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Kinetic Features of *N*-Ethylaniline Polymerization

Ya. O. Mezhuev, Yu. V. Korshak, M. I. Shtilman, S. E. Pokhil, and I. S. Strakhov

Mendeleev University of Chemical Technology of Russia, Miusskaya pl. 9, Moscow, 125047 Russia
e-mail: valsorja@mail.ru

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Abstract—Kinetics of polymerization of *N*-ethylaniline hydrochloride initiated in aqueous solution by ammonium persulfate has been studied. The auto-catalytic nature of the reaction has been revealed; the order of the catalytic stage has been determined; the rate constants of single-electron transfer and the complex formation have been calculated. Quinonediimine fragments have been found in the poly-*N*-ethylaniline; their formation mechanism has been suggested.

Keywords: aromatic amine, oxidative polymerization, kinetics, mechanism

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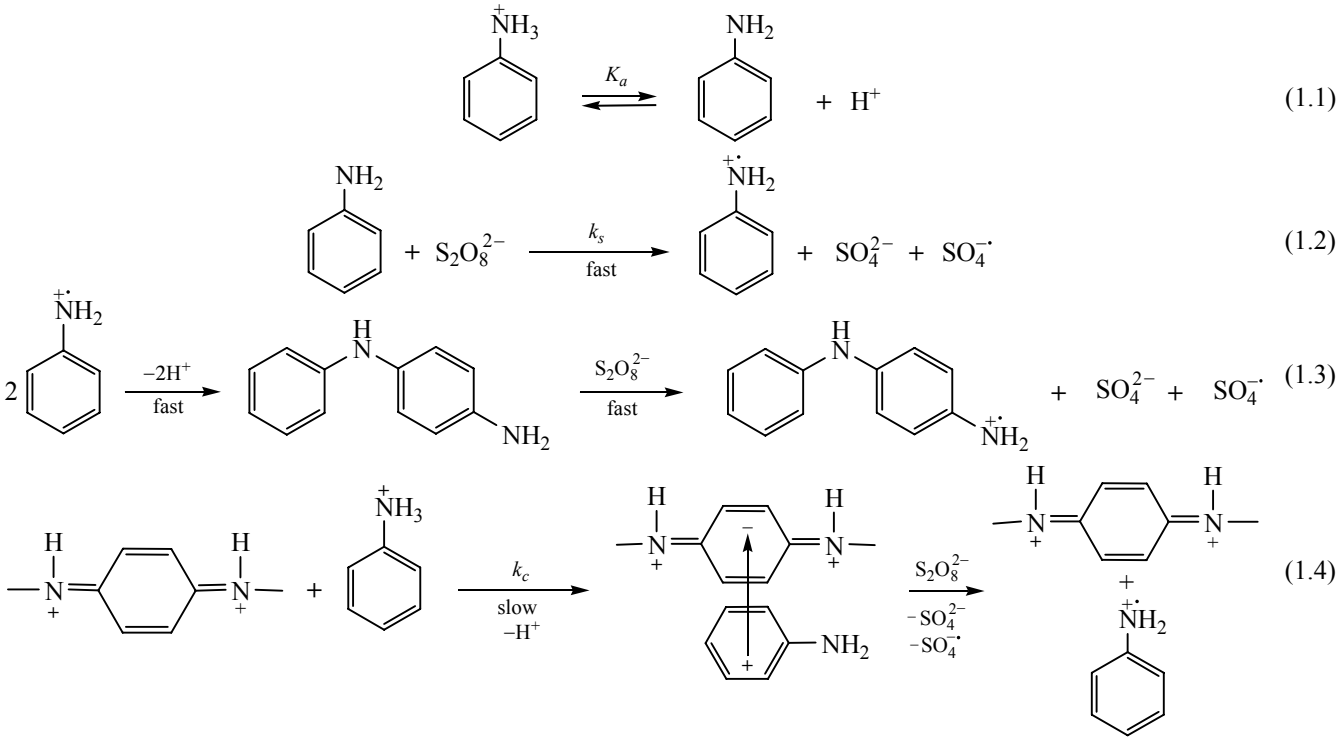
Oxidative polymerization of aniline and its derivatives is a complex auto-catalytic [1–4] heterogeneous [5–7] process, where the insoluble phase of the formed product is involved in the oxidation of the starting monomer. Despite numerous attempts to quantitatively describe the kinetics and elucidate the detailed mechanism of the oxidative polymerization [1–4, 8–10], these problems have not been solved so far. We have earlier analyzed the kinetics of oxidative polymerization of aniline hydrochloride in the aqueous solution in the presence of polyvinyl alcohol and have suggested the reaction mechanism assuming that the

Scheme 1.



single-electron oxidation of the monomer occurs in parallel to the oxidation of the monomer complex with quinonediimine fragments of the oligomeric and polymeric products (Scheme 1) [10].

The non-catalytic stage of single-electron oxidation of the monomer [Eq. (1.2)] occurs in the solution, whereas the complex formation [Eq. (1.4)] takes place in the adsorption layer (the interphase boundary between the polymer and the solution phases). The chain growth [Eq. (1.3)] is a sequence of fast stages occurring as recombination of reactive cation-radicals or oxidation of compounds electron-excessive as compared with the starting monomer [1, 2, 10].

In view of discussion on the suggested mechanism it is of interest to analyze the kinetics of polymerization of the *N*-substituted aromatic amines. Formation of the quinonediimine fragments (those responsible for the auto-catalysis effect, cf. Scheme 1) in the polymeric products is in this case seemingly blocked by the *N*-alkyl groups. In this work we investigated the kinetic features of oxidative polymerization of *N*-ethylaniline.

Accounting for the mechanism presented in Scheme 1, we have earlier [10] derived the kinetic equation (1), presumably common for polymerization processes involving aromatic amines:

$$w = -\frac{d[M]}{dt} = w_s + w_c = w_s + \frac{k_c([M]_0 - [M])[M]}{1 + K[M]}, \quad (1)$$

with w, total rate of the oxidative polymerization; w_s and w_c, the rates of single-electron monomer oxidation and the complex formation, respectively; k_c, rate constant of the complex formation; $[M]_0$ and $[M]$, initial and current concentrations of the monomer, respectively; K, constant of the equilibrium of the monomer adsorption at the surface of its n-mers; t, time.

Since differential equation (1) cannot be solved analytically, it has been considered in [10] in the two limiting cases, corresponding to the Henry ($K[M] << 1$, the second total order of the complex formation rate) and the Langmuir ($K[M] >> 1$, the first total order of the complex formation rate) adsorption equations. In both cases it has been assumed that the rate of single-electron oxidation of the monomer is significant only in the initial polymerization stage; this has led to the limiting approximation [Eq. (2)] allowing for analytical solution of the differential equation (1).

$$w_s(t = 0) = w_{s0};\ w_s(t > 0) = 0. \quad (2)$$

The integration of Eq. (1) has given kinetic equations (3) and (4) in the cases of strong (the Langmuir range) and weak (the Henry range) adsorption of the monomer, respectively [10].

$$\ln([M]_0 - [M]) = \ln(w_{s0}/k_{c1}) + k_{c1}t, \quad (3)$$

$$\ln\left(\frac{[M]_0 - [M]}{[M]}\right) = a + k_{c2}[M]_0 t;$$

$$a = \ln\left(\frac{\sqrt{[M]_0^2 + 4w_{s0}/k_{c2}} - [M]_0}{\sqrt{[M]_0^2 + 4w_{s0}/k_{c2}} + [M]_0}\right), \quad (4)$$

with k_{c1} and k_{c2}, the first- and the second-order rate constants of the complex formation, respectively.

Using oxidative polymerization of aniline as an example, we have demonstrated [10] that if the $\ln([M]_0 - [M])$ value is linear with time, then the equilibrium constant of the monomer adsorption at the surface of its n-mers is high, and the complex formation reaction follows the total first-order rate law. Similarly, is the $\ln\{([M]_0 - [M])/[M]\}$ versus time plot is linear, the adsorption equilibrium constant is low and the complex formation follows the total second-order kinetics.

If the quinonediimine fragments are absent in the formed polymer and the process follows Scheme 1, the polymerization should not be auto-catalytic, and the reaction rate [Eq. (1)] should be exclusively determined by the rate of the single-electron oxidation of the basic form of the monomer existing in the equilibrium with its salt form [Eq. (5)] [9, 10].

$$w = w_s = -\frac{d[M]}{dt} = \frac{K_a k_s [M][\mathrm{Ox}]}{[\mathrm{H}^+]}, \quad (5)$$

with K_a, dissociation constant of the conjugate acid of the monomer; k_s, rate constant of the single-electron transfer; $[H^+]$ and [Ox], current concentrations of protons and ammonium persulfate, respectively.

However, the analysis of the kinetic data on *N*-ethylaniline polymerization obtained in this work revealed that the kinetic curves were linear when plotted as $\ln\{([M]_0 - [M])/[M]\}$ versus time (Fig. 1), pointing at the second total order of the complex formation stage and the auto-catalytic nature of the process.

Rate constants of the complex formation were determined from the slopes of the linear kinetic curves,

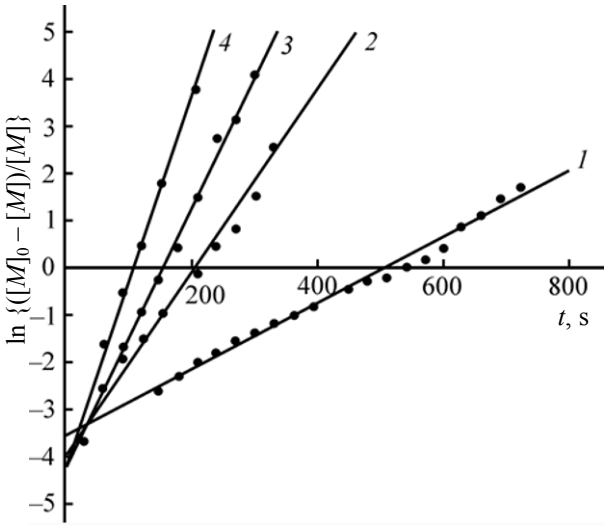


Fig. 1. Kinetic curves of oxidative polymerization of *N*-ethylaniline hydrochloride in coordinates of Eq. (4). *T*, K: (*1*) 298, (*2*) 308, (*3*) 313, and (*4*) 318.

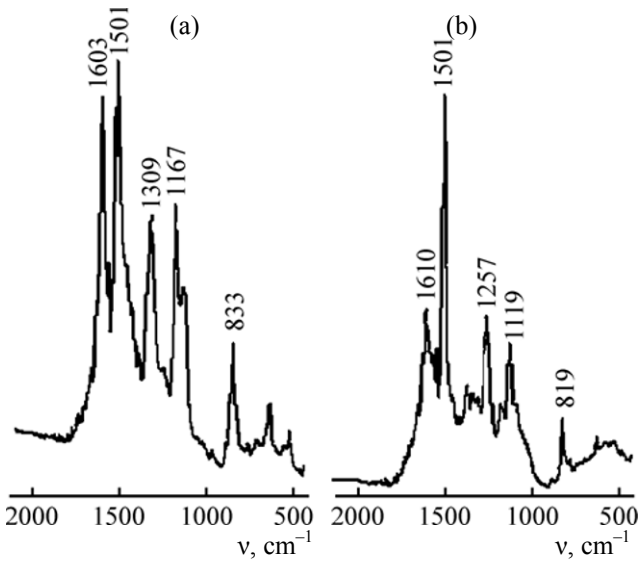


Fig. 2. IR spectra of salt forms of (a) polyaniline and (b) poly-*N*-ethylaniline.

and the rate constants of the single-electron transfer were determined from the corresponding intercepts (*a*) on the *Y* axis using Eq. (6).

$$k_s = \frac{k_{c2}[M]_0[H^+]_0}{K_a[Ox]_0}\left[\frac{e^a}{(1-e^a)^2}\right], \qquad (6)$$

with $[H^+]_0$ and $[Ox]_0$, initial concentrations of protons and the oxidizer (ammonium persulfate), respectively. The so calculated rate constants are collected in the table.

If the mechanism shown in Scheme 1 was valid, the auto-catalytic nature of the process could only be due to the formation of *N*-alkylated salt form of the quinonediimine fragments in poly-*N*-ethylaniline. The presence of such units was indirectly confirmed by high electrical conductivity and corrosion resistance of the product as well as IR and UV spectral data for the similar polymer, poly-*N*-methylaniline [11].

The presence of the band of C=N stretching vibrations of the quinonediimine fragments at 1610 cm^{-1} in IR spectrum of poly-*N*-ethylaniline (Fig. 2) (the corresponding band was found at 1603 cm^{-1} in the polyaniline spectrum) unambiguously indicated that the secondary processes of poly-*N*-ethylaniline oxidation into the *N*-alkylated salt forms took place in the reaction mixture (Scheme 2).

Furthermore, the quinonediimine fragments of conjugated amines are known to be reduced with hydrazine in the *N*-methylpyrrolidone medium, the solution being simultaneously discolored [12, 13]. Poly-*N*-ethylaniline was reduced with hydrazine in the *N*-methylpyrrolidone solution as well (within 2 h at 40°C) (Scheme 3), the dark-blue color of the reaction mixture disappearing.

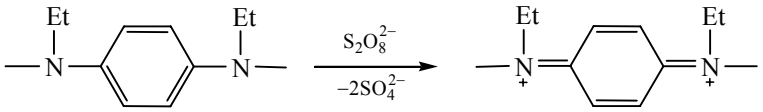
Hence, the presence of the quinonediimine fragments in poly-*N*-ethylaniline was confirmed.

The complex formation [Eq. (4.2)] occurring in parallel to the single-electron transfer [Eq. (4.1)] was seemingly the reason for the auto-catalytic nature of oxidative polymerization of *N*-ethylaniline; the men-

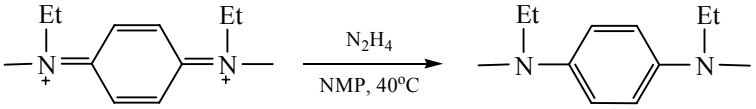
Kinetic parameters of *N*-ethylaniline polymerization induced by ammonium persulfate

T, K	298	308	313	318
$k_s \times 10^2$, L mol^{-1} s^{-1}	2.1±0.1	3.7±0.1	4.7±0.2	6.4±0.3
E_{as}, kJ/mol	43±3			
$k_{c2} \times 10^2$, L mol^{-1} s^{-1}	0.70±0.04	1.9±0.1	2.9±0.1	4.1±0.2
E_{ac}, kJ/mol	70±5			

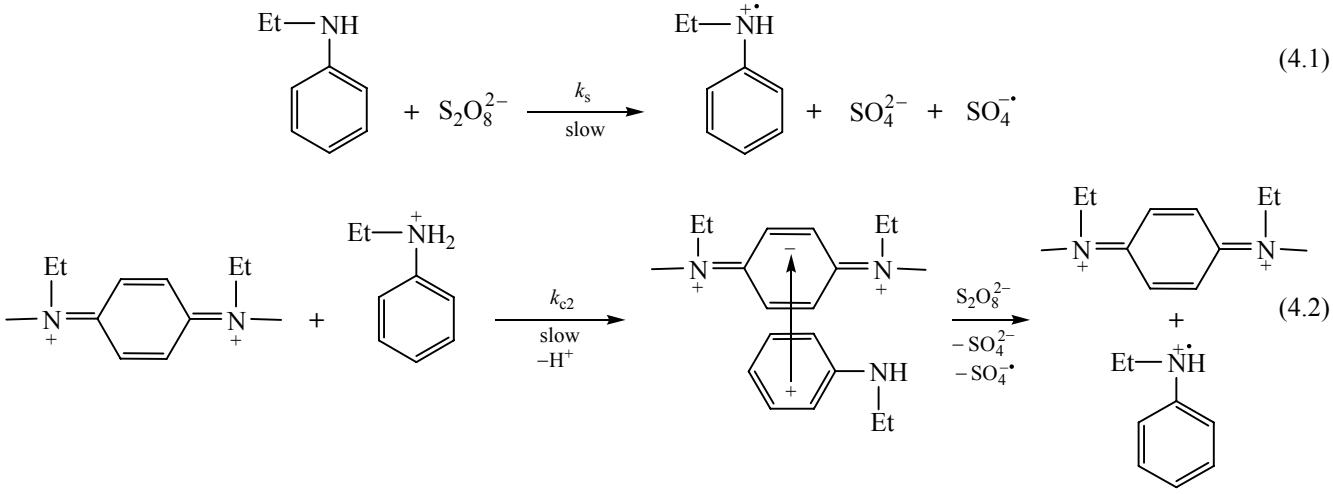
Scheme 2.



Scheme 3.



Scheme 4.



(4.1)

(4.2)

tioned processes yielded the monomer cation-radicals (Scheme 4).

To summarize, the rate-limiting stage of oxidative polymerization was presumably similar in the cases of aniline and *N*-ethylaniline. However, the complex formation stage followed the first-order rate equation in the case of aniline [10], and the second-order rate equation in the case of *N*-ethylaniline. The observed difference could be understood in the frame of the discussed polymerization mechanism (Scheme 1) to be due to the lower equilibrium constant of *N*-ethylaniline adsorption at the surface of its *n*-mers aggregates. The physical reason for the weakened adsorption of *N*-ethylaniline in comparison with aniline could be the steric hindrance caused by the ethyl groups repulsion. If so, destabilization of the charge-transfer complex itself and of the transition state leading to the complex formation in the adsorption layer should have been observed. In turn, that should have increased the activation energy of the complex formation in the course of *N*-ethylaniline polymerization as compared to that for unsubstituted aniline; that was indeed observed in the experiment (19 kJ/mol for aniline [10] and 70 kJ/mol for *N*-ethylaniline, see the table). On the contrary, the activation energy of the single-electron transfer was lower for *N*-ethylaniline (43 kJ/mol, see table) than for aniline (81 kJ/mol [10]), due to the positive inductive effect of the ethyl group stabilizing the formed cation-radical. Noteworthily, the activation energy of the single-electron transfer from *N*-ethylaniline to ammonium persulfate was close to that of *N*-methylaniline oxidation with chromic acid into the low-molecular *N*,*N*-dimethylaminequinonediimine (46.3 kJ/mol [14]).

EXPERIMENTAL

N-Ethylaniline (Aldrich) was purified by vacuum distillation. Ammonium persulfate ("analytically pure" grade) and potassium bromide (Panreac) were used as received.

Kinetic experiment. 1.21 g (0.01 mol) of *N*-ethylaniline was dissolved in 50 mL of aqueous hydro-

chloric acid (0.2 mol/L), and the solution was flushed with argon. A solution of 2.85 g (0.0125 mol) of ammonium persulfate in 50 mL of bidistilled water was prepared similarly. The solutions were kept during 15 min at the kinetic experiment temperature (25, 35, 40, or 45°C) with the pH-meter (IPL-311) electrode immersed in the solution containing *N*-ethylaniline. The oxidizer solution was then added to the monomer solution (the reaction start), and the reaction mixture pH was measured with 1 min interval until it reached a constant value (the reaction completion). The reaction was carried out at stirring, the temperature was maintained constant within (±0.1°C). The experiment was run five times at each temperature. The validity of the described method and its accuracy have been discussed earlier [10].

After the reaction was finished, the salt form of poly-*N*-ethylaniline was isolated by filtration, washed with distilled water, dried, and weighed. In all the cases the polymer yield exceeded 97% and was thus considered quantitative; that allowed calculation of the monomer current concentration as follows:

$$[M] = [M]_0\left(1 - \frac{10^{-\mathrm{pH}} - [\mathrm{H}^+]_0}{[\mathrm{H}^+]_\infty - [\mathrm{H}^+]_0}\right), \qquad (7)$$

with $[M]_0$ and $[M]$, starting and current concentrations of *N*-ethylaniline, respectively; $[\mathrm{H}^+]_0$ and $[\mathrm{H}^+]_\infty$, starting and final concentrations of protons, respectively.

IR spectra of the pellets molded from 1 mg of poly-*N*-ethylaniline and 100 mg of KBr were recorded using a Nicolet-380 specrometer.

The presence of quinonediimine fragments in the poly-*N*-ethylaniline product was confirmed by the qualitative reaction: 1 g of the polymer was dissolved at vigorous stirring in 50 mL of hydrazine solution in *N*-methylpyrrolidone (0.5 mol/L). The so prepared dark-blue solution was incubated at 40°C during 2 h.

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