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Accelerating effect of some cation radicals on the polymerization of aniline

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The chemical oxidation of aniline to polyaniline has been monitored by colour and acidity changes during dispersion polymerization. A small amount of various *p*-phenylenediamines or benzidine was found to accelerate the formation of polyaniline. The ability of such compounds to form cation radicals upon oxidation allows them to act as mediators in electron-transfer processes. Related chemicals, e.g. *o*-phenylenediamine, had little effect on polymerization, while *m*-phenylenediamine caused its retardation.

(Keywords: aniline; polyaniline; phenylenediamines)

INTRODUCTION

Polyaniline[1–3] (PANI) is an electrically conducting polymer that is easily prepared by chemical or electrochemical oxidation of aniline, typically in aqueous medium. The reaction proceeds smoothly with a good yield of polymer. The general mechanism of polymerization has been proposed by several authors[2,4–7], but its details may still need some refinement.

Autoacceleration is a typical feature of aniline polymerization: the reaction rate increases as PANI is produced during both electrochemical[8] and chemical[9] oxidation. Polyaniline seed particles introduced into the initial reaction mixture also enhance the rate of PANI formation in the dispersion polymerization of aniline[10]. Besides PANI, some low-molecular-weight organic compounds can also increase the reaction rate. The accelerating effect of several such substances is reported in this paper.

The polymerization of aniline is accompanied by changes of colour. The originally colourless reaction mixture becomes deep blue during polymerization and turns green at its final stage[9,11]. The rate of various polymerizations can thus be compared on a relative scale by measuring the time that is needed for the occurrence of the blue-to-green transition.

Polyaniline is insoluble in the aqueous reaction medium and the polymer is obtained as a fine precipitate. When polymerization is carried out in the presence of a convenient water-soluble polymer, a steric stabilizer, the macroscopic precipitation of PANI can be prevented. For example, aniline polymerized in the presence of poly(vinyl alcohol) yields dispersions of well-defined, submicrometer-sized spherical PANI particles[10–15]. Other stabilizers have also been applied successfully[16,17]. In contrast to precipitation polymerization, dispersion polymerization[18–22] proceeds under pseudohomogeneous conditions and the colour changes are more easily visible or recorded by spectroscopic methods.

According to the reaction scheme proposed by Mohilner *et al.*[4] and Stilwell and Park[5], the hydrogen atoms abstracted from aniline molecules during polymerization are released as protons. The acidity of the reaction medium is expected and indeed observed[10,23] to increase as aniline converts to PANI. Thus pH measurements can also be used to monitor the course of aniline polymerization.

In this paper, the effect of several additives on the rate of aniline polymerization is reported. Observations of the colour transition or acidity changes, or both, during the reaction were used as experimental tools.

EXPERIMENTAL

Polymerization

Aniline hydrochloride (2 mmol, 259 mg) was dissolved in 3.7 ml of water. Then 5.0 ml of 4 wt% aqueous solution of poly(vinyl alcohol) (PVAL; type 72000, Fluka, Switzerland; degree of hydrolysis >98 mol%) were added, followed by 0.01 mmol of the tested compound dissolved in 0.1 ml of 80 vol% methanol–water. The mixture was cooled to 0–2°C in iced water. Finally, 1 ml of precooled 1 M ammonium peroxydisulfate was introduced to start the reaction. The mixture was gently stirred during reaction with a magnetic bar. Concentrations of the individual components thus were :

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0.2 M aniline hydrochloride, 0.1 M ammonium peroxydisulfate, 0.45 M (vinyl alcohol units) PVAL and 0.001 M of the tested compound. The molar excess of aniline to peroxydisulfate was intentionally used to avoid potential overoxidation of PANI. The molar content of the compound tested for its catalytic effect was always 200 times lower relative to aniline, unless specified otherwise.

Colour transition

During the polymerization of aniline, the originally colourless mixture turns blue and later becomes green. Due to the intense colouration, the colour transition may not be easy to identify. Therefore, at 30 s intervals, a drop of the reaction mixture was diluted by an excess of 1 M HCl. Either the blue colour of the polymerizing species or the green colour of the completed emeraldine form of PANI could be observed. If the sample of dispersion had been similarly diluted with excess of 1 M ammonium hydroxide, a violet-to-blue transition would have been observed instead[10].

pH measurement

The changes of pH during the polymerization of aniline were recorded with a PHM64 Research pH Meter (Radiometer, Denmark), using a glass electrode with a calomel reference. The electrode gets covered with PANI film during the polymerization; it had to be well cleaned between the individual experiments to ensure reproducible results. By dipping the electrode into a dilute solution of potassium dichromate acidified with sulfuric acid (i.e. into dilute chromic acid, pH $\approx$ 1), PANI is easily oxidized to quinone and the film disappears within a few seconds. The reaction vessel and magnetic stirring bar were cleaned in the same manner.

Yield of polyaniline

The concentration of PANI in dispersions was determined next day after 60 times dilution with 1 M HCl from optical absorption at 400 nm using an absorption coefficient of $\epsilon = 31\,500\,\mathrm{cm^2\,g^{-1}}$ of polyaniline semihydrochloride[11]. The conversion of aniline to PANI typically ranged between 21 and 39%; the theoretical conversion limit[14,24] set by the concentration of peroxydisulfate is 40%.

Particle size

Particle diameter and polydispersity were determined by dynamic light scattering with an Auto-Sizer Lo-C (Malvern Instruments Inc., UK). To shorten the optical path and thus the absorption of light due to green colouration of the dispersions, a cylindrical cell of 4 mm diameter was used instead of the standard rectangular 10 mm one.

RESULTS AND DISCUSSION

Colour and acidity changes during polymerization of aniline

The changes of pH during the oxidation of aniline have a characteristic pattern[10,23]. Soon after the addition of ammonium peroxydisulfate to aniline hydrochloride solution containing PVAL (pH= 3.7), pH starts to decrease (*Figure 1*). Sometimes, maxima extending to pH $\approx$ 4–4.5 were recorded during the early stages of reaction. The concentration gradients or changes in acid–base equilibria after mixing the components, or both, are probably responsible for this effect. As discussed below, dimeric compounds are likely to be formed from aniline at this stage of the reaction. A slightly yellow tint of the reaction mixture gets darker and combines with a slowly developing transparent blue colouration. The slope of the pH dependence then becomes more negative as aniline starts to polymerize. The deep blue colour observed during polymerization can be assigned to the protonated pernigraniline[10], namely to its dication diradical form[2,5,25,26].

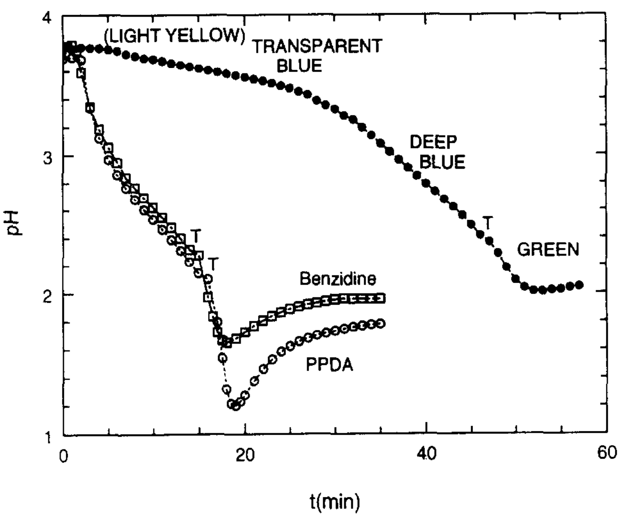
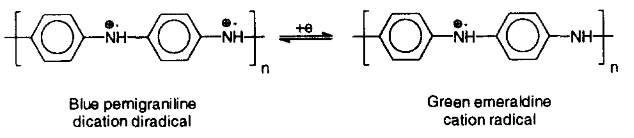


Figure 1 Time dependence of pH during the oxidation of aniline hydrochloride (0.2 M) by ammonium peroxydisulfate (0.1 M) in aqueous medium. Polymerization without additive (●, colour changes specified at the curve), and in the presence of 1 mM benzidine (□) or PPDA (○). The position of the blue-to-green transition is marked by T

After all oxidizing agent, ammonium peroxydisulfate, has been consumed, the blue reaction mixture starts turning green. During this phase, the dication diradicals are reduced by excess aniline[6] to the stable cation radical structure of protonated emeraldine[27,28]:



(1)

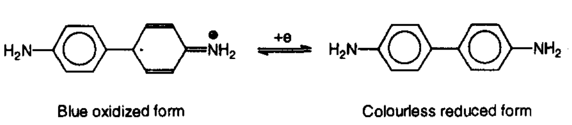
Polymerization still proceeds as aniline is oxidized to PANI by pernigraniline dication diradicals, until the reduction of pernigraniline to emeraldine is complete. Protons are released during polymerization and pH drops even more steeply (*Figure 1*).

At the final stage, the pH passes through a minimum (*Figure 1*) or levels off as the polymerization has been completed. Although the time at which the minimum is observed is well defined, the deepness of the minimum varied substantially in the individual experiments. The occurrence of the minimum may be associated with physical rather than chemical factors. For example, the formation of the film of dispersion particles on the surface of an electrode may result in its changed or delayed response. Both the time to the first observation of green colour and the time corresponding to the pH minimum can be used for relative assessment of the reaction rates of individual polymerizations. While the onset of the colour transition can be associated with the depletion of the oxidizing agent, the minimum or levelling of pH corresponds to the end of polymerization.

Compounds accelerating the oxidation of aniline

In an earlier paper[10] we reported that the oxidation of aniline is accelerated by an introduction of a small amount of PANI seed particles into the reaction mixture. Besides PANI, there are other low-molecular-weight compounds which, even at low concentration, dramatically enhance the rate of aniline polymerization (*Table 1*). All compounds which accelerate the reaction have a common feature: they form cation radicals upon oxidation.

The ability of benzidine (4,4′-diaminobiphenyl) to form coloured cation radicals is well known and benzidine has been used in analytical chemistry as a redox indicator:



(2)

Its marked effect on the chemical oxidation of aniline is demonstrated by a shift of the colour transition (*Table 1*) and the pH minimum towards shorter reaction times (*Figure 1*). Benzidine is the only compound that has a catalytic effect on the oxidation of aniline (*Table 1, Figure 1*) but does not have an aromatic ring substituted with two nitrogens in *para* positions.

Table 1 The influence of some organic compounds on the polymerization of aniline[a]. *t* is the time corresponding to the onset of blue-to-green transition occurring during the polymerization and indicating consumption of the oxidant

Compound	*t* (min)
Reference polymerizations without additives	44–49
Acceleration:	
Benzidine (4,4′-diaminobiphenyl)	13
p-Phenylenediamine	14
N-Ethyl-*N*-(2-hydroxyethyl)-*p*-phenylenediamine[b]	16
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	17
N-Phenyl-*p*-phenylenediamine	18
4,4'-Diaminoazobenzene	19
Polyaniline seed, 0.75 mM[c] (aniline units)	19
No or a little effect:	
o-Phenylenediamine	32
p-Aminophenol	38
Azobenzene	45
Hydrazobenzene	46
Retardation:	
m-Phenylenediamine	305

[a] Concentrations: 0.001 M of the tested compound, 0.2 M aniline hydrochloride, 0.1 M ammonium peroxydisulfate and 2 wt% of poly(vinyl alcohol)

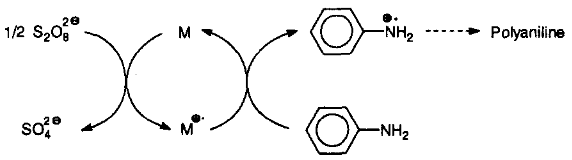
[b] Photographic developer (T32, ORWO, Germany or Activol X, Johnsons, USA)

[c] Taken from ref. 10

p-Phenylenediamine (*p*-PDA), and its derivatives substituted on one or both nitrogens up to *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine (TMPDA), yield more or less stable cation radicals when oxidized[29,30]. The radical derived from TMPDA, so-called Wurster Blue, can be isolated even in the solid state[30]. Similarly, intermediate cation radicals are formed from *p*-phenylenediamine and *N*,*N*-substituted *p*-phenylenediamines when these are used to reduce silver halides during photographic development[31].

N-Phenyl-*p*-phenylenediamine (PPDA; *p*-semidine) also belongs to the above group and, consequently, has a marked accelerating effect on the chemical oxidation of aniline (*Table 1*, *Figure 1*). This compound is believed to form cation radicals during electrochemical oxidation[2,32] and thus their formation in the chemical process is also likely. Acceleration of the chemical polymerization of aniline by introduction of a small amount of PPDA has been also observed by Fu and Elsenbaumer[24].

Koshechko *et al.*[33] have recently reported that oxidative polymerization of pyrrole is enhanced by the presence of stable cation radicals derived from *para*-substituted triphenylamines. The experimental evidence indicated that these compounds are capable of acting as homogeneous mediators of electron transfer in redox processes, i.e. in the electrochemical polymerization of pyrrole. Mediators decrease the redox potential of the reaction, like catalysts do the activation energy. By analogy, the processes involved in the polymerization of aniline can be schematically outlined as:



(3)

where M is the mediator and $M^{+\cdot}$ is the corresponding cation radical formed upon oxidation. In this sense, mediators are compounds that can easily switch from the reduced to oxidized form, and vice versa, and which have a redox potential between the potentials of sulfate/peroxydisulfate and aniline/aniline cation radical pairs.

Besides the low-molecular-weight compounds, pernigraniline and emeraldine can convert into each other by abstraction or addition of a single electron according to reaction (1). It is therefore not surprising that PANI, when introduced into the reaction mixture, has an autocatalytic effect as it promotes the polymerization of aniline[9,10] (*Table 1*) in the same manner as the other mediators.

Bacon and Adams[34] found that PPDA and benzidine are produced during the anodic oxidation of aniline in acidic medium, their molar ratio being 4:1 at pH= 2. The proportion of benzidine grew when the medium became more acidic. It is thus justified to assume that compounds of this type are also formed by recombination of aniline cation radicals during the early stages of chemical oxidation of aniline. Once they are present, they act as mediators, the resulting aniline cation radicals enter the polymerization process and later PANI itself takes over the mediator role. The introduction of these or other substances, which can form cation radicals, thus starts the polymerization of aniline much earlier and the whole process is accelerated.

Some of the compounds which promote the oxidation can homopolymerize or copolymerize with aniline, i.e. *p*-phenylenediamine[26,29,30] and PPDA[32], and even the existence of a polymer composed of benzidine units has been postulated[35]. Consequently, such compounds can start the growth of PANI chains or incorporate into their structure. The latter fact, however, does not seem to be connected directly with their mediators activity because tetramethyl-*p*-phenylenediamine, which does not form polymer chains[30], has a pronounced accelerating effect on the polymerization of aniline, too.

The effect of mediator concentration

The rate of aniline oxidation increases with increasing concentration of the mediator, as illustrated for *p*-phenylenediamine (*Figure 2a*) and TMPDA (*Figure 2b*). This is reflected again by a shift of the colour transition and the pH minimum towards shorter times. A more detailed study with TMPDA showed that the accelerating effect caused by introduction of this mediator can be observed even at concentrations as low as 10^{-5} M, i.e. at molar ratio of aniline/TMPDA= 20 000 (*Table 2*). At the same time, the conversion of aniline to PANI is not affected by the presence of the mediator (*Table 2*) and it approaches the expected 40% limit fixed by the concentration of the oxidant, ammonium peroxydisulfate, and by the stoichiometry of the reaction (molar ratio of peroxydisulfate/aniline = 0.5 in the present experiments and 1.25 mol of peroxydisulfate is needed for the oxidation of 1 mol of aniline[14,24]).

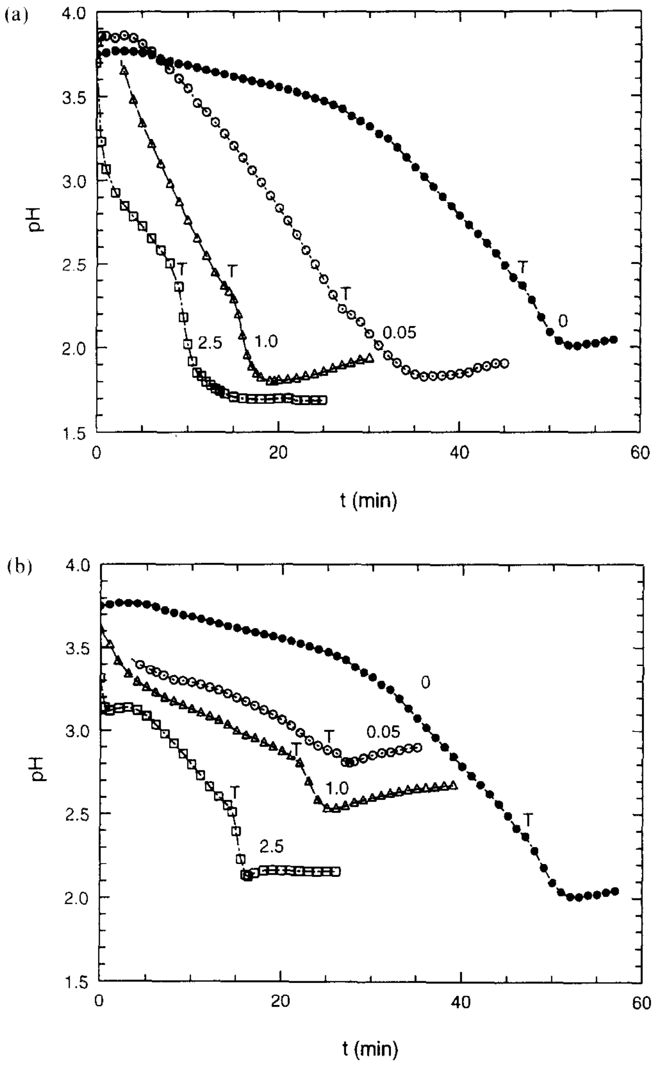


Figure 2 Time dependence of pH during the oxidation of aniline hydrochloride (0.2 M) by ammonium peroxydisulfate (0.1 M) in the presence of (a) *p*-phenylenediamine and (b) *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine. Concentration of phenylenediamines: 0 (●), 0.05 (○), 1 (△) and 2.5 mM (□). The position of the blue-to-green transition is marked by T

When the oxidizing agent is added to a solution of TMPDA in the absence of aniline, the system turns intense blue as TMPDA cation radicals (Wurster Blue) are created. After a few seconds it becomes colourless again because these are destroyed in further oxidation reactions. In the presence of aniline, the blue colouration persists, in accordance with the perpetual recovery of TMPDA postulated in reaction (3), and only later deepens gradually as PANI forms.

Table 2 The effect of varying concentration of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine, *C*, on the reaction rate and the properties of polyaniline dispersion particles[a]. *t* is the time corresponding to the onset of the blue-to-green transition indicating consumption of the oxidant, ψ is the molar conversion of aniline to polyaniline, *D* is the diameter of dispersion particles and σ^2 is the measure of their non-uniformity (statistical variance of the particle-size distribution)

$C \times 10^3$ (mol l^{-1})	t (min)	ψ (mol%)	D^b (nm)	σ^2
0	44–49	21–38	331–411	0.20–0.29
0.01	28.5	33	360	0.20
0.02	24.5	34	367	0.16
0.05	24.5	36	339	0.16
0.1	20	34	349	0.15
0.2	19	39	344	0.09
0.5	17.5	33	359	0.09
1.0	17	39	344	0.06
2.5	14.5	32	419	0.21
5.0	12.5	32	443	0.18

[a] Concentrations: the tested compound as given above, 0.2 M aniline hydrochloride, 0.1 M ammonium peroxydisulfate and 2 wt % of poly(vinyl alcohol)

[b] Relative error < 3%

In agreement with our earlier observation[14], the particle size is independent of the rate at which PANI has been produced (*Table 2*), with the possible exception of high concentrations of TMPDA. The polymerization of aniline thus seems to be followed by arrangement of PANI chains into particles, both processes being virtually separated. The reproducibility of the particle sizes obtained in the individual polymerizations in the presence of TMPDA was tolerable (*Table 2*). Also, the uniformity of the particles improved in comparison with polymerizations performed in its absence. In this sense, TMPDA has a positive effect on the quality of dispersions.

Influence of other compounds

o-Phenylenediamine, *p*-aminophenol, hydrazobenzene and azobenzene had a small or virtually no effect on the progress of polymerization (*Table 1*). Diphenylamine and 4,4′-diaminodiphenylamine belong also to this group. The results for these compounds have not been included in *Table 1* because of their limited solubility in the reaction medium.

In contrast to the other additives examined, the introduction of a small amount of *p*-aminophenol into the reaction mixture resulted in a distinct brown colouration at the early stages of polymerization, but otherwise the course and rate of the reaction were unaffected. Since common aniline contains traces of *p*-aminophenol, its further oxidation products may be responsible for the yellow to brown tint occasionally observed soon after the beginning of the reaction.

Phenylenediamines are of potential interest in modification of the PANI chain structure by copolymerization. We observed that *p*-phenylenediamine had a pronounced accelerating effect, and *o*-phenylenediamine behaved indifferently (*Table 1*). On the other hand, addition of *m*-phenylenediamine resulted in a substantial delay in the formation of PANI (*Table 1*). The character of the time dependence of the pH was similar in all three cases (*Figure 3*).

CONCLUSIONS

p-Phenylenediamine, its *N*- and *N*,*N*′-substituted derivatives, and benzidine can act as mediators in the electron-transfer processes associated with the chemical oxidation of aniline to PANI. Even at low concentration, they accelerate the process of polyaniline formation. The addition of a mediator to the reaction mixture obviously results in the omission of the first step of aniline oxidation, in which compounds of this type (i.e. benzidine and *N*-phenyl-*p*-phenylenediamine) are formed by a spontaneous recombination of aniline cation radicals. Polyaniline itself has the same ability, resulting in the autoacceleration effect observed during aniline polymerization.

The yield of polyaniline is unaffected by the presence of a mediator and the consequent increased rate of oxidation. When polymerization is carried out in the dispersion mode, the particle size is also independent of the reaction rate. The presence of a mediator could, in principle, influence the molecular weight of polyaniline. The fact that the mediator can participate in the polymerization as a comonomer is not important for its mediating role.

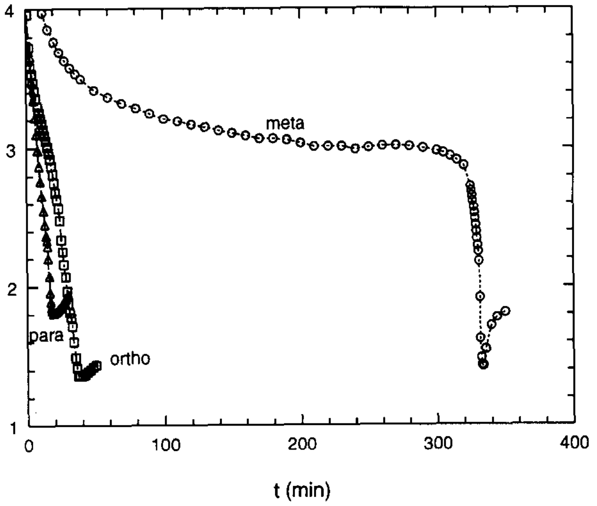


Figure 3 Time dependence of pH during the oxidation of aniline hydrochloride (0.2 M) by ammonium peroxydisulfate (0.1 M) in the presence of *o*- (□), *m*- (○) and *p*-phenylenediamines (△) (1 mM)

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Note added in proof

The acceleration of polyaniline formation by the introduction of small quantities of similar organic compounds into the reaction mixture has recently been reported by Wei *et al.* (Wei, Y., Hsueh, K.F. and Jang, G.-W. *Polymer* 1994, **35**, 3572). The addition of cerium (IV) (Fong, Y. and Schlenhoff, J.B. *Polymer* 1995, **36**, 639) or hexachloroiridate (IV) ions (Kogan, I.L., Knerelman, E.I., Shunina, I.G., Fokeeva, L.S., Estrin, Y.I. and Sokolov, D.N. *Synth. Met.* 1995, **69**, 133) was observed to have a similar effect.