ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 2, pp. 256–275. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © I.Yu. Sapurina, J. Stejskal, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 2, pp. 261–281.

Oxidation of Aniline with Strong and Weak Oxidants

I. Yu. Sapurina[a] **and J. Stejskal**[b]

[a] *Institute of High-Molecular Compounds, Russian Academy of Sciences,*
Bol'shoi pr. 31, St. Petersburg, 199004 Russia
e-mail: sapurina@hq.macro.ru

[b] *Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic,*
Heyrovského nám. 2, Prague, 16206 Czech Republic

Received March 25, 2011

Abstract—Oxidative polymerization of aniline by the action of a strong oxidant, ammonium peroxodisulfate, and a weak oxidant, silver nitrate, was studied in media with different acidities. Depending on the reaction conditions, the organic fraction of the products contained either nonconducting aniline oligomers or conducting high-molecular polyaniline. The effect of the oxidation potential on the oxidation process and formation of supramolecular structures by oxidation products was discussed on the basis of analysis of the kinetics and products of aniline oxidation by spectroscopic, conductometric, thermogravimetric, chromatographic (gel permeation), and electron microscopic methods. A relation was revealed between the morphology of composite materials and their electric conductivity.

DOI: 10.1134/S1070363212020168

Oxidation of aniline gives rise to numerous useful products such as drugs, dyes, explosives, and polymeric materials. Polyaniline (PANI) obtained by oxidative polymerization of aniline is among the most widely known representatives of conducting polymers. Polyaniline has found practical applications due to its redox and acid–base properties, high thermal stability, and electric conductivity. It is used in energy-saving devices and sensors, for electromagnetic shielding, and for the preparation of antistatic and conducting coatings; it also acts as corrosion inhibitor. Polyaniline possesses a high potential for use in medicine and heterogeneous catalysis [1].

Polyaniline is synthesized by oxidation of aniline in aqueous or aqueous–organic medium. Polymerization of aniline is a chain process, i.e., monomer units are successively appended to a polymer chain bearing an active terminal group. Wei [2] considered aniline polymerization to be a specific reactivated chain process. Chain propagation involves repeated activation–deactivation acts which imply oxidation–reduction. Inactive polymer chain is activated by the action of oxidant, but the subsequent reaction with monomer leads to reversible reduction and deactivation. During the reduction process, polymer chain extends due to addition of monomeric unit, and two protons are released thereby. Oxidation of aniline in acid medium gives regular polymer chains containing more than 95% of *para*-substituted units connected in a head-to-tail mode [3]. Regular structure determines polyconjugation and a unique set of properties intrinsic to polyaniline, in particular high electronic and proton conductivity, redox power, and paramagnetism [1]. Unlike other kinds of chain polymerization, e.g., radical polymerization where oxidant participates only in chain initiation, oxidative polymerization requires a large amount of oxidant [4] which is consumed for each act of addition of monomer unit. Therefore, molar concentration of oxidant should be comparable with the monomer concentration. Here, oxidant operates throughout the entire process until addition of the last monomer portion to polymer chain.

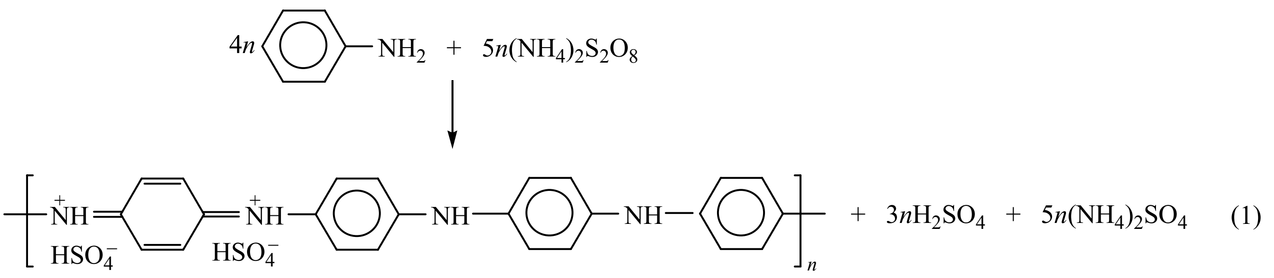
Polymerization of aniline can be performed by electrochemical or chemical methods with the use of various oxidants. In electrochemical syntheses of polyaniline, the potential at least once is raised above +1.05 V (according to the standard hydrogen scale). Chemical methods utilize most frequently strong oxidants whose oxidation potential exceeds +1.0 V. The reason is that chain initiation in acid medium requires an energy barrier corresponding to +1.05 V to be overcome [5]. Chemical syntheses of polyaniline are commonly performed using persulfates whose oxidation potential is +2.01 V. However, it was found experimentally that oxidation of aniline also occurs by the action of weak oxidants whose potential is close to 1 V or even lower. Such oxidants as $FeCl_3$ (+0.77 V) [6, 7], V_2O_5, (+0.98 V) [8–12], $AgNO_3$ (+0.8 V) [12–14], MnO_2 (+1.2 V) [15], KIO_3 (+1.1 V) [16], Pd^{+2} (+0.89 V) [17], and Au^{+3} (+1.0 V) [12, 18] are capable of oxidizing aniline not only in alkaline and neutral media but also in acid medium where the potential barrier to oxidation is fairly high.

The use of oxidants other than persulfates and especially of those possessing a low oxidation potential attracts much attention. In keeping with generally accepted views, reduced oxidation potential could favor polymerization to occur under milder conditions and formation of polymer structures with a lower number of defects and higher conductivity. From the technological viewpoint, proper choice of oxidant is important for the preparation of PANI colloidal dispersions which may be difficult to purify from by-products. The nature of oxidant affects the structure of low-molecular oxidation products. In this connection, an ideal oxidant could be hydrogen peroxide, for its reduction gives water. Finally, the reduced oxidant may be an important component of the oxidation products. Examples are metal–polymer hybrids formed as a result of oxidation of aniline with noble metal salts [13, 14, 17–19].

Another interesting aspect of using oxidants with a low oxidation potential is their effect on the PANI structure. Replacement of a strong oxidant by a weak one leads to transformation of the globular polymer structure to unidimensional, i.e., fibers and tubes are formed instead of spherical particles. Such transformations were observed when $FeCl_3$ [6], V_2O_5 [10, 11], $AgNO_3$ [13, 14], MnO_2 [15], KIO_3 [16], and CeO_2 [20] were used as oxidants. Ding et al. [21] revealed a relation between the oxidant redox potential and size of polyaniline nanofibers: reduction of the redox potential was accompanied by decrease of the diameter of PANI nanofibers. Similar relations were observed in the electrochemical oxidation of aniline [22]. Linear morphology also includes concomitant hierarchical structures like hedgehogs, flowers, and corals. Factors responsible for the observed variations of supramolecular structure of polyaniline remain unclear so far.

A number of publications [23–27] were concerned with aniline oxidation with silver nitrate ($AgNO_3$) whose oxidation potential is 0.8 V and study on the oxidation products which were composites of organic material and metallic silver. During the oxidation process the reaction mixture was subjected to various impacts, specifically to UV or gamma irradiation, ultrasonic treatment, or heating to 250°C. The formation of aniline oxidation products under these conditions was explained by activation of the monomer and reduction of its oxidation potential. The authors believed that only external action promoted oxidative polymerization of aniline; otherwise, it would be impossible. In fact, in keeping with general principles, oxidants with a redox potential lower than +1 V should be incapable of effecting polymerization of aniline provided that the potential barrier is +1.05 V. On the other hand, it was shown [13, 14, 28] that polymerization of aniline by the action of silver nitrate does occur in acid medium under normal conditions at reactant concentrations of 0.02–0.4 M in the absence of specific actions. The resulting product is characterized by spectral parameters typical of emeraldine polyaniline and by a conductivity of several S/cm. The oxidation of aniline is accompanied by reduction of silver nitrate. Stoichiometric amounts of the reduced oxidant were detected in the reaction mixture when the polymerization was complete; this indicates that the redox process involves aniline and oxidant with a low oxidation potential. It was interesting to understand factors responsible for the above transformations.

In the present work oxidation of aniline with silver nitrate was studied in comparison with the oxidation with a strong oxidant, ammonium peroxodisulfate. The mechanism of formation of polyaniline with participation of a reagent possessing a low oxidation potential is discussed, and concomitant processes of formation of supramolecular polymer structures and silver metal clusters are also considered. Apart from theoretical importance, the oxidation of aniline with silver nitrate attracts strong practical interest. The oxidation product is a hybrid material containing a polymeric semiconductor and metallic silver particles. The character of oxidation products and morphology of both components may change depending on the conditions. As a result, materials with different properties, e.g., with a conductivity varying from 10^{-2} to 10^3 S/cm, could be obtained. Development of methods for the synthesis of metal–polymer composites with specified properties is very important from the practical viewpoint. Such materials can be used as detector components in sensors and electromagnetic shields, as well as in medicine and catalysis.


(1)

Oxidation of aniline at different acidities of the medium. The oxidation of aniline was studied most thoroughly under acidic conditions with the use of a strong oxidant, ammonium peroxodisulfate. The overall process can be represented by Eq. (1).

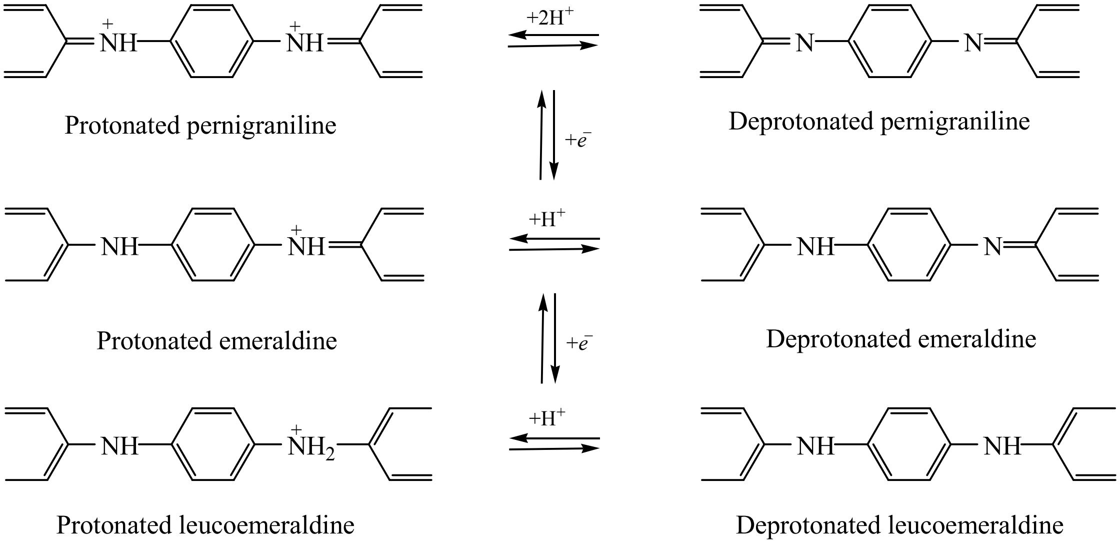
If the oxidant-to-monomer molar ratio does not exceed 1.25, the major product is emeraldine polyaniline with regular polyconjugated structure and a conductivity of 10^{-1}–10 S/cm [1, 29]. This is the most stable form of polyaniline with a medium degree of oxidation, corresponding to oxidation of every second nitrogen atom. Emeraldine contains equal numbers of amino and imino groups and is capable of being reduced or oxidized further (Scheme 1). The reduction of emeraldine gives a polymer having no oxidized nitrogen atoms, leucoemeraldine. Oxidation of emeraldine yields a structure with completely oxidized nitrogen atoms, pernigraniline. In the course of oxidation, disubstituted amino groups in the polymer are reversibly transformed into imino groups. These redox transformations of polyaniline conform to the potential ranges 0–0.2 and 0.7–0.8 V, respectively.

Nitrogen-containing moieties in polyaniline (i.e., amino and imino groups) exhibit basic properties, and they can react with an acid in reversible mode; this process is referred to as protonation [30]. Like low-molecular nitrogen-containing compounds, including aniline, amino and imino groups in PANI undergo protonation at definite pH values, so that all oxidized forms of PANI can exist as different protolytic species, depending on the acidity of the medium (Scheme 1).

As follows from Eq. (1), by-products in the oxidation process are the reduced dye and acid. Ammonium peroxodisulfate is reduced to water-soluble sulfate. Silver nitrate should be reduced to metallic silver. In the course of aniline oxidation the acidity of the medium continuously increases, for the addition of each monomer unit is accompanied by release of two protons. Variation of pH may be regarded as an independent oxidation parameter. In this the progress of aniline oxidation was monitored by measuring pH.

The most important redox interaction in oxidative polymerization of aniline is that occurring between the

Scheme 1.



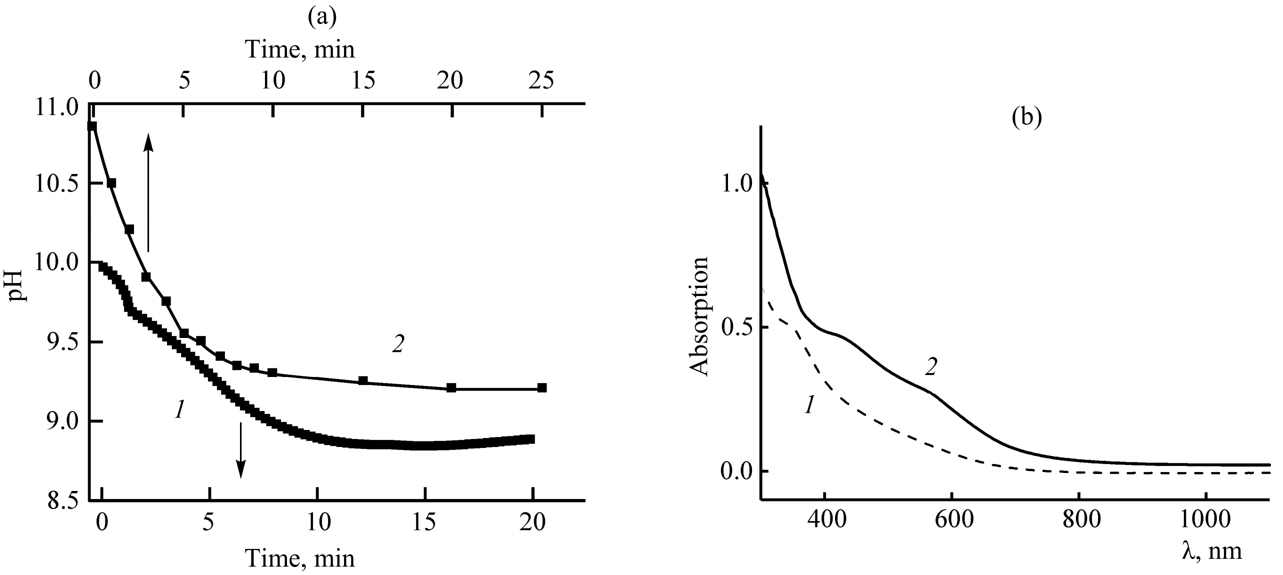


Fig. 1. (a) Variation of pH in the course of aniline oxidation with (*1*) ammonium peroxodisulfate and (*2*) silver nitrate in 0.5 M aqueous ammonia. (b) Electronic absorption spectra of products of aniline oxidation with (*1*) ammonium peroxodisulfate and (*2*) silver nitrate; solvent *N*-methylpyrrolidin-2-one.

nitrogen-containing reagents, monomer and growing polymer chain. Oxidant only activates polymer chain via oxidation to the highest oxidation state, pernigraniline, while the latter oxidizes and takes up monomer unit. Growing polymer may be regarded as mediator of aniline oxidation. During the polymerization process polyaniline "oscillates" between the highest and medium oxidation states, pernigraniline and emeraldine [31].

As shown in [32–35], the oxidation of aniline with persulfate as strong oxidant is controlled by pH. This is related to the participation in the redox process of protonated and deprotonated aniline and growing polymer chain. Neutral aniline undergoes protonation at pH 4.6 [36]. Protonation of oxidized imino groups in the polymer chain occurs at pH 2.5 (Scheme 1) [37, 38]. Disubstituted amino groups are protonated only under strongly acidic conditions (pH ~ 0) which are inappropriate for the synthesis of PANI [37].

Aniline oxidation within the pH ranges determined by the reactant protonation constants, namely at pH > 4.6, 4.6 > pH > 2.5, and pH < 2.5, follows radically different patterns. The reason is that protonation changes redox potential of nitrogen-containing species. Neutral reactants are characterized by relatively low redox potential. Neutral amino group readily loses an electron thus being oxidized even at +0.3 V; as the acidity rises, its redox potential increases. Protonation creates excess positive charge on the nitrogen atom. This leads to increase of redox potential of nitrogen-containing moiety, which can exceed +1.0 V [39].

It should also be kept in mind that variation of pH during the oxidation process due to release of protons continuously changes conditions of oxidative polymerization. The decrease in pH is the stronger, the lower the initial acidity, the higher the reactant concentration, and the faster the oxidation process. The presence of buffering agents capable of binding protons also affects pH in the oxidation process. A reaction started at pH 10 may be complete at pH 1 [32–34, 40–43]. Variation of pH is accompanied by change of redox potentials of the reactants and hence of reaction mechanism and nature and morphology of oxidation products.

Let us consider variation in the course of aniline oxidation depending on pH with the use of a strong oxidant, ammonium peroxodisulfate (oxidation potential +2.01 V) and a weak oxidant, silver nitrate (+0.80 V).

Oxidation course and properties of the products. *pH > 4.6*. At pH > 4.6 both monomer and polymer chain are not protonated, so that the reaction involves only neutral nitrogen-containing species with a low oxidation potential. As with ammonium peroxodisulfate, the oxidation with $AgNO_3$ starts immediately and goes monotonically at a high rate. Figure 1a shows variation of pH with time in the oxidation of aniline with both oxidants. The reactions in 0.5 M ammonia at an initial aniline concentration of 0.2 M and

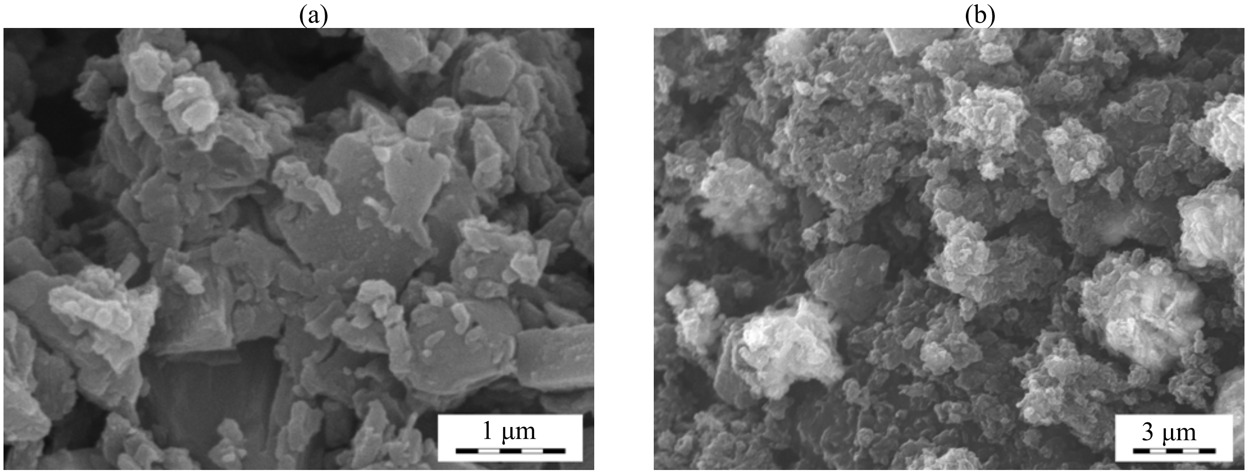


Fig. 2. Scanning electron microscopy images of products of aniline oxidation with (a) ammonium peroxodisulfate and (b) silver nitrate in alkaline medium (11 > pH > 9).

[Ox]$_e$: [An] ratio of 2.5 were complete in several minutes. In the oxidation with $(NH_4)_2S_2O_8$ the initial pH value 10.0 decreases to 8.9 by the end of the process. In the reaction with $AgNO_3$ the pH value changes from 10.8 to 9.3. These data indicate that both monomer and polymer chain do not undergo protonation throughout the process. In the oxidation of aniline with silver nitrate metallic silver deposited on the walls of the reaction vessel.

The yields of oxidation products and their properties are collected in Tables 1–3. Organic products formed in the aniline oxidation with both $(NH_4)_2S_2O_8$ and $AgNO_3$ were aniline oligomers with broken polyconjugation system [33, 34]. The electronic spectra of solutions of these oligomers in *N*-methylpyrrolidin-2-one displayed no absorption above λ 600 nm (Fig. 1b). No absorption band at λ 630 nm, typical of polyconjugated emeraldine was observed. Therefore, no emeraldine is formed in these reactions. The molecular weight of the oligomers does not exceed several thousands, which corresponds to a degree of polymerization of about several tens. The conductivity of the products obtained with the use of ammonium peroxodisulfate does not exceed 10^{-10} S/cm. The density of the material obtained in the oxidation with $AgNO_3$ was 4.22 g/cm^3 (Table 3). Taking into account that the density of polyaniline and aniline oligomers does not exceed 1.4 g/cm^3, the obtained material is a composite containing a significant fraction of metallic silver. Its conductivity was estimated at 5030 S/cm.

The oxidation of aniline with both $(NH_4)_2S_2O_8$ and $AgNO_3$ gives mainly amorphous products (Fig. 2). Silver is present therein as spherical particles with a size of 50 nm to micron level.

Table 1. Properties of aniline oxidation products with ammonium peroxodisulfate (0.25 M) under different acidities; aniline concentration 0.2 M

Parameter	0.5 M aq. NH_3, conversion 80%	0.4 M AcOH, conversion 50%	0.4 M AcOH, conversion 100%	0.1 M H_2SO_4, conversion 100%
Initial pH value	10	4.5	4.5	2.4
Final pH value	8.9	3.5	1.3	1.0
Polaron absorption maximum λ, nm	–	–	618	630
Conductivity, S/cm	$<10^{-10}$	2.4×10^{-10}	0.036	3.7
Density, g/cm^3	–	1.307	1.338	1.402
Molecular weight M_w	4090	>1000	32200	39400
Morphology	Amorphous	Two-dimensional	Nanotubes	Granules

Table 2. Properties of aniline oxidation products with silver nitrate (0.5 M) under different acidities; aniline concentration 0.2 M

Parameter	0.5 M aq. NH_3, conversion 100%	0.4 M AcOH, conversion 30%	0.4 M AcOH, conversion 70%	0.1 M HNO_3, conversion 30%
Initial pH value	10.8	5.7	5.7	2.5
Final pH value	9.3	3.5	2.5	1.8
Reaction time, h	0.24	168	540	540
Polaron absorption maximum λ, nm	–	–	618	626
Molecular weight M_w	–	–	–	41400
Morphology	Amorphous	One- and two-dimensional	Tubes	Fibers, tubes
Morphology of silver	Spheres	Layer on the oligomer surface	Spheres, rods	Spheres

Table 3. Composition and properties of aniline oxidation products with silver nitrate (0.5 M) under different acidities; aniline concentration 0.2 M

Reaction medium	pH		Yield of composite, %	Concentration of silver, wt %	Conductivity, S/cm	Density, g/cm^3
	initial	final				
0.5 M aq. NH_3	10.8	9.3	60.5	75.0	5030	4.22
0.4 M AcOH	5.7	3.5	32.7	70.8	4350–7160	3.26–3.28
0.4 M AcOH	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

4.6 > pH > 2.5. The oxidation of aniline at higher acidity was studied in carboxylic acid solutions. For example, the initial pH value in 0.4 M acetic acid containing 0.2 mol/l of aniline and 0.25 mol/l of ammonium peroxodisulfate or 0.5 mol/l of silver nitrate was 4.5 and 5.7, respectively. Under these conditions a considerable part of aniline is protonated but imino groups in polymer chains still remain unprotonated, and the oxidation sharply slows down. Figure 3a shows the pH profiles for the oxidation of aniline with both oxidants. The range 4.0 > pH > 2.5 is characterized by dramatic attenuation of oxidative processes and decrease of the rate of proton release. This pH range is intermediate between two vigorous oxidation steps with a steeper drop of pH.

In the oxidation with $(NH_4)_2S_2O_8$, the step involving slow variation of pH is complete in 30 min by vigorous exothermic reaction with fast release of protons and reduction of pH. The new step starts when the acidity attains a pH level of 2.5 which corresponds to protonation of imino groups in polymer (oligomer) chains. In the oxidation with $AgNO_3$ at the same initial reactant concentrations the process takes hundreds of hours. After 14 days, the conversion of aniline in acetic acid reaches 30%, and pH decreases to 3.5 due to liberation of protons. The oxidation goes on at a somewhat higher rate.

The yield of oxidation products in the range 4.0 > pH > 2.5 is very poor. As shown previously, ammonium peroxodisulfate as oxidant gives rise to noncomducting low-molecular oligomers, mainly dimers and trimers containing phenazine rings [32, 33, 41, 42]. In the oxidation with $AgNO_3$ homogeneous dark brown powder with a density of 3.28 g/cm^3 was isolated; its conductivity was 4350 S/cm (Table 3). As in the reaction in 0.5 M ammonia, the product contained metallic silver. The electronic absorption spectrum of the organic fraction (oxidation with $AgNO_3$) extracted into *N*-methylpyrrolidin-2-one resembled that shown in Fig. 1b. These findings indicated that the oxidation of aniline with $AgNO_3$ up to a conversion of 30% gives products with a low degree of polyconjugation.

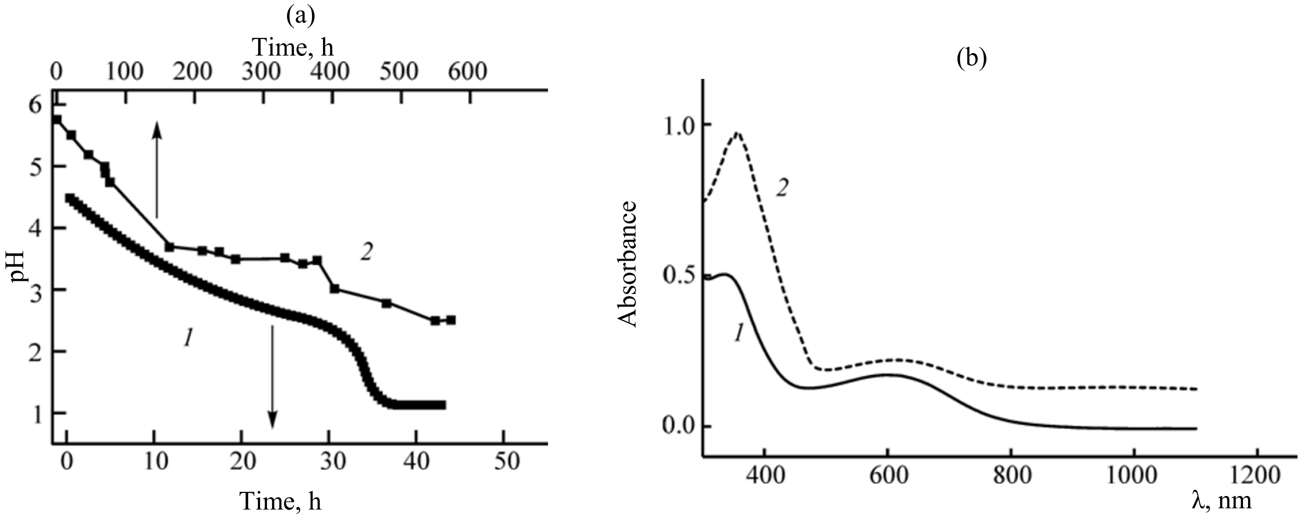


Fig. 3. (a) Variation of pH in the course of aniline oxidation with (*1*) ammonium peroxodisulfate and (*2*) silver nitrate in 0.4 M acetic acid. (b) Electronic absorption spectra of products of aniline oxidation with (*1*) ammonium peroxodisulfate and (*2*) silver nitrate (pH < 2.5); solvent *N*-methylpyrrolidin-2-one.

The supramolecular structure of the aniline oxidation products obtained as 4.0 > pH > 2.5 differs from that of the products formed in alkaline medium. The oxidation with ammonium peroxodisulfate gave flat particles with a size of about 1 μm and a thickness of 100 nm together with rods up to 200 nm in diameter (Fig. 4). Two-dimensional morphology of the oxidation products also prevailed when silver nitrate was used as oxidant. A considerable fraction consisted of micron-sized flat disk-shaped particles; also, rods and fiber-like species were found (Fig. 5). Location of metallic silver was determined by transmission microscopy. Silver decorates flat and linear particles with dark bands or forms spherical nanoparticles with a size of ~10 nm, which aggregate to produce larger particles.

pH < 2.5. The oxidation at pH < 2.5 was studied using 0.2 M aniline and 0.25 M ammonium peroxodisulfate in 0.1 M sulfuric acid, as well as 0.2 M aniline and 0.5 M silver nitrate in 1.0 M nitric acid (Fig. 6). The oxidation of aniline with silver nitrate at high substrate concentrations was also studied in acetic and formic acids when pH value dropped down to 2.5 as a result of proton release (Fig. 3).

The reaction with ammonium peroxodisulfate was complete in 10 min, but the process was not monotonic, and two steps were distinguished. The initial slow step is well known as induction period. It preceded vigorous exothermic chain propagation step accompanied by sharp decrease of pH. The yield of oxidation products approached 100%. The electronic absorption spectra of the product (Fig. 6b) contained a strong band at λ_{max} 630 nm. Taking into account other properties (Table 1), the oxidation product was identified as a typical polyconjugated polymer, i.e., emeraldine with a molecular weight of several tens of thousands; its conductivity was 1 S/cm. The polymeric product had so-called globular supramolecular structure which is most typical of polyaniline obtained in acid medium by the action of a strong oxidant. The product was represented by uniform spherical particles with a size of ~200 nm (Fig. 7a).

The oxidation with $AgNO_3$ in 1 M nitric acid was very slow. No visually detectable changes were observed during the first 100 h. After two weeks, the yield was 16%. The obtained material was characterized by a density of 3.6 g/cm^3 and a conductivity of 2200 S/cm, which indicated high concentration of metallic silver in the composite. After 3.5 weeks, the yield attained 30%, and the conductivity of the product decreased to 1000 S/cm. The electronic absorption spectra of the organic part of the composite contain a strong polaron band with its maximum at λ 626 nm (Fig. 6b). The IR spectra of deprotonated samples were also identical to the spectrum of emeraldine base [13]. Thus the organic part of the composite is a polymer with a high degree of polyconjugation.

Examination of aniline oxidation products obtained in organic acids at high conversion (when pH dropped down to 2.5) also indicated formation of a polymer

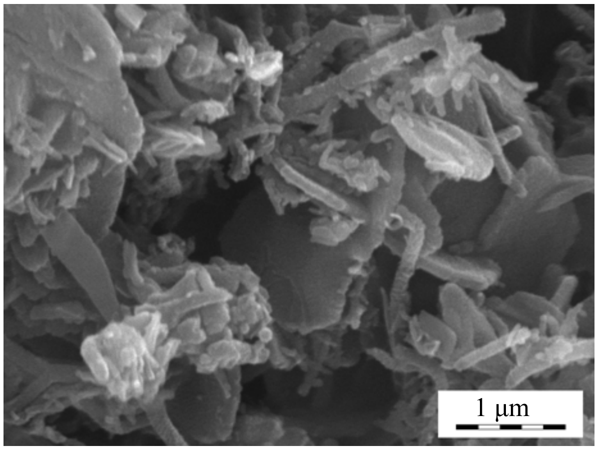


Fig. 4. Scanning electron microscopy image of products of aniline oxidation (aniline concentratin 0.2 M) with ammonium peroxodisulfate in the pH range from 4.0 to 2.5.

with extended conjugated bond system. The organic part of the composites obtained in acetic acid at a conversion of 75% (Fig. 3b) and in formic acid at a conversion of 80% [28] displayed broad absorption bands at λ 618 and 600 nm, which are typical of emeraldine polyaniline. However, the polaron absorption intensity was considerably lower than that observed for the oxidation products obtained in strong inorganic acids, which indicated low concentration of the polymer fraction. The density of the materials obtained in acetic and formic acids was 3.42 and 3.66 g/cm^3, and their conductivity was 326 and 0.85 S/cm, respectively (Table 3). Radical differences were observed in morphology of the oxidation products synthesized using $AgNO_3$ and $(NH_4)_2S_2O_8$. Instead of spherical particles (Fig. 7a) the oxidation with $AgNO_3$ afforded mainly linear structures. Nanotubes (Fig. 7b) and hierarchic nanostructures consisting of fibers 10 nm in diameter were formed together with 50-nm spherical metallic silver particles (Fig. 8a). Silver rods 300 nm in diameter and several microns long appeared in acetic and formic acids at high conversion. Silver rods were coated with a loose layer of polymer growing as fibers outward of the silver surface (Fig. 8b). Such morphology predominates for the oxidation product formed in formic acid.

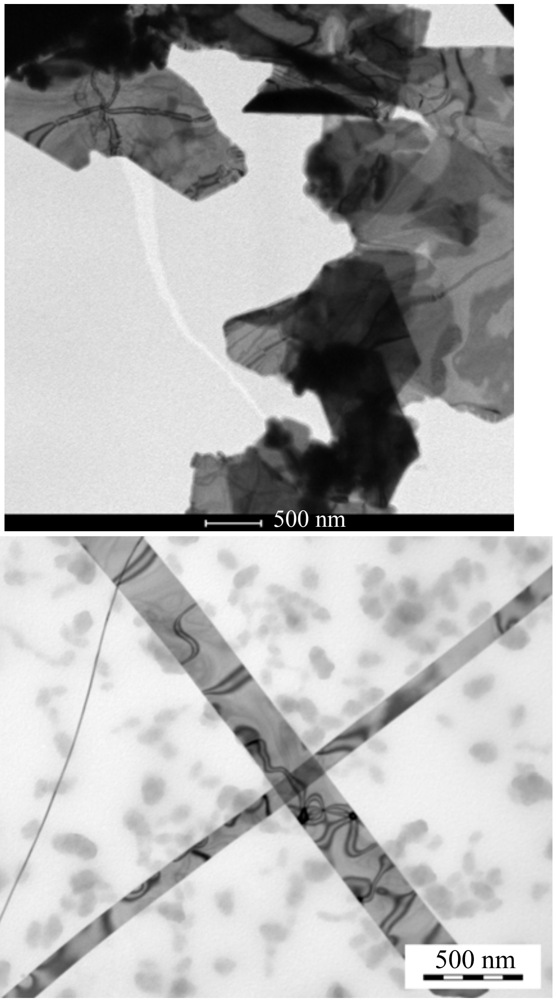


Fig. 5. Transmission microscopy images of two kinds of supramolecular structures of products of aniline oxidation (aniline concentration 0.2 M) with silver nitrate (0.5 M) in acetic acid at 4 > pH > 3.

Molecular mechanism of oxidation. The above results show that both the reaction patterns at pH > 4.6 and properties of the oxidation products obtained with the use of strong and weak oxidants are similar. The reactions involve neutral nitrogen-containing species with a low oxidation potential, so that both peroxodisulfate anion and silver cation are able to oxidize them. Presumably, like the reaction with $(NH_4)_2S_2O_8$, the oxidation with $AgNO_3$ includes the following chemical transformations. The initial step is oxidation of the monomer and formation of dimers. In the next step, oxidation of the terminal amino group in oligomer is more probable, for it characterized by a lower oxidation potential, as compared to monomer [39]. Reaction of oligomer with monomer leads to chain growth, and the degree of polymerization may attain several tens. As shown in [43, 44], the oxidation of aniline with persulfate in alkaline medium is accompanied by monotonic reduction of the open circuit potential, which suggests reduction of the oxidation potential of the products.

What is the molecular structure of aniline oxidation products obtained at pH > 4.6? Addition of monomer

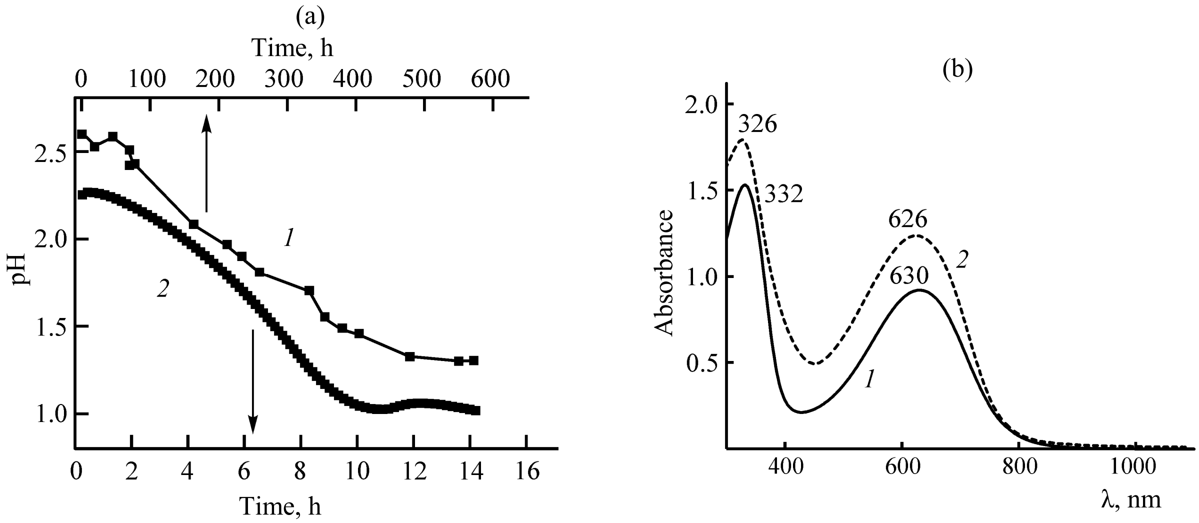


Fig. 6. (a) Variation of pH in the course of aniline oxidation with (*1*) ammonium peroxodisulfate in 0.1 M H_2SO_4 and (*2*) silver nitrate in 1 M HNO_3. (b) Electronic absorption spectra of products of aniline oxidation with (*1*) ammonium peroxodisulfate and (*2*) silver nitrate; solvent *N*-methylpyrrolidin-2-one.

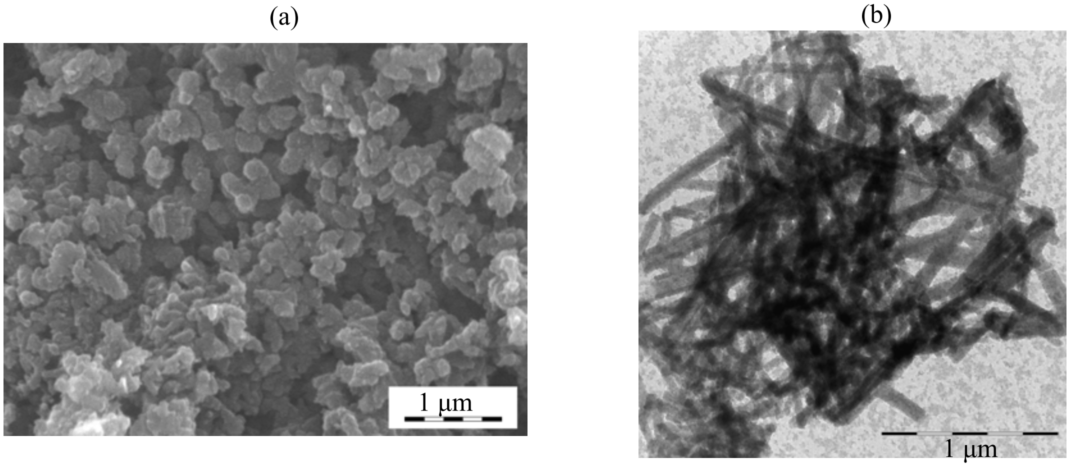


Fig. 7. (a) Scanning electron microscopy image of products of aniline oxidation (aniline concentration 0.2 M) with ammonium peroxodisulfate (0.25 M) in 0.1 M H_2SO_4. (b) Transmission microscopy image of products of aniline oxidation (aniline concentration 0.2 M) with silver nitrate (0.5 M) in 1 M HNO_3. pH < 2.5.

units follows electrophilic replacement pattern [4] (Scheme 2). Oxidized terminal imino group as electrophile replaces hydrogen atom in the benzene ring of the neutral monomer molecule. Monomer units are linked in a head-to-tail mode. In keeping with the organic chemistry rules, electrophilic attack is directed at the *ortho* or *para* position of the benzene ring, for the amino group is an electron-donating substituent. Therefore, growing polymer chains contain both *ortho*- and *para*-coupled monomer units, the former prevailing (taking into account the presence of two *ortho* positions and one *para* position in aniline molecule) [45]. Growth of polymer chain is accompanied by oxidative cyclization of *ortho*-coupled units with formation of phenazine rings. The cyclization can involve both terminal unit and *ortho*-substituted fragments inside the oligomer chain (Scheme 2). The cyclization decreases the energy of the product. However, linear chains predominate in alkaline medium; in this case, chain rapidly grows, whereas the rate of cyclization is much lower than under strongly acidic conditions [42].

Thus aniline oxidation products obtained at pH > 4.6 are not polymers with regular structure but oligomers with different structures, which contain *orto*- and *para*-coupled units together with cyclic

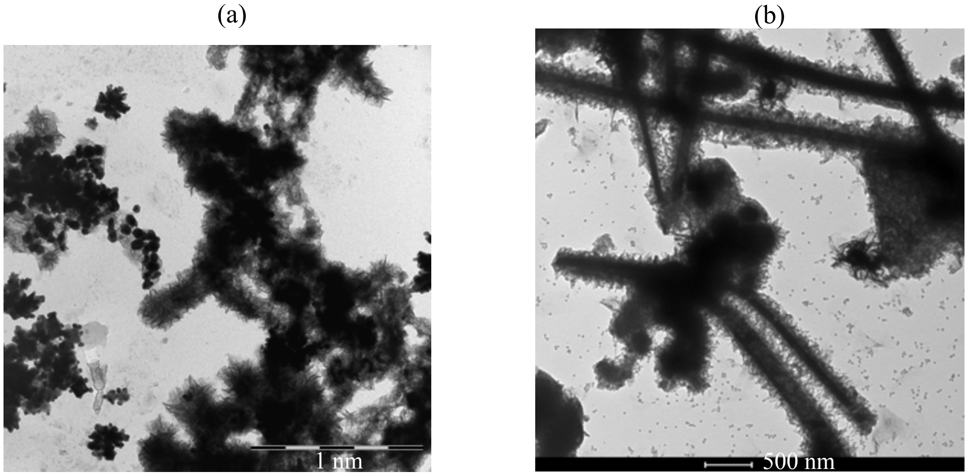


Fig. 8. Morphology of aniline oxidation products with silver nitrate in (a) acetic and (b) formic acids at pH 2.5.

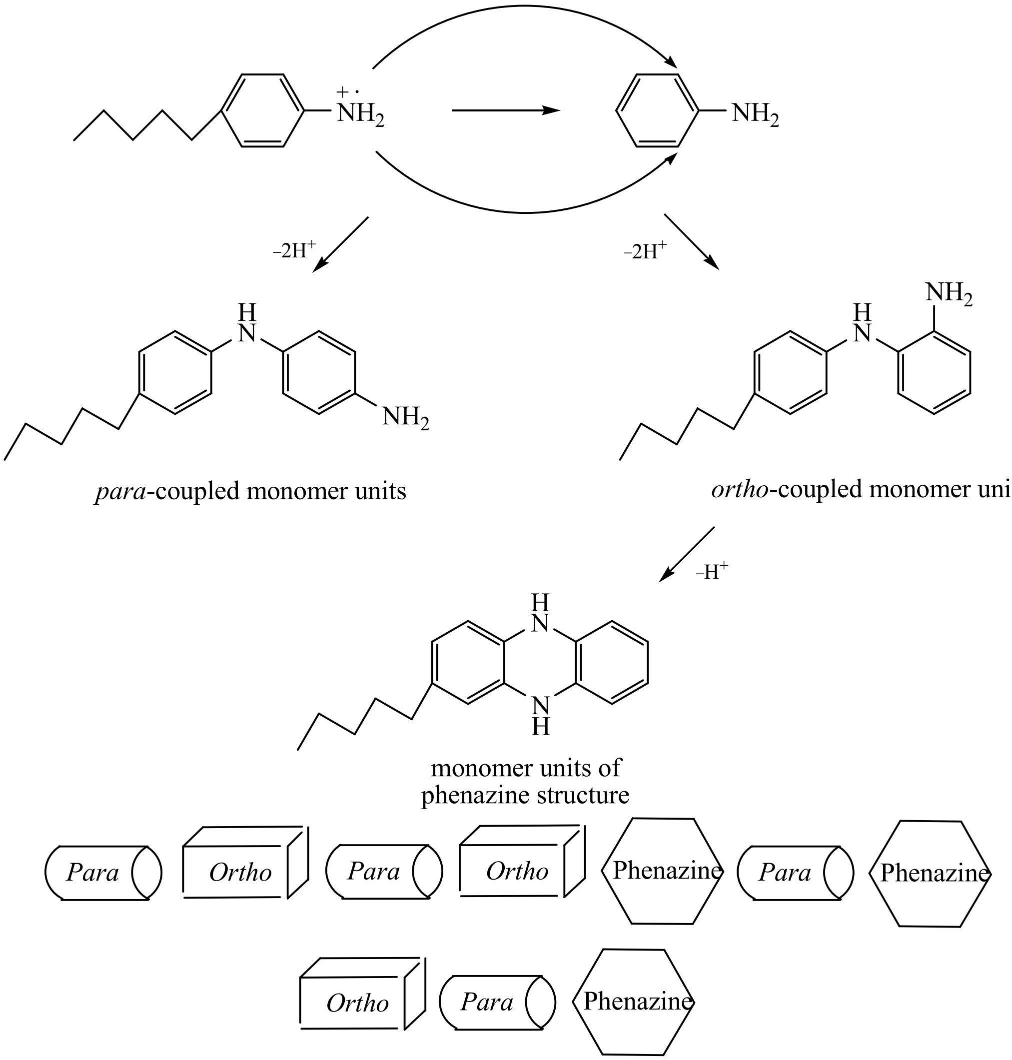
phenazine fragments. The degree of conjugation in such oligomers and hence their conductivity are low. The above mechanism of aniline oxidation is called *oligomerization*; it operates in redox interaction between neutral reactants, aniline monomer and terminal nitrogen-containing moiety in polymer chain, which are characterized by a low oxidation potential [35].

Abrupt change of the oxidation pattern in going to the pH range from 4.6 to 2.5 is related to protonation of monomer and increase of its oxidation potential. However, no protonation of imino groups in polymer chain occurs under these conditions. As a result, redox interaction becomes imbalanced. Amino structure with a low oxidation potential is unable to oxidize protonated monomer with increased oxidation potential (Fig. 9). Therefore, the redox process at $4.6 > pH > 2.5$ is maintained only by oxidation of trace amount of neutral monomer with a low oxidation potential. Neutral monomer species are supplied via displacement of the protonation equilibrium $AnH^+A^- \leftrightarrow An + H^+A^-$ [46]. Very small concentration of neutral aniline is responsible for the very low rate of electrophilic substitution reaction leading to chain extension and reduced molecular weight of the products [41, 42]. Under these conditions, the major oxidation products are *ortho*-coupled dimers [32] which generally undergo cyclization to phenazine structure (the cyclization process is favored by increased acidity) [42]. As a result, the oxidation potential of the products increases. As shown in [41], the open circuit potential slowly increases during the oxidation in the above pH range up to the start of fast exothermic step.

The formation of phenazine ring at early aniline oxidation steps was experimentally confirmed in [47, 48]. It is known that phenazine rings are capable of undergoing copolymerization and even homopolymerization [49]. In the presence of aniline oxidized phenazine moiety can "proliferate" giving rise to a polymer chain. Presumably, in acid medium phenazine structures become parent fragments (initiation centers) of future polymer chains. The oxidation potential corresponding to initiation of irreversible growth of aniline polymer chains is equal to +1.05 V [5]. Ammonium peroxodisulfate as strong oxidant can oxidize aromatic phenazine structure, so that its proliferation and growth of linear polyconjugated chain rapidly come to completion. By contrast, silver cation cannot oxidize phenazine. The oxidation potential of $AgNO_3$ is sufficient only for the initial dimerization step which includes phenazine synthesis via oxidation of neutral aniline. In the presence of a weak oxidant the reaction stops at the oligomerization step. In acid medium aromatic phenazine rings slowly accumulate as initiation centers for subsequent aniline polymerization.

The transition at pH 2.5 is the most important for aniline oxidation. This pH value corresponds to protonation of imino groups in oligomers, and their oxidative potential increases. As a result, balance in redox interaction is restored (Fig. 9). The polymer chain again becomes capable of oxidizing monomer which is now protonated rather than neutral. Chain propagation via reaction of protonated chain with protonated monomer is called *polymerization*. Like oligomerization, polymerization follows electrophilic

Scheme 2.



substitution pattern. Imino group in polymer (or oligomer) replaces one proton in the benzene ring of monomer. However, unlike oligomerization, polymerization gives rise to a strictly regular structure (Scheme 3), and the resulting polymer contains exclusively *para*-substituted units [3]. The reason for the change of the mechanism is as follows. At pH < 2.5 polymer grows in the protonated pernigraniline form where the chain possesses excess charge (positive polarons). In this case, *para* substitution becomes energetically more favorable and the only possible way of electrophilic replacement, for it gives rise to polyconjugated chain. Polyconjugation ensures delocalization of positive charges in pernigraniline and thus reduces the energy of the chain. Hence protonation of polymer chain is a factor responsible for inhibition of *ortho* substitution and formation of regular polyconjugated *para*-substituted polymers possessing a high conductivity.

Polymerization initiation center. Oxidative polymerization of aniline with formation of regular polymer chains cannot begin with reaction between aniline radical cation and protonated aniline molecule. According to quantum-chemical calculations, interaction between two small species each bearing excess positive charge is unfavorable from the viewpoint of energy [50]. A larger polyconjugated fragment capable of reducing the energy of interaction between the oxidizing center and monomer is necessary to launch regular chain propagation. Such species, phenazine units, are formed in the initial oxidation step, induction period. Phenazine moiety, being a large polyconjugated species, delocalizes positive charge of radical cation.

The induction period at pH < 2.5 is similar to the aniline oxidation in the pH range from 4.6 to 2.5, and it follows oligomerization mechanism, i.e., electrophilic substitution in neutral aniline molecule (which is characterized by low oxidation potential) leads to predominant formation of *ortho*-coupled dimers and their subsequent cyclization (Scheme 2). This slow step generates initial fragments of polymer chains, phenazine units, which (unlike the main chain) have aromatic structure and possess a high oxidation potential.

The structure of the initiation center is the subject of extensive discussion. According to [33–35], the initiation center is an unsymmetrical cyclic trimer. However, more recent studies have shown that it is symmetric and that its molecular weight conforms to an even number of monomer units [47]. Therefore, the most probable structure is cyclic aniline dimer, 5,10-dihydrophenazine. It absorbs in the visible region at λ 380 nm; such absorption band is also present in the spectrum of polyaniline. Oxidation of 5,10-dihydrophenazine gives phenazylium radical cation (Scheme 3) which absorbs at λ 420 nm. Just that band is observed at the early stage of aniline oxidation and was identified by some authors [51–53] as an absorption band belonging to intermediate in oxidative polymerization of aniline. The potential at which irreversible substitution in the nitrogen-containing 5,10-dihydrophenazine structure occurs exactly matches the oxidation potential of aniline (+1.05 V). Phenazylium radical cation is insoluble in most organic solvents and in aqueous media up to a very high acidity. It exists as dimer even in appropriate solvents at a very low concentration and may therefore be identified as aniline tetramer by molecular weight determination [41, 47].

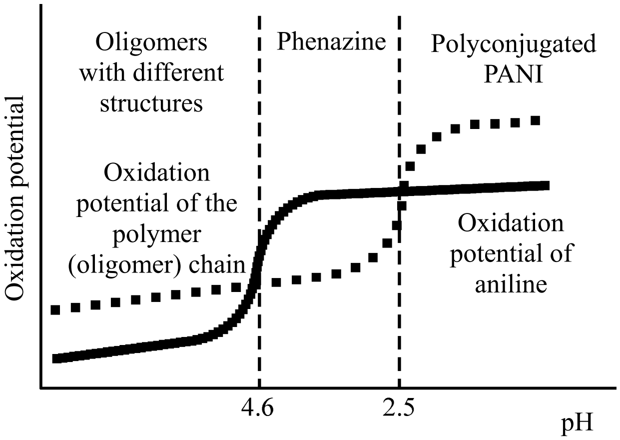
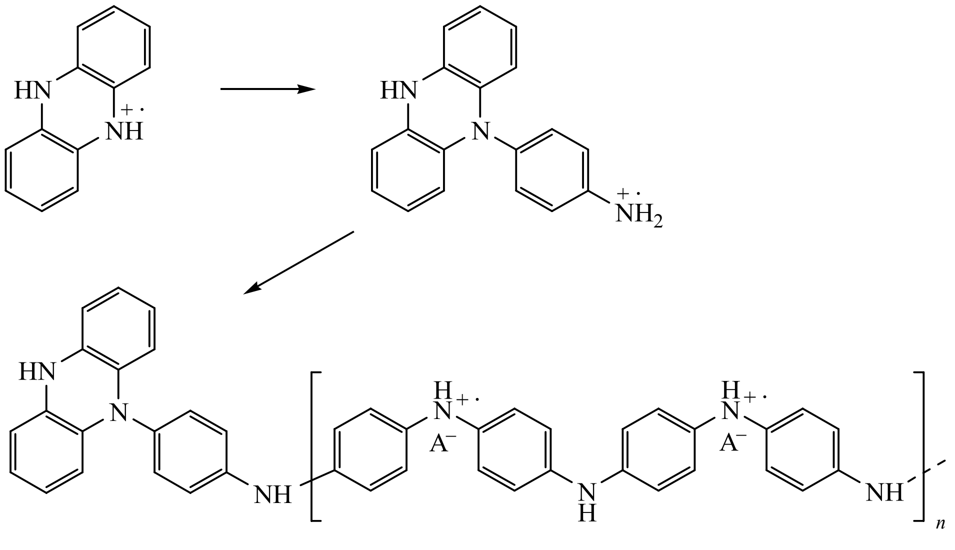


Fig. 9. Qualitative representation of variation of the oxidation potential of the monomer and growing chain against pH of the reaction medium. Indicated are oxidative polymerization products generated in the ranges pH > 4.6; 4.6 > pH > 2.5, and pH < 2.5, depending on the protonation constants of aniline and imino groups in the polymer chain.

A direct experimental proof for the phenazine structure of the active intermediate may be sorption at an electrode of aniline dimer with a crystallographic unit cell size of 0.90×1.03 nm, which is observed in acid medium at a potential value of +0.5 to +0.8 V [5, 54]. Every second nitrogen atom in the dimer is oxidized and protonated with sulfuric acid, and its elemental composition (C:N:S:O = 12:2:1:4) is very consistent

Scheme 3.



with the structure of phenazylium radical cation doped with a sulfate ion. The dimer was strongly adsorbed at an electrode, and no desorption was observed even in a high vacuum. Raising the potential to +1.05 V led to proliferation of adsorbed aniline dimers with formation of linear regular polymer chains [5].

Transition to regular chain propagation stage. The induction period is completed by growth of phenazine units to form regular chains consisting of *para*-substituted aniline fragments (Scheme 3). This transition appears as a bent on the kinetic curve, which corresponds to start of fast exothermic reaction accompanied by considerable decrease of pH. Addition of the first monomer unit to the phenazine nucleus is the most energy-consuming stage of oxidative polymerization of aniline, which determines the rate of the overall process. In electrochemical oxidation this step corresponds to so-called *first cycle potential* (+1.05 V) which is higher than potentials in the subsequent cycles [55]. Proliferation to a trimer gives an active polymerization center, and the redox potential necessary for its reaction with monomer decreases. The reaction then progresses at lower oxidation potentials.

The above mechanism is consistent with the behavior of the open circuit potential during the oxidation process. The character of potential variation in acid medium strongly differs from that observed in alkaline medium [43, 44, 56–58]. In acid medium the initial stage is accompanied by increase of the oxidation potential, which corresponds to accumulation of phenazine units. As exothermic chain propagation starts the oxidation potential decreases to a value of +0.7 to +0.8 V which is characteristic of growing pernigraniline chains. Thus the oxidation potential of aniline at pH < 2.5 passes through a maximum corresponding to the transformation of phenazine unit into active polymerization center. In order to overcome that maximum, a reagent with an oxidation potential higher than +1 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 peroxodisulfate having an oxidation potential of +2.01 V readily overcomes the barrier related to proliferation of phenazine units, and the oxidative polymerization is complete in 10 min. 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 accumula-tion of phenazine species. Nevertheless, if pH < 2.5, polymerization with formation of polyconjugated chains does occur and is characterized by a fairly high yield. Obviously, in the absence of other strong oxidants (with an oxidation potential higher than +1.05V), phenazine ring is oxidized with atmospheric oxygen whose oxidation potential is equal to +1.23 V; in addition, oxygen is soluble in water and is therefore accessible for the reactants. The formation of traces of polyaniline by the action of oxygen was reported in [59–62]. We believe that just atmospheric oxygen triggers the transition from oligomerization to polymerization, i.e., propagation of regular polyaniline chains, in the oxidation of aniline with weak oxidants. However, this stage is fairly slow.

There are examples of fast passing the energy barrier to phenazine proliferation and acceleration of polymerization. Oxidation of aniline can be performed with the use of a mixture of oxidants [8]. Addition of a small amount of a strong oxidant (its concentration is lower than several percent of the amount required for complete oxidation) initiates the polymerization process. Strong oxidant ensures formation of a sufficient number of active polymerization centers, and a weak oxidant then reacts with the main amount of aniline to accomplish chain growth at relatively low oxidation potentials.

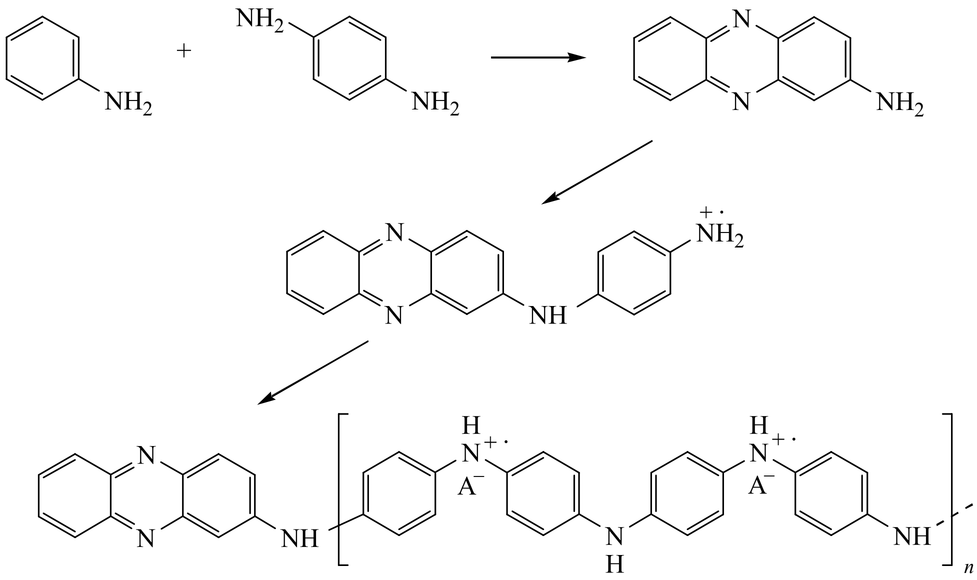
Long induction period can also be shortened by change of the chemical structure of the initiation center [33–35]. It is well known that a catalytic amount of aromatic *para*-diamines sharply shorten the induction period and hence the overall time of polymerization [63]. In our case, addition of *p*-phenylenediamine to a concentration of 0.004 M (2% with respect to aniline) shortens the oxidative polymerization process with ammonium peroxodisulfate from 10 to 3 min. Addition of the same amount of *p*-phenylendiamine in the oxidation with silver nitrate ensured formation of 90% of emeraldine polyaniline in 2 h instead of hundreds hours [64].

We propose the following mechanism of the process. Aromatic diamine is involved in the formation of phenazine unit. Its oxidation potential is lower than that of aniline; therefore, oxidation of the diamine is preferred. The reaction with aniline at the dimerization stage yields aminophenazine which is characterized by a lower oxidation potential compared to phenazine. The exocyclic amino group in aminophenazine is oxidized at a potential of +0.6 to +0.7 V [39]. Aminophenazine gives rise to regular polyconjugated chain originating from the exocyclic amino group, and high energy barrier to oxidation of aniline is thus reduced (Scheme 4). As a result, the polymerization process is strongly accelerated due to acceleration of the slowest stage. It should be noted that addition of *o*-phenylenediamine does not accelerate the process and that addition of *m*-phenylenediamine, by contrast, sharply decelerate polymerization of aniline via extension of the induction period. The latter fact is related to the formation of a defective initiation center which is incapable of promoting polyconjugated chain growth [33, 63]. After complete consumption of *m*-phenylenediamine for the formation of "defective" oligomers polymerization of aniline is resumed.

After transformation of phenazine units into active polymerization centers, the oxidation potential decreases to +0.7 to +0.8V [55], so that silver nitrate can participate again in the oxidation process. At the chain propagation stage the oxidation follows the polymerization mechanism with formation of polyconjugated *para*-coupled structure. Redox interaction involves protonated pernigraniline chain and protonated aniline whose concentration at $\mathrm{pH} < 2.5$ is high. 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 reaction completion. The final stage involves oxidation of most 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 centers. Therefore, the concentration of a strong oxidant, as well as its contribution to the overall oxidation process, may be insignificant. In the absence of other strong oxidants phenazine units can be converted into active polymerization centers by 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.

Formation of organic supramolecular structures and silver agglomerates. *Morphology of organic materials*. In keeping with the mechanism of self-organization of polymeric structures during their synthesis, aniline oligomers play the determining role in the formation of supramolecular polyaniline structures [33–35], i.e., self-organization of oligomers underlies supramolecular structure of polyaniline. Here, not only molecular structure and molecular weight of oligomers but also the rates of their accumulation and growth to produce polymer chains are significant. In media with $\mathrm{pH} > 4.6$ the oxidation yields oligomers with different molecular structures and relatively high molecular weight, which exhibit a weak tendency for self-organization. These oligomers are poorly soluble in water; therefore, they undergo agglomeration and precipitation as an amorphous material. At high pH values amorphous structures are formed in the oxidation with both ammonium peroxodisulfate and silver nitrate (Fig. 2).

Scheme 4.



Oligomers formed in the pH range from 4.6 to 2.5 differ from those obtained at high pH values. These are poorly soluble dimers having phenazine structure. Similar and compact phenazine molecules form organic crystals giving rise to particles with a definite shape. Phenazine molecules are planar aromatic systems capable of self-organization via π–π interactions. Plane-to-plane stacking of phenazine rings produces two-dimensional leaflet-like particles or one-dimensional columns. In our case, supramolecular structures formed in the range $4.6 > pH > 2.5$ are also characterized by either planar or one-dimensional morphology (Figs. 4, 5). Presumably, they consist of regularly arranged phenazine units yet having no pendant polymer chains. Insofar as assembly of phenazine units in the oxidation with $AgNO_3$ is much slower, the shape of particles thus formed is more distinct as compared to those obtained using $(NH_4)_2S_2O_8$; in the latter case, the contribution of amorphous morphology is significant. During the oxidation process metallic silver deposits on the surface of organic particles as a dark band pattern, which also confirms high degree of organization of organic particles.

At $pH < 2.5$, as well as in the range $4.6 > pH > 2.5$, similar phenazine units are formed in the initial oxidation stage, and the conditions of their self-organization determined the structure of polyaniline to be obtained. After the induction period, phenazine units proliferate to form polymer chains. The supramolecular structure at $pH < 2.5$ is largely determined by the duration of the induction period which includes formation, accumulation, and self-organization of phenazine units. Prolonged induction period favors regular assembly of phenazine units, whereas short induction period with subsequent fast chain prolixferation gives rise to random agglomeration and formation of spherical polyaniline particles. The use of persulfates which initiate fast proliferation in acid medium favor formation of polyainiline consisting of nano- and submicron-sized spherical particles, i.e., so-called globular morphology (Fig. 7a).

The oxidation with $AgNO_3$ where the induction period is extended produces mainly one-dimensional structures like tubes, fibers, and hierarchic species as corals composed of fibers (Figs. 7b, 8). Presumably, the bases of hierarchic and one-dimensional structures are generated during the long induction period. These are solitary phenazine columns or groups of columns assembled to more complex agglomerates. At the chain propagation stage phenazine columns append polymer chains and thus increase in diameter. Simultaneously the column becomes longer. The end faces of phenazine columns act as template for generation of phenazine units according to the low-energy path, whereas their generation in the bulk solution is terminated. As a result, polyaniline is formed like a polymer crystal with retention of the originally set structure [65]. It should be noted the formation of similar phenazine units always implies high degree of supramolecular organization of both oligomers and polymers with formation of one- or three-dimensional structures. In this case, unlike oligomers with different structures, no alternative exists for the formation of amorphous species.

No two-dimensional structures are formed in the oxidation of aniline under acidic conditions ($pH < 2.5$). In this case polyaniline is obtained in the form of either three- or one-dimensional structures, including hierarchic ones (Figs. 7, 8). The reason is that the solubility of two-dimensional structures tends to increase. As shown by quantum-chemical calculations, interactions between phenazine fragments lying in one plane are fairly weak, so that planar assemblies should not be stable [66]. At low pH values one-dimensional morphology predominates since π-stacking interaction between the neighboring planar aromatic systems planes is stronger. In very strongly acidic media corresponding to a sulfuric acid concentration of 2 M and higher, phenazine units undergo protonation and dissolve, which hampers not only supramolecular assembly but also formation of polyaniline. At $pH \approx -1$ the yield of polymer sharply decreases, and its conductivity also decreases [67].

Morphology of silver. Silver nitrate is reduced with aniline to produce metallic silver which is characterized by diverse morphology. Metallic silver is obtained as spherical particles 30–100 nm in diameter, which are generally joined to form loose agglomerates. In acid medium, larger silver particles of a submicron size and even hexagonal crystals with a size of up to 1 μm are also formed. In addition, silver deposits onto organic particles, giving rise to fantastic patterns consisting of extended bands. These bands are semi-transparent for transmission microscopy;this means that their thickness is no more than ten atomic layers. Finally, silver separates as one-dimensional columns up to 200 nm in diameter and up to 10 μm long. One or another morphology of silver particles predominates under definite experimental conditions.

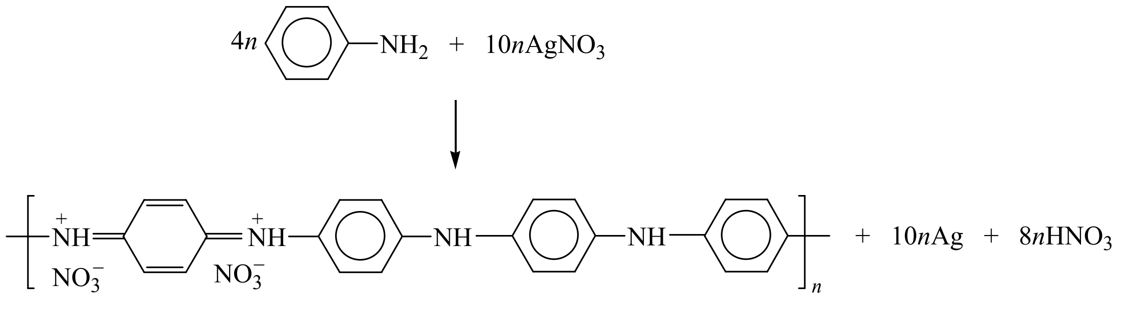
The formation of metal particles and their distribution over the organic phase are nonequilibrium processes which are affected by numerous factors. Among these, the main factors are likely to be redox potential of the reducing agent and the nature of stabilizing agent [68]. Small uniformly sized are formed under conditions of so-called mild reduction, i.e., when the reduction potential only slightly exceeds the redox potential of metal salt–metal couple. Stabilization factor is also very important; it hampers further agglomeration of nanoparticles with formation of macroscopic (compact) metal.

In the system under study, apart from aniline, silver can be reduced with aniline oligomers and emeraldine polymer. Their reduction potential is a quantity opposite to the oxidation potential. The reduction potential decreases in the series aniline > linear oligomers with different structures > polyaniline > phenazine oligomers. It is seen that phenazine ring is the mildest reducing agent with respect to silver. It is known that phenazine gives a coordination compound with silver cation [69]. This should favor even distribution of the metal over the surface of organic particles. It should also be kept in mind that the reduction potential of all nitrogen-containing structures decreases with rise in acidity as a result of protonation. Therefore, the result also depends upon pH range of the reduction process. All types of oligomers and the polymer are also capable of stabilizing metal nanoparticles, so that they simultaneously act as reducing agent and stabilizer.

According to the experimental data, the finest and most uniform distribution of silver is achieved over phenazine oligomers. Even at early oxidation stages the surface area coated with silver constitutes more than 25% of the overall surface area of oligomer particles (Fig. 5). Phenazine structures are also responsible for the formation of one-dimensional silver particles. Figure 5b shows phenazine oligomer columns with dark bands of metallic silver. Phenazine oligomer columns are formed in acetic and formic acids even at the initial oxidation stage when polymer chain propagation has not started as yet. Further reduction of silver on a column leads to complete coverage of its surface with a metal layer (Fig. 8b). The process is the most intense in formic acid, for the latter itself acts as a mild reducing agent toward silver [28]. Participation of formic acid in the reduction process follows from small increase of the concentration of silver in the composite (Table 3). At higher conversion ($pH < 2.5$) the oligomerization process changes to polymerization implying polymer chain propagation. Polyaniline chains are formed as fiber-like structures on the surface of silver columns, thus producing a loose layer on their surface.

Polymerization at $pH < 2.5$, as well as the oxidation at $pH > 4.6$ (leading to oligomers with different structures), gives rise to a different morphology of reduced silver which separates as compact spherical particles. These particles are localized near organic structures but are not distributed over the surface of the latter, as in the case of phenazine oligomers. This means that under the given conditions the reduction of Ag^+ on the surface of metal particle is energetically more favorable than on the surface of organic components.

Composition and properties of silver composites. Theoretically, oxidation of 1 g of aniline with a stoichiometric amount of $AgNO_3$ should produce 1.31 g of polyaniline and 2.9 g of metallic silver. In keeping with the stoichiometry of reaction (2), the fraction of reduced silver in metal–polymer composite should be 68.9 wt %. The oxidation to deprotonated aniline oligomers corresponds to the formation of 74 wt % of silver. The composition of metal–polymer composites can be determined by thermogravimetric analysis (TGA). The weight fraction of the metal is calculated from the amount of incombustible residue obtained after heating above 600°C on exposure to air. According to the TGA data, the fraction of silver in all composites conformed to stoichiometry of the redox process, 75% in alkaline medium and ~70% in acid



(2)

medium (Table 3). These data prove that just $AgNO_3$ is the main oxidant.

Although the concentrations of metallic silver in the aniline oxidation products were almost similar, their conductivities differed considerably. Oligomers with different structures were characterized by a conductivity of 10^3 S/cm, while the conductivities of phenazine oligomers and polyaniline were 10^2–10^3 and 10^{-1}–10^2 S/cm, respectively (Table 3). The conductivities of the doped organic components were 10^{-10} S/cm for oligomers with different structures and phenazine oligomers and 1–10 S/cm for aniline. It was reasonable to presume that the conductivity 10^3 S/cm is determined by the metal component and that the conductivity 10 S/cm and lower is limited by the organic component. In fact, study on the mechanism of charge carrier transport in metal–polymer composites [64] revealed different temperature dependences of their conductivities. The conductivity of phenazine oligomer composites in the temperature range from 100 to 300 K is metal-like, whereas the other composites exhibit semiconductor-like conductivity.

Considerable difference in the conductivity level and character may be rationalized by different morphologies of metal–polymer composites. The composites contain 20 vol % of silver and 80% of organic phase. In keeping with the percolation theory, these parameters conform to the theoretical conductivity percolation threshold. In the vicinity of percolation threshold the conductivity is very sensitive to the material structure, and it can change over a wide range. Spherical silver particles do not ensure persistent surmounting of the percolation threshold. The range of conductivity of such composites has very broad limits. Formation of relatively large silver particles in the polymerization of aniline at $pH < 2.5$ could lead to reduction of conductivity below the percolation threshold. In this case the composite exhibits a conductivity level comparable with that of emeraldine. The formation of silver nanoparticles with a size of tens nanometers could give rise to a high conductivity, but the conductivity decreases due to agglomeration of nanoparticles, i.e., due to their nonuniform distribution over the bulk material. The system keeps balance at the boundary of percolation transition. This follows from the fact that in some cases deprotonation of polymer, which is accompanied by weight loss of the organic component and decrease of its conductivity, increases the overall conductivity up to several thousands S/cm [13].

One-dimensional morphology of the conducting component is generally characterized by considerably reduced percolation threshold and increased conductivity. The formation of columnar silver particles seemed to ensure a high and steady conductivity level. Nevertheless, composites with a high concentration of silver columns have a conductivity of 0.85 S/cm, and the temperature dependence of their conductivity is semiconductor-like. The reason for the low conductivity is that each column is encapsulated in polyaniline shell which creates a barrier to conduction and hampers formation of metallic conducting paths. The highest metallic conductivity level is observed for phenazine oligomers due to uniform and fine distribution of silver over the organic material. This morphology is obtained as a result of mild reduction of Ag^+ with phenazine oligomers in combination with high level of subsequent stabilization of the metal. Aromatic phenazine rings are known to form stable complexes with metal cations and zero-valent metals with participation of π-electrons. Regular character of the reduction and fixation of silver on the surface of particles suggests cooperative effect of the oligomeric crystallite. Presumably, reduction of Ag^+ with phenazine activates nearby rings localized at a definite crystallographic axis. As a result, a geometric pattern (silver bands) appears on the surface of oligomer particles. Silver bands are ideal conducting paths ensuring high level of metal-like conductivity of the composite despite low conductivity of the organic component.

To conclude, we have shown that oxidation of aniline in both alkaline and acid media can be accomplished almost quantitatively with the aid of not only strong but also weak oxidant ($AgNO_3$) having an oxidation potential lower than +1 V. An exception is the stage at which regular conjugated polyaniline chains start to grow at $pH < 2.5$. At that stage addition of a small amount of a strong oxidant with an oxidation potential of higher than +1 V is necessary. Atmospheric oxygen can act as such oxidant.

Chain process of aniline oxidation in alkaline, weakly acid, and acid media follows different molecular mechanisms, leading to the formation of products having different molecular structures, morphologies, and properties. The reason is different oxidation potentials of the monomer and growing chain in the protonated and unprotonated states. The oxidation of aniline at $pH > 2.5$ involves deprotonated monomer and chain species having a low oxidation potential, so that the process can be accomplished with the use of a weak oxidant. The oxidation products are oligomers characterized by a low degree of polyconjugation and low conductivity.

At 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 rate-determining stage is “proliferation” of phenazine units as initiation centers of polymer chains. Phenazine has an oxidation potential of +1.05 V, and oxidative addition of monomer thereto is possible only in the presence of a strong oxidant. 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 a 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 by the action of a weak oxidant.

Chain propagation involves protonated monomer and chain possessing excess charge (positive polarons). Chain protonation constrains the reaction to produce regular polymer chains with *para*-coupled units. Regular plymer 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.

At pH < 4 supramolecular polyaniline structures are formed from insoluble phenazine species. In the initial polymerization step agglomeration of phenazine units occurs either randomly or regularly, depending on the conditions. In the presence of weak oxidants the phenazine accumulation stage is long, which favors regular assembly of phenazine units with formation of one-dimensional columns. At pH < 2.5 conducting chains grow on the basis of phenazine units. The growth of polyaniline is a heterophase process involving electron and ion conduction; polymer particles are formed following the crystal growth pattern.

Oxidation of aniline with $AgNO_3$ is accompanied by formation of metallic silver in an amount equivalent to the oxidized aniline. Depending on the conditions and structure of nitrogen-containing species, the reduced silver is characterized by different morphologies. Metallic silver is formed as spherical particles or their agglomerates weakly bound to the organic component or thin metal layers on the surface of the organic phase. The latter type is produced by reduction of $AgNO_3$ with phenazines. It ensures steady percolation of metal–polymer composites and a high level of metal-like conductivity.

EXPERIMENTAL

The following reagents were used: aniline, ammonium peroxodisulfate, and silver nitrate of analytical grade (Merck), aqueous ammonia and sulfuric, nitric, acetic, and formic acids of chemically pure grade (Vekton), and *N*-methylpyrrolidin-2-one (Merck). These chemicals were not subjected to additional purification.

Polymerization of aniline was performed at a concentration of 0.2 M at room temperature without ultrasonic treatment, irradiation with visible light, heating, or stirring in aqueous ammonia or aqueous solutions of acids over a wide range of initial pH values. Oxidative polymerization of aniline requires two electrons for addition of one monomer unit and 0.5 *e* for oxidation of every second unit to emeraldine structure. The molar ratio oxidant–monomer recalculated on one-electron transfer is $[Ox]_e : [An] = 2.5$. Ammonium peroxodisulfate is a two-electron oxidant, while silver nitrate is a one-electron oxidant. Therefore, the concentration of ammonium peroxodisulfate necessary for the oxidation of aniline to emeraldine is twice as low as that of $AgNO_3$, and we used 0.25 M $(NH_4)_2S_2O_8$ or 0.5 M $AgNO_3$ to oxidize 0.2 M aniline.

When the reaction was complete, the precipitate was filtered off and washed with water or with a solution of alkali or the corresponding acid, depending on the conditions of synthesis. The product was dried at room temperature. Protonated polyaniline was neutralized by treatment with 1 M aqueous ammonia, followed by washing with distilled water.

The conductivity of the obtained materials was determined by the van der Pauw four-point probe technique with the aid of a Solartron Schlumberger 7841 multimeter, Keithley 220 current source, and Keithley 7052 switching card. The specific conductance was measured from samples as pellets prepared under a pressure of 700 MPa, and point gold contacts were deposited onto pellets. The electronic absorption spectra were recorded on a Perkin–Elmer Lambda 20 spectrophotometer from solutions in *N*-methylpyrrolidin-2-one. Microphotographs were obtained using a Jeol JSM 6400 scanning electron microscope and a Jeol JEM 2000 FX transmission microscope. Thermogravimetric analysis for determination of silver content in the composites was performed on a Perkin–Elmer TGA 7 instrument; 100-mg samples were heated at a rate of 10 deg/min in a stream of air at a flow rate of 50 ml/min.

ACKNOWLEDGMENTS

This study was performed under financial support by the Presidium of the Russian Academy of Sciences (program no. P21), by the Federal Special-Purpose Program no. 2011-1.6-516-015-031 (state contract no. 16.516.11.6034), by the Ministry of Education and Science of the Russian Federation (project no. 16.740.11.0211), and by the Czech–Russian grant ME 847. The authors thank J. Prokeš (Charles University, Prague) and J. Kovářová and J. Hromádková (Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, Prague) for studying samples of the composites.

REFERENCES

1. *Handbook of Conducting Polymers. Conjugated Polymers: Theory, Synthesis, Properties and Characterization*, Skotheim, T.A. and Reynolds, J.R., Eds., Boca Raton: CRC, 2007, 3rd ed., p. 1238.
2. Wei, Y., *J. Chem. Educ*., 2001, vol. 78, no. 4, p. 551.
3. Hagiwara, T., Demura, T., and Iwata, K., *Synth. Met*., 1987, vol. 18, nos. 1–3, p. 317.
4. *Encyclopedia of Polymer Science and Technology. Oxidative Polymerization*, Kroschwitz, J.I., Ed., New York: Wiley, 2004, vol. 10, p. 740.
5. Yang, L.Y.O., Chang, C.Z., Liu, S.H., Wu, S.G., and Yau, S.L., *J. Am. Chem. Soc*., 2007, vol. 129, no. 27, p. 8067.
6. Ding, H., Long, Y., Shen, J., and Wan, M., *J. Phys. Chem. B*, 2010, vol. 114, no. 1, p. 115.
7. Mi, H., Zhang, H., Yang, S., Ye, X., and Luo, J., *Mater. Chem. Phys*., 2008, vol. 112, no. 1, p. 127.
8. Li, G., Zhang, C., Li, Y., Peng, H., and Chen, K., *Polymer*, 2010, vol. 51, no. 10, p. 1934.
9. Li, G., Zhang, C., Peng, H., and Chen, K., *Macromol. Rapid Commun*., 2009, vol. 30, no. 12, p. 1841.
10. Li, G., Jiang, L., and Peng, H., *Macromolecules*, 2010, vol. 40, no. 20, p. 7890.
11. Zhang, C., Wang, L., Peng, H., Chen, K., and Li, G., *Polym. Int*., 2009, vol. 58, no. 12, p. 1422.
12. Zhang, X. and Manohar, S.K., *J. Am. Chem. Soc*., 2005, vol. 127, no. 41, p. 14156.
13. Blinova, N.V., Stejskal, J., Trchová, M., Sapurina, I., and Ćirić-Marjanović, G., *Polymer*, 2009, vol. 50, no. 1, p. 50.
14. Blinova, N.V., Bober, P., Hromádková, J., Trchová, M., Stejskal, J., and Prokeš, J., *Polym. Int*., 2010, vol. 58, no. 4, p. 437.
15. Pan, L., Pu, L., Shi, Y., Song, S., Xu, Z., Zhang, R., and Zheng, Y., *Adv. Mater*., 2007, vol. 19, no. 3, p. 461.
16. Gizdavic-Nikolaidic, M.R., Stanisavljev, D.R., Easteal, A.J., and Zujovic, Z.D., *Macromol. Rapid. Commun*., 2010, vol. 31, no. 7, p. 657.
17. Li, L., Yan, G., Wu, J., and Guo, Q., *J. Colloid Interface Sci*., 2008, vol. 326, no. 1, p. 72.
18. Han, J., Liu, Y., and Guo, R., *J. Polym. Sci., Part A: Polym. Chem*., 2008, vol. 46, no. 5, p. 740.
19. Mallick, K., Witcomb, M.J., Scurrell, M.S., and Strudom, A.M., *Gold Bull*., 2008, vol. 41, no. 3, p. 246.
20. Chuang, F.-Y. and Yang, S.-M., *J. Colloid Interface Sci*., 2008, vol. 320, no. 1, p. 194.
21. Ding, H., Wan, M., and Wei, Y., *Adv. Mater*., 2007, vol. 19, no. 3, p. 465.
22. Molina, J., del Rio, A.I., Bonastre, J., and Cases, F., *Synth. Met*., 2010, vol. 160, nos. 1–2, p. 99.
23. de Barros, R.A., de Azevedo, W.M., and de Aguiar, F.M., *Mater. Charact*., 2003, vol. 50, no. 1, p. 131.
24. de Barros, R.A., Martins, C.R., and de Azevedo, W.M., *Synth. Met*., 2005, vol. 155, no. 1, p. 35.
25. Khanna, P.K., Singh, N., Charan, S., and Visvanath, A.K., *Mater. Chem. Phys*., 2005, vol. 92, no. 2, p. 214.
26. de Azevedo, W.M., de Barros, R.A., and da Silva E.F., Jr., *J. Mater. Sci*. 2008, vol. 43, no. 4, p. 1400.
27. Pillalamarri, S.K., Blum, F.D., Tokuhiro, A.T., and Bertino, M.F., *Chem. Mater*., 2005, vol. 17, no. 24, p. 5941.
28. Bober, P., Stejskal, J., Trchova, M., Hromadkova, J., and Prokes, J., *React. Funct. Polym*., 2010, vol. 70, no. 9, p. 656.
29. Stejskal, J. and Gilbert, R.G., *Pure Appl. Chem*., 2002, vol. 74, no. 5, p. 857.
30. Huang, W.S. and MacDiarmid, A.G., *Polymer*, 1993, vol. 34, no. 9, p. 1833.
31. Wei, Y., Sun, Y., and Tang, X., *J. Phys. Chem*., 1989, vol. 93, no. 12, p. 4878.
32. Stejskal, J., Sapurina, I., and Trchová, M., *Prog. Polym. Sci*., 2010, vol. 35, no. 12, p. 1420.
33. Sapurina, I. and Stejskal, J., *Polym. Int*., 2008, vol. 57, no. 12, p. 1295.
34. Stejskal, J., Sapurina, I., Trchová, M., and Konyushenko, E.N., *Macromolecules*, 2008, vol. 41, no. 10, p. 3530.

35. Sapurina, I.Yu. and Stejskal, J., *Usp. Khim*., 2010, vol. 79, no. 12, p. 1.
36. *CRC Handbook of Chemistry and Physics*, Lide, D.R., Ed., Boca Raton, FL: CRC, 1995, p. 8.
37. *Handbook of Organic Conductive Molecules and Polymers*, Nalwa, H.S., Ed., Chichester: Wiley, 1997, vol. 2, p. 50.
38. Huang, W.-S., MacDiarmid, A.G., and Epstein, A.J., *J. Chem. Soc., Chem. Commun*., 1987, no. 23, p. 1784.
39. Li, X.-G., Huang, M.-R., Duan, W., and Yang, Y.-L., *Chem. Rev*., 2002, vol. 102, no. 9, p. 2925.
40. Zujovic, Z.D., Laslau, C., Bowmaker, G.A., Kilmartin, P.A., Webber, A.L., Brown, S.P., and Travas-Sejdic, J., *Macromolecules*, 2010, vol. 43, no. 2, p. 662.
41. Ding, Z., Currier, R.B., Zhao, Y., and Yang, D., *Macromol. Chem. Phys*., 2009, vol. 210, no. 5, p. 1600.
42. Losito, I., Palmisano, F., and Zambonin, P.G., *Anal. Chem*., 2003, vol. 75, no. 19, p. 4988.
43. Pud, A.A., Noskov, Yu.V., Ogurtsov, N.A., Dmitriev, O.P., Piryatinski, Yu.P., Osipyonok, V.M., Smertenko, P.S., Kassiba, A., Fatyeyeva, K.Yu., and Shapoval, G.S., *Synth. Met*., 2009, vol. 159, no. 12, p. 2253.
44. Surwade, S.P., Dua, V., Manohar, N., Manohar, S.K., Beck, E., and Ferraris, J.P., *Synth. Met*., 2009, vol. 159, nos. 5–6, p. 445.
45. Cram, D.J. and Hammond, G.S., *Organic Chemistry*, New York: McGraw–Hill, 1964, p. 210.
46. Baizer, M.M. and Lund, H., *Organic Electrochemistry*, New York: Marcel Dekker, 1983, p. 52.
47. Ding, Z., Sanchez, T., Labouriau, A., Iyer, S., Larson, T., Currier, R., Zhao, Y., and Yang, D., *J. Phys. Chem. B*, 2010, vol. 114, no. 32, p. 10337.
48. Genies, E.M. and Lapkowski, M., *J. Electroanal. Chem*., 1987, vol. 236, nos. 1–2, p. 199.
49. Puskas, Z. and Inzelt, G., *Electrochim. Acta*, 2005, vol. 50, nos. 7–8, p. 1481.
50. Ćirić-Marjanović, G., Trchová, M., and Stejskal, J., *Collect. Czech. Chem. Commun*., 2006, vol. 71, no. 7, p. 1407.
51. Neoh, K.G., Kang, E.T., and Tan, K.L., *Polymer*, 1993, vol. 34, no. 23, p. 3921.
52. Gospodinova, N., Terlemezyan, L., Mokreva, P., and Kossev, K., *Polymer*, 1993, vol. 34, no. 11, p. 2434.
53. Huang, Y.-F. and Lin, C.-W., *Polym. Int*., 2010, vol. 59, no. 9, p. 1226.
54. Yau, S., Lee, Y., Chang, C., Fan, L., Yang, Y., and Dow, W., *J. Phys. Chem. C*, 2009, vol. 113, no. 35, p. 13758.
55. Malinauskas, A. and Holze, R., *Phys. Chem. Chem. Phys.,* 1997, vol. 101, no. 12, p. 1851.
56. Wei, Y., Hsueh, K.F., and Jang, G.-W., *Polymer*, 1994, vol. 35, no. 16, p. 3572.
57. Li, Y., Zhang, C., Li, G., Peng, H., and Chen, K., *Synth. Met*., 2010, vol. 160, no. 8, p. 1204.
58. Tran, H., Wang, Y., D'Arcy, J.M., and Kaner, R.B., *ACS Nano*, 2008, vol. 2, no. 9, p. 1841.
59. Girginer, B., Karagoz, B., Urgen, M., and Bicak, N., *Surf. Coat. Technol*., 2008, vol. 202, no. 17, p. 4176.
60. Yunus, S., Attout, A., and Bertrand, P., *Langmuir*, 2009, vol. 25, no. 3, p. 1851.
61. Zhuzhel'skii, D.V., Krylova, V.A., Ivanov, V.D., and Malev, V.V., *Elektrokhimiya*, 2009, vol. 45, no. 1, p. 145.
62. Chen, Z., Pina, C.D., Faletta E., and Rossi, M., *J. Catal*., 2009, vol. 267, no. 1, p. 93.
63. Duić, L., Kralić, M., and Grigić, S., *J. Polym. Sci., Part A: Polym. Chem*., 2004, vol. 42, no. 7, p. 1599.
64. Bober, P., Trchová, M., Stejskal, J., Prokeš, J., and Sapurina, I., *Macromolecules*, 2010, vol. 43, no. 24, p. 10406.
65. Matsumoto, S., Ihori, H., and Fujii, M., *Synth. Met*., 2009, vol. 159, no. 12, p. 2296.
66. Crispin, X., Cornil, J., Friedlein, R., Okudaira, K.K., Lemaur, V., Crispin, A., Kastemont, G., Lehmann, M., and Salaneck, W.R., *J. Am. Chem. Soc*., 2004, vol. 126, no. 38, p. 11889.
67. Blinova, N.V., Stejskal, J., Trchová, M., and Prokeš, J., *Polymer*, 2006, vol. 47, no. 1, p. 42.
68. *Nanoparticles and Catalysis*, Astruc, D., Ed., Weinheim: Willey, 2008.
69. Kokunov, Yu.V., Gorbunov, Yu.E., and Khmelevskaya, L.V., *Zh. Neorg. Khim*., 2005, vol. 50, no. 8, p. 1184.