The Mechanism of Formation of Structural Heterogeneitics in Polyaniline

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Abstract: The regularities of polyaniline formation, the influence of various additions, conditions of synthesis of the main and intermediate, including hydrolysis, products on the structure of obtained materials are studied. Making use kinetic and thermochemical methods the mechanisms of polycondensation by N-phenyl-1,4-benzoquinonodiimine, initiation macromolecules growth as result of anilines addition to electrophile quinonoimine groups of the polymer are confirmed. The chemical aspects of reactions leading to formation of structural heterogeneitics, branchings, breaching of effective conjugation, termination and sewing together of chains are analyzed.

Keywords: Polyaniline, kinetic, mechanism, synthesis, structural heterogeneitics.

1. INTRODUCTION

Polyaniline (PANi) and it`s different derivatives are being used in organic electronics, electrotechnics for displays, as solar cell, chemical sources of electricity, supercapacitors; as corrosion protection coatings, microwave absorption, materials [1-3]. In spite of their large application of those polymers, many problems concerning their structure are not clear. Cited in literature different mechanisms of their receipt very often are contradictory and are unable to explain many experimental facts [3-5]. The oxidation of aniline and it`s derivatives with persulfates is the key stage in synthesis of conjugated polyamines. The initial reaction product is the amine`s cation-radical, which depending on the reaction medium nature, may be undergo to different changes, which result in the formation of many products of condensation [6]. The obtained products are active for further polycondensation and as a rule form polymer chains leading to many structural dissimilarities. They cannot be evaluated quantitatively and strongly influence on the structure and the properties of the final polymer [5-9]. It is established, that at chemical as well at electrochemical aniline's oxidation in water, it`s cation-radical is being formed which irreversibly dimerizes principally forming N-phenylene-1,4-phenylenediamine (D). The reaction is being complicated as result of the possibility molecules of joining 'head to head' or 'tail to tail', which result is the formation either benzidene or diphenylhydrazine [4, 6, 11]. All formed products take part in polycondensation processes. For this reason, the properties of the final polymer essentially depend on the nature of the initial products of condensation [2, 7,10]. In spite of large quantity of investigations the mechanism of amine`s (A) oxidative polycondensation remains no clear [3-13].

The chain propagation is being considered as a process, which occurs by means of cation-radical mechanism as a variant of cationic polymerization [2, 3, 9].

$$\text{Initiation}\quad \mathrm{A}\xrightarrow{k_1}\mathrm{A}^{\bullet+}+\mathrm{e}^-\qquad \mathrm{d}[\mathrm{A}^{\bullet+}]/\mathrm{d}t=k_1[\mathrm{A}]\qquad \text{(I)}$$

$$\text{Propagation}\quad \mathrm{A}_n^{\bullet+}+\mathrm{A}\xrightarrow{k_2}\mathrm{A}_{n+1}{}^{\bullet+}\qquad -\mathrm{d}[\mathrm{A}]/\mathrm{d}t=k_2[\mathrm{A}][\mathrm{A}_n^{\bullet+}]\qquad \text{(II)}$$

$$\text{Termination}\quad \mathrm{A}_n^{\bullet+}+\mathrm{A}\xrightarrow{k_3}\mathrm{A}_{n+1}-\mathrm{e}^-\qquad -\mathrm{d}[\mathrm{A}_n^{\bullet+}]/\mathrm{d}t=k_3[\mathrm{A}_n^{\bullet+}][\mathrm{A}]\qquad \text{(III)}$$

If the case of chain initiation stage is obvious, then the chain propagation and termination stages disagree with obtained experimental results. A two-stage model for the formation of emeraldine base is proposed. In the first stage of the reaction the pernigraniline salt (PS) oxidation state is formed. In the second stage, pernigraniline is reduced to the emeraldine salt (ES) as aniline monomer is oxidized to the radical cation. In the third stage, this radical cation couples with ES. For two-step process of polycondensation the equation (1V) is found [2],

$$dA/dt = k_1[A]\ Ox]+k_2\sigma[A]\ P \qquad (1V)$$

where [A] is the molar concentration of aniline, [Ox] is the molar concentration of the oxidant, k1 is the rate constant of the initial step (induction period) of polymerization, k2 is the rate constant for the polymer chain propagation, σ is the surface factor, P is the surface of the reaction medium interface. However, even in this case the authors failed to reveal the physical meaning of both σ and P parameters.

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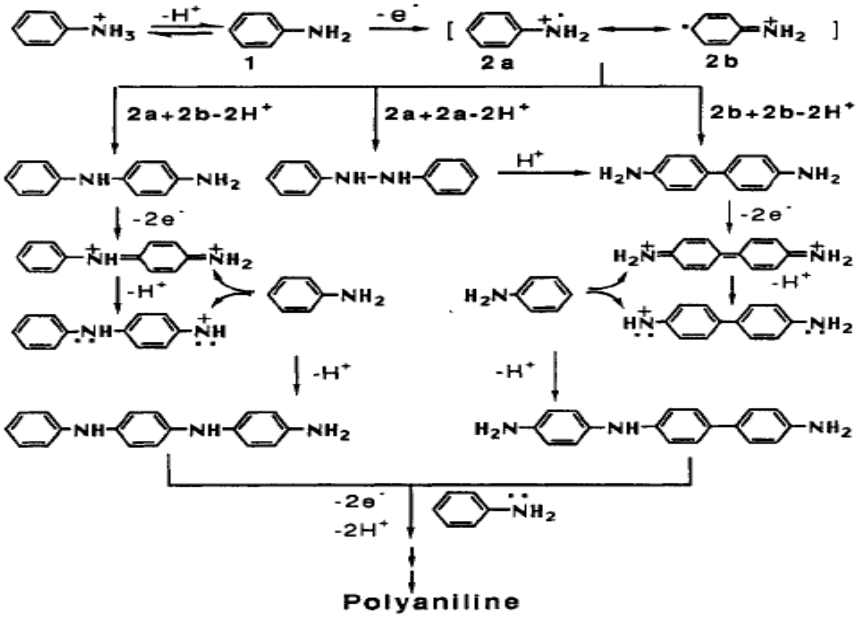
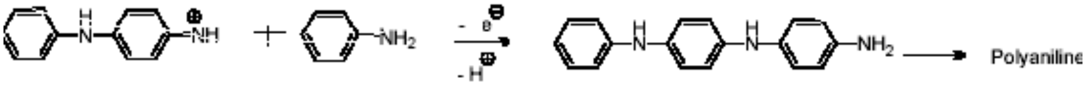


Scheme 1:



Scheme 2:

Efforts to explain the peculiarities of polyaniline synthesis by the mechanism of nitronium ion formation stage [4, 15] (Scheme **2**), also were unsuccessful and were disproved in some subsequent publications.

We have studied the regularities of aniline polycondensation initiated with ammonium persulfate (Ox) at different conditions and we tried to specify the aspects of occurring reactions, to generalize and explain the obtained experimental results as well literature data.

2. EXPERIMENTAL PART

Aniline (chemically pure) is distilled in vacuum before its use, formic acid and methanol again "chemically pure", are also distilled before use. Ammonium persulfate, sodium hydrosulfite were "chemically pure" grade, and N-phenyl-1,4-diphenylene diamine (D) (Aldrich production) are used without supplementary purification. "Pure" hydroquinone recrystallizes from aqueous solution. The polyaniline synthesis is carried out at intensive stirring of aniline's solution ([A] = 0.05 – 0.35 M) and [Ox] = 0.06 – 0.35 M solubilized in either hydrochloric (0.05-3.0 M) or formic acids. The initial temperature changed in the interval 263-310 K. The process is controlled by continuously measuring the potential and temperature of the reaction mixture. To pick out the intermediate reaction products the process has stopped adding 1M aqueous solution of $Na_2S_2O_3$. The polyaniline is filtered and washed with water and methanol. To obtain the polymer in emeraldine form the samples supplementary are treated with 0.5 M ammonia solution during 10 h, washed with water and dried during 7 h at 323 K. Kinetic measurements are carried out making use thermochemical and potentiometric methods [14,16]. Reaction rate (R) was determined by the change of the potential of open circuit**.**

The temperature profiles of the process are obtained measuring the temperature at isothermal conditions. To evaluate the heat, which evolves during the synthesis, the reaction is carried out in calorimeter at adiabatic conditions. The temperature is measured with accuracy ± 0.3^oC. The chain potential is determined by the method described in [16] making use platinum and glass electrodes 'ESL-43-07' on device 'Ionomer-FT-74'. The readings of the potentiometer are restarted through every 15 sec. The accuracy of the measured potential was ± 5 mV.

The ESR studies are carried out making use modified ESR device prepared in the Institute of

Chemical Physics of the Russian Academy of Sciences (Moscow) with working frequency equal to 9.4 GHz, modulation frequency equal to 100 kHz. The modulation amplitude was 0.3 Hz. Equal volumes of freshly prepared solutions of A (0.2 M) and P (0.2M) in formic acid are mixed in quartz ampoule during 10-15 sec and it is placed in the ESR device resonator (T = 298K). The rate of formation of the radical cation is determined by the relative intensity ($I = I_t/I_0$) ESR signal.

The IR spectrums are registrated for polymer`s emeraldin form either in KBr tablets or as films. In this case, Fourier spectrophotometer (Perkin Elmer 1600) is used. When powders are used method of breached full internal reflection with ZnSe crystals (ATR-FTIR) is applied making use “Nicolet/NEXUS” device.

The measurements of volume electroconductivity of purified polymer samples are carried out for polymer ES brought on tablets of diameter equal to 0.4 cm and of thickness equal to 0.1 cm. The samples are prepared pressing the purified powder under pressure equal to 100 MPa. The samples for resistance measurement are prepared making use copper electrodes on which 0.5 ml of reaction suspension is spread. The samples are dried at 298 K during 24 h and during 4 h at 323 K. The elemental composition of emeraldin form of polymers is determined making use analysator “EUR VECTOR EA 300”.

3. THE OBTAINED RESULTS AND THEIR DISCUSSION

The kinetic study of polyaniline formation as result of aniline oxidation with ammonium persulfate in aqueous solution of hydrochloric acid shows that quick polymerization starts to run after a prolonged induction period. Then follows a prolonged after polymerization plot, where the viscosity, electroconductivity and the yield of the polymer are being diminished (Figure **1**).

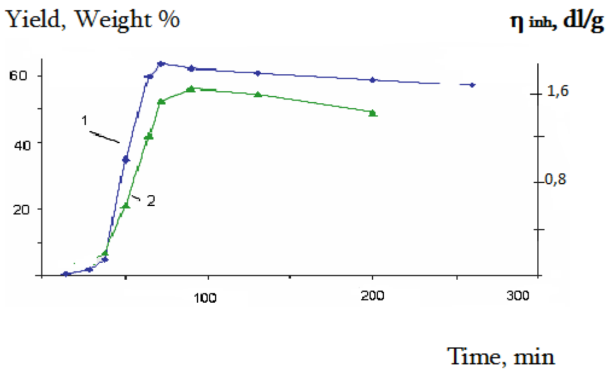


Figure 1: Polyaniline yield (1) and viscosity (2) dependence on reaction time.

[A] = 0.13 mol/L; [Ox] = 0.12 mol/L; [HCl] = 1 mol/L; T= 0°C.

The induction period is due to the accumulation of low molecular products of aniline condensation as N-phenyl-1,4-phenylendiamine, benzydene and azobenzene [3, 14, 17]. The authors of more late works have revealed too [2, 5, 8]. In water medium by chromatographic method the formation of 6 products are stated from which already apart known other intermediate products are identified: (tetramer) 2,5-dianilino-N-phenylbenzoquinondiimine, 2,5-dianilino-N,N-diphenylbenzoquinonediimine (pentamer) and in formic acid 2-aminodiphenylamine [12,18]. The polycondensation rate in formic acid is more, the molecular mass and the electric conductivity of polyaniline is less. At the initial stage of the synthesis in the region, which corresponds to the induction period, increase of the ESR signal intensity is being observed. ESR signal (Figure **2**) with width of 7-8 G and with concentration 10^{18} spins per g is characteristic for semiquinone type complex of cation-radical with initial amine.

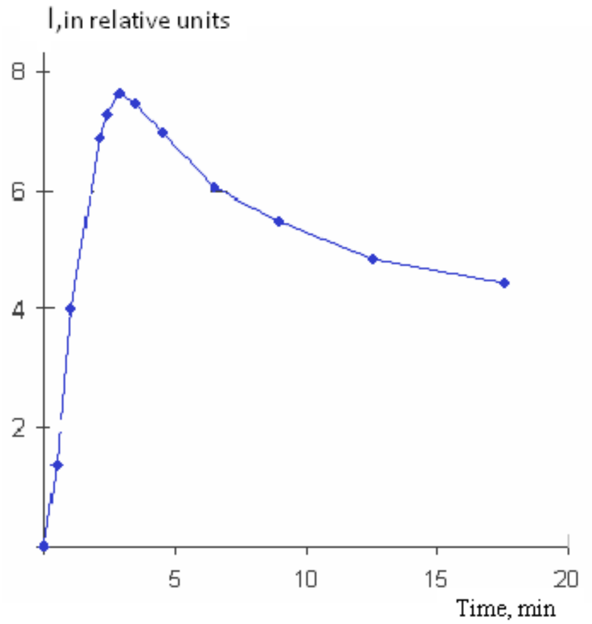
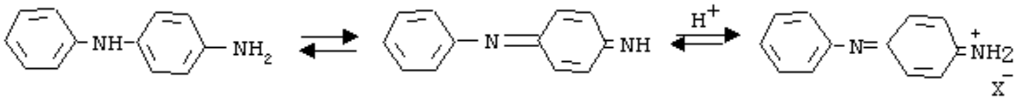


Figure 2: Kinetics of aniline cation-radical formation in formic acid, method ESR.

[A]= 0.2 mol/L; [Ox] = 0.2 mol/L; T = 25-27°C.

It is well known that the aniline cation-radical is stable in strong acidic medium [19-21], but this is not enough to detect it. In formic acid solution, the complex stability increases so much that at the initial stage of aniline oxidation it becomes possible to register the ESR spectrum of the radical corresponding to the aniline molecule. At T = 268 °K the complex of aniline-cation-radical is being educed from the solution [12].



Scheme 3:

The formation of low molecular products during induction period is being controlled by the complex stability. In moderate acidic mediums, the main primary product is D. Potentiometric measurements of reaction medium acidity in polyaniline synthesis process show that in the induction period stage the medium pH diminishes with high rate (R). It is due to the aniline`s dimer formation and it`s oxidation to quinoneimin with educing of 4 protons, then begins slow process of it`s salt formation. After this process begins the polycondensation with educing of two protons from 1 mole of aniline, with pH decrease and isolation of polyaniline from the reaction medium.

Great attention is given in the literature [3, 4, 10] to the mechanism of aromatic amines dimerization at their oxidation. From the analysis of literature as well from our experimental data it follows, that the main product which is being formed at the initial stage of aniline oxidative polycondensation is D, which in presence of persulfate anions is being oxidized with formation of N-phenyl-1,4-benzoquinonediimine (Dx) (Scheme **3**).

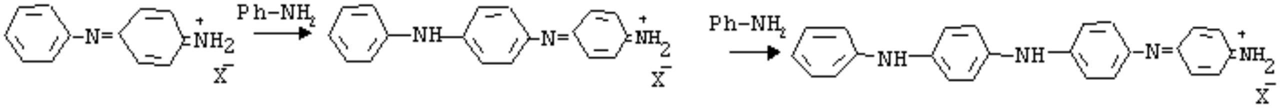
Accumulated in acidic medium Dx in the initiation stage forms salts, which react with aniline or with other nucleophiles. Spectral studies show the presence of absorption at 1445 and 1414 cm^{-1} in IR spectrum and a pick at 420 nm in UV spectrum. These data confirm the quinoneimine formation at the initial stage of polycondensation. The oxidation potential of the formed dimer (D) (E_D=0.52 V) is essentially lower than the aniline oxidation potential (E_A=1.03V). This shows that the formed N-phenyl-1,4-phenylene diamine may be oxidized with persulfate with formation of the corresponding quinoneimine. According to [18] the evaluated equilibrium constant of the following reversible reaction

$A\bullet + D\bullet \leftrightarrow A + Dx$ is of the order $K = 10^8$.

Therefore, in equilibrium state intermiadetly formed aniline cation-radical reacts with p-aminophenylimine by disproportionation, which results in the Dx accumulation in the reaction mixture. Probably it brings to the inhibition of aniline`s further oxidation. This conclusion agrees with results obtained by means of electrochemical measurements. From those data it follows the appearance of aniline`s oxidation pick on voltamperograms. It becomes apparent only in the first cycle of scanning [13]. The dimer concentration is very low (of the order 10^{-5}M) [17]. For this reason it`s condensation with Dx and with other oligomers and polymer is very improbable.

Considering the studies concerning the influence of different aromatic additions on the aromatic amines oxidation it is proposed the possibility of “aniline`s nucleophilic substitution by nitronium ion’’ or by cation-radical [3, 4, 21]. Later was shown that the chain growth and the formation of branching`s at aniline polymerization may be explained assuming the aniline addition to electrophile center (the quinoneimine group) of the macromolecule [17, 18, 22, 23]. The formed trimmer is being oxidized forming the corresponding quinoneimine because it`s redox potential is more lower than the Dx redox potential (Scheme **4**).

The further aniline`s addition results in tetramer formation. Therefore, as result of successive oxidation of the intermediate amine and of addition of the initial monomer to the polymer is being formed. Considering the fact that as result of chain propagation the general quantity of quinoneimine groups increases the reaction rate is increases too. This mechanism explains some peculiarities of aniline polycondensation, for example, the renewal of the polycondensation after the addition of the consumed component, the ability of copolymer formation with other nucleophilic monomers, the process rate increases in presence of some aromatic amines or polyaniline. If those assumptions is true, the aniline addition rate (the polycondensation rate) must be increased with increasing the concentration and the electrophility of the quinoneimine. We have established that in polyaniline presence the rate of aniline oxidative



Scheme 4:

polycondensation increases, the induction period decreases. The decrease is proportional to the quantity of the added nanosized polyaniline suspension. In these conditions the viscosity of the obtained polymer solution decreases due to the enhance of growing centers (quinoneimine groups) concentration. The polycondensation rate increases as result of protons concentration increase (Figure **3**). This affirms the quinoneimine electrophility enhance at transition from imine to its salt.

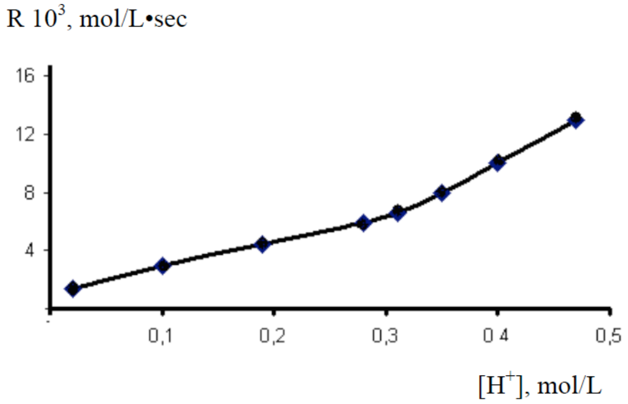


Figure 3: Dependence of polycondensation rate (R) on medium acidity (proton concentration).

[A]= 0.13 mol/L; [Ox] = 0.1 mol/L; T = 0-2°C.

The break on the kinetic curve may be explained assuming that in quinoneimine molecule there is trigonal carbon atom (C=N), therefore it is stronger base than the amine and in acidic medium easily forms two kinds of salts (pK_1=1.05, pK_2=2.55) [24].

The assumed polymer`s growth mechanism is being confirmed also considering the fact, that increasing the added dimer concentration, the polycondensation rate increases too, at the same time the induction period decreases. At [D] =10^{-4} mol/L the reaction occurs without induction period. Taking into consideration the increase of growing centers concentration at the cited conditions it results in mean molecular mass decrease (the intrinsic viscosity diminishes from 0.9 to 0.3). Inhibitors, which hinder the dimer formation as result of their reaction with aniline cation-radical, decrease the reaction rate and increase the induction period practically by an order. It is more clearly noticeable in the case of hydroquinone (Figure **4**, curve 3).

The obtained results confirm that namely Dx is the polycondensation initiator and not the nitronium cation or phenazine oligomers as was assumed in [4, 5, 8, 15]. Moreover, we have shown that the presence of 2, 2-diaminophenazene (0.005 M) in the reaction mixture has negligible influence on the aniline polycondensation rate.

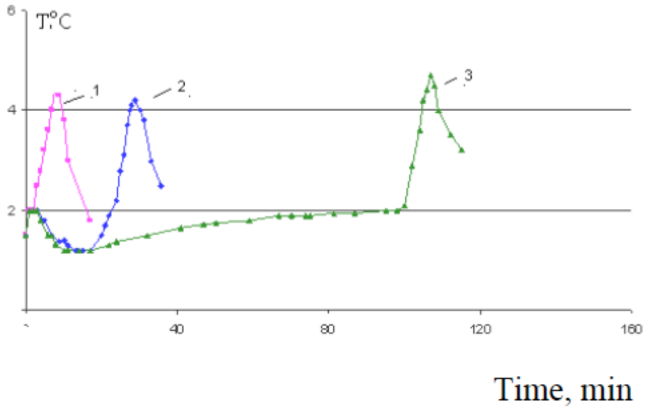


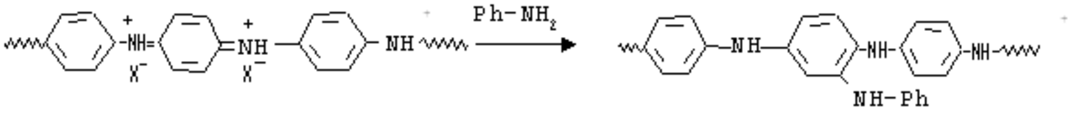
Figure 4: Temperature profile of aniline polycondensation in presence of additions: 0.004 mol/l N-phenyl-p-phenilene diamine (1); without addition (2); 0.007 mol/l hydroquinone (3); [A] = [Ox] = 0.12 mol/L; [HCl] = 1 mol/L.

As the polymerization occurs the quantity of terminal quinoneimine groups decreases, but the general quantity of disubstituted quinoneimine groups increases. The probability of monomer interaction with them increases in spite of low electrophiles in comparison with terminal quinoneimines.

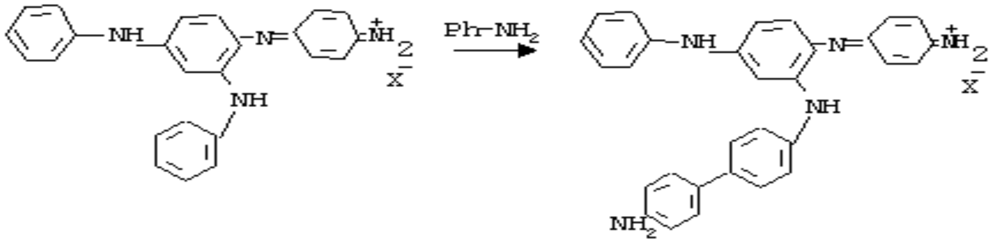
Already in the trimer there are two isomeric Quinone imines, but in the tetramer it cannot be equal to four. The aniline addition to the di-substituted quinoneimines may be occurred only *via* nitrogen atom according to the following scheme (Scheme **5**).

From this scheme follows that as the macromolecule grows the chain branching probability increases. It seems that it may bring to macromolecules growth stopping. However, the experimental data show the formation of polyaniline with a mean MM equal to 10^{5}. This contradiction may be explained taking into consideration the possibility of occurring some side reactions, concerning the aniline condensation. The fact is that the formed terminal phenyl groups at para position are sufficiently active and under the action of the oxidant, they can be condensed with aniline *via* cation-radical mechanism analogous to the benzydene formation (Scheme **6**).

While soluble oligomer polyamines, which are in conjugated chains, are able to condense with aromatic groups. Such kind of reactions occur at oxidative polycondensation of di- and triphenylamines at sufficiently mild conditions [24, 25]. The aniline addition to the terminal phenyl group as ‘head to head’ at addition reaction conditions results in appearance of amine terminal groups which favor the chains growth, their branching and sewing.



Scheme 5:



Scheme 6:

The reaction becomes complicated as result of polymer falling out. Already the tetramer is insoluble in the reaction medium and does not form polymer in the reaction conditions [17]. Therefore, the chain growth in heterogeneous conditions occurs at forced conditions at the expense of the monomer – aniline mobility and the reactivity of its para-position.

This allows to explain some peculiarities of aniline`s derivatives polycondensation, the passivity of p-substituted anilines, diphenylamine, the essential changes in the structure and properties of D polycondensation product. It is indispensable to discuss also other reactions, which play a great role in the PANi structure formation and of other aromatic polyamines.

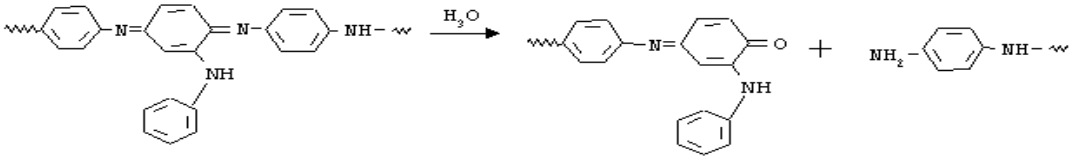
This is the hydrolysis of the imine group in acidic medium in presence of oxidant, which is discussed in detail in the review [3] (Scheme **7**).

Experimentally (see Figure **1**) this is expressed in the decrease of polymer yield, viscosity and electroconductivity in the region of post polymerization as result of chains rupture, appearance of o- and m-substituted aromatic nucleus in the polymer main chain. Those structure no uniformities – "defects", especially the o- and m-substituted fragments of the chain, as is known, decrease the effective conjugation, which results in its turn deterioration of electrophysical, mechanical and other properties of the polymer. As the hydrolysis rate is less than the chain growth rate for this reason, that process is revealed on the whole in the post polymerization region when aniline`s concentration becomes less.

The hydrolysis proceeding is confirmed considering some decrease of polymer yield at the end of the reaction and of heat evolution during polycondensation in strong acidic mediums. As result of hydrolysis absorption at 1680 cm^{-1} appears. The pick at 1635 cm^{-1} (C=O) becomes wider and the pick intensity in the region 3480 cm^{-1} decreases. These data concern secondary amines.

In acidic medium quinoneimine groups are enough reactive and may add different nucleophile groups as HO$^-$, Cl$^-$ and other anions. This results inculcation of covalently bonded Cl (to 1.8%), hydroxyl (to 2.5%) in the macromolecular of discussed compounds. At the same time this results in decreases of carbon content in PANi up to 76%. This fact more than once is discussed [3, 5, 7, 17]. It is known that as result of reaction phenyl group may be chipped of, as during N, N`-diphenyl-p-phenylenediamine polymerization [10].

The studies of polyaniline's IR spectrums show that out flatness deformation vibrations of the C-H bond of



Scheme 7:

the p-substituted aromatic nucleus become wider in the region 830 cm^{-1}, in spectrum is being appeared absorption at 790 and 880 cm^{-1} combined with absorptions at 1111-1117 cm^{-1}, which is characteristic for three and four substituted aromatic groups. The double absorption pick of C-N bond absorption in the regions 615 and 1232 cm^{-1} and in the interval 1340-1350 cm^{-1} are also characteristic for 1,2,4- and 1,2,4,5-substituted aromatic derivatives [26, 27].

It must be noted that the widening of the absorption picks at 1620, 1345, 1115 and 850 cm^{-1} are characteristic for phenazine cycles. The appearance of multiplet in the interval 1620-1700 cm^{-1} in the case of polyaniline at high temperatures testifies the formation of phenazine fragment`s structures mainly under thermal action. Based on obtained by experimental data and us we propose a kinetic model of polymerization of aniline and its derivatives.

4. CONCLUSIONS

So we have established that at the reaction first stage an induction period is being observed which is due namely to Dx formation [2-4, 28-29], which initiates the polyaddition (polycondensation) monomer. Kinetic models of reactions are presented in Scheme.

Active center formation (initiates):

$A + Ox \leftrightarrow [K_1]$

$[K1] \leftrightarrow A+\cdot$ $(H_2N\text{-}Ph - e^- \rightarrow H_2N\text{-}Ph+\cdot)$

$A+\cdot + [K_1] \rightarrow A_2$ (N-phenylene-1,4-phenylenediamine)

$A_2 + Ox \leftrightarrow [K_2]$

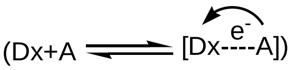
$[K_2] \leftrightarrow A_2x$ $(D - e^- \leftrightarrow D+\bullet - e^- \leftrightarrow Dx)$

The inhibition of that process (hydroquinone, diphenylamine at or radical inhibitors) results in the reaction rate decrease with an essential extent.

Macromolecules growing occurs by addition of monomer molecules to the active centers [7, 23, 29]. In the dimer presence the polyaddition rate increases, at the same time the induction period, as well the polyaniline solution viscosity, are being decreased. The addition of aniline to the terminal quinoneimine group results in linear chain growth.

Propagation:

$[A_2x] + [A] \leftrightarrow [Q]$



$[Q] \rightarrow A_3$

$A_3 + Ox \leftrightarrow [K_3]$

$[K_3] \leftrightarrow A_3x$

……….

$Anx + A \rightarrow An_{+1}$ (polymers)

Were [K] are the complexes of amines and oligomers with oxidants.

[Q] symbolizes the complexes of oligomers quinoneimines with monomers.

[A], [Ox], [An] - are the current concentrations of aniline, oxidant and oligomers.

The reaction of aniline with disubstituted quinoneimine group favours chains branching, the appearance of o-and m-substituted fragments in macromolecules and the breach of conjugation. We proposed scheme for aniline poly-addition process, which explains the growth characteristics of macromolecules. The hydrolysis of imine groups brings to decrease of polyaniline mean molecular mass, appearance of structure defects, sewing of chains and to worsening of material properties.

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