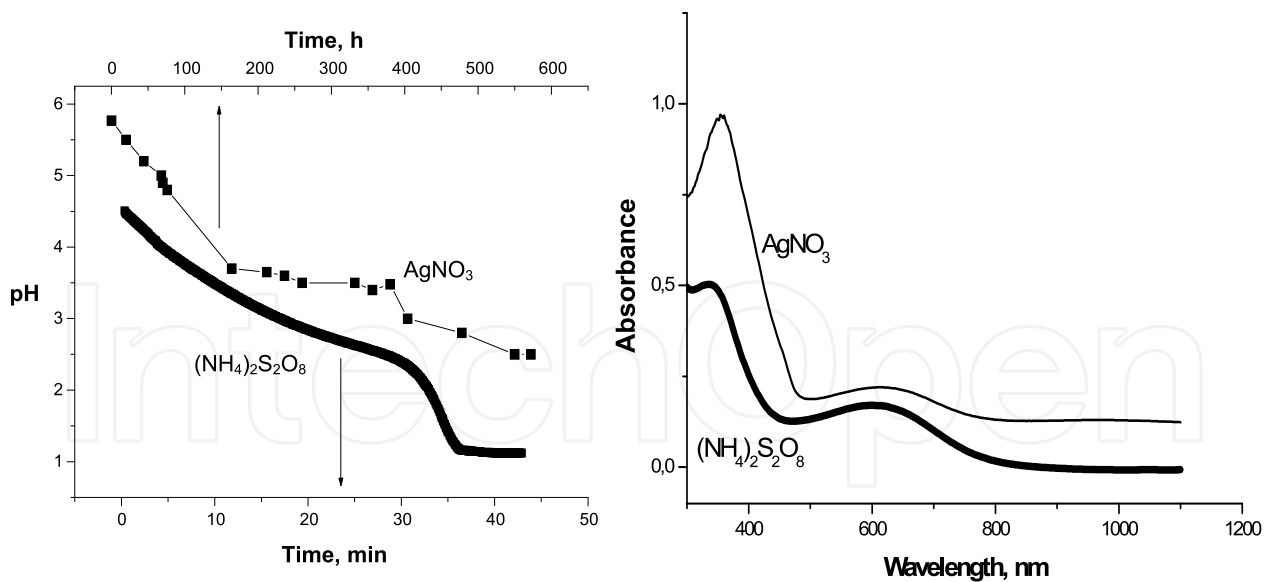


Figure 7. (a) Change of pH in the course of oxidation of aniline with ammonium persulfate and silver nitrate in 0.4 M acetic acid. (b) Electronic spectra of products of aniline oxidation with ammonium persulfate (100% conversion) and silver nitrate (70% conversion, $\text{pH} < 2.5$); samples are dissolved in N-methylpyrrolidone.

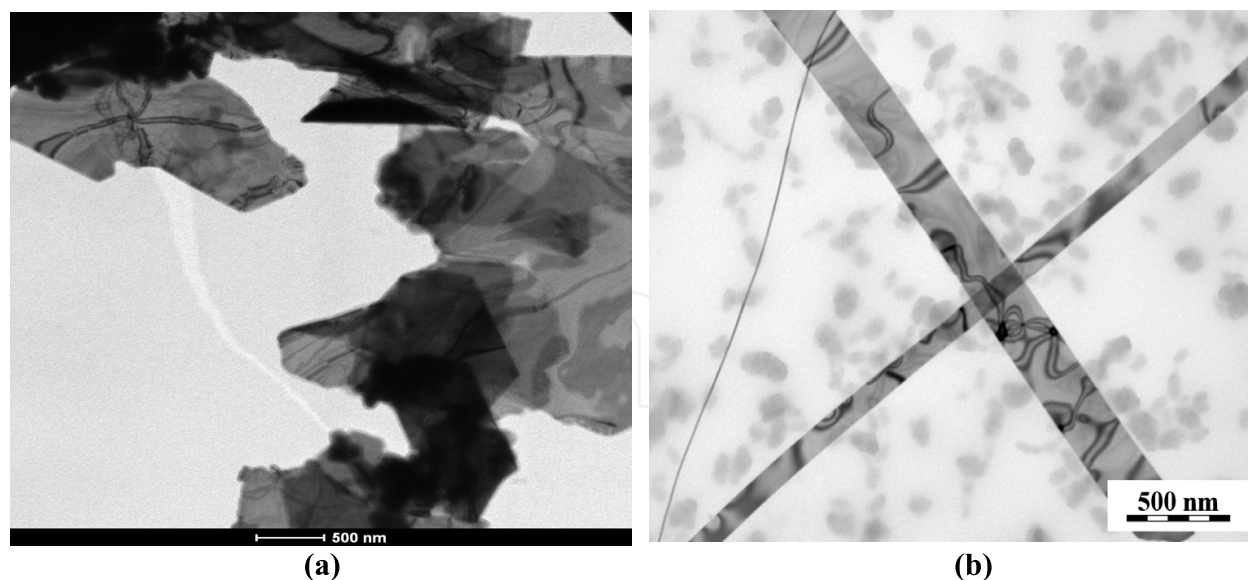


Figure 8. Two types of supramolecular structures of products of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with AgNO_3 ($0.5 \text{ mol}\cdot\text{L}^{-1}$) within the 2.5 - 4.5 pH range (TEM images).

Parameter	0.5 M NH_4OH , 100% conversion	0.4 M CH_3COOH , 30% conversion	0.4 M CH_3COOH , 70% conversion	0.1 M HNO_3 , 30% conversion
Initial pH	10.8	5,7	5,7	2.5
End pH	9.3	3.5	2.5	1.8
Oxidation time, (h)	0.24	168	540	540
Wavelength of polaron absorption band, (nm)	-	-	618	626
Molecular mass M_w	-	-	-	41400
Morphology of organic fraction	Amorphous	Two-dimensional One-dimensional	Fibers Tubes	Fibers Tubes
Morphology of silver	Spheres	Layer on oligomer	Spheres + sticks	Spheres

Table 3. Morphology and properties of composites formed in the course of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with silver nitrate ($0.5 \text{ mol}\cdot\text{L}^{-1}$) at various pH values.

5.2.3. Oxidation at $\text{pH} < 2.5$

Oxidation process at $\text{pH} < 2.5$ is illustrated by the reaction between $0.2 \text{ mol}\cdot\text{L}^{-1}$ solution of aniline and $0.5 \text{ mol}\cdot\text{L}^{-1}$ solution of AgNO_3 in 1.0 M nitric acid (Fig. 9a,b), as well as in acetic and formic acids (0.4 M) at high conversions of aniline; release of protons leads to decrease in pH down to 2.5 (Fig. 7a,b). The reference reaction was interaction between aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) and ammonia persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$) in 0.2 M sulfuric acid.

Two-step reaction between aniline and ammonia persulfate was completed in 10 minutes. The yield of emeraldine with a molecular weight of 40 000 and conductivity of $1 \text{ S}\cdot\text{cm}^{-1}$ is close to 100% (Table 1). Polymer consists of granules (which is characteristic of PANI obtained in acidic medium under the action of strong oxidants, Fig. 4d).

Oxidation in the presence of AgNO_3 in 1 M nitric acid proceeds very slowly. During the first 100 hours, no visible signs of oxidation appear. The 16% yield is achieved in two weeks. The density of the product is $3.6 \text{ g}\cdot\text{cm}^{-3}$, it has a conductivity of $2200 \text{ S}\cdot\text{cm}^{-1}$ which indicates the presence of a large amount of metallic silver in the composite. In three weeks and a half, the yield is 30%, and conductivity of the product decreases down to $1000 \text{ S}\cdot\text{cm}^{-1}$ (Table 3, 4). Electronic spectra of organic fraction of the composite include intensive polaron absorption band with a maximum at 626 nm (Fig. 9b). IR spectra of deprotonated samples are also similar to those of emeraldine (Blinova et al. 2009). Thus, organic fraction of the composite is a polymer with high degree of polyconjugation.

The studies of products of aniline oxidation obtained in organic acids at high conversion (when pH decreases down to 2.5) also showed that the polymer with long conjugation system is formed. For example, organic fraction of composites obtained in acetic acid at a conversion of 75% (Fig. 7b) and in formic acid at a conversion of 80% demonstrates wide absorption bands in the spectra at 618 nm and 600 nm characteristic of emeraldine. However, intensities of polaron absorption bands are much lower than these in the case of reaction in a stronger (nitric) acid, this fact indicating that the content of polymer fraction is low. The densities of samples obtained in acetic and formic acids are 3.42 and $3.66 \text{ g}\cdot\text{cm}^{-3}$, and conductivities are 326 and $0.85 \text{ S}\cdot\text{cm}^{-1}$, respectively (Table 4).

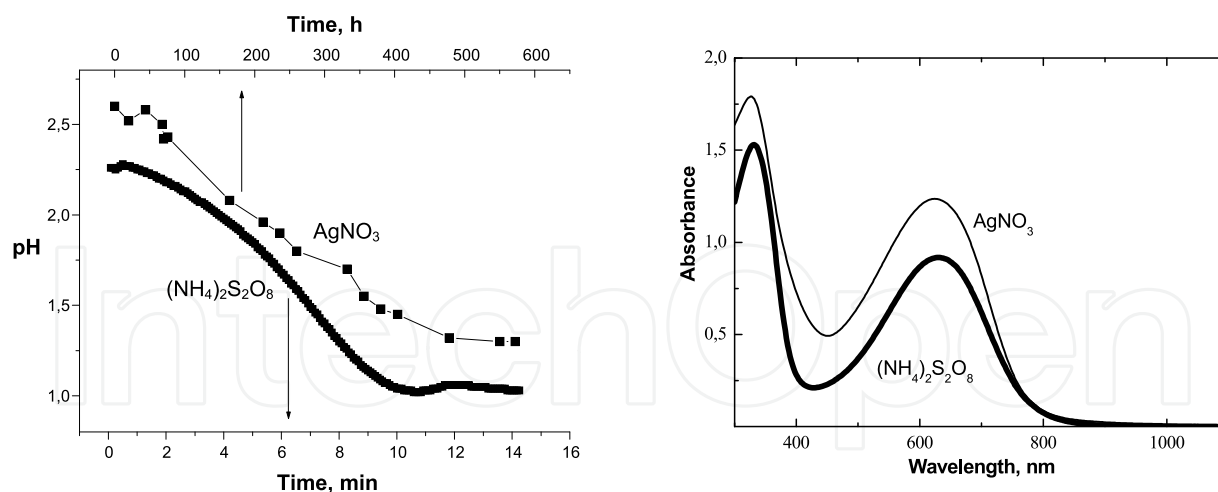


Figure 9. (a) Change of pH in the course of aniline oxidation under the action of ammonium persulfate in 0.1 M sulfuric acid and silver nitrate in 1 M nitric acid. (b) Electronic spectra of products of aniline oxidation with ammonium persulfate and silver nitrate; samples are dissolved in N-methylpyrrolidone.

Although at $\text{pH} < 2.5$ both the strong and weak oxidants oxidize aniline to the emeraldine state, supramolecular structures of products are fundamentally different. In the case of AgNO_3 , instead of spherical particles typical for the products of persulfate oxidation (Fig. 4d), one-dimensional particles prevail. PANI in the form of nanotubes and hierarchical structures

consisting of fibers with a diameter of 10 nm includes spherical particles of metallic silver with a diameter of 50 nm (Fig. 10 a, b). At high conversions, in acetic and formic acids silver “sticks” several μm in length and with a diameter of up to 300 nm appear. These sticks are covered with loose layer of polymer which starts to grow from silver surface as fibers (Fig. 10 c, d). In the product obtained in formic acid, this morphology prevails.

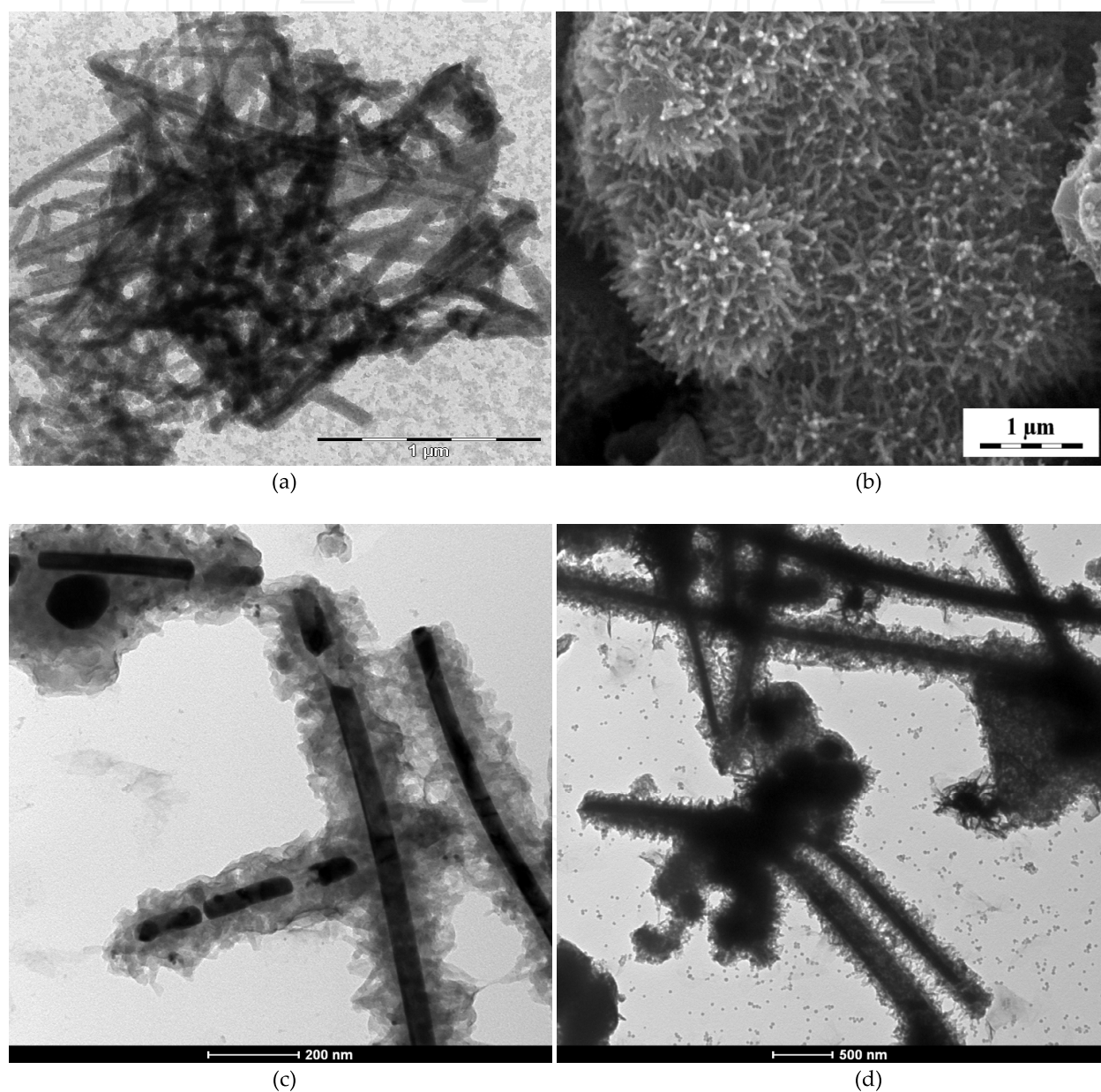


Figure 10. (a,b) Morphology of products of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with AgNO_3 ($0.5 \text{ mol}\cdot\text{L}^{-1}$) in 1 M nitric acid (SEM image). (c, d) Products of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with AgNO_3 ($0.5 \text{ mol}\cdot\text{L}^{-1}$) in acetic and formic acids at high conversions ($\text{pH} < 2.5$) (TEM image).

5.3. The composition of PANI/Ag materials

Oxidation of one gram of aniline with a stoichiometric amount of AgNO_3 theoretically yields 1.31 g of PANI and 2.9 g of metallic silver. Therefore, according to stoichiometry of the reaction (2), the content of reduced silver in metal/polymer composite should be 68.9 wt%.

Oxidation to nonconducting aniline oligomers gives the composite with 74 wt% of silver. Thermogravimetric analysis allows to establish composition of silver-containing products. Mass fraction of metal is determined as a mass of incombustible residue left after heating of sample in air flow up to more than 600°C. According to TGA data, silver content in all the composites corresponds to the stoichiometry of redox process: in alkaline media it is 75 wt%, and in acidic media – about 70 wt% (Table 4). These data prove that it is AgNO_3 that acts as the main oxidizing agent.

Reaction medium	pH		Yield of composite, %	Content of Ag, wt%	Conductivity, $\text{S}\cdot\text{cm}^{-1}$	Density, $\text{g}\cdot\text{cm}^{-3}$
	initial	end				
0.5 M NH_4OH	10.8	9.3	60.5	75.0	3300-5030	4.22
0.4 M CH_3COOH	5.7	3.5	32.7	70.8	4350-7160	3.26-3.28
0.4 M CH_3COOH	5.7	2.5	75.7	69.0	326	3.42
0.4 M HCOOH	-	-	79.8	72.6	0.85	3.66
1.0 M HNO_3	2.5	1.8	30.0	70.7	709-1080	3.54

Table 4. Composition and properties of products of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with AgNO_3 ($0.5 \text{ mol}\cdot\text{L}^{-1}$) at various pH values.

5.4. Oxidation potential as an important factor in aniline oxidation

Comparison of results of oxidation of aniline with strong and weak oxidants shows that both the strong oxidant (persulfate) and weak one (AgNO_3) at $\text{pH} < 2.5$ oxidize aniline to give PANI in the emeraldine oxidation state, while at higher pH in both cases aniline oligomers without developed conjugation system are formed. The courses of these two reactions occurring in acidic media are different. While in alkaline medium both persulfate and AgNO_3 oxidize aniline in several minutes, and kinetic curves of oxidation are comparable. In going to acidic media, rate of oxidation drops considerably. The reaction proceeds for hundreds of hours; the lower the initial pH, the lower the conversion at any given instant of time. At the same time, the general views of time “profile” of pH for reactions with persulfate and AgNO_3 are similar. In the media with $\text{pH} > 3.5$ and $\text{pH} < 2.5$, faster pH change is observed, while in the pH range 2.5 to 3.5, oxidation becomes slower.

Another interesting aspect of using oxidant with low potential is its influence on PANI morphology. At $\text{pH} \leq 2.5$ and high concentrations of reactants, oxidation by persulfate leads to the formation of a polymer with granular structure. Replacing strong oxidant by a weaker one leads to the formation of fibers, tubes and hierarchical structures. These transformations were observed not only in the case of AgNO_3 (Blinova et al. 2009), but also in the reactions with another oxidants having low potential: FeCl_3 (Ding et al. 2010), V_2O_5 , (Li et al. 2010;), MnO_2 (Pan et al. 2007), KIO_3 (Gizdavic-Nikolaidic et al. 2010), CeO_2 (Chuang et al 2008). The authors of (Ding et al. 2007) revealed interrelation between the value of oxidation potential of oxidizing agents and diameter of one-dimensional PANI particles: lowering the potential leads to decrease in fiber diameter. Similar regularities are observed during electrochemical oxidation of aniline (Molina et al. 2007). In addition to one-dimensional objects, hierarchical structures (urchins, flowers, corals) are formed. Thus, transformation of supramolecular structure of PANI when employing weak oxidant is of a universal character.

The important feature of process with the use of AgNO_3 is the formation of metallic silver. In the course of the reaction, at any initial values of pH silver is reduced in stoichiometric amounts with respect to oxidized aniline. This fact proves that silver cation serves as an oxidizing agent. Depending on synthesis conditions, reduced silver precipitates in the form of various nano-dimensional structures (spheres, sticks or bands covering oligomer particles). The presence of silver provides high conductivity of the obtained materials, and these composites have many possible applications in polymer electronics. It is interesting that depending on synthesis conditions, in spite of equal silver content, conductivity of PANI/Ag composites changes over wide range (from 10^{-2} to $7\,000\text{ S}\cdot\text{cm}^{-1}$). Morphology and properties of PANI/Ag composites, as well as reasons for this difference in conductivity, are discussed in (Sapurina & Stejskal, 2012).

6. Molecular mechanism of aniline oxidation

In this section, we will discuss molecular mechanism of oxidative polymerization of aniline with the key factors responsible for chain formation being pH of reaction medium and oxidation potential of reactants (related to pH) (Sapurina & Stejskal 2008; Stejskal et al. 2010). The concepts of mechanism were formed not only on the basis of the given results. A vast amount of experimental data available in the literature give us additional information.

Fig.11 shows a typical kinetic curve of aniline oxidation (for the case of reaction proceeding in the wide pH interval, $6 > \text{pH} > 1$). Temperature and pH profiles change synchronously with time and demonstrate three regions with different oxidation rates. Transitions between these regions are observed at pH values of 3.5 and 2.5. These pH values coincide with protonation constants of aniline ($\text{pK} = 3.5$) and imino groups of polymer chain ($\text{pK} = 2.5$). At $\text{pH} > 2.5$, oligomers without polyconjugation chain are formed; these materials possess low conductivity. At $\text{pH} < 2.5$, high molecular weight PANI can be synthesized; it demonstrates high degree of polyconjugation and high conductivity, its chains contain 95-98% of *para*-substituted monomer units. Dramatic change in the properties of products takes place at a pH value of 2.5 corresponding to the protonation constant of growing polymer chain.

Therefore, at pH 2.5, mechanism of polymer formation changes, and mixed irregular addition gives way to regular polymerization. These general features are in effect for different oxidants and protonating acids over a wide concentration range.

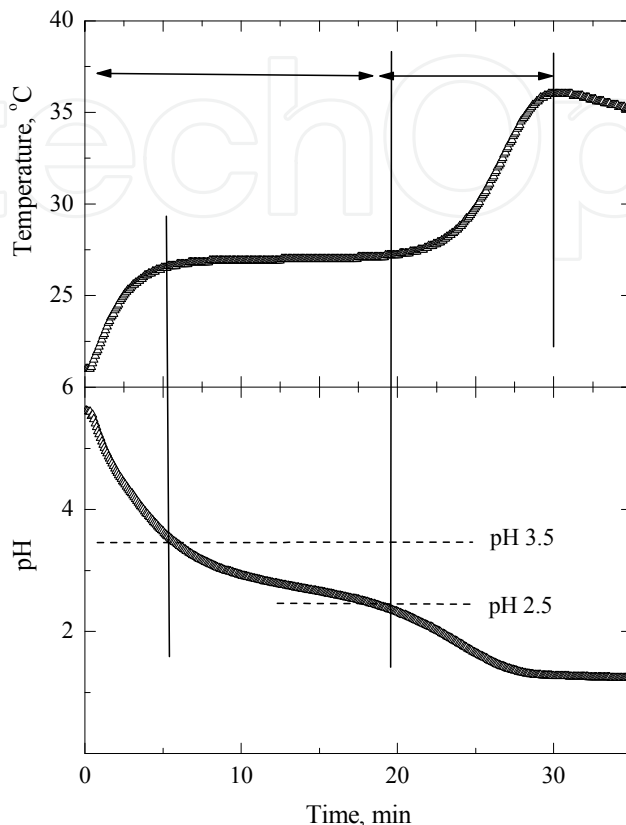
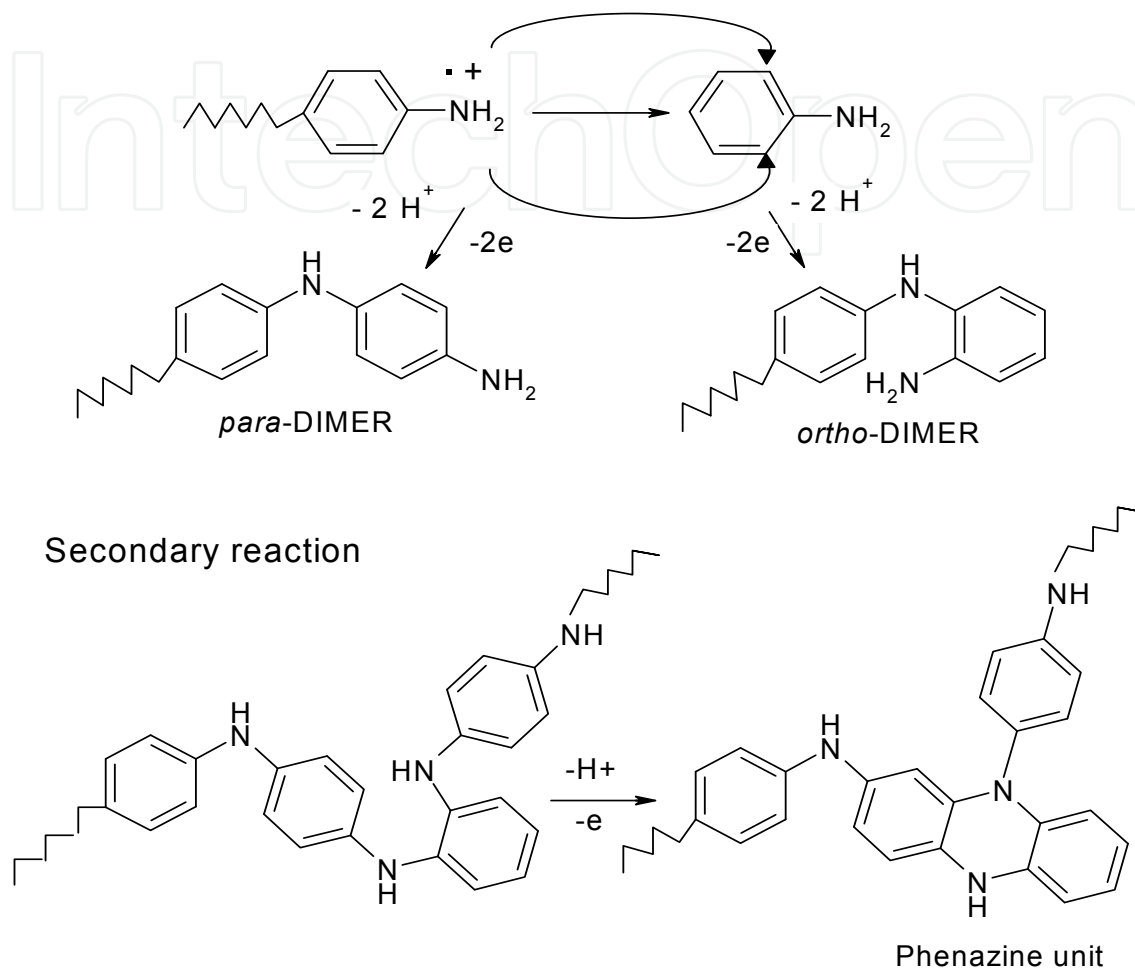


Figure 11. Temperature and pH profiles of oxidation of aniline ($0.2 \text{ mol}\cdot\text{L}^{-1}$) with ammonium persulfate ($0.25 \text{ mol}\cdot\text{L}^{-1}$) in water solution.

6.1. Oxidation at pH > 3.5

At pH > 3.5 both monomer and growing chain are deprotonated, and oxidation of aniline (chain reaction of electrophilic substitution) proceeds in full accordance with concepts of theoretical organic chemistry. The most probable process is oxidation of nitrogen-containing structure of monomer and oligomer and linking monomer units in the “head-to-tail” fashion. However, other substitution paths are also possible, e.g., the process leading to “head-to-head” structures. Due to the presence of amino group (electron donor substituent) in aniline, the attack of oxidized polymer fragment is directed at *ortho*- and *para*-positions of monomer phenyl ring. Since phenyl ring contains two vacant *ortho*-positions, monomer units with *ortho*-structure should prevail. Chain growth is accompanied by secondary reactions. Monomer units of *ortho*-structure have low oxidation potential and undergo further oxidation leading to the formation of phenazine rings (Scheme 5). These reactions may be both intramolecular (similar to these in *o*-phenylenediamine oxidation) and intermolecular (with the participation of monomer). Thus, in addition to linear *ortho*- and

para-monomer units, polymer chains should contain phenazine fragments. Scheme 4 demonstrates the most probable paths of electrophilic substitution leading to the formation of *ortho*- and *para*- monomer units; intramolecular oxidative cyclization of *ortho*-units and their transformation into phenazine rings are also shown.



Scheme 6. Formation of monomer units of *para*- and *ortho*-structure after attack of aniline cation radical directed at *para*- and *ortho*-positions of aniline phenyl ring. Secondary reactions intramolecular oxidative cyclization of *ortho*-units and their transformation into phenazine rings are shown.

However, the probability of formation of other structures is also more than zero. Besides, hydrolysis and formation of quinones may take place in products in the presence of an oxidant. Thus, at medium and high pH values, oxidation of aniline should give chains with heterogeneous structure and prevailing linear or cyclized *ortho*-units (the presence of the latter was proved by spectroscopic methods (Stejskal & Trchova, 2012)). Oxidation of deprotonated forms of reactants proceeds at low potentials (+0.3 - +0.5 V) and may take place under the action of weak oxidants; reaction rates in the cases of strong and weak oxidants are comparable. Monotonous decrease in open circuit potential taking place in the course of the reaction (Surwade et al 2009) is due to the fact that monomer oxidation gives way to oxidation of end amino group of di- and trimer (which possess lower oxidation potentials). However, in the case of longer oligomers, the difference is smoothed, this fact

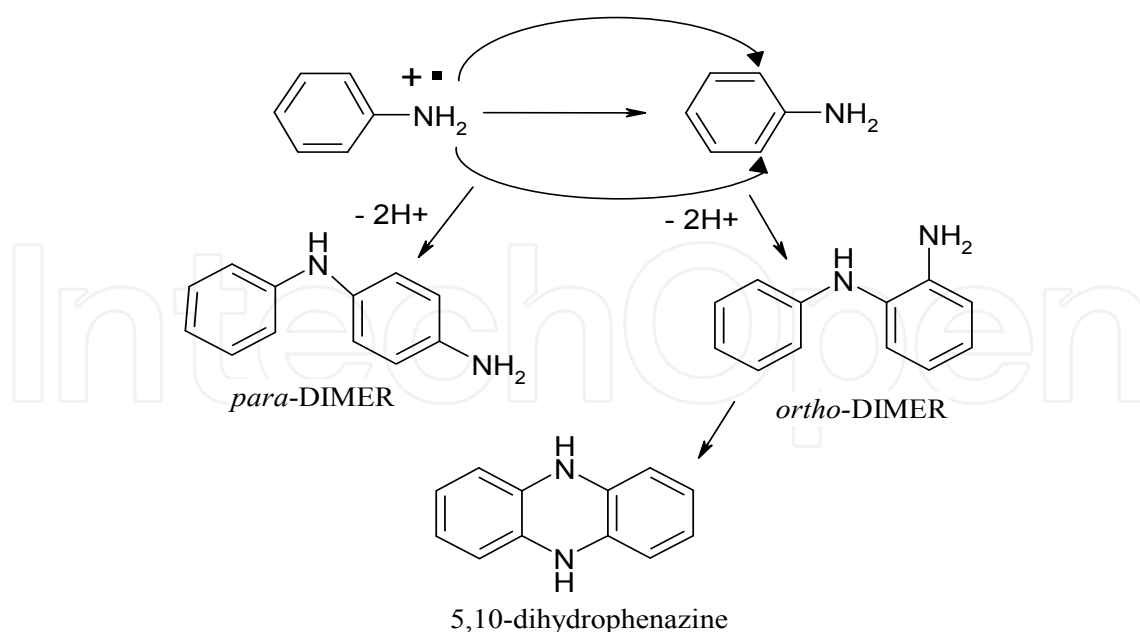
accounting for low molecular masses of oxidation products. In alkaline media, linear chains prevail, since chain propagation proceeds faster than cyclization processes (Losito et al. 2003). In oligomers with heterogeneous chain structure, no polyconjugation is observed, and we should expect low conductivity (see Tables 1 and 2). The process of aniline oxidation with the participation of deprotonated reactants (monomer and growing polymer chain) which yields aniline oligomers of heterogeneous structure lacking in polyconjugation will be termed “oligomerization”.

6.2. Oxidation at $3.5 > \text{pH} > 2.5$

At pH values ranging from 2.5 to 3.5, the major portion of aniline is protonated, and its oxidation potential increases. At the same time, under these conditions, imino groups in polymer chains are still not protonated, this resulting in imbalance of redox interaction between monomer and growing chain. The chain possessing low oxidation potential cannot oxidize protonated monomer with increased oxidation potential. Within the pH range 2.5 to 3.5, oxidation is drastically decelerated. Redox process proceeds only at the expense of oxidation of traces of neutral monomer (which has low oxidation potential). Neutral monomer is fed through shift of deprotonation equilibrium $\text{AnH}^+\text{A}^- = \text{An} + \text{H}^+\text{A}^-$ (Baizer & Lund, 1983).

How does pH change affect the structure of polymerization products? Oligomers obtained in alkaline media are mainly linear, and their degree of polymerization does several tens (Tables 1, 2). As oxidation slows down (i.e., pH decreases, and neutral aniline is spent), length and composition of oligomers change. The rate of monomer addition (i.e., chain growth) decreases, and intramolecular cyclization prevails. This change leads to the formation of short cycle-containing molecules. At $\text{pH} < 3.5$, the main product of oxidation is aniline dimer with *ortho*-structure (Stejskal et al., 2010). Virtually all these dimers undergo intramolecular cyclization to produce phenazine structures, since cyclization rate in acid media is higher than that in alkaline media (Losito et al. 2003).

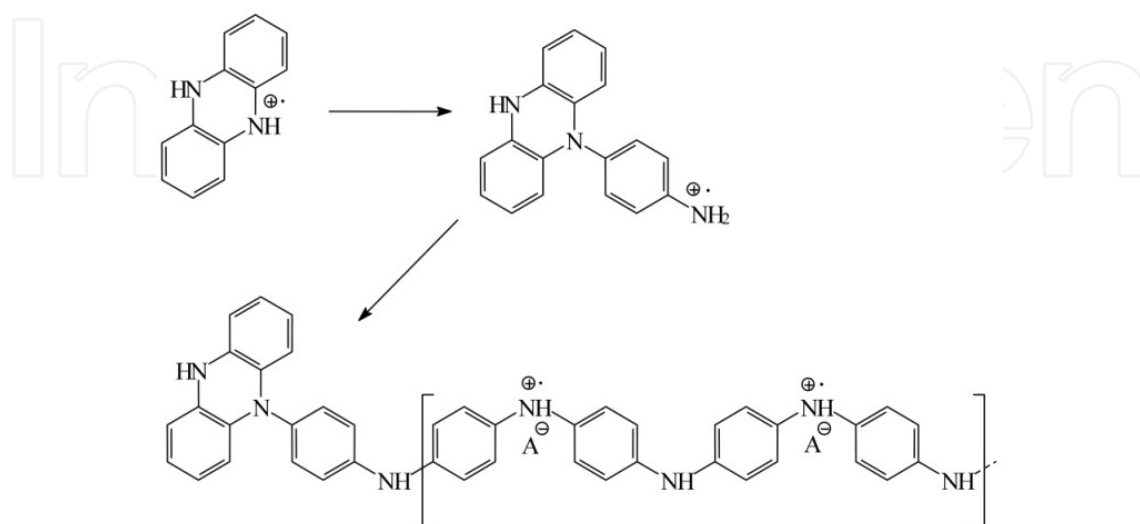
Aniline dimerization and cyclization of dimers occur at low potentials and may start under the action of weak oxidants. As a result, aromatic phenazine rings with high oxidation potential are formed. This fact is corroborated by the slow increase in open circuit potential taking place in the course of oxidation in the pH range 2.5 to 3.5 (Ding et al. 2009; Ding et al. 2010). It is well-known that phenazines can take part in copolymerization and even homopolymerization, but phenazine starts adding monomer molecules (“germinates”) at high oxidation potential (+1.05 V) (Inzelt & Puskas, 2004; Puskas & Inzelt, 2005). The value of “germination” potential of phenazine is similar to the potential of PANI growth start (Yang et al, 2007), and, consequently, we suppose that phenazine ring serves as a nucleate of future polymer chain. Thus, in the pH range 2.5 to 3.5, according to Scheme 6, slow accumulation of aromatic phenazine rings takes place; these rings have high oxidation potential and are intermediates of polymerization and nucleates of future polymer chains.



Scheme 7. Accumulation of aromatic phenazine rings.

6.3. Oxidation at pH < 2.5

The growth of polymer chains with regular structure becomes possible after the next protonation step. At pH < 2.5, the most important pH transition in aniline polymerization takes place. The protonation of monomer amino groups is followed by protonation of imino groups in oligomers, and their oxidation potential increases. This process restores balance of redox interaction between reactants. The chain is once again able to oxidize and add monomer, although in the protonated form which dominates in this pH range. The chain growth taking place at the expense of interaction between protonated chain and protonated monomer and leading to the formation of polyconjugated conducting polymers will be called “polymerization” (Scheme 8).



Scheme 8. The “germination” of phenazine nucleate and propagation of PANI chain.

6.3.1. The limiting step of oxidation

However, in acidic medium (where the majority of monomer molecules are protonated), oxidative polymerization of aniline cannot start with the reaction between cation radical of monomer and protonated aniline molecule, since (according to quantum-chemical calculations) interaction of two small particles bearing excess positive charge is not energy-favored (Ćirić-Marjanović, 2006). To start growth of regular chains, larger polyconjugated fragment is needed; only this fragment is able to lower the energy of interaction between oxidizing site and monomer. These particles are formed in the initial stage of oxidation ("induction period"). We suppose that they are phenazine rings. The role of phenazine as a bulk polyconjugated particle involves delocalization of positive charge of cation radical. At $\text{pH} < 2.5$, this induction period is similar to aniline oxidation in 2.5 – 3.5 pH range and proceeds according to the "oligomerization" mechanism. Aniline cation radical and deprotonated monomer (having low oxidation potential) take part in electrophilic substitution with preferential formation of *ortho*-dimers and their subsequent cyclization (Scheme 7).

Chain growth begins with addition of monomer unit to phenazine nucleate with cyclic structure and high oxidation potential. This is a limiting step of the whole process; its energy barrier corresponds to a potential of +1.05 V. After addition of monomer unit, the nature of growing end changes. Instead of tertiary nitrogen atom embedded into aromatic ring, new active site (end amino group) is formed; its structure is repeated in the process of polymer growth. Oxidation potential of amino group is lower than that of phenazine, and this fact leads to considerable acceleration of polymerization (Li et al., 2002).

The presented mechanism agrees with the behavior of open circuit potential. The character of variation of this potential in acid medium strongly differs from that observed in alkaline medium (Surwade et al 2009; Geng et al., 1998). In acid medium, the initial stage is accompanied by increase in the oxidation potential, which corresponds to accumulation of phenazine nucleates. As exothermic chain propagation starts, the oxidation potential decreases down to a value of +0.7 to +0.8 V which is characteristic of growing pernigraniline chains. Thus, the oxidation potential of aniline at $\text{pH} < 2.5$ passes through a maximum corresponding to the transformation of phenazine nucleate into active polymerization site. In order to overcome that maximum, a reagent with an oxidation potential higher than +1.05 V is necessary. On the other hand, oxidants with a potential lower than +1 V ensure both initial and final stages of oxidative polymerization.

Ammonium persulfate (having an oxidation potential of +2.01 V readily overcomes the barrier related to "germination" of phenazine nucleates, and oxidative polymerization is completed in several minutes. Weak oxidants, such as silver nitrate, cannot oxidize phenazine structure. Therefore, the induction period in the reaction with AgNO_3 takes hundreds of hours. The oxidation stops at the stage of generation and accumulation of phenazine nucleates. Nevertheless, if $\text{pH} < 2.5$, polymerization with the formation of polyconjugated chains does occur and is characterized by a fairly high yield. Obviously, in the absence of other strong oxidants phenazine ring is oxidized with atmospheric oxygen

whose oxidation potential is equal to +1.23 V; in addition, oxygen is soluble in water and therefore accessible for the reactants. The formation of traces of polyaniline under the action of oxygen was reported in (Liao & Gu. 2002).

After “germination” of phenazine nucleates, i.e., transformation of these nucleates into active sites of polymerization, the oxidation potential decreases to +0.7 - +0.8 V (Geng et al. 1998) and, therefore, oxidants with low potential are again able to participate in oxidation process. Thus, weak oxidants, including silver nitrate, are capable of keeping both the initial aniline oxidation step (generation of phenazine units) and polymer chain propagation until the reaction is completed. The final stage involves oxidation of most part of monomer, and it consumes an equivalent amount of AgNO_3 . The presence of a strong oxidant with a potential higher than +1.05 V is necessary only at the stage corresponding to the transformation of phenazine units into active polymerization sites. Therefore, the concentration of a strong oxidant, as well as its contribution to the overall oxidation process, may be insignificant.

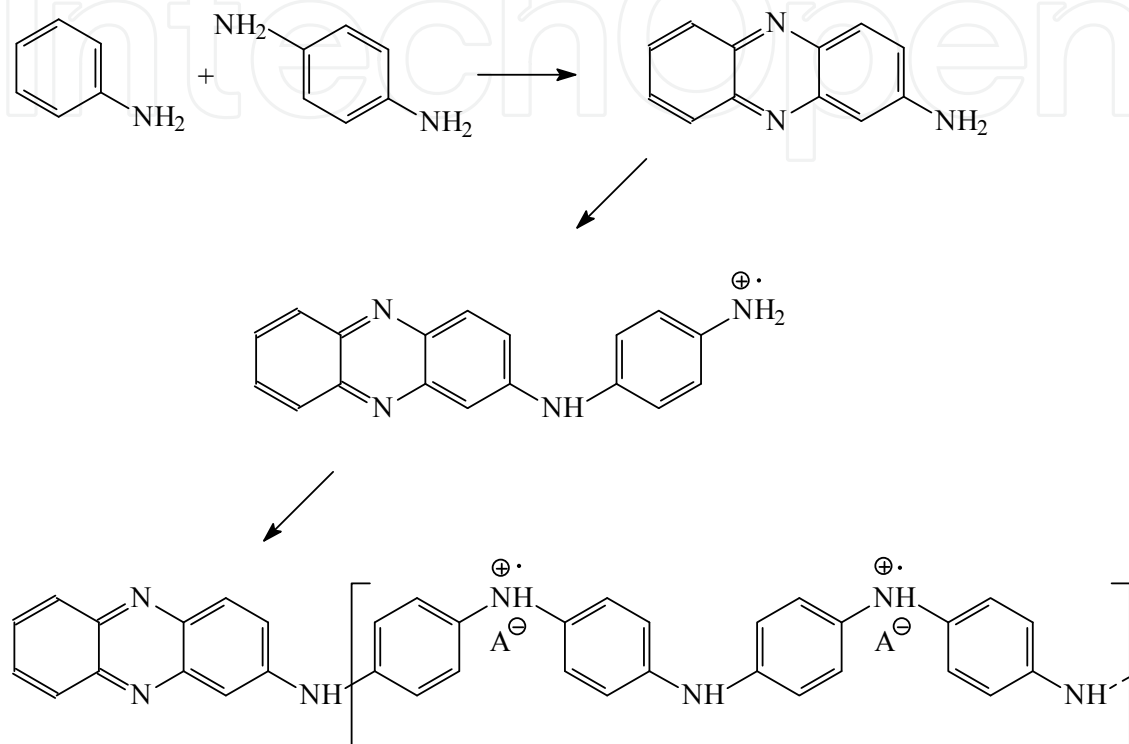
6.3.2. The overcoming the “germination” stage

We believe that the oxidation of aniline to the emeraldine form in the absence of strong oxidants can be held under the influence of a weak oxidant with oxygen. Phenazine units can be converted into active sites of polymerization under the action of atmospheric oxygen, but in this case the reaction is slow. An exception is likely to be a combination of atmospheric oxygen with Fe^{3+} which is known to catalyze oxidation processes (Davied et al. 1995). There are other examples of fast passing the energy barrier of phenazine “germination” and acceleration of polymerization. Oxidation of aniline can be performed with the use of a mixture of oxidants (Bober et al., 2011). Addition of a small amount of strong oxidant (when its concentration is lower than several percent of the amount required for complete oxidation) initiates the polymerization process. This allows to overcome high energy barrier and obtain a sufficient amount of active sites of polymerization. Weak oxidant then reacts with the main amount of aniline to accomplish chain growth at relatively low oxidation potentials.

Long induction period can also be shortened by change of the chemical structure of the nucleate. It is well-known that catalytic amounts of aromatic *para*-diamines sharply shorten the induction period and hence the overall time of polymerization (Tran et al. 2008; Bober et al., 2010). We propose the following mechanism of the process. Aromatic diamine is involved in the formation of phenazine nucleate. Its oxidation potential is lower than that of aniline; therefore, oxidation of diamine is preferred. The reaction between diamine and aniline at the dimerization stage yields aminophenazine (Scheme 9).

This aminophenazine nucleate gives rise to regular polyconjugated chain originating from exocyclic amino group, and high energy barrier of oxidative polymerization of aniline is thus reduced in the nucleate “germination” stage. As a result, the polymerization process is strongly accelerated due to acceleration of its slowest step. It should be noted that addition

of *o*-phenylenediamine does not accelerate the process and that addition of *m*-phenylenediamine, by contrast, sharply decelerates polymerization of aniline via extension of induction period. The latter phenomenon is related to the formation of "defect" initiation site which cannot promote the growth of polyconjugated chain. After complete consumption of *m*-phenylenediamine for the formation of "defect" oligomers, polymerization of aniline is resumed.



Scheme 9. Formation of aminophenazine nucleate giving rise PANI chain grows.

6.3.3. The growth of polyconjugated chains

Aniline polymerization, as well as oligomerization, proceeds according to electrophilic substitution mechanism. However, as opposed to oligomerization, the former yields polymers with strictly regular structure. The polymer containing only *para*-substituted units is formed. The reason for changes in reaction mechanism and transition from mixed *ortho*- and *para*-substitution into highly selective formation of *para*-structures is thus the following. At pH < 2.5 polymer grows in the protonated pernigraniline form where the chain bears excess charge (positive polarons). In this case, *para* substitution becomes energetically more favorable and is the only possible way of electrophilic substitution, since it reduces the energy of the chain. Only in the case of *para*-substitution, polyconjugation is formed which ensures delocalization of positive charges in pernigraniline and decreases repulsion energy. Thus, protonation of polymer chain forbids *ortho*-substitution (the most typical for aniline), as well as all other types of electrophilic substitution ("head-to-head", "tail-to-tail") and leads to the formation of regular polyconjugated *para*-structure and polymer chains possessing high conductivity.

6.4. Termination of chain growth

Polymerization stops after depletion of one or other reactant (monomer or oxidant). The state of PANI after termination depends on the strength of the used oxidant, as well as on molar ratio oxidant/monomer. When strong oxidant is taken in excess, the resulting polymer remains in pernigraniline form. If the reaction is carried out under stoichiometric conditions, or with aniline in excess, pernigraniline is reduced to emeraldine at the end of the reaction.

Pernigraniline is much less stable than emeraldine and takes part in irreversible reactions with electron donor agents. Apparently, during PANI synthesis and after its termination, end imino groups of polymer undergo hydrolysis. This supposition is corroborated by the presence of oxygen in deprotonated PANI samples, as well as by the presence of absorption bands of hydrolyzed structures in IR and NMR spectra of polymers (Kriz et al., 2011; Kellenberger et al., 2011). In the opinion of the authors (Gospodinova et al., 1994), hydrolysis of active sites proceeds continually both during oligomerization and after termination of polymer growth. The hydrolyzed terminal amino group effectively blocks any further growth reactions, because it cannot add monomer; therefore, aniline oxidation cannot be considered as a process proceeding without termination (i.e., "living" polymerization).

6.5. Concluding remarks

As a final matter, it should be noted that chain reaction of aniline oxidation in alkaline, weakly acidic and acidic media proceeds according to different molecular mechanisms, and, as a result, products with different molecular structures, morphologies and properties are formed. This is caused by the existence of monomer and growing chain in protonated and deprotonated forms which possess different oxidation potentials. Oxidation of aniline at $\text{pH} > 2.5$ occurs with the participation of deprotonated monomer and growing chain which have low oxidation potentials; therefore, it may be performed entirely under the action of weak oxidant. The products of this reaction are oligomers with low degree of polyconjugation and low conductivity.

At $\text{pH} < 2.5$, the reaction occurs in a stepwise mode, and variation of the oxidation potential during the process is described by a curve passing through a maximum. In the induction period, the oxidation follows low-energy path at a potential of +0.5 V and yields cyclic dimers having phenazine structure. The limiting stage is "germination" of phenazine rings (nucleates of future polymer chains), when the growth of linear polyconjugated chain starts. Phenazine has an oxidation potential of +1.05 V, and oxidative addition of monomer to this fragment is possible only in the presence of strong oxidants. If the oxidant has a potential lower than +1 V, the process is inhibited at the stage of formation of phenazine units. However, addition of 1 mol % of strong oxidant is sufficient to overcome this barrier. At the chain propagation stage, the oxidation potential again drops down to +0.7 V, and the reaction can proceed further under the action of weak oxidant.

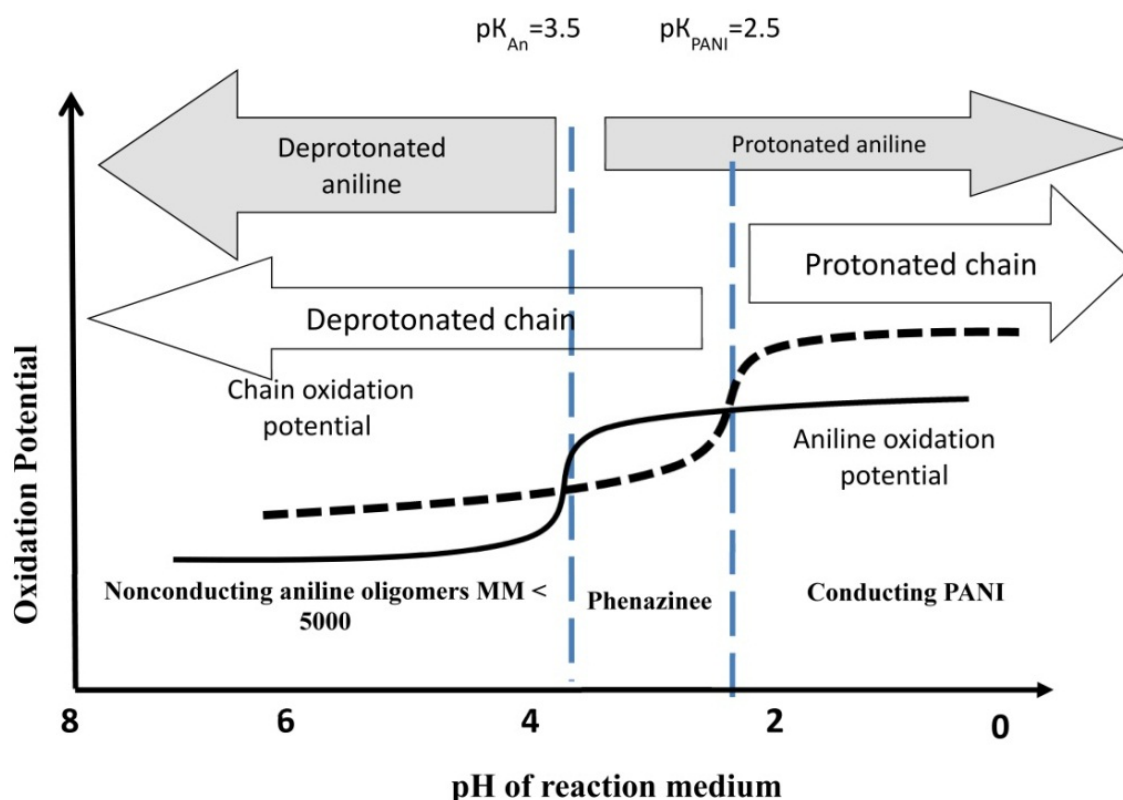
Chain propagation involves protonated monomer and the chain possessing excess charge (positive polarons). Chain protonation constrains the reaction to produce regular polymer

chains with *para*-coupled units. Regular polymer chain possessing extended conjugation system is characterized by the lowest energy due to delocalization of positive polarons over the conjugation system. Growth of other structures is terminated, since they become unfavorable from the viewpoint of energy.

According to protonation constants of nitrogen-containing groups of monomer and chain taking part in polymerization, the process can be divided into three ranges (Scheme 10):

- $\text{pH} > 3.5$, where all types of nitrogen-containing groups are deprotonated, and oxidation proceeds according to regularities of synthesis of typical dielectric polymers (e.g., phenols) with the formation of irregular chains having molecular masses of up to 5 000.
- $3.5 > \text{pH} > 2.5$, where monomer is protonated, while imino groups of chains are not; imbalance of redox processes is observed, this leading to slow formation of cyclic dimmers with phenazine structure.
- $\text{pH} < 2.5$, where imino groups of chains, as well as monomer, are protonated, the balance of electron exchange between chain and monomer is restored, but all growth patterns except *para*-substitution are forbidden. This leads to the formation of regular polyconjugated chains with high molecular weight.

Thus, regular structure of PANI responsible for its unique properties is formed at $\text{pH} < 2.5$ due to protonation of imino groups in polymer chain.



Scheme 10. Oxidation of aniline depending on protonation constant of monomer pK_{An} and that of chain imino groups pK_{PANI} .

7. The formation of polyaniline supramolecular structures

The important feature of PANI synthesis is heterophase nature of polymerization. As a rule, synthesis begins under homogeneous conditions, since both aniline and oxidant are well soluble in acidic aqueous media. However, already in the initial step, the reaction becomes heterophase. This process is called “precipitation polymerization”, because it gives a precipitate (insoluble polymer). However, PANI precipitation cannot be considered as irregular agglomeration. Complex morphology of particles and layers formed by macromolecular chains in the course of polymerization gives evidence that self-organization of macromolecules occurs during synthesis. From theoretical and practical points of view, the mechanism of PANI self-organization and reasons for unusually high selectivity of oxidative polymerization of aniline are the main problems. It is the pattern of assembly of polymer chains in macroscopic sample and molecular structure of these chains that determine properties of material and application areas.

7.1. Types of supramolecular structures

Recently, numerous types of PANI supramolecular structures have been obtained. Their synthesis and potentialities are discussed in several reviews (Bhadra et al. 2009; Stejskal et al. 2010; Wang et al 2011). The basic structures are one-dimensional (nanofibers, nanotubes and nanorods) (Fig 4c, 8b, 10a, 12a,b); two-dimensional (ribbons, plates) (Fig 4b, 8a), and three-dimensional (granules, microspheres and nanospheres) (Fig 4d,f 12c). Their combination and more complicated organization give rise to a vast diversity of structures. Different hierarchical formations are built of fibers coming from the common centre or axis (Fig. 10 b, c, d.). One-dimensional structures can be packed in bundles or form a sort of network, flowers (Fig. 12 e) or dendrites. PANI fibers can also form two-dimensional structures called “micromats”. These are rhomboid particles, “weaved” to produce mats of several layers of fibers coming from the vertex of the rhombus and crossing at right angle (Fig.12 d). Among three-dimensional structures, microspheres and hollow microspheres should be mentioned (Fig 4 a). Their outer diameters fall in the range from a half of micrometer to several micrometers, and the thickness of their walls varies from nano- to submicrometer sizes. The spheres can serve as centers of fiber growth or, conversely, the fibers 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.

PANI supramolecular structures may form not only in the volume of reaction medium, but also on the interface between two phases. In the course of aniline polymerization, thin films of polymer are generated on the surfaces contacting with polymerization medium (Malinauskas, 2001). These surfaces are reactor walls, macroscopic support immersed in polymerization medium, or nanoscopic carriers dissolved or dispersed in this medium. When the synthesis is completed, all these surfaces become covered with PANI layer with a thickness ranging from several nanometers to hundreds of nanometers. PANI layers, as a rule, have homogeneous thickness and are strongly attached to the surface. Adsorption onto macroscopic support leads to the formation of films, and combination of PANI with nanoscopic carrier may give colloidal dispersions of polymer (Sapurina & Stejskal, 2008).

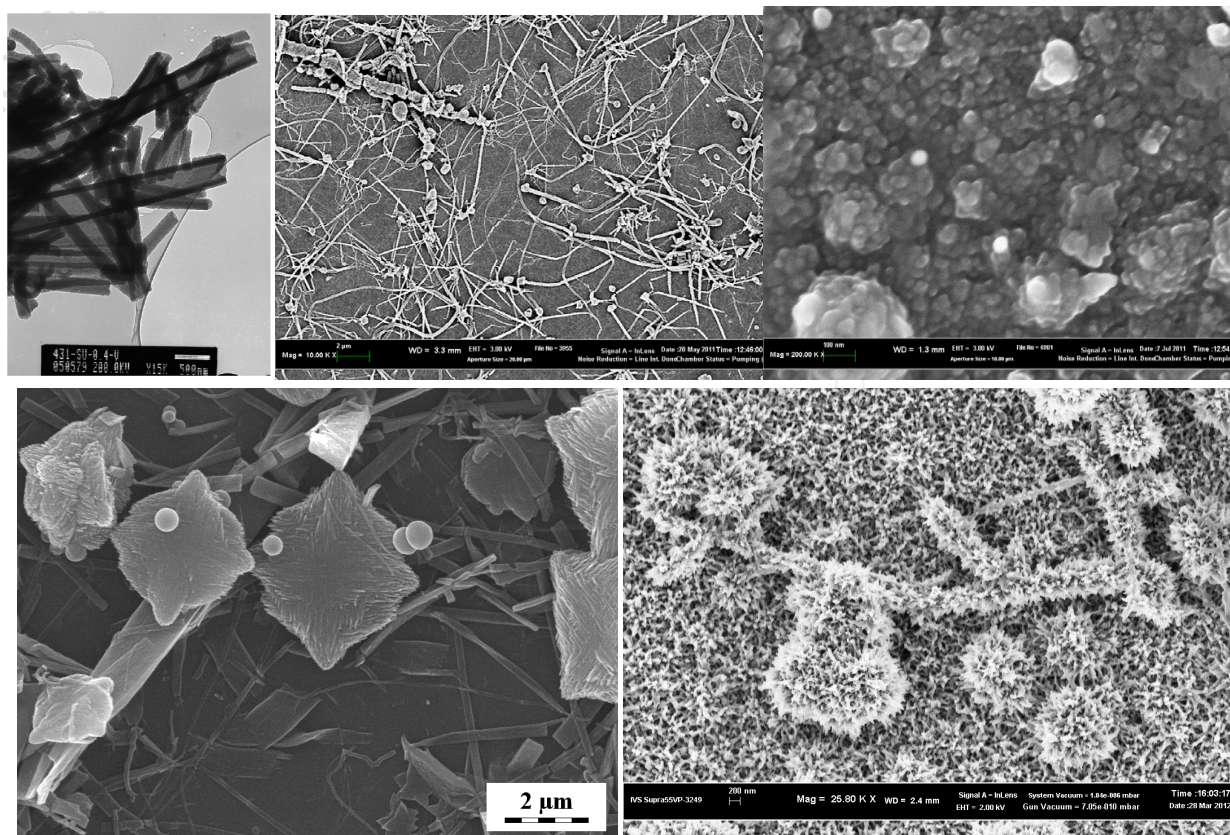


Figure 12. Supramolecular structures of PANI and aniline oligomers: a) PANI nanotubes, b) nanofibers, c) PANI granules. d) The structure of two-dimensional oligoaniline, “nanomats”, in the presence of nanospheres and nanoribbons. e) Hierarchical nanostructure of PANI flowers.

All the 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 (Steskal et al 1998; Stejskal et al 2008; Ding et al., 2008; Laslau et al 2009). In a number of publications, the stages of formation of supramolecular structures in the course of the synthesis are traced, the data on increase in globule diameter, lengthening of tubes and fibers are given. All these data evidence the processes of specific self-organization occurring during aniline polymerization and ceasing after its termination.

Recent studies have clearly shown that ability for self-organization of polymer chains is inherent to PANI (Huang & Kaner, 2006). The mechanism of formation of PANI supramolecular structures is common regardless of the results (thin films, stabilized colloids, precipitated particles of one-, two- or three-dimensional structure). Self-organization processes are the logical continuation of molecular reactions of synthesis allowing to explain the formation of a given type of morphology under different experimental conditions.

7.2. Mechanism of polyaniline self-organization during the synthesis

The suggested mechanism of PANI self-organization is based on the concepts of adsorption and agglomeration of nucleates (phenazine rings) (Sapurina & Stejskal 2008). According to molecular mechanism of synthesis, oxidation in pH range 2.5 – 3.5, as well as the initial step of oxidation at pH < 2.5, yields aniline oligomers having cyclic phenazine structure. It is known that phenazines are planar aromatic rings with high π -electron density. Phenazines are insoluble in aqueous reaction medium and tend to adsorb to surfaces and agglomerate. Phenazine adsorption occurs at the expense of π -electron interaction (one of the most energy-consuming types of physical bonds). Its energy is much higher than that of common van der Waals forces, it is comparable with hydrogen bond energy and estimated to be tens of kcal·mol⁻¹ (Hoeben et al. 2005). Phenazines are planar aromatic structures belonging to the class of discotics. They are prone to crystallization with the formation of stacks and one-dimensional columns or two-dimensional planar templates. Intermolecular binding leading to the formation of columns occurs due to π - π interaction between aromatic rings. The processes of regular assembly of phenazine heterocycles are the most energetically favorable. However, they are not always realized during the synthesis and may give way to the formation of chaotic spherical agglomerates. We suppose that regular and chaotic types of phenazine ring agglomeration create different types of templates which then give rise to polymer chains. This hypothesis allows to explain the formation of various PANI supramolecular structures and gives insight into a number of important properties of the polymer.

7.3. The interrelation between processes of formation of PANI supramolecular structures and molecular reactions of PANI synthesis

The process of formation of polyaniline supramolecular structures corresponds to the paths of molecular reactions. In common with molecular reactions, it depends on pH of reaction medium and oxidation potential of oxidizing agent. Let us consider general rules of formation of supramolecular structures under different experimental conditions.

7.3.1. *The role of acidity and oxidation potential*

7.3.1.1. *Oxidation at pH > 2.5*

In alkaline media, aniline oxidation leads to the formation of oligomers with heterogeneous molecular structure and molecular masses of 3 000 – 5 000; these chains are little capable of self-organization. Oligomer chains are poorly soluble in alkaline medium, and, therefore, during oxidation, trivial aggregation and precipitation of amorphous structures occur. These heterogeneous oligomers form amorphous precipitate (Fig.4e; 6), inhomogeneous films possessing low adhesion to the surface and micro- and nanospheres (Fig 4a). The reason for the formation of spheres is a poor solubility of aniline at high pH and the conditions peculiar to emulsion polymerization (Sapurina & Stejskal 2010). In alkaline medium, aniline is present in the non-protonated form and hence poorly soluble. It exists as droplets in the

reaction medium. These droplets may be stabilized by anions or surfactants present in the solution; consequently, microemulsions or nanoemulsions with sufficiently narrow particle size distribution appear. The oxidation proceeds mainly on the surfaces of droplets; they are covered with a layer of oligomer, but can contain the non-consumed monomer in their internal areas. In this case, hollow spheres are formed (see Fig.16). After addition of acid to the solution, the majority of products obtained in alkaline medium dissolve (as a result of protonation of nitrogen-containing structures). Most of these products are also soluble in organic solvents, such as chloroform, tetrahydrofuran, alcohols (Laska & Widlarz, 2005). Oligomers do not retain their initial morphology under heating; they melt and form monolith (Stejskal & Trchova 2012).

In going to neutral or weakly acidic media, molecular mass of oligomers decreases, and the content of phenazine rings rises. Oligomers become more homogeneous in composition and are prone to crystallization and self-organization. Products of oxidation in weakly acidic media demonstrate planar two-dimensional or one-dimensional morphology (Fig. 4b, f; 8a). These are particles like plates and bands or rhombic micromats and sticks (Fig 12d). We suppose that they are formed as a result of assembly of phenazine columns, as well as tri- and tetramers containing phenazine rings. Two-dimensional and one-dimensional structures differ in durability. Bands and plates with rather weak bonds between phenazines lying in one plane tend to dissolve at $\text{pH} < 4$ and rearrange to form fibers (Yu et al., 2011). At low pH, two-dimensional morphology is not formed; one-dimensional structures with interactions at the expense of more strong π, π -overlapping of adjacent planes prevail.

In the pH range 2.5 to 3.5, the majority of oligomers are phenazines insoluble in water. Compact phenazine molecules of the same type organize into particles of certain geometry. The materials obtained within this pH range possess the highest degree of crystallinity (Prathap & Srivastava. 2011). Here one-dimensional structures (needle-shaped crystallites with smooth surface or fibers which, as a rule, are assembled into more complex formations) prevail (Fig.8b). They consist of columns made of phenazine nucleates which have not yet started growing polymer chains. The formation of all types of oligomers proceeds at low oxidation potentials (starting from +0.4 V) according to oligomerization pattern, i.e., oxidation of reactive deprotonated form of aniline. Therefore, the reaction may proceed under the action of weak oxidants. Due to the absence of polyconjugation, these materials demonstrate low conductivity ($< 10^{-8} \text{ S}\cdot\text{cm}^{-1}$).

7.3.1.2. Oxidation at $\text{pH} < 2.5$

At $\text{pH} < 2.5$, in the initial stage of the synthesis, as well as in the 2.5 – 3.5 range, phenazine nucleates of the same type are formed. There are no long oligomers of heterogeneous structure in this case. Aggregation of phenazines leads to the formation of template of future polymer particle, its shape being programmed in the first stage of synthesis. When the induction period is completed, nucleates start to grow polymer chains and reproduce shape of the template. In spite of the presence of only one type of nucleation centers, the structure of future PANI may vary. In this case, structure is determined by the conditions of self-

organization of phenazine nucleates. At $\text{pH} < 2.5$, type of supramolecular structure depends on the duration of induction period (the stage of formation, accumulation and self-organization of nucleates). The long induction period favors organized assembly of phenazine into columns and is followed by the growth of one-dimensional structures, while short induction period resulting in fast “germination” of nucleates leads to chaotic agglomeration of nucleates and formation of spherical PANI particles (Sapurina & Stejskal 2012).

The use of a strong oxidant (e.g., persulfate) which initiates fast “germination” of nucleates and does not allow them to reach concentrations sufficient for assembly leads to the polymer assembled from granules (Fig.12c). In the presence of weak oxidants, when induction period is long, and phenazine cannot “germinate”, mainly one-dimensional structures are formed (Fig.12a, b). The frames of hierarchical and one-dimensional structures are single phenazine columns or groups of columns assembled into more complex agglomerates. Phenazine agglomerates start growing polyconjugated chains under the action of a strong oxidant with a potential higher than + 1.05 V. In the absence of this oxidant, the transition occurs under the action of oxygen (+1.23 V).

Growth of polyconjugated chains leads to the formation of conducting material possessing properties of organic semiconductor. Supramolecular PANI structures were shown to be very stable; they are not destroyed during polymer carbonization and apparently soluble only in N-methylpyrrolidone. Carbonization of PANI does not lead to melting, as opposed to that of oligomers. The structure of one-dimensional and three-dimensional particles is retained, although their dimensions decrease (Zhang & Manohar 2006). We suppose that high energy of binding of initial phenazine fragments and interchain interactions cause high stability and low processability of PANI.

7.4. The condition of different types of supramolecular structures formation

All supramolecular structures were discovered accidentally when refining the methods of PANI synthesis. The combination of synthesis parameters leading to the prevalence of a certain type of PANI particles is called “method of the synthesis of a supramolecular structure”. In the literature, special consideration is given to obtaining one-dimensional structures in the absence of any structuring template. Methods of synthesis of PANI fibers and tubes were developed by different researchers under different experimental conditions. Let us consider experimental conditions of different methods in terms of the suggested mechanism of formation of one-dimensional supramolecular structures. According to the mechanism, type of PANI supramolecular structure should be determined by the duration of induction period. Long induction period favors organized assembly of phenazines and formation of one-dimensional structures, while short induction period followed by fast “germination” of phenazines leads to chaotic agglomeration and formation of spherical particles. Analysis of synthesis conditions and polymerization process shows that this rule works for the following methods known from the literature.

- *The dilution method* (Zhang et al 2006). Polymerization of aniline is performed under the action of persulfate at $\text{pH} < 2.5$ and at low concentrations of reactants ($< 0.001 \text{ mol}\cdot\text{L}^{-1}$). Conducting PANI has the morphology of fibers several tens of nanometers in diameter and several micrometers in length. Here, long induction period (the stage of accumulation of phenazine nucleates) is observed, since at low concentrations of reactants, rate of nucleate “germination” decreases.
- *The method of soft templates* (Ding HJ et al 2008). Polymerization of aniline is performed in the presence of weak organic acids under the action of both strong and weak oxidants; concentrations of reactants are higher than $0.1 \text{ mol}\cdot\text{L}^{-1}$. Nanofibers and nanotubes with external diameters of 50–500 nm and lengths of up to $10 \mu\text{m}$ are produced. In the presence of weak organic acids, the initial acidity of the reaction mixture is above $\text{pH} 3$. Thus, the reaction conditions enter the pH interval from 2.5 to 3.5, where the rate of aniline oxidation is dramatically reduced, and long induction period is observed. Under these conditions, reactions of chain growth are reduced and only slow accumulation of phenazine nucleates takes place.
- *The method of decreasing pH* (Stejskal et al 2010). Polymerization of aniline ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$) proceeds under the action of different oxidants at low concentrations of strong acids or in the absence of any acids. Polymerization yields nanofibers and nanotubes with external diameters of 50–200 nm and lengths of up to micrometers. Equivalent to *soft templates method* at low concentrations of strong acids or in the absence of any acid oxidation falls within the acidity interval with $\text{pH} > 2.5$ characterized by slow accumulation of nucleates.
- *The method of polymerization at the interface* (Huang & Kaner, 2006). Polymerization proceeds at the interface of organic phase containing aniline ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$) and aqueous phase containing an oxidant (persulfate, Fe^{+3}). The reaction is carried out in the presence of acids dissolved in one phase. PANI nanofibers grow at the liquid–liquid interface separating the reactants. There are two reasons for the formation of PANI nanofibers at the interface between immiscible liquids: (1) decrease in medium polarity at the organic solvent/water interface and suppression of protonation of nitrogen-containing structures (which is equivalent to increase in pH and going to the acidity interval $\text{pH} > 2.5$, where slow accumulation of nucleates occurs); (2) decrease in polymerization rate which is limited by diffusion of reactants at the interface (which is equivalent to dilution).
- *The method of mixed solvents* (Zhou et al, 2007). Aniline ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$) is oxidized with persulfate in the mixed water/alcohol medium in the presence of acids. The reaction gives PANI fibers. Similarly to polymerization at the interface, dilution of water with organic solvent leads to decrease in medium polarity. This process suppresses protonation of reactants, and the reaction falls within the acidity interval with $\text{pH} > 2.5$ characterized by slow accumulation of nucleates.
- *Methods based on cycling of electrical potential or on galvanostatic technique* (Guo & Wang, 2008; Gao & Zhou 2007; Molina et al, 2010). Polymers are produced during the electro-oxidation of aniline at $\text{pH} < 2.5$ in the galvanostatic regime or during potential cycling when the initial potential of more than $+1.05 \text{ V}$ is reduced down up to negative values.

Nanofibers or a network of nanofibers are formed on an electrode. Decrease in oxidation potential suppresses “germination” of phenazine nucleates and promotes accumulation of these nucleates.

- *Methods of weak oxidants* (Sapurina & Stejskal 2012). The methods are equivalent to electrochemical techniques.
- *The method of catalytic additives of aromatic diamines with para-structure.* (Tran et al., 2008) Polymerization of aniline ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$) proceeds under the action of persulfate at $\text{pH} < 2.5$ in the presence of catalytic amounts of *para*-semidine, *para*-phenylenediamine etc. Shortening of induction period leads to the presence of higher fraction of one-dimensional structures (fibers) in the products. This method is the only known exception to the general rule. Apparently, introduction of diamines leads to changes in nucleate structure and fast accumulation of high concentrations of nucleation centers (according to the Scheme 9) promoting the formation of one-dimensional templates.

In all cases, decrease in temperature favors processes of self-organization of phenazine rings into columns and decreases fractions of other morphology types, while increase in acidity results in transformation of one-dimensional structures into granules.

7.5. Stages of self-assembly occurring in the course of PANI synthesis

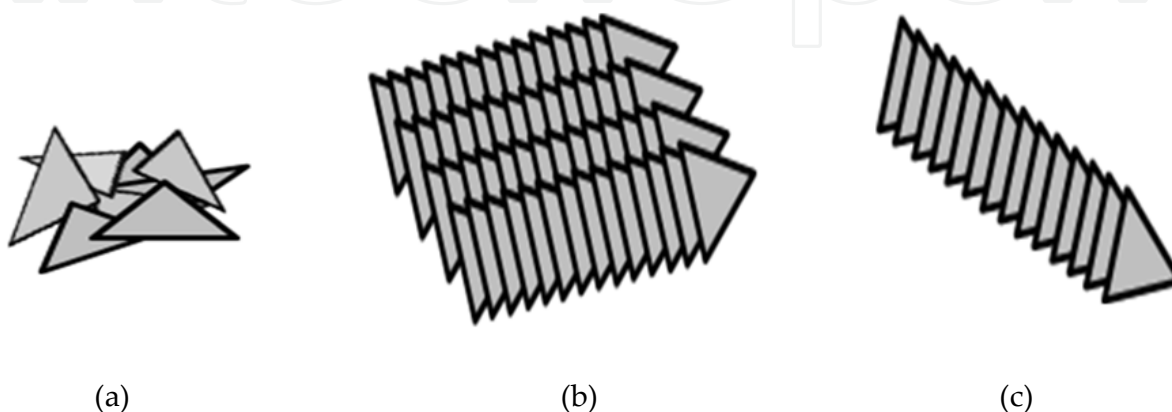
At $\text{pH} < 2.5$, synthesis of PANI involves two steps: induction period and growth of polymer chains. The process of formation of supramolecular structures also may be divided into two stages; we term these stages “nucleation period” and “period of polymer formation”. These phases fully coincide with the steps of molecular synthesis; let us examine the processes included in these steps.

7.5.1. Induction (nucleation) period

In acidic media (at $\text{pH} < 2.5$) conducting PANI (emeraldine) can be obtained as an insoluble precipitate or nanolayer on template surface or dispersion of polymer in aqueous (or organic) phase. Polymer particles included in these formations may have various morphologies (granular, one-dimensional or dendroid). How are all these structures formed? The induction period (formation of insoluble cyclic dimers) is at the same time nucleation stage (i.e., adsorption and association of phenazine nucleates and creation of all types of supramolecular structures). Adsorption of nucleates onto support leads to the formation of PANI films and adsorption onto stabilizer carrier to formation of colloidal particles (Stejskal & Sapurina, 2005). Association of phenazine oligomers results in the appearance of templates of presepitate (Scheme 11).

While phenazine aggregation in reaction medium depends only on synthesis conditions, formation of films and colloids is influenced by the nature of support and carrier. Analysis of literature shows that morphology of thin films and colloidal PANI particles is formed in accordance with the concept of selective interaction between phenazine and surface:

- PANI films grow more actively on negatively charged “anionic” surfaces than on positively charged “cationic” ones (Onoda et al 2006; Shinkai et al 2005).
- The rates of PANI layer growth on hydrophobic templates are higher than those of growth on hydrophilic materials (Onoda et al, 2006; Shinkai et al 2005).
- PANI morphology depends on hydrophilicity/hydrophobicity of the template. Films with homogeneous thickness are formed on hydrophobic surfaces, while on hydrophilic templates, island-like films or polymer layers with rough profiles are grown (Scheme 11) (MacDiarmid 1997).



Scheme 11. Aggregation of phenazine nucleates: (a) chaotic agglomeration b) formation of two-dimensional and c) one-dimensional templates.

Peculiarities of film growth and morphology of these films can be explained by the fact that phenazine nucleate is a hydrophobic organic base. As a base, it interacts strongly with anionic sites and is distributed more uniformly on hydrophobic surfaces. Specific influence of magnetic materials and magnetic field on the growth of PANI film was also revealed. Particularly, some authors observed preferential growth of polymer layer on the boundaries of ferrite domain walls (Fig.13) (Babayan et al. 2012), change of film morphology under the action of magnetic surface, influence of magnetic field on the rate of film formation and its structure (Cai et al. 1997; Ma et al. 2008). The above-listed phenomena may be related to magnetic cation-radical nature of phenazine nucleates showing up under the conditions of synthesis.

The influence of dispersed forms of carrier favoring the formation of PANI colloidal dispersions is also very specific. Depending on the chemical nature of the carrier, it can accelerate aniline polymerization; the more its surface area, the higher the polymerization rate (Stejskal et al. 2003). According to the molecular mechanism, nucleation stage proceeds at low oxidation potential, but culminates in the energy-consuming stage (addition of first monomer unit to phenazine). Certain types of carriers are able to activate phenazine rings and accelerate their “germination”. Activating carriers include ferrites and carbon materials (soot, graphite, carbon nanotubes). In the presence of these additives, induction period can be considerably shortened, and polymerization rate increases many times (Konuychenko et

al. 2006b; Babayan et al. 2012). It was also established that on electrodes made of carbon materials, aniline polymerizes at lower potentials than on platinum electrode (Matsushita et al. 2005). Apparently, in the case of carbon electrode, activation takes place due to the influence of π -electron structure of carbon on π -electrons of phenazine rings, and in the case of ferrites, activation is caused by magnetic interactions. After addition of first monomer unit to phenazine, chain growth proceeds with a relatively low oxidation potential. Thus, "germination" is an "energy barrier" between nucleation stage and the stage of polymer formation. After the start of chain growth, nucleation is virtually terminated. Polymer is formed on the basis of the grown nucleation centers.

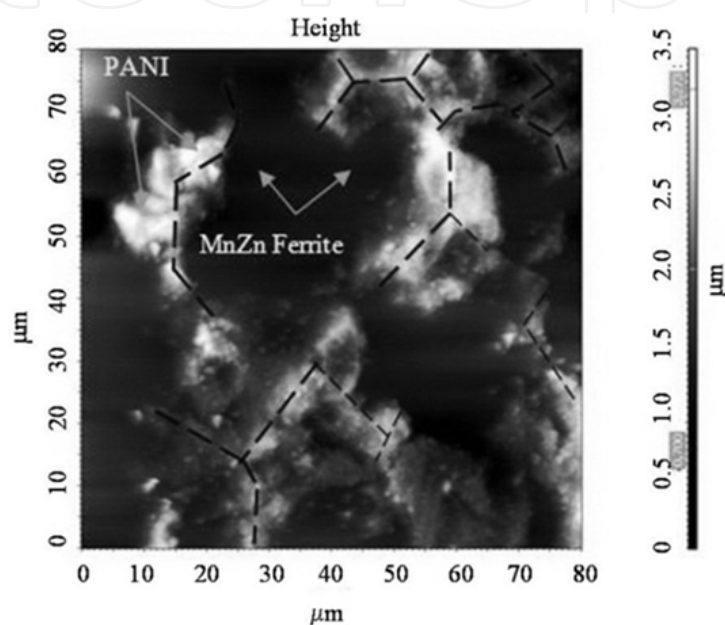
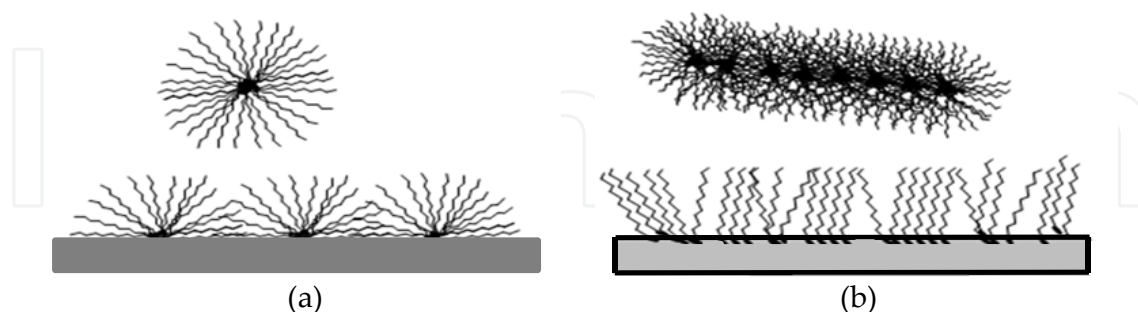


Figure 13. Thin PANI film with a «honeycomb» structure that repeats the microstructure of ferrite grain boundaries prepared on the surface of MnZn ferrite by *in-situ* polymerization



Scheme 12. The formation of PANI supramolecular particles of 3D and 1D morphology and films on (a) hydrophilic and (b) hydrophobic support.

7.5.2. Synchronous growth of PANI supramolecular structures

The existence of "energy barrier" between nucleation and growth stage has an influence on polymer morphology. Rather frequently PANI consists of particles of one type with

practically similar dimensions. Fig. 14 shows spherical particles of PANI colloid and polymer nanotubes. In both cases, low size polydispersity is observed. This result is due to the fact that all growth processes proceed under similar conditions and during similar periods of time, i.e., growth starts and ceases simultaneously for all particles. With the start of growth reaction, nucleation is terminated, and new nucleation centers are not supplied any more. Only nucleates which have had sufficient time to start growth can now take part in propagation. Reaction is completed also synchronously after one of reactants is exhausted. All these processes are responsible for the fact that in the absence of secondary aggregation, PANI particles with a very narrow size distribution are formed. Polydispersity of spherical colloidal particles and globules comprising PANI precipitate is 1.05 – 1.1 (Stejskal et al.1996) Nanofiber diameters and nanotube wall thicknesses also have narrow size distributions.

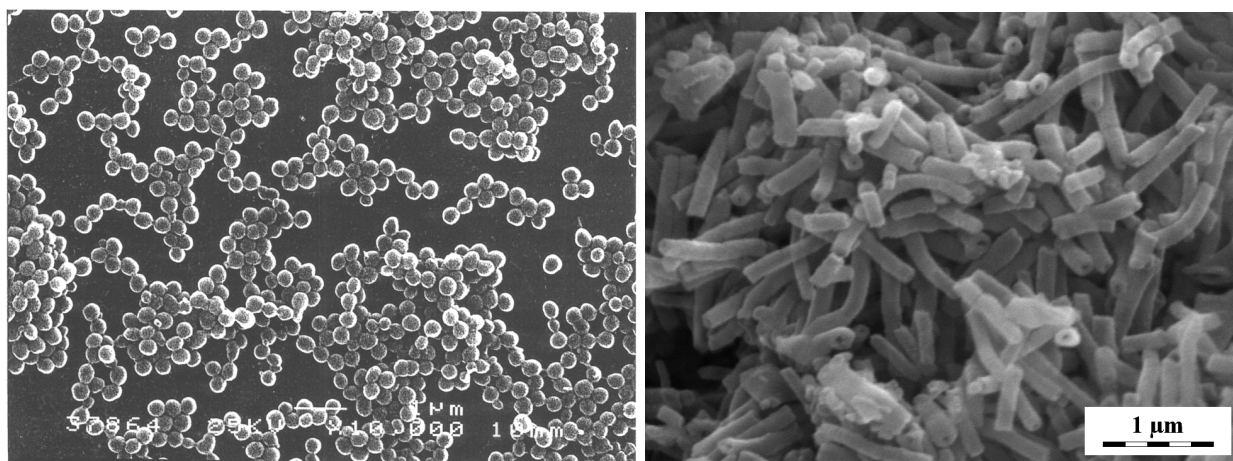


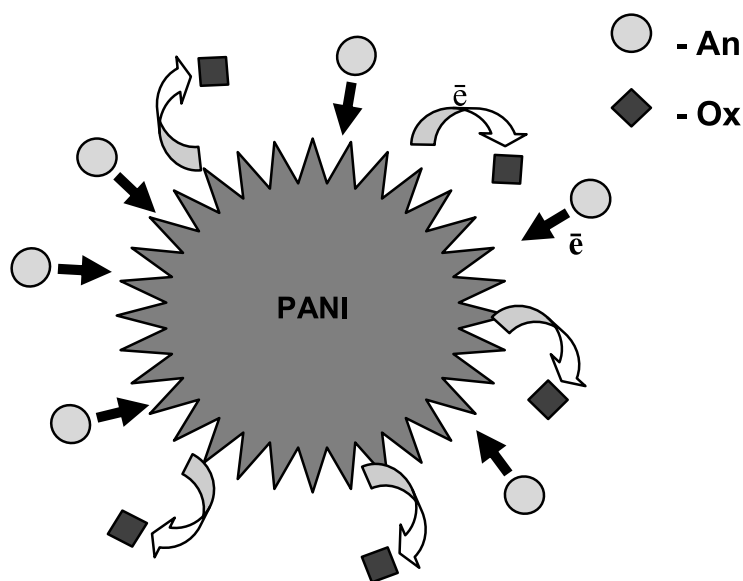
Figure 14. PANI colloidal particles a) and PANI nanotubes b) with low polydispersity of particle size. Scanning electron microscopy.

7.6. The growth of polymer chains possessing electronic and ionic conductivity

By the beginning of the growth stage, initial fragments of future polymer chains are already associated or attached to the surface, and the foundations of supramolecular “architecture” of PANI are laid. During exothermic growth reaction, templates (aggregated phenazine nucleates) which have added monomer units proceed to increase polymer mass at a high rate. The growth of PANI and other conducting polymers is dramatically different from the well-known propagation of dielectric polymers. Conducting polymer grows not as an individual chain, but as a conglomerate of chains possessing electronic and ionic conductivity (Blinova et al. 2007). During the growth process, both monomer and oxidant are soluble, i.e. dispersed at the molecular level. At the same time, growing chains are agglomerated; they are already bound at the expense of interactions between phenazine nucleates and/or between phenazine nucleates and the surface and therefore “feel” each other.

Molecular weight of the polymer increases in the following manner (Scheme 13). Oxidant oxidizes one terminal amino group in agglomerate of polymer chains. Positive polaron

generated after oxidation is easily delocalized within the whole agglomerate and stabilized by mobile acid anion. Oxidation sites created by oxidant are redistributed within the whole conducting particle and minimize its energy. This redistribution determines the following additions of monomer units. Addition of monomer unit may occur not in the point where interaction with oxidant took place. PANI particle takes part in redox interaction as a single entity (Sapurina & Stejskal, 2008; Stejskal et al. 2010). Conducting polymer propagates as a self-organizing agglomerate of polymer chains; these chains response to oxidation/reduction processes as a single object and control shape of polymer particles. Cooperative interaction between oxidant, polymer particle and monomer increases probability of the process manifold and serves as a factor accelerating polymerization (the so-called "autoacceleration").



Scheme 13. Mechanism of heterophase PANI growth involving electronic and ionic transport processes (see text).

7.7. Peculiarities of formation of three-dimensional and one-dimensional structures

PANI granules, as well as spheres, belong to three-dimensional formations, but their structure and properties differ dramatically. Spherical shape is created by aniline droplet which turns into an agglomerate of non-conducting oligomers after oxidation. The basis of conducting granule is a chaotic cluster of phenazine nucleates which has initiated growth of regularly packed polyconjugated chains.

The formation of granules proceeds according to the diffusion-limited aggregation mechanism. Initial phenazines form a cluster, and this cluster starts growth of polyconjugated chains. Then, the second cycle of cluster-cluster diffusion-limited aggregation may take place, and a particle resembling blackberry is formed. The second cycle is observed in the beginning of the propagation step and inherent to particles which are not bound with surface. Apparently, this process is caused by growth of polymer chains

and changes in surface properties of the initial cluster and, therefore, its interactions with medium. "Granule" is a common term for a particle assembled from clusters. In the course of the propagation step, granule grows at the expense of increase in dimensions of individual clusters, while the number of clusters in the particle remains constant. The cluster is a sphere; the granule has a quasi-spherical shape. In the final stage of the synthesis, insoluble granules aggregate to form micrometer-size particles of irregular shape (Spivak et al. 2010).

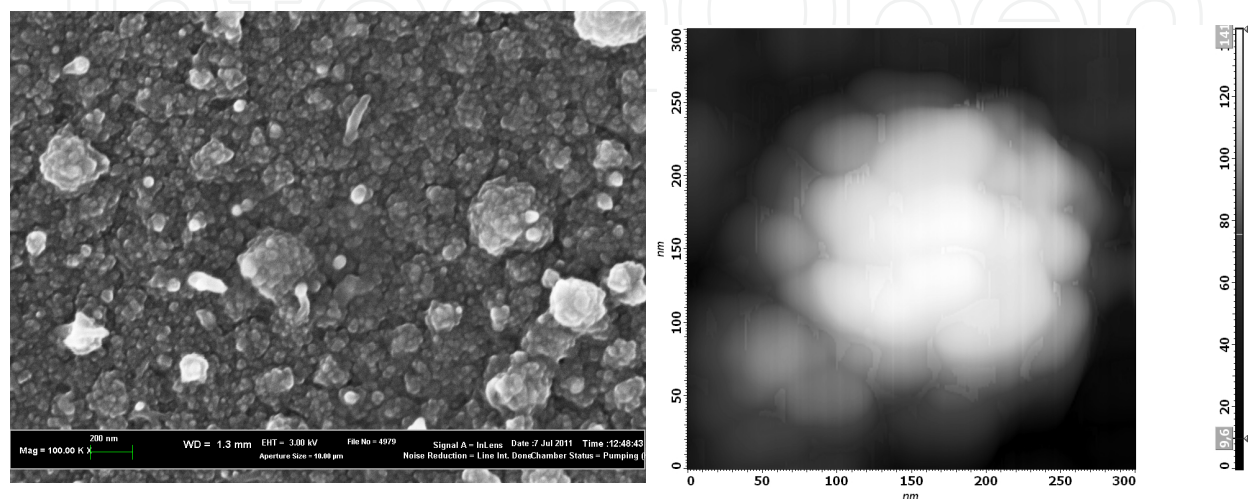


Figure 15. Hierarchical structure of PANI granules. a) SEM image, b) Atomic Force microscopy.

Similarly to granules, one-dimensional structures (fibers and tubes) grow in the course of propagation. Individual column of phenazine nucleates may serve as a template for fiber growth. The presence of larger initial template is necessary for tube growth; this template should shape the inner cavity of polymer nanotube. Depending on synthesis conditions, templates may vary. The most frequently observed templates are crystalline oligomers of aniline forming tubular needle-shaped structures (Stejskal et al. 2006). However, PANI tubes with square and rectangular cross-sections were also obtained; these structures arise with the participation of inorganic crystals (Ding et al. 2009). Template should not necessary be one-dimensional and have the length corresponding to tube size. In the propagation step, lengthening of fibers occurs, and, by analogy with fibers, tube length also increases with retaining the initial shape of this tube. We suppose that during growth, central rod of one-dimensional structure lengthens at the expense of build-up of new cyclic oligomers. However, the formation of phenazine rings occurs not in the solution, but directly on the surface of butt end of growing fiber or tube. In essence, this process is analogous to growth of organic single crystal. It is less energy-consuming than formation of new phenazine sites in solution and occurs at lower oxidation potential (Sapurina & Stejskal 2008). Simultaneously, wall thickness also increases. Polymer chains arising in heterogeneous medium are regularly organized and interact with adjacent chains via hydrogen bonds. Apparently, the outer diameter of lengthening one-dimensional structure is controlled by the fact that the wall-forming chains "feel" their environment. The whole system, in common with crystal, controls its dimensions during growth.

Heterophase growth of polymer particles (involving processes of electronic and ionic transport of oxidation sites) allows to reach high level of self-organization. With that, a certain shape of particle (from spheres with clear boundaries to tubes with definite diameters) is formed. One is tempted to compare oxidative polymerization of aniline with the processes of nucleation and growth of crystals. Slow and energy-consuming stage of formation of initial crystallites occurs in solution. The subsequent crystal growth proceeds directly on the surface of a crystallite and develops very fast. Just as crystallite surface catalyzes processes of "assembly" of crystal structure, redox-active conducting polymeric agglomerate catalyzes and organizes assembly of monomer units.

To summarize the section devoted to stages of assembly of PANI supramolecular structures and influence of oxidation potential and pH of reaction medium on PANI morphology, we should note the following points. The formation of uniform phenazine nucleates always leads to high supramolecular order (be it organization of oligomers or polymer chains). In contrast with the case of oligomers of heterogeneous structure, there are no amorphous formations. The assembly proceeds according to reactions of molecular synthesis. Supramolecular architecture of conducting PANI laid down in the induction period (during organization of phenazine rings) is fixed and completed in the propagation step during the formation of hydrogen bonds between regularly packed polymer chains. These types of intermolecular interactions are the basis of a diversity of supramolecular PANI structures.

8. The principle of organization of PANI supramolecular structures

Comparison between different types of PANI supramolecular structures obtained under similar experimental conditions reveals many common features. Not only particles of one type (e.g., granules) have similar dimensions; linear dimensions of structures of different types also coincide. Thus, in one reaction vessel, PANI films and colloids may be obtained simultaneously (or films and granular precipitate). Radii of colloidal particles are equal to film thicknesses, dimensions of precipitated PANI granules are also in good agreement with the thicknesses of films (Riede et al. 2002; Sapurina et al 2002). Thickness of nanotube walls is always identical to radius of fibers and simultaneously equal to thickness of walls of nanospheres obtained in the same experiment as one-dimensional structures (Fig.16). These facts indicate that all the supramolecular PANI objects have common structure. The correspondence between linear dimensions of supramolecular objects (film thickness, thickness of polymer tube wall, fiber radius) and molecular mass of PANI forming a given structure was also revealed. Moreover, thickness of an object coincides with the length of stretched polymer chain (when calculation of chain length was performed with regard for zigzag structure (Sapurina et al 2002) and with the use of experimentally established number-average molecular weight of polymer).

Experimental data concerning correlation between linear dimensions of different types of supramolecular structures and dependence between dimensions and molecular mass of polymer can be explained by the hypothesis that PANI structures are organized on the principle of radial arrangement of polymer chains. In spherical particles, polymer chains

radiate from the center. Fibers and walls of PANI tubes consist of polymer chains organized perpendicularly to the axis of one-dimensional structure, and PANI films attached to a surface have a structure of polymer brush. This type of organization may be promoted by diphilic nature of growing chain. PANI chain consists of cyclic nucleate and linear "tail". Under synthesis conditions, phenazine nucleates are deprotonated, and, being deprotonated nitrogen-containing structures, they are hydrophobic. At the same time, growing polymer chains are protonated and hydrophilic. Naturally, hydrophilic chains grow mainly towards aqueous phase, and away from hydrophobic nucleate. Diphilic "nucleate-chain" structure resembles micelle-forming surfactant molecule, with the difference that hydrophobic fragments of PANI chains are strongly attached to each other or a surface.

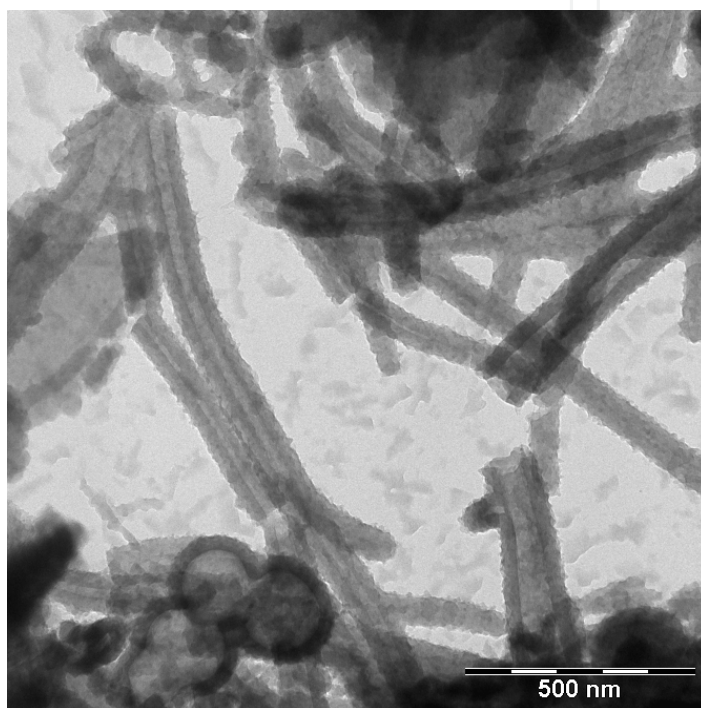


Figure 16. PANI nanotubes and nanowires together with hollow PANI spheres. (TEM image)

9. Supramolecular structure of polyaniline – The model of inhomogeneous metal

Since the end of the 1980s, mechanism of charge transport in conducting polymers has been studied with the use of four representatives of this class (polyacetylene, polyaniline, polypyrrole and polythiophene) as examples (Skotheim, 2007). All these conducting polymers demonstrate similar features. In the doped conducting form, they possess comparatively low conductivity (less than 10^2 S·cm⁻¹ and 10^4 S·cm⁻¹ for polyacetylene) characteristic more of semiconductors than metals. Activation character of temperature dependence of conductivity is also typical for a majority of samples. At the same time, the data obtained in the studies of magnetic, optical, dielectrical properties, as well as thermopower, indicate the presence of conduction electrons in doped polymers. Thus, polymers demonstrate dual character and reveal properties of both semiconductors and

metals. Low charge carrier mobility ($10^{-1} - 10^{-4} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ for PANI (Harima et al., 2001) and their high concentration ($3 \cdot 10^{20} \text{ spin} \cdot \text{g}^{-1}$) comparable with carrier concentration in metals provide evidence that there are mechanisms of localization of charge carriers in macroscopic samples.

To explain all these experimental data, the model of structurally inhomogeneous conducting polymer was suggested; in this model, the sample is considered as an inhomogeneous metal. The polymer is represented as “a system of conducting islands in dielectric matrix”. According to the model, crystalline “islands” assembled of regularly packed polyconjugated chains exhibit metallic conductivity. Charge carrier mobility and polarizability inside this island are high. However, islands are distributed in a weakly conducting medium which creates a barrier for charge transport. The medium with low conductivity is a set of separate transport paths connecting these conducting islands into one common net. This model presents the best description of properties of conducting polymers, allows to explain localization of charge carriers and one-dimensional transport which is frequently observed and corresponds to the linear dependence $\sigma = f(T^{1/2})$ (Epstein et al, 1994; Alechin 2006).

The conductivity of a crystalline island is estimated to be about $10^6 \text{ S} \cdot \text{cm}^{-1}$, i.e., 4-6 orders of magnitude higher than that of a typical macroscopic sample. It was shown that the island possesses three-dimensional metallic conductivity. Crystalline areas demonstrate rather narrow size distribution and are uniformly dispersed in amorphous matrix. Depending on the used method of synthesis, doping and subsequent treatment, dimensions of crystalline areas may vary from 5 nm to 100 nm (Mazerolles et al., 1999). The level of conductivity of macroscopic sample is determined by degree of overlapping between boundaries of conducting “islands” and may vary over wide limits.

In deprotonated polymers, volume fraction of islands is low, but it increases with increasing degree of doping. Transition from non-doped polymer to doped one demonstrates percolation character. At the doping degree of 20%, percolation transition occurs, and conducting paths between metallic islands start to form; therefore, conductivity increases dramatically. The transport between islands requires activation. With increasing temperature, activation barriers between conducting elements may be more easily overcome, and conductivity grows. Changes in conductivity and inductive capacity depend on temperature and degree of protonation, and this dependence demonstrates fan-like pattern. Increase in the volume of crystalline island during swelling in organic solvent also may promote transition of macroscopic sample into metallic state. The suggested model of “disorganized metal” explains the presence of metallic state in conducting polymers, low level of macroscopic conductivity and activation-requiring transport in macroscopic sample (caused by inhomogeneity in polymer structure).

The model of structurally inhomogeneous PANI was proved directly in the experiment. Inhomogeneous morphology of the polymer, as well as inhomogeneity in the properties of macroscopic samples, was revealed by X-ray structural analysis, luminescence, ellipsometry, electron and atomic force microscopy (Leite et al 2008; Lux et al 2003). Crystalline islands were observed as dense inclusions in amorphous matrix with the aid of high-resolution

transmission electron microscopy and atomic force microscopy (Mazerolles et al 1999). (Fig.17). The model of inhomogeneous metal describes properties of conducting polymers well, but it has a drawback: the reasons for appearance of island structure are not understood. While molecular structure of polyconjugated PANI chains demonstrates very high homogeneity, the mechanisms leading to the formation of this considerable inhomogeneity in structure and properties of macroscopic sample are unclear.

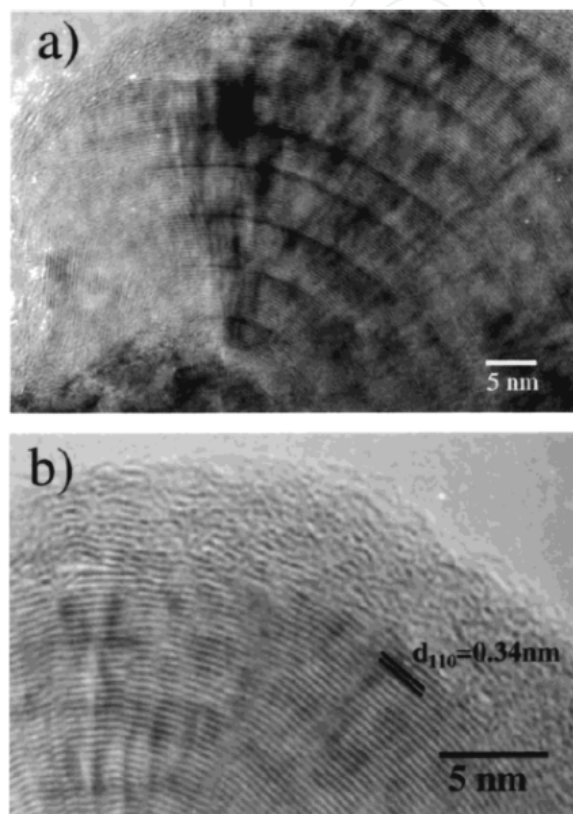


Figure 17. High resolution TEM image of PANI particles of granular structure.

From Mazerolles L, Folch S, Colombari P. Study of polyanilines by high-resolution electron microscopy. *Macromolecules* 1999;32:8504–8.

The mechanism of self-organization of polymer chains during doping process is an attempt to explain the formation of crystalline islands (Zuo et al, 1987; Zuppiroli et al 1994). According to this mechanism, appearance of polarons in solid phase of polymer is accompanied by processes of local self-ordering of chains and self-assembly to crystalline island structures, while disappearance of polarons leads to destruction of polymer islands. The suggested mechanism of self-organization in the course of doping is beneath criticism. Driving forces of this self-organization are unclear. The reasons for very irregular “gathering” of polymer chains in crystalline conglomerate (so that densities of neighbor areas of a sample differ by several times) are not understood either. According to this mechanism, we have to assume that self-organization into island structures occurs due to motions of macromolecules in solid polymer. Therefore, it is difficult to understand how high degree of chain ordering inside island leading to “metallic” transport is achieved. It is also impossible to explain the extremely high rate of

self-organization processes. Changes in polymers proceed at the rates corresponding to mobility of low-molecular weight compounds in liquid phase (doping and dedoping of PANI may occur with a frequency of up to 30 Hz).

In our opinion, self-organization of PANI with the formation of "island" structures occurs in the stage of polymer synthesis. The formation of inhomogeneous structure of polymer proceeds according to the mechanism of heterophase growth of PANI as individual particle (Sapurina & Stejskal 2008). We suppose that the PANI particles formed during polymerization are the inhomogeneous elements ("island" and its surrounding area).

Let us consider granular structure of PANI. Typical dimensions of spherical PANI clusters are tens of nanometers; these parameters are in agreement with sizes of conducting islands. The central part of a particle demonstrates high degree of organization of polymer chains. Similarly to the "island", this is a three-dimensional crystal, and it may support three-dimensional metallic conductivity (Joo et al 1994). On the periphery of a particle, organization is disturbed; every crystalline island is surrounded by amorphous mantle. This fact explains why at high degree of polymer crystallinity (60% for PANI) (Stejskal et al 1998) transport mechanism most often remains activation-dependent. Conductivity of macroscopic sample is limited by intervals between crystalline zones; here, transport is carried out via transport paths, this being in agreement with the frequently observed one-dimensional conductivity. Synchronous growth of particles of one type in the course of PANI synthesis guarantees uniform distribution of crystallites of the same size within polymer sample.

Behavior of PANI under external influence and during aging also agrees well with the model "particle – inhomogeneity element" (Travers et al, 1999). Oxidation/reduction, protonation/deprotonation and thermal aging of PANI result in changes on the periphery of a particle. These processes first cause response from the Curie spins present in amorphous zone. As a rule, they do not affect the central area of a particle. Reduction and deprotonation of emeraldine do not lead to complete disappearance of polarons. Non-conducting forms of PANI contain unpaired spins (10^{16} spin·g⁻¹), as well as acid which stabilizes positive polaron. It was shown that the content of the Pauli spins (populating crystalline areas) does not decrease after deprotonation. Loss of conductivity does not cause considerable reorganization of supramolecular structure (Pouget et al., 1994). The problem of structural inhomogeneity of PANI is very important, since it is the heterogeneity on supramolecular level that limits conductivity of polymers.

10. Concluding remarks

This review attempts to consider synthesis of PANI from a general viewpoint, starting with molecular reactions and assembly of supramolecular structures and ending with comparison between general concept of synthesis and the model of inhomogeneous metal explaining properties of conducting polymers. The information is presented succinctly, and we have no opportunity to give experimental proof of different points, but it can be found in the given references.

Apparently, PANI synthesis is not unique. Similar regularities are observed during synthesis of other conducting polymers by oxidative polymerization. During oxidation, pyrrole, thiophene and their derivatives demonstrate dependence between their properties, pH of reaction medium and oxidation potential; they are self-organized in the course of synthesis and form different types of supramolecular structures. There are reasons to believe that, similarly to PANI, high selectivity of synthesis and formation of polyconjugation in other polymers are related to the presence of excess positive charge on the growing chain. Evidently, the formation of aggregates between growing chains of conducting polymers involves electronic and ionic transport. Processes of molecular synthesis and assembly of supramolecular structures determine properties of conducting polymers. Understanding these processes would allow us to obtain materials with better characteristics.

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