$(NH_4)_2IrCl_6$ and other promoting agents of the chemical polymerization of aniline

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It has been found that some transition metal salts considerably decrease the induction period of the chemical polymerization of aniline. The efficiency of the promoting agents decreases in the series $(N)_2IrCl_6 > MoCl_5 > NiCl_2$.

Key words: aniline hydrochloride, polymerization, promoting agents.

The polymerization of aniline promoted by ammonium persulfate[1] is characterized by a pronounced induction period, the duration of which abruptly increases as pH increases and as temperature decreases. For instance, when the latter decreases to $-15\div-20$ °C, the duration of the initial stage increases to several hours. After this the reaction evolves uncontrollably due to its exothermic character. Here we report that the introduction of the transition metal salts $(NH_4)_2IrCl_6$, $MoCl_5$, and $NiCl_2$ into the reaction medium considerably decreases the induction period.

Experimental

Aniline was dissolved in hydrochloric acid in the ratio required to obtain a 0.1 *M* aniline hydrochloride solution. The resulting solution, to which the neccessary amount of promoter was added, was mixed in a beaker with an aqueous solution of 0.08 *M* ammonium persulfate in a 1:1 (v/v) ratio, then rapidly transfered into the measuring cell of a Specord spectrophotometer. The pH of each reagent was adjusted to the desired value with 0.1 *M* HCl or NH_4OH solutions. Molybdenum pentachloride was added to the reaction medium as a solution in 0.1 *M* HCl, in which $MoCl_5$ was partially hydrolyzed.[2]

For elemental analysis, a sample of polyaniline was allowed to stand in excess 1 *M* NH_4OH for 12 h, filtered off and dried at 60 °C. Found (%): C, 70.9; H, 6.29; N, 15.7 $(C_6H_7N)_n$. Calculated (%): C, 77.4; H, 7.5; N, 15.1 $(C_{12}H_{14}N_2O)_n$. Calculated (%): C, 71.3; H, 6.93; N, 13.9.

These results suggested that polyaniline can form a complex with oxygen at the stage when it is converted into the base form or during drying.

Using atomic absorption spectroscopy (AAS-1 spectrophotometer) for the base form of the polymer, it was found that 1 g polyanilinecontains 0.714 mg of iridium, which corresponds to about 1 atom of the metal per 2700 monomeric units.

The molecular weight distribution of polyaniline in *N*-methylpyrrolidone was estimated with a Millichrom chromotograph using a column packed with unmodified silica gel Lichrospher Si 500 A. Using the polystyrene standards, the linear calibration range for this sorbent was found to be $2\cdot10^4$—$6\cdot10^5$.

The plots of optical density versus retention volume during chromatography of the polyaniline solutions, which reflect the molecular weight distribution (MWD) of the polymer samples, are given in Fig. 1; one of these polymers was obtained in the presence of a promoting agent (10^{-3} *M*), and the other without it. As follows from this data, the samples investigated have a

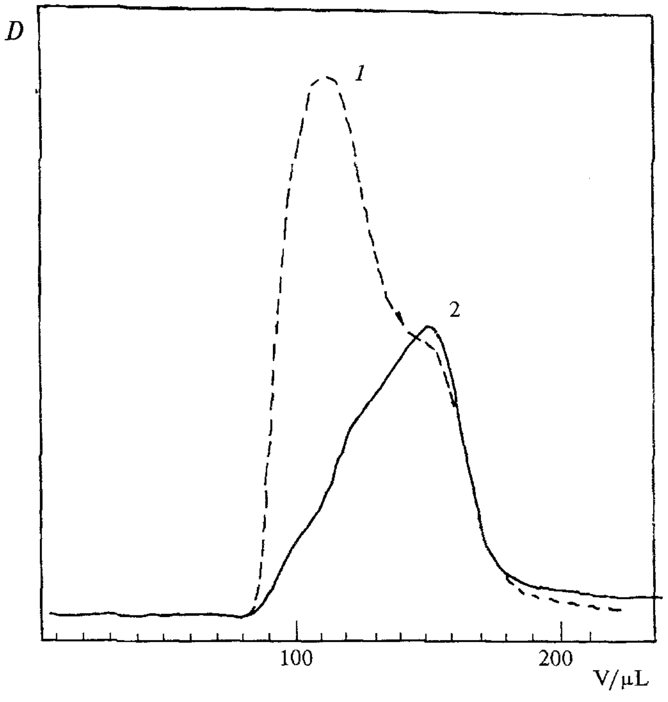

Fig. 1. Plots of optical density versus retention volume during gel chromatography of solutions of polyaniline synthesized in a medium containing $(NH_4)_2IrCl_6$ (*1*) and in the absence of promoting additive (*2*).

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bimodal MWD, and the maximum of the MWD curve of the polymer synthesized in the presence of the iridium salt is shifted to the high molecular weight region by at least two orders of magnitude. According to the calibration used, the second peak falls in the region of MW 100000—200000 D.

The kinetics of the polymerization was monitored photometrically in the visible region at 24240 cm^{-1} (412.5 nm). The evolution of the absorption spectra during the polymerization was given in our previous study.[2] Most probably we were photometrically following the formation of the dimer and accumulation of the polymer in solution.

The electrochemical experiments were carried out using a standard cell, which included glassy-carbon working and auxiliary electrodes, as well as a silver chloride reference electrode (Ag/AgCl/3.5 *M* KCl). Decimolar solutions of aniline in HCl were used as the electrolytes; their pH was adjusted to the desired values with an aqueous solution of NH_4OH.

In order to study the properties of the polymer produced, the synthesis of polyaniline was carried out at −15 °C using agents in the above-mentioned ratio. After filtration and washing with water, the polymer was converted into the base form by treatment with excess 0.1 *M* NH_4OH followed by drying *in vacuo* at 60 °C. A conductive film was obtained by precipitation from a *N*-methylpyrrolidone solution.

The reagents were purified using standard procedures. Aniline and *N*-methylpyrrolidone were distilled *in vacuo*, ammonium persulfate was recrystallized. Sulfuric acid, ammonium hydroxide, and the salts that were used as promoting agents, were "pure" grade and were used without any additional purification.

Results and Discussion

The plots of the optical density of the reaction medium versus time at various pH values are given in Fig. 2. For each experiment, the curve for the solution without additive is compared with that obtained in the presence of 10^{-3} mol · L^{-1} of $(NH_4)_2IrCl_6$. As judged from the curves obtained, in each case a significant change in the induction period is observed, which increases as the pH of the solution increases.

The results of the study of the electrochemical polymerization of aniline are shown in Fig. 3. It follows from the data presented that the introduction of $(NH_4)_2IrCl_6$ considerably decreases the threshold potential of polymerization in the range of pH 1—3.

There are at least two more compounds, whose introduction into the reaction medium decreases the induction period. It follows from Fig. 4 that $MoCl_5$ and $NiCl_2$ have a similar influence on the induction period, however their effeciency is slightly lower. The capacity for reducing the induction period decreases in the sequence $(NH_4)_2IrCl_6 > MoCl_5 > NiCl_2$. Increasing the promoter concentration results in augmentation of its efficiency.

The films produced retained their mechanical strength after being kept in 38% sulfuric acid.

The electrical conductivity of the polyaniline films synthesized in the presence of a promoting additive and precipitated by *N*-methylpyrrolidone was 12 Ohm · cm^{-1}. Polyaniline films prepared by standard procedures have an electric conductivity of 5—7 Ohm · cm^{-1}.

It is well known that one can distinguish at least three stages in polyaniline synthesis: 1) induction period, 2) chain growth, and 3) formation of the polymer solid phase. Chain growth can be accomplished either by the addition of a monomer or a dimer, and the induction period is caused by autocatalytic oxidation of a monomer into a dimer.[3] Indeed, to oxidize a mono-

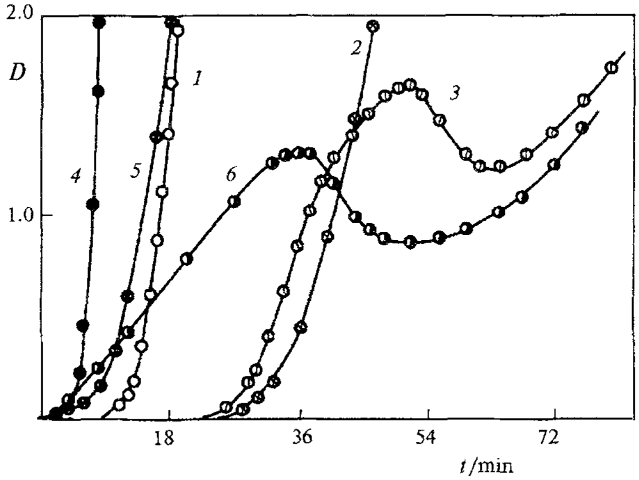

Fig. 2. Plots of optical density versus time during the chemical polymerization of aniline promoted by ammonium persulfate in the absence (*1, 2, 3*) and in the presence of 10^{-3} mol · L^{-1} $(NH_4)_2$ $IrCl_6$ (*2, 4, 6*). pH = 1 (*1, 4*), 2 (*2, 5*), 3 (*3, 6*).

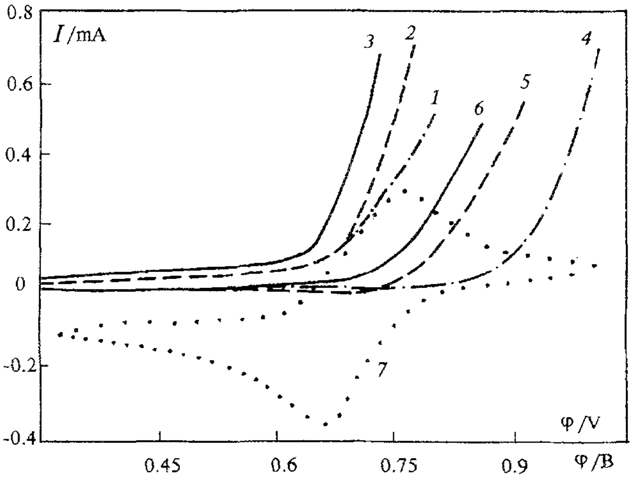

Fig. 3. Voltammograms of the electrochemical synthesis of polyaniline in the absence (*1, 2, 3*) and in the presence of 10^{-1}mol · L^{-1} $(NH_4)_2$ $IrCl_6$ (*2, 4, 6*). pH = 1(*1, 4*), 2 (*2, 5*), 3 (*3, 6*), 7 is voltammogram of 10^{-3} mol · $L^{-1}(NH_4)_2IrCl_6$ at pH = 1.

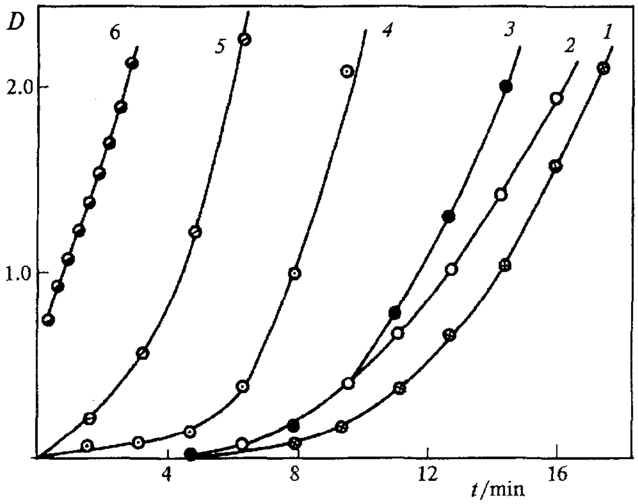

Fig. 4. Plot of optical density versus time during the chemical polymerization of aniline with ammonium persulfate in the presence of $(NH_4)_2IrCl_6$, $MoCl_5$, $NiCl_2$ at pH = 1:
1 — without initiation agent; *2* — 10^{-4} mol · L^{-1} $NiCl_2$;
3 — 10^{-3} mol · L^{-1} $NiCl_2$; *4* — 10^{-3} mol · L^{-1} $MoCl_5$;
5 — 10^{-4} mol · L^{-1} $(NH_4)_2IrCl_6$; *6* — 2.3 10^{-2} mol · L^{-1} H_2IrCl_6.

mer, it is neccessary to apply a significantly higher potential than that needed to oxidize a dimer.

The reasons given above are fundamental to understanding the role of the inorganic promoting agent. The latter has a lower oxidation potential than that required for conversion of aniline into a radical cation. This fact is supported by the voltammetric curve for a solution of $(NH_4)_2IrCl_6$ in water, which is shown in Fig. 3. It is apparent from the data obtained that the oxidation threshold of the promoter matches the polymerization threshold that aniline would have in the absence of overvoltage. Thus, the inorganic additive is oxidized to a state with excess positive charge, which is transfered to the monomer to begin the chain, which growths further by successive addition of monomer molecules. The promoting agent seems to form a weak complex with aniline immediately after mixing. This results in facilitation of the charge transfer to the monomer. The small amounts of irridium found in the polymer also support the mechanism suggested.

If the foregoing reasons are correct, it is possible to assume that the stage of oxidation of the monomer into a dimer is supressed and the overall process proceeds *via* monomer addition under mild conditions. These mild conditions of polymer growth in the absence of abrupt changes in temperature, in turn, might increase the values of electrical conductivity and molecular mass of the polymer. Increasing the temperature has been reliably found to be accompanied by a decrease in molecular weight[4] and electrical conductivity.

Thus, it has been demonstrated that it is possible to reduce the induction period of aniline polymerization by addition inorganic promoters, whose efficiency decreases in the sequence $(NH_4)_2IrCl_6$ > $MoCl_5$ > $NiCl_2$.

References

1. B. V. Nekrasov, *Osnovy obschei khimii,* Khimiya, Moskva, 1973, **1**, 376 (in Russian).
2. Y. L. Kogan, G. I. Davidova, E. I .Knerel'man, G. V. Gedrovich, L. S. Fokeeva, L. V. Emelina, and V. I. Savchenko, *Synth. Met.*, 1991, **41/3**, 887.
3. Yen Wey, Xun Tang, and Yan Sun, *J. Pol. Sci. part A: Polymer Chemistry*, 1989, **27**, 2385.
4. Y. L. Kogan, L. S. Fokeeva, and V. I. Savchenko, *Synth. Met.*, 1990, **37**, 75.

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