

Influence of chemical polymerization conditions on the properties of polyaniline

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The chemical polymerization of aniline in aqueous solutions was studied as a function of a wide variety of synthesis parameters, such as pH, relative concentration of reactants, polymerization temperature and time, etc. The polymer was synthesized using a number of different oxidizing agents and different protonic acids. It was found that the reaction yield was not sensitive to most variables. By contrast, the inherent viscosity of the polymer, measured in solutions in concentrated sulphuric acid, was strongly dependent on the synthesis parameters. Optimum reaction conditions are outlined for the chemical polymerization of aniline, for post-treatment with aqueous HCl solutions, and for compensation of the emeraldine salt into its base form. Under such conditions, high-quality polyaniline base was synthesized with an inherent viscosity (0.1% w/w polymer in sulphuric acid) as high as 2.32 dl g⁻¹.

(Keywords: polyaniline; synthesis; conductivity; electrically conducting polymers; viscosity)

INTRODUCTION

Polyaniline has attracted considerable attention since MacDiarmid *et al.* reinvestigated this material as a conducting polymer¹. Polyaniline is unique among conducting polymers in that its electrical properties can be reversibly controlled both by charge-transfer doping and by protonation. The wide range of associated electrical, electrochemical and optical properties, coupled with good stability, make polyaniline potentially attractive for application as an electronic material.

Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization². Considerable effort has been devoted to development of relationships between synthesis conditions and the properties of polyanilines obtained by electrochemical polymerization^{3,4}. By contrast, relatively little attention has been paid to the chemical polymerization of aniline. The latter polymerization process is of particular importance since this synthesis is the most feasible route for the production of polyaniline on a large scale. Recently, Pron *et al.*⁵ compared the electrical conductivity and the reaction yield of polyaniline, polymerized with four different oxidizing agents and at different aniline/oxidant ratios. These authors concluded that the redox potential of the oxidizing agents is not a dominant parameter in the chemical polymerization of aniline; most oxidizing agents gave similar results. Armes *et al.*⁶ studied the polymerization of aniline at 20°C using ammonium persulphate as oxidant. In their study of the effect of the oxidant/monomer initial mole ratio, they concluded that the conductivity, yield, elemental composition and degree of oxidation of the resulting polyaniline are essentially

independent of this ratio when its value was below 1.15. On the basis of elemental analysis, the authors concluded that over-oxidation of polyaniline occurs at higher oxidant/monomer mole ratios. Asturias *et al.*⁷ investigated the influence of the polymerization atmosphere (air or argon) on the degree of oxidation of chemically prepared polyaniline, using (NH₄)₂S₂O₈ as an initiator.

To our knowledge, no systematic studies have been reported on the relationship between the chemical polymerization conditions and the principal macro-molecular properties of polyaniline, such as the viscosity or molecular weight. The lack of such studies is due, of course, in part to the presumed intractability of polyaniline, which has impeded solution characterization of the polymer.

Recently, we found⁸ that both the salt and the base form of polyaniline can be completely dissolved at room temperature, up to a polymer concentration of more than 20% w/w, in several concentrated strong protonic acids such as H₂SO₄, CH₃SO₃H and CF₃SO₃H. We established that dissolution took place without detectable degradation and that the solutions were stable at room temperature at least for several days. The polyaniline salt was recovered from such solutions in partially crystalline form by precipitation in water or methanol⁸. This solubility enabled the use of viscosity measurements as a means of estimating molecular weights.

Employing this finding, we initiated a systematic investigation aimed at establishing the relations between a variety of synthesis variables and the characteristics of the polyanilines produced. In this paper, we present results on the effects of the type of oxidizing agents and protonic acids, aniline/oxidizing agent mole ratio, pH, polymerization temperature and time, etc., on a range of polymer properties, with special emphasis on the viscosity and conductivity. The former, we believe, is of paramount importance for the manufacturing of high-quality polyaniline products, such as fibres and

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films. In addition, we briefly discuss various compensation conditions for the preparation of polyemeraldine base, as well as procedures for reprotonation of as-polymerized polyaniline, widely used in the preparation of fully protonated, conducting polyaniline.

EXPERIMENTAL

Materials

Reagent-grade aniline (Aldrich) was vacuum distilled under nitrogen prior to use. All other reagents were used as received.

Synthesis

The preparations were carried out in aqueous protonic acid solutions. The type and concentration of oxidizing agents and protonic acids were widely varied, as shown in the following sections. The polymerization temperature was controlled by placing the reaction vessel in a regulated cooling bath while monitoring the temperature with a thermometer that was inserted directly into the reaction mixture.

Addition of oxidant was carried out in two different ways:

(a) *Method A*: 250 ml of protonic acid solution of the oxidizing agent was slowly added, under vigorous stirring, to 250 ml of a protonic acid solution of the same molarity that contained 20 ml (0.219 M) aniline.

(b) *Method B*: 50 ml of aqueous solution of oxidizing agent without protonic acid was added very slowly into 200 ml HCl solution containing 20 ml aniline. The final concentration of HCl in the reaction mixture was maintained constant, as indicated below.

After all the oxidant was added (over a period of 1–3 h, unless otherwise indicated) the reaction mixture was left stirring at constant temperature during a specific period of time. The oxidation of aniline is *highly exothermic*; therefore, the rate of addition of the oxidant was adjusted in both methods to prevent any increase in the temperature of the reaction mixture. Over the whole period of addition, the temperature of the polymerizing mixture was held within 1°C of that of the temperature bath.

The precipitated polyaniline was recovered from the polymerization vessel, filtered and then washed with distilled water until the washing liquid was completely colourless. In order to remove oligomers and other organic by-products, the precipitate was washed with several portions of methanol until the methanol solution was colourless. Finally, the material was twice washed with ethyl ether and subsequently dried at room

temperature for 48 h in dynamic vacuum, until constant mass was reached. The polymer yield was calculated, for reasons of simplicity, assuming that the products were completely protonated, 50% oxidized poly(*p*-phenylene-amineimine) $[4(C_6H_4NH)^{2+}(2A^-)]_n$; here A is the corresponding counter-anion from the protonic acids used in the synthesis.

Extractions of polyaniline by tetrahydrofuran (THF) or dimethylformamide (DMF) were carried out using a Soxhlet extractor or washing onto a porous glass filter, followed by washing with methanol and ether and, finally, drying.

The pristine polyaniline salt was converted to the base form by treatment with aqueous NH_4OH solutions of different concentrations, subsequently followed by washing with distilled water, methanol and ethyl ether. Reprotonation of polyaniline salt or base was accomplished at room temperature by stirring with an HCl solution, followed by filtration and drying at room temperature in dynamic vacuum until constant mass was reached.

Characterization

The inherent viscosities of the polyanilines were determined at 25°C in 0.1% w/w solutions in concentrated sulphuric acid, using an Ubbelohde viscometer. Solutions of polyaniline salt or base were prepared by dissolving 0.0368 g of the polymer in 20 ml 97% sulphuric acid. The mixture was left overnight at room temperature under moderate stirring, to yield a homogeneous solution.

Electrical conductivities of the as-polymerized polymers were measured on dry pressed pellets employing the usual four-probe method under laboratory conditions. The estimated error in the latter measurement is about 20%.

U.v.-vis. spectra were recorded with a Perkin-Elmer Lambda 9 UV/VIS/IR spectrophotometer.

RESULTS AND DISCUSSION

Oxidizing agents

Table 1 summarizes the data obtained for the range of oxidizing agents used in this study as initiators of aniline polymerizations. The polymerizations were carried out under standard conditions, but for varying polymerization times. Note that the aniline/oxidant ratio was adjusted in order to normalize the aniline/oxidant molar ratio to $k=2.5$ for all oxidizing agents (as proposed by Pron *et al.*⁵). Here, $k=2.5M_{an}/M_{ox}M_e$, where M_{an} =number of moles of aniline, M_{ox} =number of moles of oxidizing agent and M_e =number of electrons necessary to reduce

Table 1 Effect of oxidizing agent on polyaniline properties^a

Oxidant	An/Ox	Time (h)	Yield (%)	σ (S cm ⁻¹)	η_{in} (dl g ⁻¹)	$E_{ox}(H_2/2H^+)$
(NH ₄)S ₂ O ₈	2	4	37	1.2	1.17	2.00
K ₂ Cr ₂ O ₇	6	18	42	0.7	1.05	1.33
KIO ₃	6	24	29	0.4	0.64	1.09
FeCl ₃	6	24	10.7	0.3	0.37	0.77
KMnO ₄	5	24	8.1	9×10^{-4}	0.30	1.49
KBrO ₃	6	24	0.9	3.5×10^{-2}	0.11	1.44
KClO ₃	6	24	1.8	5.6×10^{-3}	0.12	1.45

^a Polymerization parameters: HCl concentration, 1.5 M; normalized aniline/oxidant ratio, $k=2.5$; reaction temperature, 0°C; method of addition, A

one molecule of the oxidizing agent. It is assumed that oxidation of aniline to polyemeraldine withdraws, on average, 2.5 electrons from each aniline monomer.

As can be inferred from the results presented in Table 1, the characteristics of the polyaniline varied markedly with the nature of the oxidizing agent. Three different groups can be discerned. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ resulted in high polymerization yield, electrical conductivity and viscosity. The second group, KIO_3 and FeCl_3 , yielded polyaniline of electrical conductivity similar to that of the first group, but with much lower viscosity. Although these oxidizing agents exhibited a reasonable polymerization rate, the resulting products contained a large fraction of water- and methanol-soluble oligomers. As a result, the final polymer yields were much lower than that of the first class. Although KMnO_4 also developed a reasonable polymerization rate, the electrical conductivity of the polymer was much lower than commonly observed for polyaniline. Infra-red spectra of this material differed slightly from that of the usual polyaniline, indicating a difference in the main-chain structure. With the third group of oxidation agents (KClO_3 and KBrO_3), the polymerization rate was low and the yield and the viscosity of the products were very low.

In the last column of Table 1, we list the standard redox potential of these oxidizing agents. There was no obvious correlation between the properties of polyaniline and the redox potential of the initiator. We observed, for example, that, although the ClO_4/Cl^- couple (1.37 V versus H^2/H^+) has a similar redox potential as $\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}$, NaClO_4 did not initiate chemical polymerization of aniline under otherwise similar reaction conditions. These facts indicate that the mechanism of oxidative polymerization of aniline is more complex than previously proposed; evidently, further studies are necessary to elucidate the polymerization mechanism.

The aniline/oxidizing agent ratio had a minor effect on the electrical conductivity of the polyanilines produced. By contrast, the polymer yield was strongly dependent on this ratio (see Table 2). For both $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, the lower aniline/oxidizing agent ratio resulted in a lower final yield

Table 2 Dependence of polyaniline properties on aniline/oxidant mole ratio

Oxidant	An/Ox	k	Yield (%)	σ (S cm^{-1})	η_{in} (dl g^{-1})
$(\text{NH}_4)_2\text{S}_2\text{O}_8^a$	8	10	9.9	0.8 (9.8) ^c	0.80
	4	5	20.0	0.5 (12.6)	0.78
	2	2.5	38.0	2.7 (10.6)	0.90
	1.5	1.88	60.2	0.9 (12.1)	0.83
	1	1.25	75.1	0.6 (12.0)	0.67
$(\text{NH}_4)_2\text{S}_2\text{O}_8^b$	8	10	9.0	0.4	0.94
	2	2.5	36.9	1.2	1.17
	1	1.25	75.8	1.2	0.75
$\text{K}_2\text{Cr}_2\text{O}_7^b$	24	10	10.7	1.7	1.00
	12	5	20.8	0.5	1.08
	6	2.5	41.9	0.7	1.05
	4	1.66	46.0	0.5	0.89
	3	1.25	83.7	2.8	0.74

^a Method of addition, B; HCl concentration, 1.2 M; reaction time, 24 h; reaction temperature, 0°C

^b Method of addition, A; HCl concentration, 1.5 M; reaction time, 4 h for $(\text{NH}_4)_2\text{S}_2\text{O}_8$, 24 h for $\text{K}_2\text{Cr}_2\text{O}_7$; reaction temperature, 0°C

^c After treatment by 1.0 M HCl for 2 h

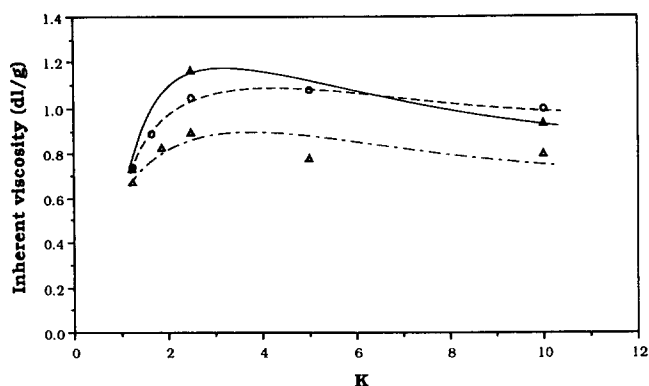


Figure 1 Viscosity vs. normalized aniline/oxidizing agent ratio: Δ , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, method B of oxidant addition; \blacktriangle , $(\text{NH}_4)_2\text{S}_2\text{O}_8$, method A of oxidant addition; \circ , $\text{K}_2\text{Cr}_2\text{O}_7$, method A of oxidant addition; for other polymerization parameters, see footnote of Table 2

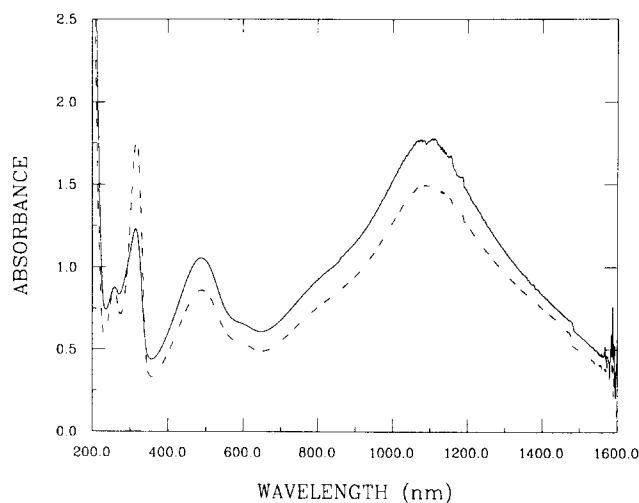


Figure 2 U.v.-vis. spectra of polyaniline, synthesized with aniline/oxidizing agent ratio $k=10$ (—) and $k=1.25$ (---)

of polyaniline. It is clear that this was due to the high concentration of oxidant, which promoted the formation of oligomers and yielded a large amount of water- and methanol-soluble material.

Figure 1 shows the viscosity as a function of the normalized aniline/oxidizing agent ratio. Oxidation by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ produced polyaniline of similar viscosity, but exhibited somewhat different behaviour in the k -dependence. In the case of $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, the viscosity saturated at values of k exceeding 2.5; for $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidation, a maximum viscosity was observed at $k=2.5$. Thus, for maximum reaction yield and molecular weight, the optimum normalized aniline/oxidizing agent ratio was $k=2.5$ for both $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation, i.e. an aniline/oxidant mole ratio of 2 for ammonium persulphate and 6 for potassium chromate.

Figure 2 shows u.v.-vis. (sulphuric acid) solution spectra of polyaniline synthesized with aniline/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ molar ratios of 1 and 8, respectively. In both cases we observed features⁹ typical for polyemeraldine salts. I.r. spectra of polyaniline obtained with different aniline/oxidizing agent ratios are similar and also typical of polyemeraldine salt⁹. We concluded that the aniline/oxidant ratio did not affect the degree of oxidation of the polyaniline chain within the wide range of

$k=1.25-10$, for both ammonium persulphate and potassium chromate oxidation.

Protonic acid medium

In their early work, MacDiarmid *et al.*¹ indicated the strong effect of the acidity of the polymerization medium on the electrical conductivity of synthesized polymer. Here we systematically re-examined this acidity influence. The data in Table 3 show that, at $\text{pH} < 4$, the electrical conductivity and reaction yield remained unaffected, within experimental error, while the viscosity was

Table 3 Effect of HCl concentration on polyaniline properties^a

Method of addition	HCl conc. (M)	pH	Yield (%)	η_{in} (dl g ⁻¹)	σ (S cm ⁻¹)
B	0.86	4	37.6	0.41	1.4
	0.96	3	40.3	0.55	2.2
	1.0	1	43.0	0.71	1.2
	1.2	<1	38.0	0.90	2.7
	1.5	<1	38.9	0.84	2.9
	2	<1	38.8	0.83	2.2
	3.0	<1	38.5	0.80	2.5
	4.0	<1	38.0	0.73	1.7
A	0.75	<1	38.3	0.87	1.0
	1.5	<1	36.9	1.17	1.2
	3.0	<1	36.5	0.86	8.9

^a Polymerization parameters: normalized aniline/oxidant ratio, $k=2.5$; reaction temperature, 0°C; reaction time, 4 h for A, 24 h for B

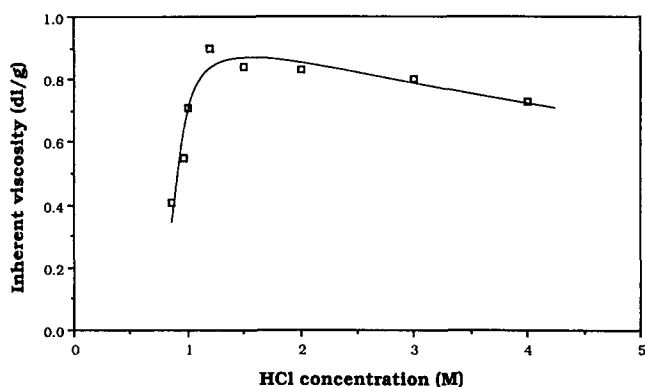


Figure 3 Viscosity vs. HCl concentration; for other polymerization parameters, see footnote of Table 3

Table 4 Effect of protonic acids on polyaniline properties^a

Acids	Yield (%)	$\eta_{in,salt}$ (dl g ⁻¹)	$\eta_{in,base}$ (dl g ⁻¹)	σ (S cm ⁻¹)	$\text{p}K_a$
HCl	36.9	1.17	1.64	1.2	-7.0
H ₂ SO ₄	30.6	0.99	1.35	0.7	1.82
HBF ₄	43.5	0.57	0.90	1.1	
HF	43.3	0.55	0.85	0.5	3.17
CH ₃ SO ₃ H	31.4	1.05	1.19	1.8	-1.2
CF ₃ SO ₃ H	28.3	0.98	1.19	1.0	-0.26
CF ₃ COOH	31.9	0.92	1.21	1.1	0.3
HClO ₄	41.3	0.45	0.66	4.4	
HCOOH (88%)	33.6	0.72	0.87	1.0	3.75
CH ₃ COOH (80%)	28.1	- ^b		2.5×10^{-3}	4.75
CH ₃ COOH	16.1	0.11		1.5×10^{-7}	4.75

^a Polymerization parameters: acid concentration, 1.5 M, except HCOOH and CH₃COOH; reaction time, 24 h, except for HCl and HClO₄, 4 h; reaction temperature, 0°C; method of addition, A; compensation condition, 3% NH₄OH, 2 h

^b Only partially soluble in 97% H₂SO₄

significantly dependent on the acidity, for both methods of addition of oxidizing agent (see also Figure 3). From these results we concluded that for (NH₄)₂S₂O₈ oxidation, a HCl concentration of 1.2–2.0 M yielded polyaniline of optimum quality and high viscosity, i.e. molecular weight.

It will be shown in the following sections that high acidity accelerates hydrolysis of the polyemeraldine chains. The dependence of the molecular weight of polyaniline on the acidity of the reaction medium clearly indicated that two competing processes (polymerization and degradation due to hydrolysis) controlled the polyaniline synthesis.

We found that not only the concentration but also the nature of the protonic acid affected the quality of the polymerization products. Table 4 describes the results of aniline polymerizations carried out in different media of mineral and organic acids, under otherwise identical synthesis conditions. We noted that the yield and electrical conductivity were not sensitive to the acid used, much like the concentration, except in the case of 3 M acetic acid. By contrast, the viscosity was found to be strongly dependent on the nature of acid. Because of difference in molecular weight of counter-anions, we listed for comparison also the viscosity of the corresponding emeraldine base that was prepared under identical conditions. The origin of the strong dependence of the polymer viscosity on the nature of the acid is not clear at this stage. There was not a quantitative correlation between the strength of the acid and the polymer viscosity; this can be inferred from the viscosity and the $\text{p}K_a$ data of these acids listed in Table 4. Qualitatively, however, the stronger acids yielded polyaniline of higher viscosity.

Polymerization temperature, time and additives

Table 5 reveals that the viscosity of polyaniline is sensitive to the polymerization temperature. This was true for both methods of oxidant addition. The viscosity of the polyaniline (salt or base) increased on decreasing the polymerization temperature to -5°C (see Figure 4). However, at -10°C the polymer viscosity decreased, although the polymerization rate was still reasonably high. The reduction in viscosity at this low temperature was probably due to the precipitation of the aniline hydrochloride salt. Further decrease of the reaction

Table 5 Effect of reaction temperature on polyaniline properties^a

T (°C)	Yield (%)	$\eta_{in,salt}$ (dl g ⁻¹)	$\eta_{in,base}$ (dl g ⁻¹)	σ (S cm ⁻¹)
-10	38.4	0.82	0.97	1.7
-5	38.8	0.98	1.19	1.3
0	38.7	0.95	1.13	1.0
10	39.2	0.80	0.98	1.0
25	37.7	0.62	0.81	1.5

^a Polymerization parameters: HCl concentration, 1.5 M; aniline/ammonium persulphate mole ratio, 2.0; reaction temperature, 0°C; reaction time, 6 h; method of addition, A

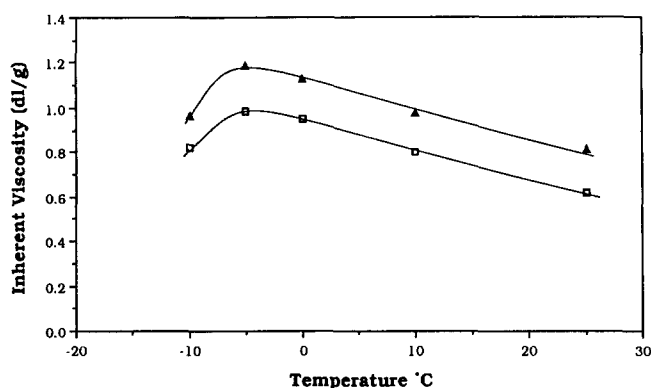


Figure 4 Viscosity vs. polymerization temperature: □, as-polymerized salt; ▲, emeraldine base; for other polymerization parameters, see footnote of Table 5

temperature was limited by the solubility of ammonium persulphate in aqueous solutions. We found the reaction yield and electrical conductivity to be virtually independent of the polymerization temperature (Table 5). Thus, we concluded that chemical polymerization of aniline by ammonium persulphate or potassium perchromate oxidation should be executed at a temperature between 0 and -5°C.

Commonly, chemical polymerizations of aniline are carried out over a period of 10–90 h^{6,7}. We found that long polymerization times do not, in fact, favour the synthesis of high-molecular-weight polyaniline. Table 6 shows typical results for (NH₄)₂S₂O₈ oxidation of aniline at various polymerization times at 0°C. This table shows that the reaction yield was almost the same over periods from 1 to 24 h; however, reduced viscosities were observed at polymerization times exceeding 4 h. These results indicate that the polymerization occurred relatively rapidly and was essentially completed in 4 h. Prolonged periods seemed to lead to slow hydrolysis, resulting in a decrease of the viscosity. Thus we conclude that, for ammonium persulphate oxidation, very long polymerization times are not necessary, and, in fact, are harmful. On the other hand, a reaction time of 1 h, which was proposed by MacDiarmid *et al.*¹, was not sufficient to achieve maximum molecular weight.

It was found that the viscosity of polyaniline was also sensitive to the method of addition of oxidant. It can be concluded from Table 2 that, for ammonium persulphate oxidation, method A yielded polyanilines with slightly higher viscosities. As emphasized above, the oxidative polymerization of aniline is exothermic; thus the rate of addition of oxidant may affect the temperature of the reaction mixture, and, therefore, affect the quality of the resulting polyaniline. In previously published studies on the chemical polymerization of aniline, various oxidant

addition rates have been used, ranging from pouring in all the oxidant solution at once⁶ to 'slow adding'^{2,5}. In a more elaborate study of this topic, we specifically investigated the rate at which the oxidant solution was added to the reaction mixture by method of addition B. In this study we maintained the total reaction time constant (10 h), as well as all concentrations (HCl concentration 1 M, aniline/(NH₄)₂S₂O₈ molar ratio 2:1, aniline 13.3 ml), but varied the polymerization temperature and, independently, the rate of oxidant addition. The resulting polyaniline was converted to the base form by treatment with 3% aqueous NH₄OH solution for 2 h. Figure 5 shows the results of inherent viscosity of the resulting polyemeraldine base vs. rate of oxidant addition. As concluded earlier the optimum temperature for the polymerization of this system was between 0 and -5°C. We found that rate of addition mostly affected the viscosity of the polymer between 350 ml min⁻¹ (pouring in all the oxidant solution at once) and 1.17 ml min⁻¹ (dripping over a period of 30 min) (Figure 5). A change was also noticed in the powder morphology of the precipitated polyaniline. At the fastest rate, the powder was extremely fine. In all other cases the particles produced were substantially more coarse. From the results in Figure 5, we concluded that rates that lead to a total addition time of 60 min seemed adequate, since lower rates did not yield a significant increase in inherent viscosity. In our opinion, the former rate simply ensures, under the present conditions, that oxidant addition occurs without a significant increase in reaction temperature.

In order to increase further the molecular weight of polyaniline, we attempted to polymerize aniline in mixtures of organic and aqueous media. This concept is based on the idea that use of organic solvents in which polyaniline partially dissolves may prevent the immediate precipitation of the growing polyaniline chains from the

Table 6 Effect of polymerization time on polyaniline properties^a

Time (h)	Yield (%)	η_{in} (dl g ⁻¹)	σ (S cm ⁻¹)
1	40.9	0.64	6.1
4	39.9	1.17	1.2
8	40.6	1.10	1.1
24	38.5	0.81	3.1

^a Polymerization parameters: HCl concentration, 1.5 M; aniline/ammonium persulphate mole ratio, 2.0; reaction temperature, 0°C; method of addition, A

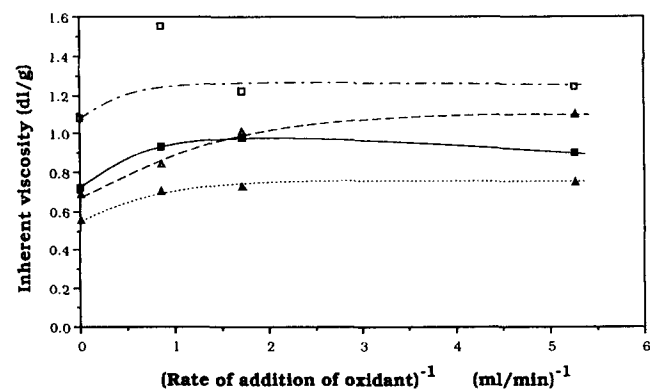


Figure 5 Inherent viscosity as a function of rate of oxidant addition; □, -5°C; △, 0°C; ■, 10°C; ▲, 30°C

reaction mixture. It was inferred from the data in Table 7 that all these additives had no beneficial effect on the polymerization process. The polyanilines polymerized in mixed solvent systems, in fact, exhibited slightly lower viscosities than those synthesized in pure aqueous solutions; the reaction yields and electrical conductivities were virtually identical. Further efforts in this direction are in progress.

Reprotonation with aqueous HCl solution

As-polymerized polyaniline obtained by the procedures described in this paper exhibit a degree of protonation of about 0.15–0.20 as determined by elemental analysis. Pristine polyaniline powder is generally protonated by treatment with 1–4 M HCl aqueous solution for long periods of time (usually 24–48 h)^{1,6}. Such treatment generally increases the electrical conductivity by about one order of magnitude. As evidenced by the results in Table 8, we observed that such long-time exposure to aqueous HCl may lead to a significant decrease in the viscosity of polyaniline. This table shows that high HCl concentrations and long duration of the reprotonation process lead to reduced viscosity of the resulting polyaniline. These data indicate unambiguously that degradation occurred, probably due to hydrolysis of the imine nitrogen–carbon bond. We noted that, at HCl concentrations of about 0.5 M, the reduction of the viscosity became much less pronounced. In fact, stirring with 0.1 M HCl solutions resulted in a slight increase of viscosity, in comparison with that of the initial polyaniline. The increase of both electrical conductivity and Cl/N ratio excluded the possibility of deprotonation as a possible explanation for this phenomenon. At this point

we are inclined to attribute the slight increase in viscosity to an increase of the molecular weight due to chain branching. (It is difficult to envision a mechanism for the increase of chain length during stirring with dilute HCl solution, as opposed to hydrolysis with more concentrated solutions.) As a matter of fact, at very long reprotonation times, occasionally partly insoluble material was produced, which further corroborates this view.

From these results we concluded that the preparation of fully protonated, highly conductive polyaniline (without loss in molecular weight) should be carried out in aqueous HCl solutions of a concentration less than 0.5 M for 2 h.

Compensation procedure

Pristine emeraldine salt can be converted to the emeraldine base by treatment with aqueous NH₄OH solutions. We observed that the quality of the emeraldine base produced was strongly dependent on the concentration of the NH₄OH solution and the duration of the reaction. Long-time stirring with concentrated ammonium hydroxide solution resulted in a marked decrease of the viscosity of the final emeraldine base. From the data listed in Table 9, we concluded that polymer degradation in the compensation process can be prevented by stirring with very dilute solutions (about 0.3%) for 24 h. Alternatively, treatment with 3% NH₄OH for 2 h gave satisfactory results; the viscosity of the resulting emeraldine base was only slightly lower than in the former compensation process. Elemental analysis revealed that both processes were adequate to yield fully converted

Table 7 Effect of the additives on polyaniline properties^a

Additives ^b	Yield (%)	η_{in} (dl g ⁻¹)	σ (S cm ⁻¹)
DMF	40.2	0.78	1.5
NMP	39.9	0.67	2.6
THF	37.2	0.73	1.1
Acetone	39.5	0.80	1.1
Isopropanol	37.6	0.86	1.3

^a Polymerization parameters: HCl concentration, 1.5 M; aniline/ammonium persulphate mole ratio, 2.0; reaction temperature, 0°C; reaction time, 24 h; method of addition, A; water/additive = 6/4

^b DMF, dimethylformamide; NMP, *N*-methylpyrrolidinone; THF, tetrahydrofuran

Table 9 Effect of compensation procedure on the viscosity of polyemeraldine base

NH ₄ OH solution (%)	Time of stirring (h)	$\eta_{in,salt}$ (dl g ⁻¹)	$\eta_{in,base}$ (dl g ⁻¹)
30	24	1.17	1.14
30	24	0.90	0.67
30	0.5	1.17	1.45
3	18	1.17	1.49
3	2	1.17	1.62
3	2	0.90	1.20
3	0.5	1.17	1.64
0.3	24	1.17	1.76
0.3	12	1.17	1.70
0.3	2	1.17	1.74
0.3	0.5	1.17	1.65

Table 8 Reprotonation of as-polymerized polyaniline with aqueous HCl solution

HCl solution (M)	Time (h)	Initial properties ^a		Final properties		
		η_{in} (dl g ⁻¹)	σ (S cm ⁻¹)	η_{in} (dl g ⁻¹)	σ (S cm ⁻¹)	Cl/N ^b
1.5	22	1.17	1.2	0.60	13.5	
1.5	0.5	1.17	1.2	0.66	12.5	0.49
1.0	2	1.17	1.2	0.85	8.9	0.47
1.0	15	1.63 ^c	<10 ⁻⁹	0.42	16.9	
0.5	24	1.17	1.2	1.01	13.2	0.46
0.5	2	1.17	1.2	1.12	9.3	0.49
0.1	24	1.17	1.2	1.41	9.6	0.43
0.1	2	1.17	1.2	1.58	8.3	0.44

^a Cl/N for initial polyaniline salt is 0.17

^b Determined by elemental analysis

^c Polyaniline base after extraction by THF

Table 10 Extraction of polyemeraldine base with THF

η_{in} (initial base) (dl g ⁻¹)	Yield (THF-insoluble) (%)	η_{in} (resulting base) (dl g ⁻¹)	η_{in} (THF-soluble) (dl g ⁻¹)
1.20	81	1.63	0.18
1.64	85	2.32	
1.66	90	2.27	

emeraldine base (the chlorine content was below the detection limit, <0.3%).

In our studies, we found that the amount of THF-soluble (oligomeric) material of the emeraldine base decreased with decreasing concentration of the ammonium hydroxide solution and time of conversion. This soluble fraction exhibited nearly identical i.r. spectra (in KBr pellets) and u.v.-vis. spectra in sulphuric acid as the THF-insoluble material. Clearly, these two fractions differed only in molecular weight, as evidenced by the viscosity data presented in *Table 10*. The data in this table also indicate that the removal of the THF-soluble fraction from the emeraldine base leads to a significant increase in the viscosity of the remaining powder. Using this extraction technique we obtained polyaniline base with an inherent viscosity as high as $\eta_{in} = 2.32 \text{ dl g}^{-1}$. From comparison with data for this polymer and viscosities measured under identical conditions of nylon-6 and poly(*p*-phenyleneterephthalamide) and the Mark-Houwink relations^{10,11} for these polymers, we estimated that the corresponding molecular weight of the polyaniline was between 20×10^3 (rigid-chain limit) and 100×10^3 (flexible-chain limit).

Remarkably, attempts to extract emeraldine base with DMF, in which emeraldine base dissolves more readily, failed. After room-temperature extraction with DMF, the emeraldine base was completely insoluble in sulphuric acid. I.r. spectra indicated the presence of C=O vibrations in this DMF-washed polyaniline. This observation implies that chemical reaction had taken place during the extraction process, resulting in crosslinking of the polyaniline chains.

CONCLUSIONS

We studied the relationships between the chemical polymerization conditions and the physicochemical properties of polyaniline. We established optimum synthesis conditions for the polymerization of aniline by ammonium persulphate oxidation with respect to viscosity, electrical conductivity and reaction yield. We found that the reaction yield was not strongly sensitive to most synthesis variables, while the viscosity, or molecular weight, and the electrical conductivity of the as-polymerized and/or post-treated polyaniline salt were found to be markedly affected. In the present study we focused on macroscopic phenomena, such as yield, viscosity, etc. In forthcoming studies we will report in detail on the effects of the various polymerization parameters on the chain architecture.

The present results do not permit conclusions regarding the molecular-weight dependence of the conductivity, due to the wide variations in polymerization conditions, protonation, post-treatments, etc. This spectrum of synthesis variables affected, among other characteristics, purity, particle size and morphology, grain boundaries in the compressed pellets used for the conductivity measurements, and the like. This multitude of variables, of course, obscures the unambiguous unveiling of a molecular weight-conductivity relation. This topic will be dealt with in a systematic manner in a forthcoming paper.

In addition, we reported that the commonly employed procedure for protonation of polyemeraldine salt (long-time stirring of as-polymerized polyaniline powder with concentrated aqueous HCl solution) leads to significant degradation of polyaniline. On the other hand, stirring with dilute hydrochloric acid caused a slight increase in the viscosity of polyaniline. Furthermore, we found that polyemeraldine was not resistant against long treatment with concentrated alkaline solutions. We presented optimum reaction conditions for both full protonation and compensation procedures. In addition, we observed that the removal of low-molecular-weight polyaniline, by careful extraction of emeraldine base with THF, resulted in a significant increase in the polymer viscosity. Based on the techniques presented in this work, we succeeded to produce high-quality polyemeraldine base with an inherent viscosity in H₂SO₄ (0.1% w/w polymer) as high as 2.32 dl g^{-1} with an estimated molecular weight between 20×10^3 (rigid-chain limit) and 100×10^3 (flexible-chain limit).

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