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Oxidative polymerization of aromatic amines: kinetic features and possible mechanisms

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The state-of-the-art studies into the synthesis of electrically conducting polymers by oxidative polymerization of aromatic amines are surveyed. The attention is focused on polyaniline, the most important representative of this class of polymers. The concepts of possible mechanisms, types of active sites and kinetic features of the oxidative polymerization of aromatic amines are analyzed and integrated. Considerable attention is paid to the formation of the new phase having a catalytic action. Numerous effects reported in the literature are explained in terms of the views on oxidative polymerization of aromatic amines as a heterogeneous autocatalytic process.
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I. Introduction

Oxidative polymerization forms a separate class of reactions used for the synthesis of polymers, characterized by a number of common features and occupying a special place among methods of polymer synthesis. The specific character of oxidative polymerization is related to the fact that its features cannot be explained relying on the classical views on the kinetics and mechanism of stepwise chain reactions involved in the synthesis of macromolecules. Suffice it to say that even the overall scheme of oxidative polymerization does not look as a usual reaction of polymer synthesis, but implies the formation of polyconjugated systems *via* oxidation of low-molecular-mass compounds that possess simultaneously a sufficient electron excess and aromaticity, such as phenols, benzenethiols, pyrroles, thiophenes, aromatic amines and diamines.[1–7]

Aniline is historically the first and the most studied monomer of oxidative polymerization. The accomplished polymerization of aniline marked not only the beginning of synthesis of polyconjugated systems, but also transition to the age of synthetic polymers. Apparently, the starting point of this age is 1840, when Fritzche[8] described the preparation of a dark-green powder by oxidation of aniline, which was well before the proper notion of 'polymer' appeared. More than two decades later, polyaniline was again prepared by electrolysis of aniline sulfate;[9] subsequently, the structures of leukoemeraldine and emeraldine aniline forms and the pernigraniline state were characterized.[10] In the subsequent years, the oxidative syntheses of polymers or oligomers did not attract much attention, and their products were usually treated as being due to undesirable resinification. An exception was the aniline black dye, which was first obtained in 1907 (Ref. 11) and is currently used to a limited extent.

The renaissance of the research into polymers of aniline and other polyconjugated systems started with the synthesis of electrically conductive polyacetylene[12] and was fuelled by the idea to generate high temperature superconductivity. Superconductors based on polyaromatic amines have never been prepared; however, the specific electrical conductivity of doped polyconjugated systems varies from a few to several thousand siemens per centimetre.[13] The specific

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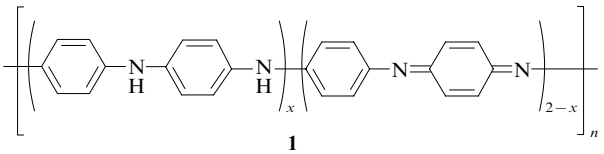
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conductivity of the proper polyaniline varies over a range of ten orders of magnitude, depending on the conditions of synthesis (first of all, pH of the medium, temperature, oxidant to monomer molar ratio and the nature of the dopant), and reaches 10 S cm^{-1} with thoroughly controlled preparation conditions.[13–16] Apart from the high electrical conductivity, polyaniline possesses high chemical and thermal stability,[17–19] redox activity[20,21] and controlled absorption spectrum.[5,22] These properties determined its application as a component of anticorrosion and antistatic coatings with shielding ability against electromagnetic radiation, supercapacitors, electrorheological fluids, sensors, membranes, catalytic systems and materials for medical and biological applications.[23–44]

The oxidative polymerization of aniline can be induced by various oxidants — $S_2O_8^{2-}$, $Cr_2O_7^{2-}$, ClO_3^-, VO_3^-, MnO_4^-, IO_4^-, H_2O_2, Ce^{4+}, Fe^{3+}, Cu^{2+}, Ag^+ or $H[AuCl_4]$.[5,45–52] Of considerable interest is the possibility to conduct this reaction under the action of oxygen or ozone using copper(II) salts [53] or iron(III) salts [54] as catalysts, respectively. The methods of oxidative polymerization of aniline are not limited to processes induced by chemical oxidants, but also include electrochemical,[55–60] photochemical,[61–63] plasma-assisted [64] and enzymatic [65,66] oxidative polymerization processes. Polyaniline can also be obtained by processes other than oxidation,[5,45] *e.g.*, by polycondensation of *p*-dichlorobenzene with sodium amide.

In the general case, the polyaniline chain (structure **1**) consists of aminobenzoic and quinonediimine moieties, and the ratio between them determines the degree of oxidation of the chain.[5,20,21] In addition, each degree of oxidation can exist as either salt or base.[67,68] Thus, polyaniline is involved in both redox and acid-base equilibria, in particular, those with Lewis acids,[69–73] and the position of these equilibria determines the polyaniline form of existence and properties.[5]

Structures 1



1

$x = 0$, pernigraniline; 1, emeraldine; 2, leukoemeraldine

By oxidative polymerization, it is also possible to obtain polymers of aromatic amines other than aniline and the corresponding copolymers. For example, oxidative polymerization and copolymerization reactions have been carried out for toluidines,[74] xylidines,[75,76] anisidines,[75,77–81] 3-aminobenzoic acid,[81] anthranilic acid,[82] nitroanilines,[83] *N*-phenylanthranilic acid,[84] *p*-semidine,[85] *o*-hydroxyaniline,[86] *N*,*N*-dimethylaniline,[87] *N*-ethylaniline,[88] 2-aminopyridine,[89] 2-aminopyrimidine [90] and other monomers.[5] A special place among the monomers is occupied by phenylenediamines, which form ring chain polymers upon oxidative polymerization and copolymerization.[75,90–97]

The oxidative polymerization can be used not only to prepare new types of polymers and copolymers, but, in some cases, also to control the morphology of the products. In this connection, it is necessary to mention the vigorously developing research into the synthesis of specific morphological forms of polyaniline such as three-dimensional globules, nanotubes, nanofibres, and various polyaniline-based nanocomposites.[14,98–103]

Thus, oxidative polymerization of aromatic amines opens up new, in principle, opportunities for the preparation of polymers and copolymers with extended systems of conjugated bonds along the macromolecule.[74–97] In some cases, these compounds possess a certain specific morphology.[14,98] However, despite numerous studies into the mechanism of oxidative polymerization of aromatic amines, neither the sequence of elementary steps nor even the nature of active sites participating in them is ultimately clear now.[98] Moreover, the mechanisms presented by different authors often contradict one another.[14,22,76,79–81,88,95,98,104–107]

Over the last three decades, the scope of synthetic applications of oxidative polymerization has extended to such an extent that an exhaustive survey of published data on this subject would have required a huge review. The kinetics and mechanism of oxidative polymerization traditionally receive much less attention in the literature sources than the synthesis and the possible applications of new electrically conductive polymers and composite materials. Some issues associated with the effect of various factors on the course of oxidative polymerization of aromatic amines are addressed in a number of reviews [14,22,68,98] and in a monograph;[5] however, no publications integrating the kinetic and mechanistic studies of these processes are now available. Therefore, here we focus on the kinetic features and critical analysis of various views on the mechanism of oxidative polymerization of aromatic amines. The review mainly covers publications of the last 15 years with inclusion of earlier papers that contain fundamentally important results.

II. General features of oxidative polymerization of aromatic amines

In view of the abundance of factual information that mainly refers to special cases and the diversity of approaches to interpretation of the observed trends, it is necessary to enumerate the fundamental aspects of the oxidative polymerization of aromatic amines. In our opinion, these aspects include the reliably established facts listed below.

1. The oxidative polymerization of aromatic amines is a kinetically complex and autoaccelerating reaction.[105–107]

2. The rate of oxidative polymerization is considerably affected by introduction of some compounds. For example, the addition of π-electron donors such as 2,6-di-*tert*-butyl-4-methylphenol and 2,3- dimethoxybuta-1,3-diene inhibits the oxidative polymerization, whereas *p*-phenylenediamine and *p*-semidine, conversely, substantially accelerate the oxidative polymerization.[108–110] The addition of *o*-phenylenediamine does not affect the rate of oxidative polymerization of aniline, while the introduction of *m*-phenylenediamine even retards the reaction.[14] The oxidative polymerization rate can also be changed by introduction of inert materials, such as Al_2O_3, carbon, silica gel and some polymers, into the reaction system.[111–115] A considerable acceleration of oxidative polymerization occurs if pre-synthesized polyaniline is added to the reaction system.[111]

3. Oxidative polymerization of aromatic amines starts in a homogeneous system, which becomes heterogeneous as a result of fast decrease in the solubility of aniline *n*-mers with

increasing degree of polymerization. Indeed, the solubility of the aniline dimer is still rather high, while the aniline trimer and especially tetramer are insoluble in acidic aqueous solutions and, therefore, do not polymerize.[5, 16, 105, 111, 116, 117]

4. The molecular mass of the aniline oxidation products can vary from a few hundreds to a few hundreds of thousands† and is mainly determined by the temperature of synthesis, pH of the medium and the initial monomer to oxidant molar ratio in the reaction system.[98, 118, 119] The preparation of high-molecular-mass polyaniline requires an oxidant with a redox potential > 1.1 V,[13] pH < 2.5 (Ref. 98) and reduced temperature.[119]

5. Despite the variability of views on the nature of active sites of oxidative polymerization, almost all of the authors[79, 85, 105, 120, 121] recognize that the chain is built up *via* direct interaction of either the pristine monomer or the active sites formed upon the monomer oxidation with the terminal active site of the macromolecule. Therefore, the question of the nature of chain propagation steps is actually equal to the choice between assumptions on the nature of active sites of oxidative polymerization; furthermore, this process can be considered as either a chain reaction or as recombination of active sites of the *n*-mers of aromatic amine with the monomer active site. The impossibility of recombination of the active sites of different *n*-mers of aromatic amines during oxidative polymerization is presumably attributable to the lack of their solubility in the reaction medium.[5, 16, 105, 111, 116, 117]

6. The more electron excessive the monomers, the higher their reactivity towards oxidative copolymerization.[83, 89, 90] For example, the oxidative polymerization of nitroanilines occurs at a negligibly low rate, while in the presence of small amounts of aniline, fast copolymerization takes place.[83]

7. The oxidative polymerization of aniline is a very exothermic reaction, which is caused by formation of polymeric products stabilized by conjugation. According to the data of calorimetry, the heat of this process does not depend on the ammonium persulfate : aniline molar ratio in the initial reaction mixture up to 1.25 and then linearly increases (Fig. 1). The increase in the heat of oxidative polymerization of aniline in the presence of an excess of ammonium persulfate attests to oxidation of the emeraldine salt chain, resulting in accumulation of quinonediimine moieties.

8. It is also known that polyaniline can undergo destruction to give *p*-benzoquinone. This process usually occurs at a relatively low rate during the chemical oxidative polymerization of aniline in moderately acidic media and is noticeable only in the post-polymerization period [117, 123] or in the electrochemical polymerization.[107, 123]

Despite the indisputability of the above-listed experimental results, there is still no common concept that could account for all of them. In the kinetic analysis of oxidative polymerization, the formation of new phase is not quantitatively taken into account; the nature of the autocatalysis of this reaction is unclear; there is no ultimate understanding of the essence of reactions resulting in the polymer chain growth; and the views about the nature of active sites of oxidative polymerization are also disputable.

† The published data on the average molecular masses of polyaniline should be interpreted with caution, taking into account the fact that the macromolecules are prone to association in solutions to give supramolecular aggregates, which obviously results in overestimated average molecular-mass characteristics. Therefore, the available values for the average molecular mass of polyaniline may at best be used as qualitative comparative characteristics, provided that they have been determined by one and the same method under identical conditions.

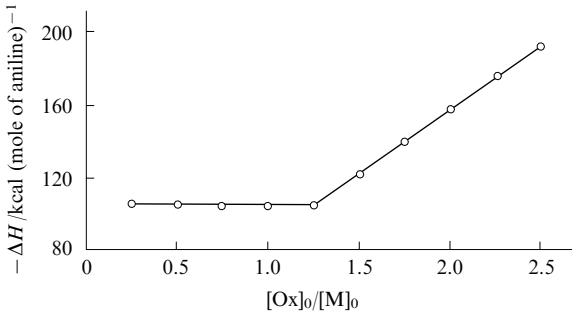


Figure 1. Enthalpy variation during the oxidative polymerization of aniline with ammonium persulfate *vs.* the initial molar ratio of the monomer ($[M]_0$) and oxidant ($[Ox]_0$) concentrations.[122]

III. Kinetic features of the oxidative polymerization of aromatic amines

The kinetics of oxidative polymerization of aniline is addressed in a number of original studies.[76, 79 – 81, 85, 88, 95, 104 – 107, 124] The kinetic curves of oxidative polymerization usually have a long induction period, which is followed by a sharp increase in the monomer conversion with time (Fig. 2).[79, 81, 88, 98, 111, 124] This shape of the kinetic curve attests to a complex character of the reaction.

Meanwhile, some researchers used the formal kinetic tools to determine the orders of the reaction with respect to the monomer and the oxidant applying kinetic equations with one rate constant. For example, in a kinetic description of the oxidative polymerization of aniline in the presence of iron(III) chloride with the assumption of first order with

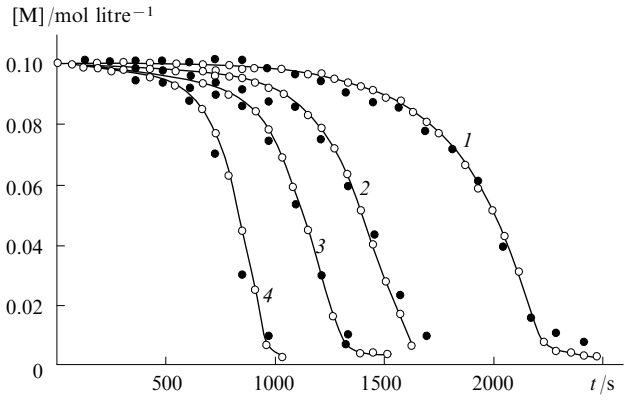


Figure 2. Kinetic curves of oxidative polymerization of aniline (0.1 mol litre^{-1}) in the presence of ammonium persulfate ($[Ox]_0 : [M]_0 = 1.25$) measured at different temperatures by potentiometry (light dots) and UV spectroscopy (dark dots).[124]
T /°C: (*1*) 15, (*2*) 25, (*3*) 30, (*4*) 35.

respect to the monomer, the order with respect to the oxidant was found to be 0.18, as given by the following equation:[104]

$$\frac{d[M]}{dt} = k\,[M][Ox]^{0.18} \quad (1)$$

where k is the reaction rate constant.

The order with respect to the oxidant determined while conducting the aniline polymerization up to high degrees of conversion was 0.18; meanwhile, it is known for sure that in the initial period this order is equal to unity;[76] hence, the order of the reaction decreased as the monomer conversion increased. The decrease in the order of reaction with increasing conversion is a formal sign of autoacceleration.

In a description of the kinetics of oxidative polymerization of 3,5-dimethylaniline in the presence of ammonium persulfate under pH-static conditions, agreement between kinetic equation (2) and experimental data was achieved for various pH values at low monomer conversions (Fig. 3 *a*–*e*).

$$\frac{d[H^+]}{dt} = (1-\alpha)k\,[M][Ox] = (1-\alpha)k([M]_0-[H^+])\times \quad (2)$$
$$\times\left([Ox]_0 - \frac{[H^+]}{2}\right)$$

where $[H^+]$ is the proton concentration, α is the degree of protonation of 3,5-dimethylaniline.

It can be seen that as the fraction of the salt form of 3,5-dimethylaniline decreases, the oxidation rate substantially increases, which attests to higher reactivity of the base form of the monomer. Thus, during the induction period, it is the base form of the monomer that is oxidized,[76] which is consistent with the results obtained by other researchers.[88, 111, 124] Conversely, in the region of high monomer conversions, the experimental reaction rates exceed the values calculated by Eqn (2) (see Fig. 3 *b*,*d*,*e*), which is in line with the presence of autoacceleration effect noted in a number of papers.[79, 81, 98, 105, 106, 124]

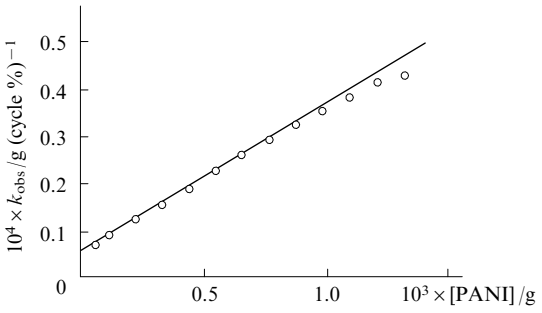


Figure 4. Observed rate constant (k_{obs}) *vs.* the amount of polyaniline formed.[106]

Apparently, the attempts to describe the kinetics of oxidative polymerization using *n*th-order equations with one rate constant may provide the description of the experimental temperature – concentration dependence for a certain range of monomer conversions,[76, 104] but they are of limited utility, because a reaction that has an induction period and autoacceleration behaviour cannot consist of only one stage.

There are various approaches to interpretation of the autoacceleration effect in the oxidative polymerization (see below); meanwhile, it has been reliably ascertained that the introduction of pre-synthesized polyaniline into the reaction system accelerates the reaction.[98, 111] A linear dependence of the observed rate constant k_{obs} on the amount of polyaniline [PANI] formed was established for electrochemical polymerization of aniline (Fig. 4).[106]

The analytical form for the linear plot shown in Fig. 4 is given by the following equation:

$$k_{obs} = k_1 + k_2[PANI] \quad (3)$$

where k_1 is the intercept term, k_2 is the slope of the k_{obs} – [PANI] linear dependence.

Meanwhile, it has been shown that the rate of electrochemical oxidative polymerization of aniline (W) follows

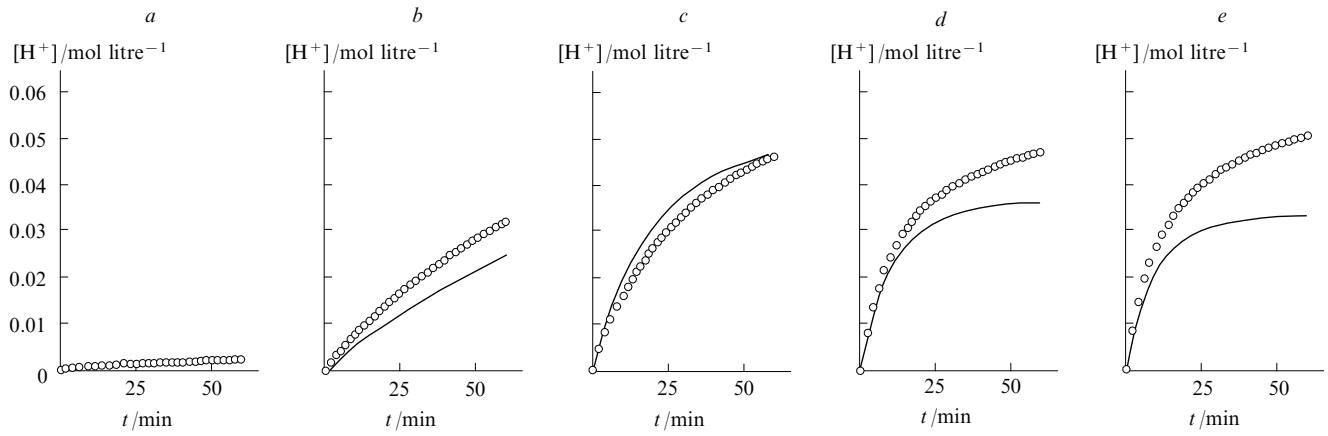


Figure 3. Theoretical (continuous lines) and experimental (dots) kinetic curves measured for the oxidative polymerization of 3,5-dimethylaniline in the presence of ammonium persulfate at various pH of the medium.[76]
(*a*) pH 3, α = 0.99; (*b*) pH 4, α = 0.91; (*c*) pH 5, α = 0.53; (*d*) pH 6, α = 0.10; (*e*) pH 7, α = 0.011.

first-order kinetics with respect to the monomer concentration

$$W = k_{obs}[M] \quad (4)$$

Expressions (3) and (4) considered together give rise to the following equation describing the kinetics of electrochemical oxidative polymerization of aniline ‡

$$W = k_1[M] + k_2[M][PANI] \quad (5)$$

Kinetic equation (5) attests to an autocatalytic effect of polyaniline.[106] An identical kinetic equation was derived in another study addressing the electrochemical oxidative polymerization of aniline.[125] In order to take into account the oxidative destruction of polyaniline during the electrochemical oxidative polymerization of aniline, Eqn (5) was modified by introduction of a term assuming a decrease in the polymer concentration according to first-order kinetics, which resulted in the equation

$$W = k_1[M] + k_2[M][PANI] - k_{od}[PANI] \quad (6)$$

where k_{od} is the rate constant for the polyaniline oxidative destruction.

Equation (6) is in better agreement with experimental results for high monomer conversions than the initial equation (5).[107]

For quantitative description of the kinetics of chemical oxidative homopolymerization of *o*-anisidine[79] and its copolymerization with 3-aminobenzoic acid,[81] the following kinetic equation was used:

$$W = -\frac{d[M]}{dt} = k_1[M][Ox] + k_2[M][P] \quad (7)$$

where P is the polymer formed.

Equation (7) is in line with experimental kinetic curves for oxidative polymerization of *o*-anisidine in the presence of sodium persulfate, which have been measured at different temperatures with the current concentrations of *o*-anisidine being found by ^{1}H NMR spectroscopy (Fig. 5).

Analysis of published data [79, 81, 88, 105 – 107, 124, 125] showed that the kinetics of electrochemical and chemical oxidative polymerization of aromatic amines can be described by Eqns (5) and (7), respectively. It can be seen that these equations differ only in the order of the first term with respect to the concentration of the oxidant; in the case of the electrochemical reaction, the oxidant is represented by the anodically polarized electrode. The validity of kinetic equations (5) and (7) attests to the presence of two rate-limiting stages in the oxidative polymerization of aromatic amines. When the monomer conversion is low and so is the concentration of the products of oxidative polymerization ([P] ≈ 0), the reaction rate is determined by the first term. When the concentration of the polymer increases, the oxidative polymerization rate is determined by the second term, because, according to the results of several studies,[108, 111, 126, 127], $k_1 \ll k_2$.

For taking into account the heterogeneous nature of the oxidative polymerization, it was proposed to replace the amount of the polymer in Eqn (7) by the total surface area of polymer particles (*s*) and to use the following equation:[111]

$$W = -\frac{d[M]}{dt} = k_1[M][Ox] + k_2\sigma[M]s \quad (8)$$

where σ is the surface factor.

Since the surface factor is empirical and the interfacial area present in the system is determined by the amount of polymer formed, Eqns (7) and (8) are equivalent.

Although the kinetic equations we discuss are general, they are empirical.[111] For fitting together the kinetic data and the results presented in the preceding Section, several mechanisms of oxidative polymerization have been proposed.

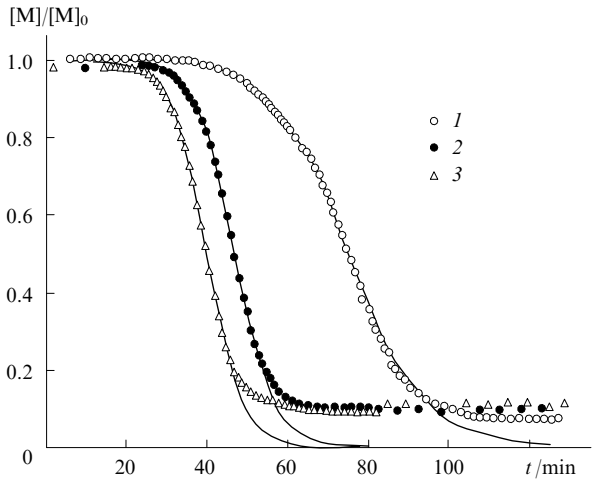


Figure 5. Kinetic curves of oxidative polymerization of *o*-anisidine in the presence of sodium persulfate measured at temperatures of 5 (*1*), 15 (*2*), 25 °C (*3*) ([M]$_0$ = [Ox]$_0$ = 0.05 mol litre^{-1}).[79]

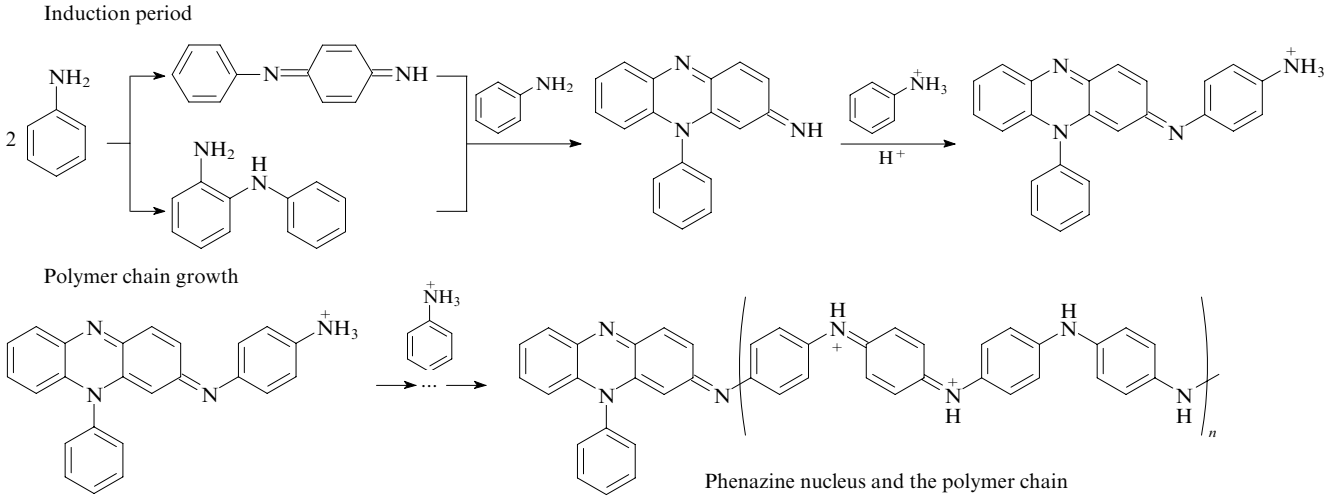
IV. Mechanisms of oxidative polymerization of aromatic amines

Currently, the mechanism of oxidative polymerization of aromatic amines is not entirely clear. The lack of a unified, non-contradictory concept for the oxidative polymerization mechanism is indicated by the presence of quite a few papers [14, 76, 79, 81, 98, 104 – 106, 124] in which diversified and often mutually exclusive approaches are proposed. The main disputable issues include the active sites of oxidative polymerization (various authors have proposed radicals, cations or radical cations) and the nature of autoacceleration effect.

The oxidative polymerization of aromatic amines is possible only in highly acidic media.[14, 98] In relation to aniline oxidation, it has been shown that the molecular mass of the products formed in weakly acidic or alkaline medium (pH > 4) is < 3000; furthermore, the reaction gives a complex mixture of products, which are partly soluble in water, amorphous and typical dielectrics.[14] In the pH range from 2.5 to 4, the reaction also yields water-insoluble, low-molecular-mass products with dielectric properties, which were identified as the aniline tetramer or phenazine dimers.[14] When pH < 2.5, polymeric products are formed,

‡ This kinetic description is also valid for many aniline derivatives.

Scheme 1



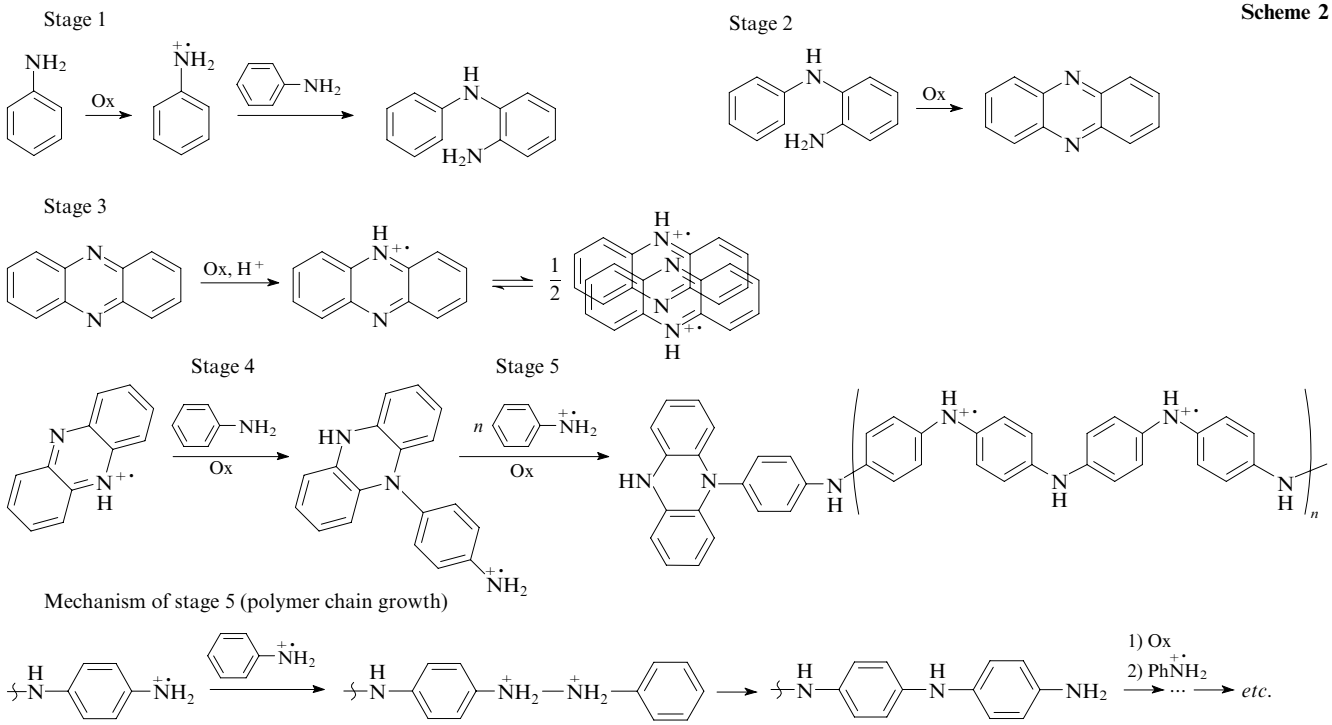
possessing high electrical conductivity, considerable degree of crystallinity and often also a certain specific morphology.[98]

In recent years, particular attention has been attracted by the synthesis of polyaniline of a specified morphology,[98] which can be quite diverse[99] and depends appreciably on the conditions of oxidative polymerization.[100–103] The self-assembly of polyaniline chains to supramolecular structures has been interpreted[98] in terms of a scheme that assumes that phenazine moieties are already formed in an early stage of the oxidative polymerization of aniline (Scheme 1).

The assumption of formation of phenazine moieties in early stages of the reaction is confirmed by the data of electronic spectroscopy,[128] IR spectroscopy[129] and cyclic voltammetry[130] and largely accounts for the trends of formation of supramolecular structures in the oxidative polymerization of aniline.[98] However, the presented mechanism (see Scheme 1) should rather be considered as an overall scheme, as it tells nothing about the active sites or elementary steps of oxidative polymerization. Moreover, a variety of explanations have been proposed for the formation of particular supramolecular structures in polyaniline synthesis.[98, 99]

Sapurina and co-workers[14, 131] changed the sequence of stages presented in Scheme 1 with the assumption of predominant formation of *o*-semidine (rather than *p*-semidine) as the primary product of aniline oxidation (Scheme 2, stage 1) acting as the precursor of phenazine[14, 96, 131] (stage 2). It is assumed that at pH < 2.5, the formed phenazine is further oxidized to give the radical cation, which exists in equilibrium with its dimer (stage 3) and can function as an electrophile towards aniline (stage 4). The semidine rearrangement (stage 5), which occurs under mild conditions in highly acidic media, is taken to be the reaction

Scheme 2



providing growth of the macromolecule.[14] If the pH of the medium is in the range from 2.5 to 4, the oxidation of aniline ends in the formation of phenazine, while stages 4 and 5 do not proceed.[14]

The intermediate formation of *o*-semidine and phenazine in the oxidative polymerization of aniline is indicated by numerous results of spectral and electrochemical investigations.[14, 98, 128 – 133] The assumption of the intermediate formation of phenazine and its subsequent oxidation to give radical cations existing in equilibrium with dimers[14, 133] may account for the absence of an EPR signal from the reaction system in the initial period of oxidative polymerization.[14]

However, the mere fact of detection of *o*-semidine and phenazine in the reaction system does not rule out the possibility that *p*-semidine is formed as the major intermediate product of polyaniline synthesis; furthermore, it is known that *p*-semidine is oxidized at lower potentials than *o*-semidine,[14] which promotes its faster consumption. In addition, it is known that the addition of *o*-phenylenediamine to the reaction system does not influence the rate of oxidative polymerization of aniline,[14] which casts doubt on the mechanism presented in Scheme 2. Indeed, if we adhere to this mechanism, we should expect acceleration of the oxidative polymerization of aniline after the introduction of *o*-phenylenediamine into the reaction system, since it can be oxidized to give phenazine derivatives,[96] the reaction of which with aniline is supposed to determine the reaction rate (see Scheme 2) according to the assumption made by the authors.[14]

Propably, *o*-semidine and phenazine are side products of the oxidative polymerization of aniline, as has also been noted in the literature.[117] Meanwhile, this does not rule out the participation of the formed phenazines in chain self-assembly, as they are capable of copolymerization with aniline.[134, 135]

It is also noteworthy that the reported[14, 98, 116, 136] data on the variation of the open-circuit potential with time during the oxidative polymerization of aniline cannot serve as the crucial evidence for identification of the key intermediates, because this potential depends on not only the concentration of compounds in the reaction system, but also on their ability to be adsorbed on the electrode. Published data[98, 136, 137] attest to high adsorption of phenazine and the products of its oxidation on various surfaces; this may account for a maximum detected in the time dependences of the open-circuit potential in the induction period of aniline oxidative polymerization.[116, 136]

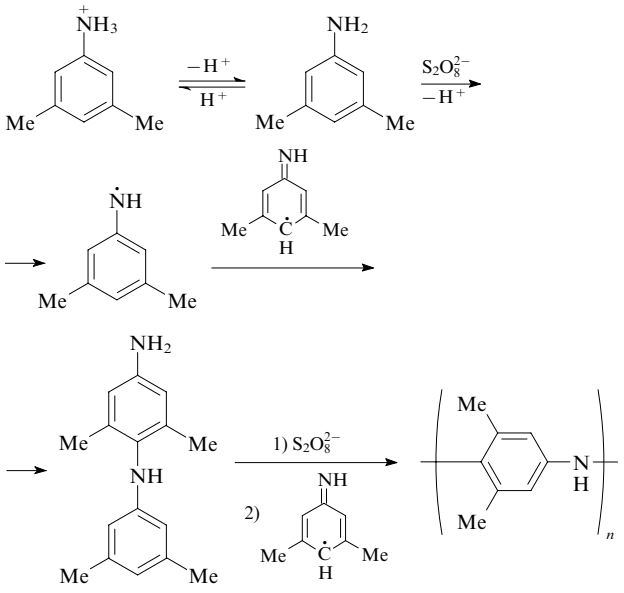
Thus, to date it is unclear how many phenazine rings are formed in the early stage of aniline oxidative polymerization and whether this is the major reaction pathway. Indeed, some publications (for example, Refs 117, 138 and 139) report that phenazine rings are mainly formed in the final stages.

In our opinion, the absence of a signal in the EPR spectrum of the reaction mixture in early stages of aniline oxidative polymerization cannot be attributed to the equilibrium between the monomer and dimer of the phenazine radical cation (Scheme 2, stage 3), as described by Sapurina *et al.*,[14] because unpaired electrons are retained in the proposed structure of the dimer. In addition, the possibility of existence of the phenazine radical cation shown in Scheme 2 seems doubtful, since a species of this type should bear a double rather than single positive charge, which would make it highly unstable. The most likely cause for the absence of the EPR signal from the reaction system in early stages of the oxidative polymerization of aniline is too short lifetime of the aniline radical cations, which precludes recording of their signal.

Finally, the assumption about the semidine rearrangement taking place in the polymer chain growth stage after the head-to-head recombination of radical cations (see Scheme 2),[14, 140, 141] which is in agreement with kinetic data,[14] seems to contradict the possibility of formation of high-molecular-mass polyaniline. Indeed, *N*,*N*′-diphenylhydrazines are known to be prone to oxidation to azo compounds,[142] in particular, in the presence of ammonium persulfate,[143] and this should result in fast chain termination. The issue of spin density distribution in the aniline radical cation is also disputable. According to some publications,[141, 144] the radical cation is located on the nitrogen atom. Conversely, quantum chemical calculations by the AM1 method indicate that the unpaired electron is largely concentrated on the carbon atom located in the *para*-position relative to the amino group.[145] The latter result implies that the head-to-head recombination of aniline radical cations cannot be the predominant process. The electrostatic repulsion between the positively charged nitrogen atoms of the aniline radical cations is also unfavourable for the head-to-head recombination.

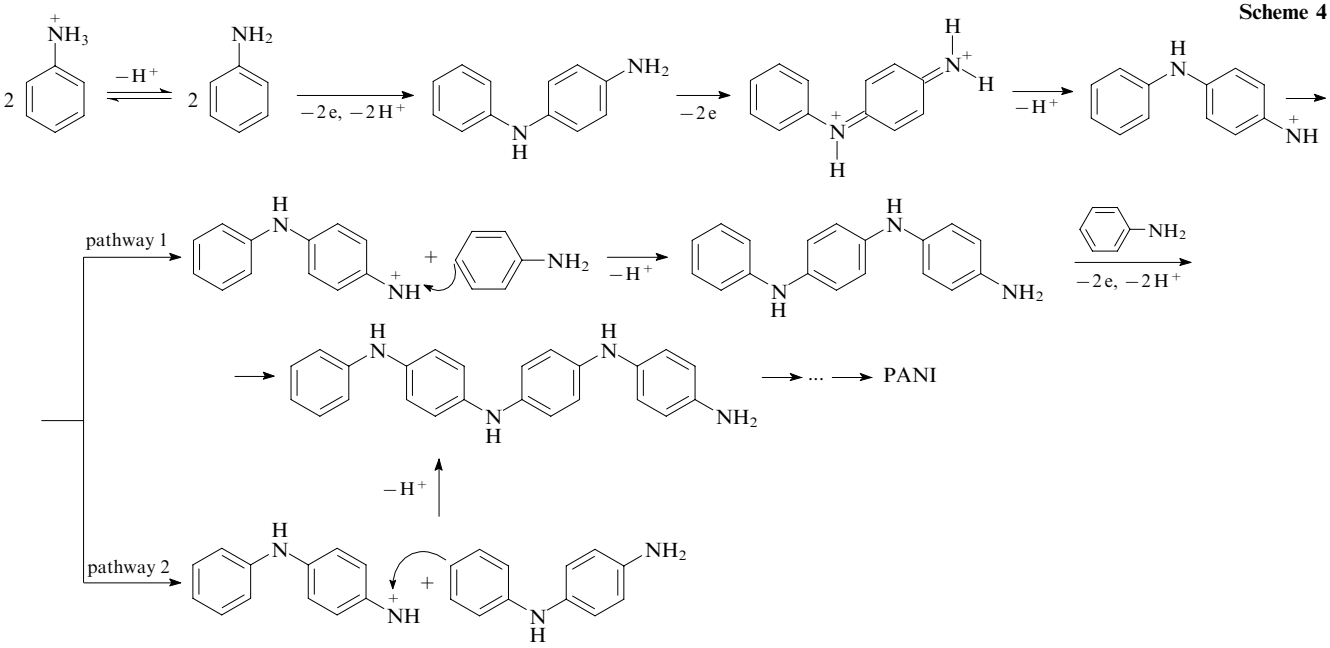
A kinetic study of the oxidative polymerization of 3,5-dimethylaniline provided the conclusion about the intermediate formation of aromatic amine radicals as active sites (Scheme 3).[76]

Scheme 3



The presented mechanism does not account for the autocatalytic oxidative polymerization; in addition, it is at variance with the fact that the monomers that contain electron-withdrawing groups stabilizing the presumed aromatic amine radicals by resonance are unreactive in oxidative polymerization.[83] The enhanced activity of the monomers with electron-donating substituents prompts the idea that the arising intermediates are positively charged, *i.e.*, the active sites are of a cationic or a radical cation

Scheme 4



nature. The possibility of formation of nitrenium cations as the active sites of oxidative polymerization is being widely discussed in the literature (Scheme 4).[22, 105, 106, 117, 130, 146]

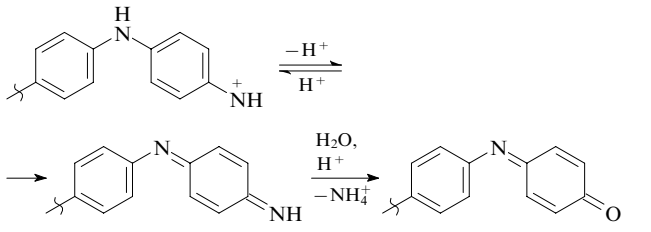
According to the mechanism presented in Scheme 4, the oxidative polymerization of aniline starts with slow oxidation of the base form of the monomer to the dimer (*p*-semidine), which undergoes the further fast oxidation to *N*-phenylbenzoquinone-1,4-diimine and deprotonation to give the nitrenium cation. The latter acts as the electrophile in the reaction with the monomer (the dimer, which is considerably soluble in the reaction medium, is also suggested to participate in the growth of the polymer chain). Thus, the steps of polymer chain growth in the oxidative polymerization represent the electrophilic aromatic substitution, the polyaniline formation being a chain process.[105, 106, 117]

However, some experimental facts are at variance with this mechanism. Since aniline oligomers are more reactive towards the electrophilic aromatic substitution than the monomer, chain branching and subsequent cross-linking should inevitably take place. However, it is known that ~98% of polyaniline units have no branchings; moreover, they are constructed through *para*-coupling.[147] The absence of cross-linking between polyaniline chains is evidenced by the solubility of its base form in *N*-methylpyrrolidone.[5]

Meanwhile, the nitrenium cations should occur in the protolytic equilibrium with N-unsubstituted quinonediimines, which are known to be hydrolytically unstable in acidic media (Scheme 5).[148] Therefore, assuming nitrenium cations to be active sites, one can hardly expect the formation of high-molecular-mass polyaniline [119] and, even more so, the increase in the molecular mass with increasing acidity of the medium.[98]

There are also other factors that obviously contradict the proper possibility of growth of the polymer chain *via* electrophilic aromatic substitution. It is evident that under conditions of oxidative polymerization, aniline is almost fully protonated; furthermore, protons are released in the reaction; hence, the equilibrium additionally shifts towards the phenylammonium cation. Unlike the base form of aniline, the phenylammonium cation is unreactive towards electrophilic aromatic substitution; together with the decrease in the pH during the oxidative polymerization, this should result in retardation of the reaction and is at variance with the autoacceleration effect observed experimentally. Finally, although aromatic amines with electron-withdrawing substituents are known to have low reactivity towards oxidative polymerization, the addition of small amounts of aniline results in the formation of the copolymer at acceptable rates and in acceptable yields.[83] This is also inconsistent with the assumption that nitrenuim cations act as the active sites for polymer chain growth by the electrophilic aromatic substitution mechanism.

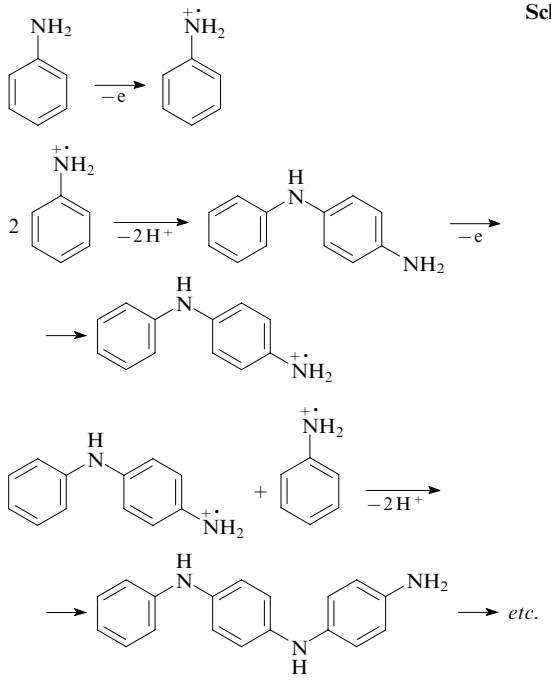
Scheme 5



One more type of active sites for oxidative polymerization are radical cations of aromatic amines.[14, 22, 72, 79, 81, 88, 95, 98, 104, 124, 149, 150] Initially, the idea of intermediate formation of radical cations from aromatic amines was utilized to explain the formation of a polymer chain during the oxidative polymerization; however, this did not account for the autocatalytic effect of the process (Scheme 6).[14, 104]

According to this scheme, the macromolecule grows *via* recombination of radical cations of aniline *n*-mers only with the monomer radical cations; this precludes classification of the oxidative polymerization as either chain or stepwise process. It is assumed that recombination of the radical cations of aniline *n*-mers with each other is virtually

Scheme 6

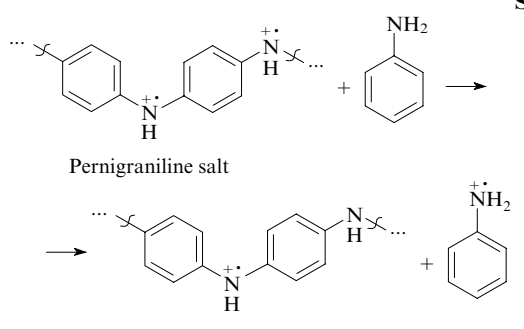


impossible, as they are insoluble in the reaction system and form a new phase.[85, 105]

Formally, the oxidative polymerization can be treated as a chain process giving rise to macromolecules, with chain propagation occurring upon addition of the monomer to the end of the growing macromolecule.[79, 85, 98, 105, 120, 121, 124] The monomer addition (recombination) proceeds through re-oxidation steps of both the monomer and the *n*-mers; in terms of the theory of chain reactions, this corresponds to chain propagation *via* termination. Also, the growth of the polymer chain in the oxidative polymerization can be considered as a stepwise poly-recombination of the oligomer radical cations with the monomer radical cations.[85, 98] The above considerations concern only the terminology; it is clear that oxidative polymerization is a separate class of reactions giving macromolecules, which has its own fundamental features.

The concept of formation of the radical cations does not contradict the known data on the reactivity of aromatic amines; however, the (very simplified) radical cation mechanism, which is shown in Scheme 6, cannot account for the autocatalytic effect of oxidative polymerization; furthermore, it is being criticized.[14]

Scheme 7



Pernigraniline salt

Emeraldine salt

In order to explain the autocatalytic effect in the oxidative polymerization of aromatic amines under the hypothesis of intermediate formation of radical cations, a mechanism has been proposed assuming the oxidation of the monomer by the formed pernigraniline (Scheme 7).[5, 79, 81, 111, 151]

Pernigraniline is known to possess clear-cut oxidizing properties; [5, 22, 111, 151] however, the formation of this compound during oxidative polymerization requires the presence of an even more potent oxidant, namely, the peroxydisulfate ion, which would compete favourably with pernigraniline for the common reducing agent — aniline. Therefore, it seems unlikely that aniline would be oxidized with pernigraniline in the presence of the peroxydisulfate ion and also that pernigraniline would be already formed at low conversion of the monomer, where the autoacceleration effect starts to be manifested [124] (see Figs 2 and 5). Meanwhile, to interpret the autocatalysis effect in the oxidative polymerization of aromatic amines, one should merely assume the possible formation of the charge transfer complex between the monomer (donor) and the *n*-mers containing quinonediimine moieties (acceptors) and the subsequent fast oxidation of this complex to give radical cation (Scheme 8).[88, 124, 152]

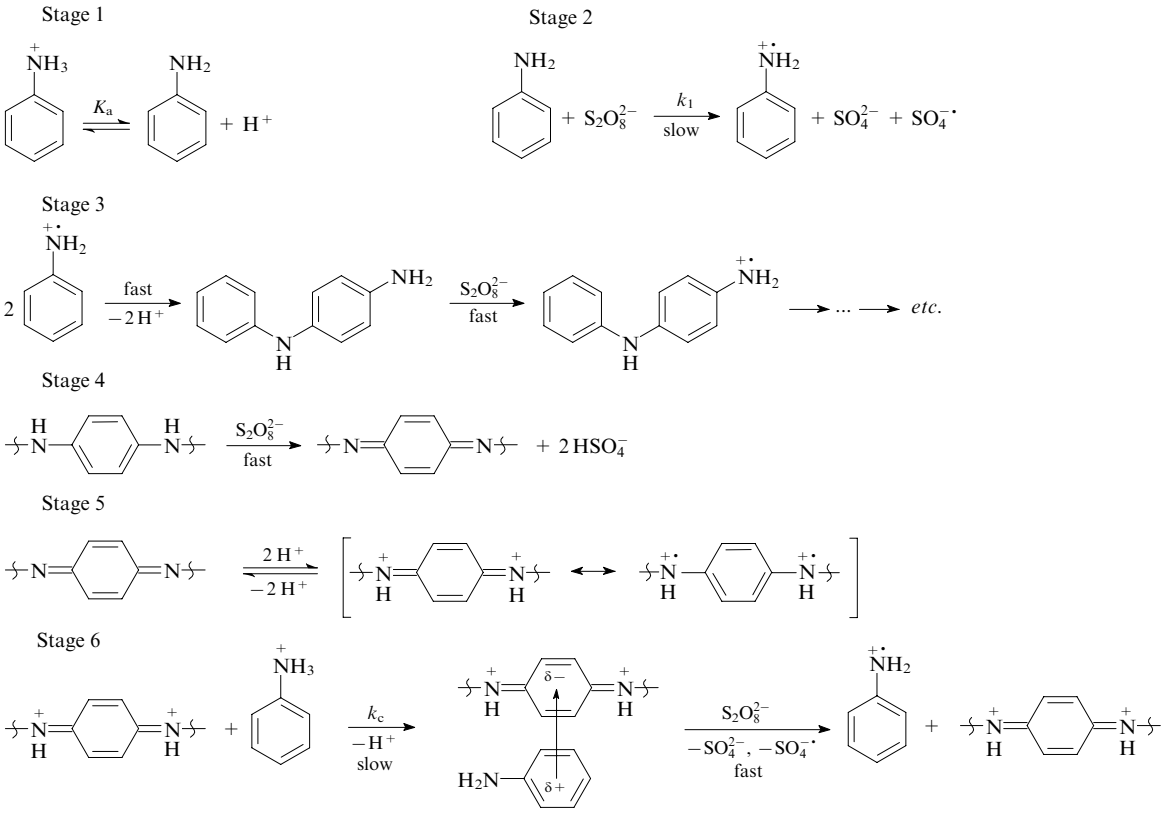
The mechanism of oxidative polymerization of aromatic amines presented in Scheme 8 includes the catalytic and non-catalytic rate-limiting stages. The non-catalytic stage determines the reaction rate at low monomer conversions and consists in slow one-electron oxidation of the base form of the monomer (Scheme 8, stage 2), which exists in protolytic equilibrium with the salt form (stage 1). The catalytic stage includes the slow formation of charge transfer complex followed by its fast oxidation (stage 6). Since the *n*-mers of aromatic amines bearing the electron-withdrawing protonated quinonediimine moieties are almost insoluble in the reaction medium and form a new phase upon aggregation, the formation of the charge transfer complex should be preceded by adsorption of the monomer, with the charge transfer complex being formed on the surface of aggregated *n*-mers of aromatic amines.[88, 124, 152]

Both the catalytic and non-catalytic stages give rise to the monomer radical cations. The monomer radical cations participate in fast recombination steps with each other to give dimer and with the radical cations of aromatic amine *n*-mers (see Scheme 6 and Scheme 8, stage 3). Note that the reducing activity of the aromatic amine oligomers substantially increases with increasing degree of polymerization, as shown by several authors,[22, 79, 81, 105, 106] which means that the rate of the whole oxidative polymerization process is limited by the monomer oxidation rate.

If one accepts the validity of the mechanism shown in Scheme 8, it becomes possible to interpret all of the above noted (see Section II) features of the oxidative polymerization of aromatic amines. Indeed, the autoacceleration effect in oxidative polymerization is attributable to the catalytic action of the protonated forms of quinonediimine moieties, while the induction period is due to the necessity of accumulation of a sufficient amount of these moieties.[124, 152]

The possibility of formation of high-molecular-mass polyaniline only in the region pH < 2.5 (Ref. 98) can be explained by the fact that the formation of the charge transfer complex requires a considerable electron deficiency

Scheme 8



on the acceptor quinonediimine moieties, which arises upon protonation (Scheme 8, stage 5).

The inhibition of the oxidative polymerization of aniline by π-electron donors, for example, 2,6-di-*tert*-butyl-4-methylphenol, can be attributed to competition with the monomer for the electron-withdrawing quinonediimine moieties. Conversely, the increase in the rate of oxidative polymerization upon the addition of aromatic amines that are more electron-excessive than aniline, such as *p*-semidine and *p*-phenylenediamine, is explained by the higher rate of one-electron oxidation of these amines compared with the oxidation rate of aniline, which also results in accumulation of catalytically active protonated forms of quinonediimine moieties in the system.[85, 95, 108 – 110] However, the effect of compounds added to the reaction system on the oxidative polymerization rate is due not only to their reducing activity, but also to their structural details. Indeed, although the oxidation of both *o*-phenylenediamine and *m*-phenylenediamine starts at lower potentials than the oxidation of aniline, the introduction of the former does not change the rate of oxidative polymerization of aniline, while addition of the latter to the reaction system markedly decreases the rate.[14] Probably, *o*-phenylenediamine is oxidized in the reaction system to give phenazine derivatives,[96, 131] which can copolymerize with aniline [134, 135] at a rate that does not exceed the rate of aniline homopolymerization and, hence, this does not affect the reaction rate. *m*-Phenylenediamine cannot be directly oxidized to give quinonediimine moieties exhibiting a catalytic action; this apparently accounts for the observed increase in the induction period of oxidative polymerization of aniline in the presence of this compound.

The elongation of the induction period of aniline oxidative polymerization in the presence of *m*-phenylenediamine can also be explained in a different way. According to the assumption of polymer chain growth *via* the semidine rearrangement, the introduction of *m*-phenylenediamine leads to accumulation of 'defective' oligomers that are unable to propagate the chain *via* the semidine rearrangement.[14]

The reduced reactivity of aromatic amines containing electron-withdrawing substituents towards the oxidative homopolymerization may be attributed to the lack of stability of the radical cations formed. In the case of copolymerization with aniline, which is the first to be oxidized, protonated quinonediimine moieties are accumulated in the system; they are able to form charge transfer complexes with aromatic amines containing an electron-withdrawing group, thus involving these amines into the reaction.[83]

Under the assumption that the formation of the adsorption charge transfer complexes precedes the steps of polymer chain growth, a quantitative approach has been proposed to the description of the oxidative polymerization kinetics taking into account the heterogeneous nature of the reaction.[124, 152, 153]

Let the rate of one-electron oxidation of the monomer (non-catalytic stage) be designated by W_s and the rate of the catalytic stage be designated by W_c. Since the monomer radical cations arise as a result of monomer consumption in both the one-electron oxidation and catalytic stage occurring in parallel, the overall oxidative polymerization rate (W) will be given by the sum of the rates of these reactions

$$W = -\frac{d[M]}{dt} = W_s + W_c \quad (9)$$

The non-catalytic stage of oxidative polymerization taking place in the solution follows overall second-order kinetics, with the orders with respect to the monomer base form and the oxidant being equal to unity.[79, 124]

Considering the particles of the dispersed phase as spheres with a surface area equivalent to that of the aggregates of aromatic amine *n*-mers, the rate of the catalytic stage, which is a heterogeneous reaction, can be described by the equation:

$$W_c = \frac{k\theta_{eq}S}{V} = \frac{4\pi r^2 k\theta_{eq}N}{V} \quad (10)$$

where k is the rate constant for the reaction between the adsorbed monomer and electron-deficient moieties of the polymer; θ_{eq} is the equilibrium degree of coverage of the surface of *n*-mer aggregates with the monomer; S is the total interfacial area in the system; N, r is the number and the average radius, respectively, of the spheres equivalent in the surface area to the aggregate particles of aromatic amine *n*-mers; and V is the volume of the system.

The total number of aggregate particles of aromatic amine *n*-mers can be calculated from the equation

$$N = \frac{m}{m_a} \quad (11)$$

where m is the current value for the total weight of the aggregates of aromatic amine *n*-mers formed, m_a is the average weight of a single aggregate.

If the total weight of all aggregates is expressed in terms of the current monomer concentration, relation (11) is transformed into the following equation:

$$N = \frac{3([M_0] - [M])VM}{4\pi\rho r^3} \quad (12)$$

where ρ is the density of the aggregates of aromatic amine *n*-mers, M is the monomer molar mass.

With the assumption that the monomer adsorption on the surface of *n*-mer aggregates obeys the Langmuir isotherm, it is possible to calculate the degree of surface coverage from the equation

$$\theta_{eq} = \frac{K[M]}{1 + K[M]} \quad (13)$$

where K is the adsorption equilibrium constant for the monomer on the surface of *n*-mer aggregates.

By combining Eqns (10), (12) and (13), we obtain the relation for description of the rate of the catalytic stage

$$W_c = \frac{3KkM([M]_0 - rm[M])[M]}{\rho r(1 + K[M])} \quad (14)$$

By introducing an overall rate constant for the catalytic stage

$$k_c = \frac{3KkM}{\rho r}$$

into Eqn (14) and taking account of sum (9), we get an equation for calculating the overall rate of oxidative polymerization

$$W = -\frac{d[M]}{dt} = W_s + \frac{k_c([M]_0 - [M])[M]}{1 + K[M]} \quad (15)$$

It can be seen that kinetic equations (7) and (8) are special cases of Eqn (15) and are valid if the inequality $1 \gg K$ [M] holds. Indeed, in this case, Eqn (15) takes the form

$$W = -\frac{d[M]}{dt} = W_s + k_{c2}([M]_0 - [M])[M] \quad (16)$$

where k_{c2} is the second-order rate constant for the catalytic stage.

If $1 \ll K$[M], then Eqn (15) can be transformed into the following expression:

$$W = -\frac{d[M]}{dt} = W_s + k_{c1}([M]_0 - [M]) \quad (17)$$

where k_{c1} is the first-order rate constant for the catalytic stage.

It can be seen that Eqns (16) and (17) presume the autocatalytic course of the oxidative polymerization. The polymerization kinetics for the vast majority of aromatic amines, including phenylenediamines, obeys Eqn (16).[79, 80, 88, 95] The rate constant k_{c2} of Eqn (16), which coincides with the rate constant k_2 of Eqn (7), remains invariable up to high degrees of monomer conversion.[79, 80, 88, 124, 152, 153] According to Eqn (14), this implies that the aggregates of aromatic amine *n*-mers, which form the new phase, have a constant radius. This behaviour is possible if the arising primary aggregates form a coagulation structure permeable for the solvent (water), the monomer and the oxidant. The formation of regular coagulation supramolecular structures during the oxidative polymerization of aniline is evidenced by numerous literature data, which are integrated in a review,[98] in which consistent theoretical views on the mechanism of their formation are introduced for the first time.

This approach provides explanation for the influence of inert compounds on the oxidative polymerization rate;[111 – 115] probably, these compounds act as adsorption sites even for lower oligomers of aromatic amines and, therefore, they affect the surface concentration of the protonated quinonediimine moieties accessible for the formation of charge transfer complexes with the monomer.

Kinetic descriptions of the oxidative polymerization of various monomers using Eqns (7), (16) and (17) have shown that the activation energy of the non-catalytic stage is always higher than the activation energy of the catalytic stage, which is also in line with the assumption about the autocatalytic nature of oxidative polymerization.[79, 80, 88, 95, 152, 153]

The integration of Eqns (16) and (17) has been reported;[124] however, for further consideration, it is important that the integrated form of equation (16) is linear in the $\ln[([M]_0 - [M])/[M]] - t$ coordinates, while the integrated form of equation (17) is linear in the $\ln([M]_0 - [M]) - t$ coordinates.

Interesting results have been obtained in a kinetic study of the dispersion oxidative polymerization of aniline in

aqueous solutions of polyethylene oxide,[153] which acts as a stabilizer. The addition of poly(ethylene oxide), which is hydrogen-bonded to the aniline *n*-mer chains, results in a change in the order and the activation energy of the catalytic stage. If conditions of the oxidative polymerization of aniline without poly(ethylene oxide) are chosen in such a way that the catalytic stage follows the overall first-order kinetics ($1 \ll K[M]$) and Eqn (17) holds, then in the presence of poly(ethylene oxide) with a molecular mass exceeding some definite value, the catalytic stage switches from the overall first- to second-order kinetics ($1 \gg K[M]$) and obeys Eqn (16). Apparently, the change in the overall order of the catalytic stage is a consequence of decreasing adsorption equilibrium constant of monomer K, which is presumably associated with shielding of the surface of *n*-mer aggregates by poly(ethylene oxide) chains. Indeed, switching of the catalytic stage of aniline oxidative polymerization from the overall first- to second-order kinetics occurs as the poly(ethylene oxide) molecular mass increases from 3000 to 6000, that is, a certain chain length must be reached to make possible the shielding effect (Fig. 6). The activation energy of the catalytic stage of the oxidative polymerization of aniline conducted in aqueous solutions of poly(ethylene oxide) with the molecular mass of 12 000 is much higher than the activation energy determined in the absence of poly(ethylene oxide), which is also indicative of shielding effect and is consistent with the assumption that the rate-limiting steps of oxidative polymerization occur with participation of the adsorbed monomer.[153]

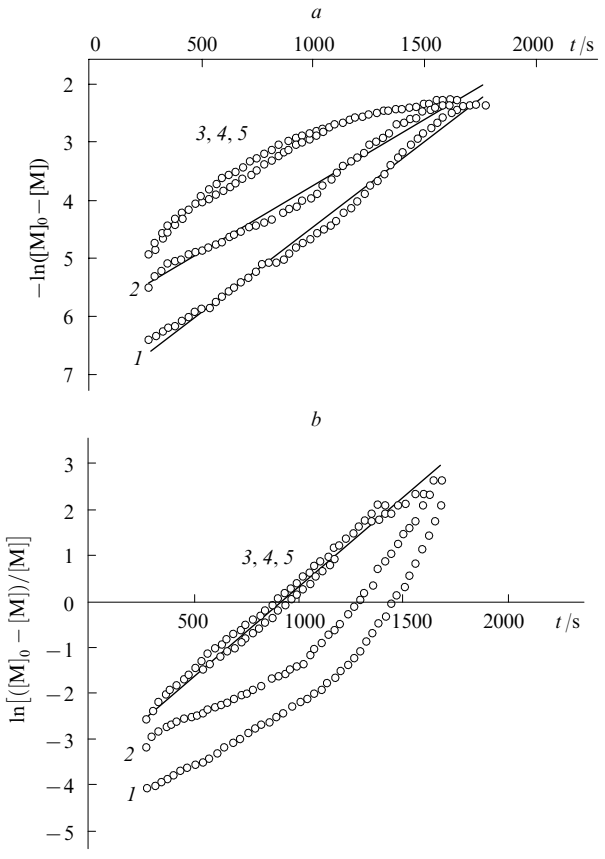


Figure 6. Linearized kinetic curves in the coordinates $\ln([M]_0-[M])-t$ (*a*) and $\ln[([M]_0-[M])/[M]]-t$ (*b*) for the oxidative polymerization of aniline hydrochloride (0.1 mol litre^{-1}) induced by ammonium persulfate (0.125 mol litre^{-1}) in an aqueous solution of poly(ethylene oxide) (0.1 base-mol litre^{-1}) with the molecular weight 300 (*1*), 3000 (*2*), 6000 (*3*), 12 000 (*4*), 35 000 (*5*) at a temperature of 25 °C.[153]

It is noteworthy that kinetic equations (9) – (17) can also be derived under the assumption of complete electron transfer from aniline to pernigraniline (see Scheme 7) if this transfer is supposed to occur slowly [79, 81] after the fast establisment of the adsorption equilibrium between the monomer and pernigraniline.

Irrespective of whether the electron transfer from the monomer to the electron-withdrawing moieties of the *n*-mers is complete (formation of the radical cation, Scheme 7) or partial (formation of the charge transfer complex, Scheme 8), kinetic equations (15) – (17) assume that the adsorption equilibrium is established rapidly. A piece of indirect evidence supporting the assumption of fast establishment of the adsorption equilibrium between the monomer and *n*-mer aggregates is the fact that the second-order rate constant for the catalytic stage (k_{c2}), which is determined by the slope of the kinetic curves in the $\ln[([M]_0-[M])/[M]]-t$ coordinates, does not depend on the molecular mass or concentration of poly(ethylene oxide) after they have reached the threshold values.[153]

The assumption of formation of charge transfer complexes between the monomer and protonated quinonediimine moieties in the *n*-mers, which we made for the first time, provides an explanation for the autoacceleration effect, without resorting to the assumption of formation of pernigraniline even at low monomer conversions. Furthermore, the influence of various compounds added to the reaction system on the oxidative polymerization rate is also rationally explained, and the views on the monomer adsorption taking place before oxidation make it possible to theoretically substantiate the empirical relations for the oxidative polymerization rate established earlier.

Generally, the performed analysis of published data attests to participation of the oxidative polymerization products, which form a new phase, in the formation of monomer active sites, which are apparently represented by the radical cations of aromatic amines.

V. Conclusion

Despite the considerable advances made in the synthesis and applications of polymers of aromatic amines, the mechanism and kinetics of polymerization are still subjects of versatile discussion. To date, no common theory of oxidative polymerization has been developed, which restricts the possibility for targeted control of this class of reaction. Meanwhile, using the theoretical approaches considered above, it is possible to explain some regular features of oxidative polymerization. Further development of the synthetic approaches to the preparation of electrically conductive polymers and composite materials based on them would, apparently, be closely related to the progress in understanding of the mechanism of oxidative polymerization.

The oxidative polymerization of aromatic amines is a separate class of reactions used for the synthesis of macromolecules, which is distinguished by a number of fundamental kinetic and mechanistic features not inherent in other methods for polymer synthesis. The nature of the

active sites of oxidative polymerization is still a controversial issue; however, there is convincing evidence for the intermediate formation of radical cations, and it is assumed that the macromolecule grows as a result of recombination of radical cations of aromatic amine *n*-mers only with the monomer radical cations. The oxidative polymerization starts in a homogeneous system, which then becomes heterogeneous because of the lack of solubility of even lower oligomers of aromatic amines in the reaction medium, and the new phase being formed has a catalytic action. Thus, the oxidative polymerization of aromatic amines is a kinetically complex, heterogeneous, autocatalytic process.

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