Influence of hydrolysis on the chemical polymerization of aniline

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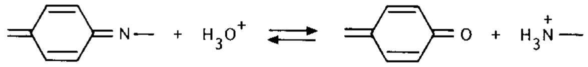
The influence of hydrolysis on the process of oxidative polymerization of aniline was evaluated through the effect of polymerization temperature on the yield of polyaniline (PANI) in different pH regions where the polymerization took place. The synthesis parameters were chosen based on the dependence of the polymerization and hydrolysis processes on the pH of the medium, and considering the opposing thermal effects of the two processes (exothermic polymerization and endothermic hydrolysis). The yield of PANI was evaluated from the conductivity of composite films cast from aqueous dispersions of PANI prepared by chemical oxidative polymerization of aniline using poly(vinyl alcohol-*co*-acetate) as a steric stabilizer. It was found that the influence of hydrolysis is most pronounced in slightly acidic ($pH > 4$) and strongly acidic ($pH < 1.5$) media. This imposes the requirement for the polymerization of aniline to be carried out at low temperature (0–5°C) in order for hydrolysis to be suppressed. When the initial stage of polymerization takes place at $4 < pH < 1.5$, hydrolysis does not play a significant role and polymerization proceeds with a high yield irrespective of the temperature changes.

(Keywords: polyaniline; dispersion polymerization; hydrolysis)

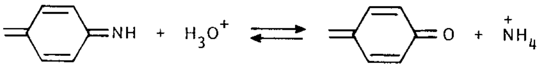
INTRODUCTION

As far as the authors are aware, there are only a few reports on the influence of hydrolysis of the imine nitrogen–carbon bonds on the chemical polymerization of aniline (ANI) and properties of polyaniline (PANI). Thus, Cao *et al.*[1] have observed that treatment of PANI powder with 1–4 M HCl aqueous solution for long periods of time resulted in a reduced inherent viscosity of the polymer measured in solutions of concentrated sulfuric acid.

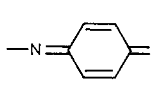
Further, elemental analysis data of PANI, prepared by chemical oxidative polymerization at high HCl concentration (2–4 M), have revealed a deficit of nitrogen atoms (with respect to carbon atoms), which equalled the number of oxygen atoms introduced into the chain[2]. This was explained by the hydrolysis of imine nitrogen–carbon bonds, which may result in either chain breaking:


(1)

or nitrogen elimination if an end-group is involved:

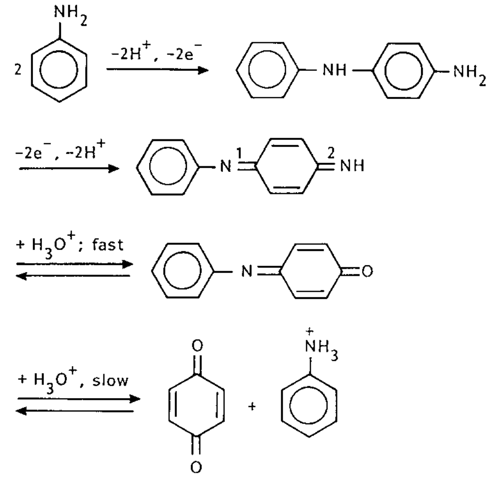

(2)

The hydrolysis that occurred in more acidic media became significant for PANI exhibiting higher oxidation state (OS) than that of emeraldine, in which groupings were more abundant[2]. Results from the investigation of the electrochemical oxidation of PANI films have shown[3] that hydrolysis of imine nitrogen–carbon bonds leading to deterioration of the electrochromic properties of PANI proceeded at higher potentials (more that 0.7 V vs. SCE).



The importance of hydrolysis in the processes of electrochemical and chemical oxidation of ANI have been studied in detail under conditions when PANI has not been formed, i.e. at constant electrode potential higher than 0.75 V, or at a large excess of oxidant[4–7]. The oxidation of ANI under those conditions resulted in the formation of *N*-phenyl-1,4-benzoquinonediimine (PBQ) and was accompanied by hydrolysis of the PBQ formed.

Summarizing the experimental results from the electroanalytical studies, preparative electrolysis and preparative chemical oxidation of ANI in 0.5 N and 6 N H_2SO_4, Hand *et al.*[4] have suggested the following mechanism of formation and hydrolysis of PBQ:



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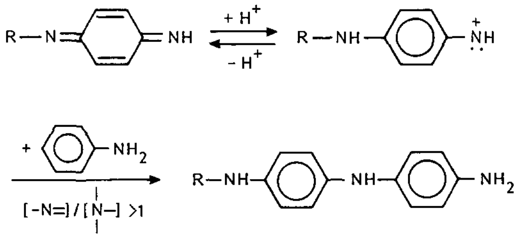
However, this mechanism was based on the identification of the final products and on Hückel molecular-orbital (HMO) calculation of the fully protonated diimine, but not on the experimental observation of the intermediates[6]. Intermediates both in this mechanism (hydrolysis in position 2), as well as in the only plausible alternative mechanism (hydrolysis in position 1), have not been detected. In view of the experimental evidence, or the lack thereof (especially the absence of either intermediate), it was not possible to determine which mechanism was operative, though according to Hand *et al.*[4] the former was favoured on the basis of HMO calculations. It was supposed that the oxidative polymerization of ANI during the initial stage proceeded by the formation of PBQ[7] and PANI of the highest OS (pernigraniline)[8].

Our investigations on the mechanism of polymerization of ANI have shown[9,10] that the initial stage of PBQ formation took place in the whole pH range, whereas the following propagation of the chains (reduction step by addition of ANI to the active sites) occurred solely in an acidic medium:



(4)

It was shown that the activity of the propagating species (nitrenium cations) depended on the extent of oxidation of the chains and on the pH of the medium. It was concluded that the necessary conditions for chain growth are: first, the OS has to be higher than that of emeraldine (i.e. the rate of the oxidation step must be higher than that of the reduction step); and secondly, the pH of the medium in the case of PBQ has to be lower than 2, and in the case of longer chains $pH < 6$[10]. Decreasing pH resulted in an increased rate of the reduction step. In contrast, the rate of formation of the oxidized species (including PBQ and oxidized forms of trimer, tetramer, etc.) dropped on decreasing pH.

Therefore, depending on pH, either hydrolysis and polymerization can proceed simultaneously or one of those processes proceeds preferably.

Hydrolysis has to result in decreased yield and/or molecular weight of PANI. The influence of hydrolysis on the electrical properties of PANI could hardly be distinguished in pure (100%) PANI. But in the case of polymer blends, prepared *in situ* by polymerizing ANI in the presence of non-conducting thermoplastic constituent, hydrolysis, which lowered the yield of PANI, has to affect substantially the electrical conductivity of the blends, which is very important in their application.

In the preparation of both the individual polymer and the polymer blends by chemical oxidative polymerization of aniline, the determination of PANI yield is related to the nitrogen determination by elemental analysis. The concentration of the nitrogen-containing products, however, does not necessarily correlate to the content of conducting PANI, since non-conducting products like residual aniline and its oligomers, and the reduction products of ammonium peroxydisulfate, contain nitrogen as well. Therefore, this method of direct determination of the yield is not useful in the study of the influence of hydrolysis on the yield of the conducting constituent in composite films.

Previously, we have described the preparation of PANI as a stable aqueous dispersion in the presence of poly(vinyl alcohol-*co*-acetate) (PVAL) as a steric stabilizer[11,12]. When the initial concentration of ANI in the polymerizing system containing 10 wt% PVAL decreased below $0.2\,\mathrm{mol\,l^{-1}}$, an abrupt drop in conductivity corresponding to the decreased PANI content was observed[12]. In this paper the influence of hydrolysis of the imine nitrogen–carbon bonds on the process of chemical oxidative polymerization of ANI in aqueous dispersions stabilized by PVAL was studied in the range of the abrupt dependence of conductivity on the PANI content in the blends. As an indirect measure of the yield of the conductive constituent, the electrical conductivity of the blend was used.

EXPERIMENTAL

Reagent-grade ANI (Fluka) was vacuum distilled prior to use. All other reagents were purchased also from Fluka and were used as received.

PANI dispersions were prepared by oxidative polymerization of ANI as described previously[11,12] at a molar ANI concentration of $0.2\,\mathrm{mol\,l^{-1}}$ and molar ratio ANI/oxidant = 1. The initial pH value (pH_0) and temperature (T_0) were determined immediately after addition of ANI and oxidant (ammonium peroxydisulfate) to the aqueous solution of PVAL. The polymerization temperature (T) was controlled by placing the reaction vessel in a thermostated bath of temperature T_0 while monitoring the temperature T with a thermometer inserted directly into the reaction mixture.

In situ pH measurements of the reaction mixture were performed at $T_0 = 23°C$.

Conductivity measurements of free-standing films cast from dispersions containing both PANI and PVAL were performed using the conventional four-probe technique.

RESULTS AND DISCUSSION

Summarizing the available data on the mechanism of oxidative polymerization of ANI and on the concomitant hydrolysis, it can be suggested that hydrolysis occurs mostly when its rate (rate constants 10^{-2}–$10^{-1}\,s^{-1}$ according to Hand *et al.*[5]) is comparable to the rate of the reduction process, since the rate of the oxidation step limits neither the polymerization[8,9] nor the hydrolysis[4] processes. Therefore, the influence of pH of the medium on the process of PANI preparation reflects on the ratio of the main (polymerization) and the side (hydrolysis) reaction rates.

Another parameter that considerably affects the ratio of the rates of polymerization and hydrolysis is the polymerization temperature T. Since aniline polymerization is highly exothermic, while hydrolysis is endothermic, it can be expected that the hydrolysis rate has to decrease substantially on decreasing T. Therefore, in the pH range where profound hydrolysis can occur, the temperature decrease has to result in a sharp increase in the yield of PANI and in the conductivity σ of the corresponding films obtained.

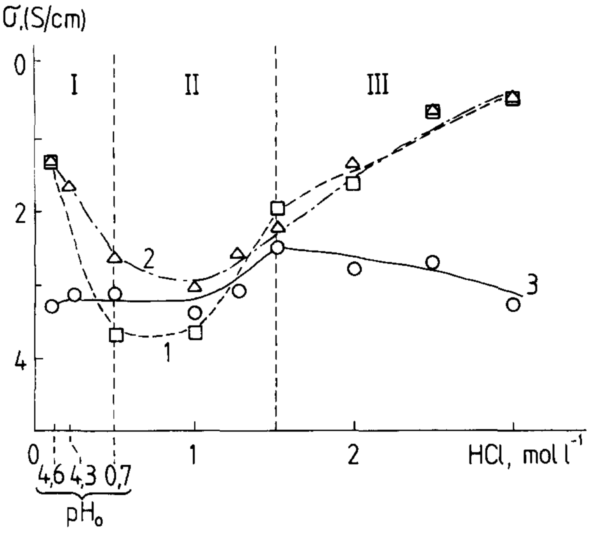


Figure 1 Conductivity of composite (PANI + PVAL) films *versus* HCl concentration in the polymerizing mixture at various initial temperatures T_0: curve 1 (□), 2°C; curve 2 (△), 4°C; curve 3 (○), 30°C. Concentration of ANI, 0.2 mol l^{-1}; molar ratio of ANI/OX, 1; concentration of PVAL, 10 wt%

The plots of conductivity of films vs. HCl concentration and T presented in *Figure 1* revealed three regions of HCl concentration differing in the extent of its effect on the yield of the conducting constituent.

In the first region (I), the initial values of pH of the reaction system were changed within wide limits: from $pH_0 = 4.6$ for 0.1 M HCl up to $pH_0 = 0.7$ for 0.5 M HCl (*Figure 1*). In the slightly acidic region (pH > 4), the conductivity of the films increased considerably (about two orders of magnitude) on decreasing the initial temperature T_0 from 30 to 4–2°C, whereas at ca. pH 0.7 the influence of temperature was not substantial (compare curve 3 with curves 1 and 2 in region I of *Figure 1*), and even decreasing T_0 did not result in increased conductivity of the films. This last tendency of relatively low yield of PANI and its independence of temperature was observed also in the second region (II) of HCl concentration (from 0.5 M up to 1.5 M). Further increase of HCl concentration (region III, *Figure 1*) resulted in a situation analogous to the slightly acidic region, i.e. decreased T_0 resulted in an abrupt increase in conductivity of the films obtained (compare curves 1 and 2 with curve 3 in region III of *Figure 1*).

Based on these results it can be supposed that the hydrolysis effect is substantial in the whole range of HCl concentration studied. However, strong hydrochloric acid is not suitable for elucidation of the influence of hydrolysis on the PANI yield. First, a variation of its concentration in a very narrow range results in an abrupt change of pH_0 of the medium; and secondly, as a strong acid it does not possess a buffering ability. Thus, it is not possible to keep a constant pH in a certain time interval during the polymerization in the presence of hydrochloric acid.

Besides, it was interesting to find exactly the ranges of pH (but not the concentration of a particular acid) where the influence of hydrolysis on the chemical oxidative polymerization of ANI is most pronounced, as pH can be regarded as a parameter summarizing the influence of both the concentration and the strength of the acids and bases present in the system.

For that purpose we studied the polymerization of ANI at different initial pH values, pH_0, from 5 to 0, and for various rates of change of pH during the process. For that reason, except for the strong hydrochloric acid, various other acids of pK_a in the range of 2–5 (orthophosphoric, monochloroacetic, formic, acrylic and acetic acids) were used. The influence of hydrolysis was evaluated by the dependence of the PANI yield (i.e. electrical conductivity of the films obtained) on pH_0, T_0 and the range of pH where the polymerization took place. The most illustrative results are shown in *Figures 2a* and *2b*.

Based on these results, three main pH regions differing by the extent of the influence of hydrolysis on the yield of PANI can be distinguished. In the first region ($pH_0 > 4$) (*Figure 2a*) the effect of hydrolysis is substantial, as judged by the low conductivity ($\sigma = 10^{-3}$–$10^{-4}\,S\,cm^{-1}$) of the films obtained from dispersions prepared at $T_0 = 23°C$. The conductivity of these films increased considerably (about two orders of magnitude) on decreasing the initial temperature from 23 to 4–2°C.

In the second range, $1.5 < pH_0 < 4$ (*Figure 2b*), films of higher conductivity ($\sigma = 10^{-2}$–$10^{-1}\,S\,cm^{-1}$) can be obtained at $T_0 = 23°C$ and the conductivity of the films does not depend on polymerization temperature in the whole range studied ($T_0 = 2$–$30°C$). These experimental facts suggest the negligible effect of hydrolysis on the yield of PANI in this pH range.

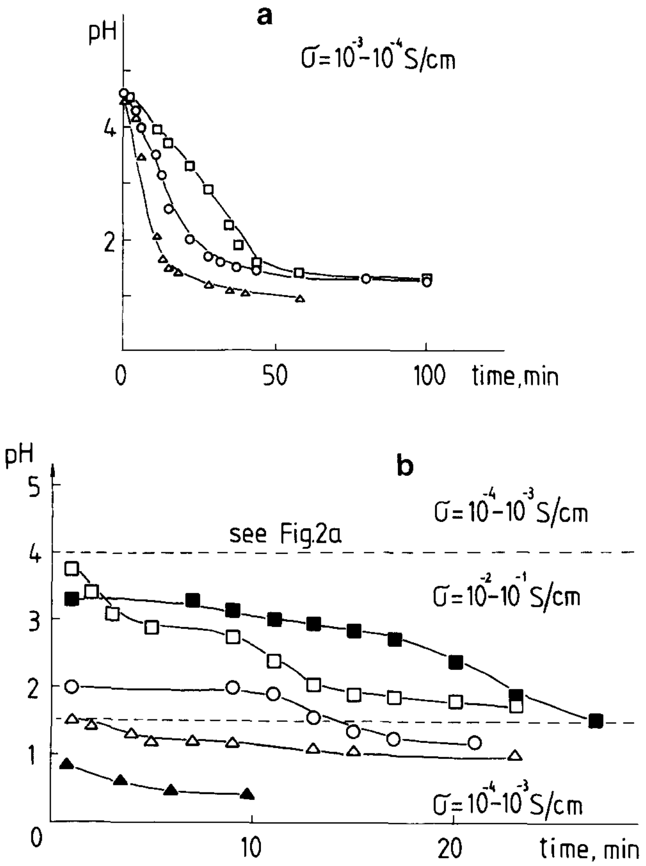


Figure 2 Variation of pH during the polymerization of ANI in the presence of various acids: (a) 0.1 M formic acid (□), 0.1 M hydrochloric acid (△), 0.15 M orthophosphoric acid (○); (b) 1 M monochloroacetic acid (□), 1 M orthophosphoric acid (△), 1 M formic acid (■), 5 M formic acid (○), 0.5 M hydrochloric acid (▲). Concentrations of ANI and PVAL and molar ratio of ANI/OX as shown in *Figure 1*; $T_0 = 23°C$

In the third range ($pH_0 < 1.5$), a strong influence of hydrolysis on the yield of PANI similar to that described above for slightly acidic medium ($pH_0 > 4$) was observed.

All these experimental results can be explained as follows.

In our previous study[9] on the polymerization of ANI in acidic medium ($pH \sim 0$) by using *in situ* electron absorption spectroscopy, it was shown that at the initial stage of the process (8–10 min at room temperature) oxidized oligomers and pernigraniline have been formed. The rate and the extent of their following reduction increased on decreasing the pH of the medium, reaching emeraldine oxidation state at $pH \sim 0$. It is natural to suggest that, exactly in this stage of the polymerization process (i.e. at the stage of oxidized forms of oligomers and PANI), the hydrolysis of imine nitrogen–carbon bonds would have the most substantial effect, depending on the ratio of the rates of reduction and hydrolysis.

Further, our previous investigations[10] on the polymerization of ANI in slightly alkaline, neutral and slightly acidic media have revealed that reduction of PBQ proceeded with a measurable rate only at $pH < 2$, in contrast to the longer oxidized chains where reduction took place at higher pH values as well. Therefore, in polymerization of ANI under conditions when $pH_0 \gg 2$, an initial time interval should exist (before reaching the value of pH 2) when PBQ formation and its hydrolysis take place, but reduction practically does not proceed. This actually occurred when polymerization took place at $pH_0 > 4$, i.e. at low concentration of the acid (*Figure 2a*). Evidence that, in polymerization at $pH_0 > 4$, hydrolysis considerably affects the yield of the conductive constituent (and thus the conductivity of the films obtained) is the above discussed dependence of the yield of PANI on T_0.

Additional confirmation of the suggestion that hydrolysis affects mainly the initial stages of polymerization (at $pH_0 > 4$ the stage of PBQ formation) is the decreased conductivity of the film obtained by polymerizing ANI in 0.1 M HCl at $T_0 = 23°C$ ($\sigma = 10^{-3}\,S\,cm^{-1}$), as compared to a similar film obtained at $T_0 = 30°C$ ($\sigma = 10^{-4}\,S\,cm^{-1}$) under conditions when the highest polymerization temperature, T_{max}, is equal in both cases (*Figure 3*).

When polymerization (initial stage) proceeds at $pH_0 < 4$, and especially at $pH_0 \sim 2$, conditions exist that are probably more favourable for reduction than for hydrolysis both of PBQ and of longer oxidized chains. Such conditions could be created when acids of medium strength (formic, monochloroacetic) were used. In a fairly large range of concentration they correspond to the above stated conditions in respect to pH_0 ($1.5 < pH_0 < 4$). Under those conditions, pH at the initial stage was kept between 4 and 1.5 due to the buffering ability of these acids, which bound the protons released in both oxidation and reduction steps of oxidative polymerization of ANI. As a result, films of conductivity 10^{-2}–$10^{-1}\,S\,cm^{-1}$ were obtained (*Figure 2b*). As a consequence of the negligible effect of hydrolysis on the yield of PANI under these conditions, the conductivity of the films does not depend on polymerization temperature in the whole range studied ($T_0 = 2$–$30°C$).

When the polymerization took place in initially strongly acidic medium, conditions were again created where hydrolysis and reduction proceeded as competitive processes. As a result, films prepared at $pH_0 < 1.5$ and $T_0 = 23°C$ revealed conductivity in the range of 10^{-3}–$10^{-4}\,S\,cm^{-1}$ (*Figure 1*, regions II and III; *Figure 2b*).

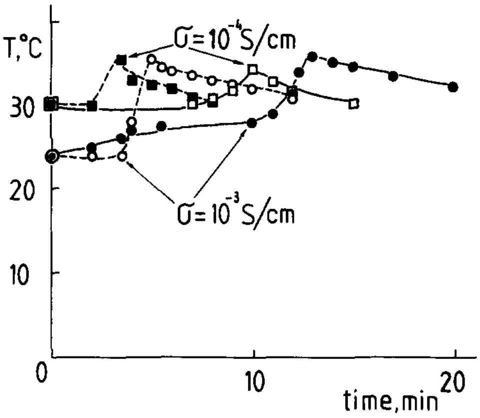


Figure 3 Variation of T during the polymerization of ANI at different HCl concentrations: (●, □) 0.1 M; (○, ■) 3 M. Concentrations of ANI and PVAL and molar ratio of ANI/OX as shown in *Figure 1*

It is worth noting, however, that the dependence of the PANI yield on the reaction temperature, which, in our opinion, is an indirect measure of the influence of hydrolysis on the process of ANI polymerization, differs considerably in the pH ranges $0 < pH_0 < 1$ (concentration of HCl 0.5–1.5 M) (*Figure 1*, region II) and $pH_0 \sim 0$ (HCl concentration higher than 1.5 M) (*Figure 1*, region III).

As seen from *Figure 1*, the increase in conductivity of the films on decreasing T_0 was observed only at HCl concentration higher than 1.5 M (region III). According to our statement, hydrolysis in this pH range is competitive with polymerization. The decrease of T_0 down to 2–4°C allows PANI of high yield (conductivity $10^{-1}\,S\,cm^{-1}$) to be obtained even in a strongly acidic medium. By analogy with slightly acidic medium ($pH_0 > 4$), in this case temperature affects most considerably the initial stage of polymerization too, i.e. the yield of PANI is affected by T_0. Thus, the increase of T_0 from 23 to 30°C when polymerization took place in 3 M HCl resulted in decreased conductivity of films from 10^{-3} to $10^{-4}\,S\,cm^{-1}$ (*Figure 3*).

In the concentration range 0.5–1.5 M HCl (*Figure 1*, region II), however, the change of T_0 from 2 to 30°C practically did not change the conductivity of the films; a conductivity of 10^{-3}–$10^{-4}\,S\,cm^{-1}$ was observed even at low temperature, with a following slight increase at the border line between regions II and III (*Figure 1*).

Probably, the range $0 < pH_0 < 1$ corresponding to II is not only characterized by the substantial effect of hydrolysis on the yield of PANI, but also is not favourable for the polymerization of ANI itself, which results in the lower yield of PANI. Similar results have been obtained by Duic *et al.*[13] when the electrochemical polymerization of ANI at different pH_0 values was studied. As a possible reason for such a phenomenon, the unfavourable ratio of the oxidative potentials of the growing nitrenium cations and aniline could be supposed.

Another approach we have used to illustrate the dependence of PANI yield on pH_0 and on the pH range where the initial stage of polymerization proceeds was polymerizing ANI in 1 M solution of acids of different pK_a: hydrochloric, orthophosphoric, monochloroacetic, formic, acrylic, acetic. This selection of acids of different

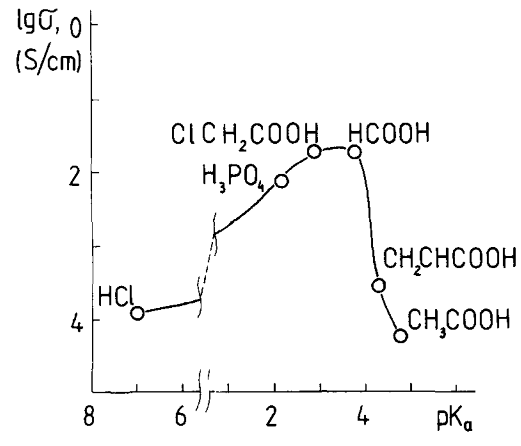


Figure 4 Conductivity of composite (PANI + PVAL) films cast from dispersions prepared in 1 M solution of various acids *versus* pK_a of the acids. Concentrations of ANI and PVAL and molar ratio of ANI/OX as shown in *Figure 1*; $T_0 = 23°C$

strength enabled us to cover all the pH range, using the same (1 M) concentration.

Thus, the dependence of the conductivity of films, prepared at $T_0 = 23°C$ by using 1 M solutions of the above-mentioned acids, on their pK_a (*Figure 4*) reflects the influence of the pH range where polymerization takes place on the PANI yield. The dependence obtained reflects in a generalized form the information presented in *Figures 2a* and *2b*. It enabled us to draw the conclusion that in the presence of acids of medium strength ($2 < pK_a < 4$) the influence of hydrolysis on the polymerization of ANI was reduced to a minimum, and films of the highest conductivity were obtained.

In conclusion, the following ranges of pH$_0$, which differ in the extent of the influence of hydrolysis on the oxidative polymerization of ANI, can be distinguished:

(i) At $pH_0 > 4$ and $pH_0 < 1.5$ hydrolysis has a profound effect and cooling down at least to 5°C is a necessary condition for its elimination.

(ii) At $1.5 < pH_0 < 4$ the effect of hydrolysis is negligible and polymerization with a high yield proceeds in a wide range of temperature. As the pH of the medium decreases during oxidative polymerization of ANI, it is advisable to use acids of medium strength ($2 < pK_a < 4$) in order to keep a nearly constant pH value at the initial stage of the polymerization (stage of oxidized products).

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