Evolution of polyaniline structure during synthesis

K. G. Neoh* and E. T. Kang
Department of Chemical Engineering, National University of Singapore, Kent Ridge, Singapore 0511

and K. L. Tan
Department of Physics, National University of Singapore, Kent Ridge, Singapore 0511
(Received 29 October 1992; revised 14 January 1993)

The oxidative polymerization of aniline by $(NH_4)_2S_2O_8$ in dilute solutions of $HClO_4$ or HCl of various concentrations was investigated. The reactions were terminated at various times and the solid products were isolated and analysed using Fourier transform infra-red and ultraviolet–visible absorption spectroscopy and X-ray photoelectron spectroscopy. The ultraviolet–visible absorption spectra of the reaction mixtures and the structure of the initial solid products indicate different initial reaction pathways and intermediates occurring under the conditions tested. At low acid concentrations, the solids that are initially precipitated out are salts of short-chain oligomers with the anions from the protonic acid as well as sulfate anions. In contrast, at low pH, the long-chain, *para*-disubstituted nature of the solid is evident at the initial stages and the counterions are predominantly supplied by the protonic acid. With decreasing acid concentration, although the polymerization rate decreases, a long-chain *para*-disubstituted polymer is ultimately obtained, albeit with an increase in the proportion of sulfate anions serving as counterions and in the amount of unprotonated imine units. A comparison of the thermal stability of the various polymers indicates a significantly lower decomposition temperature for the polymers obtained at low acid concentrations or short reaction time.

(Keywords: polyanilines; synthesis; structure; oxidative polymerization; spectroscopy; *FT*i.r.; X.p.s.; u.v.–vis.)

INTRODUCTION

The polymerization of aniline can be achieved by either chemical or electrochemical means. It is generally accepted that the polyaniline family can exist in a range of oxidation states, and the structures of the base form can be represented as:

$$[(\text{-B-NH-B-NH-})_{1-y}(\text{-B-N=Q=N-})_y]_n$$

where B represents a benzenoid ring while Q represents a quinoid ring[1,2]. Most of the studies on the mechanisms of polyaniline formation have focused on electrochemical polymerization[3–7]. These studies have proposed that the initial oxidation of aniline results in a radical or nitrenium cation and the dimer, *p*-aminodiphenylamine, is an intermediate. Unreacted aniline and the dimer have also been extracted from the reaction mixture during the course of chemical polymerization of aniline in 1 M HCl[8]. From the concentrations of the monomer and dimer, as determined by linear sweep voltammetry, the oxidation of aniline to generate *p*-aminodiphenylamine has been proposed to be the slow step in the polymerization[8]. Beyond the dimer stage, a firm understanding of the polymerization mechanism and the structural changes is still lacking.

In this paper, we present the results from the structural investigation of the products obtained at various reaction times during the course of chemical polymerization of aniline in different acidic media. The analytical techniques used for structural characterization include ultraviolet–visible (u.v.-vis.) and Fourier transform infra-red (*FT*i.r.) absorption spectroscopy and X-ray photoelectron spectroscopy (X.p.s.). The latter technique, in particular, is well suited for elucidating the proportions of amine (–NH–), imine (–N=) and positively charged nitrogen (N^+) species in polyaniline[9–11].

EXPERIMENTAL

Chemical polymerization

The chemical polymerization of aniline was carried out using $(NH_4)_2S_2O_8$ either in dilute HCl or $HClO_4$, or in deionized water under N_2. The acid concentration was varied from 0.002 to 1 M. For all runs, 5×10^{-3} mol of aniline in 100 ml of acid solution or H_2O and a monomer/oxidant mole ratio of 1 were used. The polymerization was carried out either at 0–5°C or at room temperature (25°C). The product was filtered out after selected time intervals and washed with acid of concentration similar to that used in the polymerization

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* To whom correspondence should be addressed

0032-3861/93/183921-08

process for acids of 0.1 M or lower. For polymerization in 1 M acid, 0.1 M acid was used as the washing medium. Drying was carried out under dynamic vacuum. The base polymers were obtained by treating the as-synthesized polymer salts with NH_4OH solution.

Instrumentation

*FT*i.r. absorption spectra of the samples dispersed in KBr were measured on a Shimadzu FTIR 8101M spectrophotometer. The u.v.-vis. absorption spectra of the reaction mixtures and *N*-methylpyrrolidinone (NMP) solutions of the products were determined using a Shimadzu UV-260 spectrophotometer. Thermogravimetric (t.g.) analysis was carried out using a Netzsch STA 409 simultaneous thermogravimetric–differential thermal analyser to determine the thermal stability and degradation behaviour of the products in N_2. The X.p.s. measurements of the powder samples were made on a VG Escalab MkII spectrometer with a Mg Kα X-ray source (1253.6 eV photons). The samples were mounted on the standard sample studs by means of double-sided adhesive tape. A take-off angle of 75° was used in all X.p.s. runs. The X-ray source was run at 12 kV and 10 mA. The pressure in the analysis chamber was maintained at 10^{-8} mbar or lower during measurements. To compensate for surface charging effects, all binding energies were referenced to the C(1s) neutral carbon peak at 284.6 eV. In spectral deconvolution, the full width at half-maximum (f.w.h.m.) of the Gaussian peak components was kept constant in a particular spectrum. The peak area ratios for various elements were corrected by experimentally determined instrumental sensitivity factors and may be subject to a maximum of ±10% error.

RESULTS AND DISCUSSION

Product yield

The rate of solid precipitation is highly dependent on the pH of the acid used and the reaction temperature. The product/monomer ratio (by weight) obtained after 5 h reaction time at 0°C when 1 M $HClO_4$ is used is almost 20 times that obtained with 0.01 M $HClO_4$. The variation of yield with temperature is illustrated in *Figure 1a* for the case of the 0.01 M $HClO_4$. In this figure, the data points are marked by letters, which will be used to denote the products obtained at different times for the subsequent discussion. At room temperature, the reactions are almost completed after 3 h, as evidenced by the levelling off of the product yield, and after the filtration of the product, no further precipitation of solids in the filtrate was observed. In this case, a rapid decrease in the pH of the reaction medium was observed after an induction period of approximately 45 min (*Figure 1b*). The pH change is substantial and can be readily followed in this case owing to the low acid/aniline ratio, and the decrease in pH is consistent with proton elimination occurring in the polymerization process[12]. The results in *Figure 1* indicate that the structure of the products obtained during the first 2 h at 25°C should be quite different from those obtained at longer reaction times. The shape of the product yield curve obtained from the 25°C experiments indicates that the initial reaction rate is slow but increases rapidly before finally levelling off. This behaviour is consistent with the self-catalysis or autoacceleration phenomenon observed in the electrochemical polymerization of aniline[13]. It is postulated that since the initial oxidation of aniline is the rate-determining step and the dimer and succeeding oligomers have lower oxidation potentials than aniline, the increase in reaction rate is achieved by incorporating the monomeric aniline into the oligomeric species[4,8]. The structure of the products obtained at different reaction times shows the largest variation when acid of 0.01 M or lower is used (as compared to 1 M acid). Thus, the results obtained with 0.01 M acid will be discussed in detail and a comparison with the results obtained with acids of other concentrations is made in the last section.

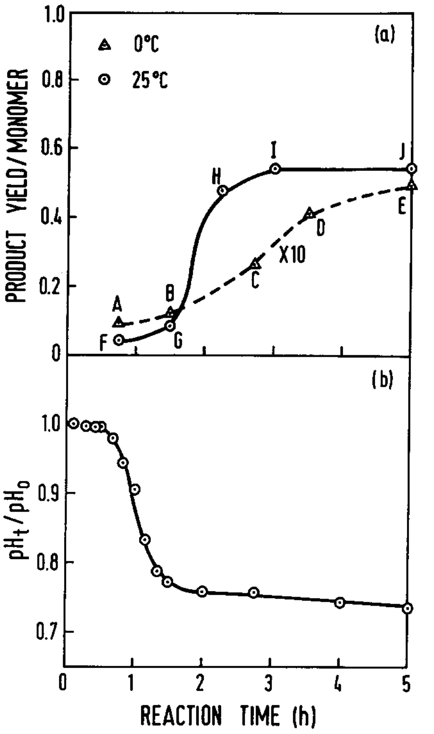

Figure 1 (a) Product yield/monomer ratio (by weight), and (b) ratio of pH of reaction medium at any time *t* (pH_t) to that immediately after oxidant addition (pH_0), for polymerization of aniline in 0.01 M $HClO_4$

FT*i.r. and u.v.-vis. absorption spectra*

The *FT*i.r. absorption spectrum of the product from aniline polymerization in 0.01 M $HClO_4$ after 5 h at 0°C (product E) is compared with those of the products obtained after various times at 25°C in *Figures 2a* to *2d*. The spectra in *Figures 2a*, *2b* and *2c* (corresponding to products E, F and G) are rather similar but they show distinct differences from that of product H in *Figure 2d*. The i.r. absorption spectra of products obtained at reaction times longer than 2 h 15 min are similar to *Figure 2d*. The long absorption tail in *Figure 2d* masks the NH stretching bands in the 3100–3500 cm^{-1} region[14]. This feature together with the intense band at 1140 cm^{-1} has been associated with 'doped' polyanilines[14,15]. The characteristic absorption band for the ClO_4^- anion is at 630 cm^{-1} (ref. 16). However, the presence of sulfate anion will also contribute to absorption in this region[16]. The absorption bands in the 650–900 cm^{-1} region are characteristic of the substitution pattern on the aromatic ring. The band at 820 cm^{-1} is assigned to the C–H out-of-plane bending vibration of the 1,4-disubstituted ring, while the two bands at 690 and

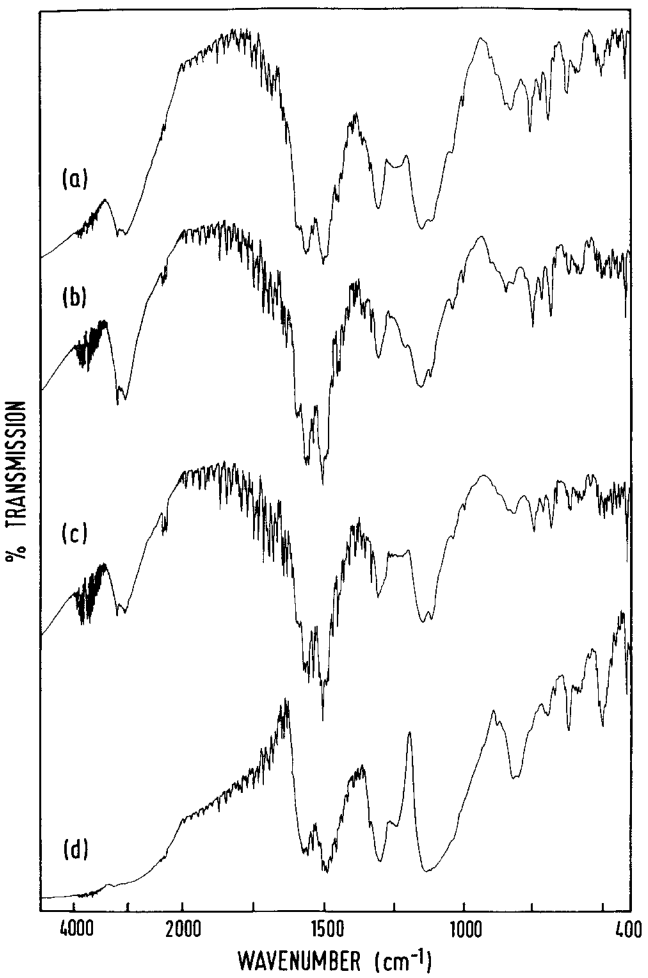

Figure 2 *FT*i.r. absorption spectra of products from aniline polymerization in 0.01 M $HClO_4$: (a) product E, (b) product F, (c) product G and (d) product H

750 cm^{-1} are attributed to the corresponding vibrations of the monosubstituted benzene ring[17]. Thus, it can be established from the *FT*i.r. absorption spectroscopy results that the polymerization products obtained after a reaction time of 2 h in 0.01 M $HClO_4$ at 25°C consist predominantly of *para*-disubstituted chains. On the other hand, the products obtained at shorter reaction times or even at 5 h at 0°C have a much smaller degree of polymerization, as indicated by the comparable intensities of the bands attributed to both *para*-disubstituted and monosubstituted rings. It is likely that products A, B, C, D, E, F and G are salts of aniline oligomers. The drastic difference between the *FT*i.r. absorption spectra of the products obtained after 1 h 30 min and 2 h 15 min (*Figures 2c* and *2d* respectively) is consistent with the rapid increase in polymerization rate in this time interval (*Figure 1a*).

Although the *FT*i.r. absorption spectra have been useful in revealing the differences in the degree of polymerization at different reaction times, other important information such as the oxidation state and degree of protonation of the products have to be obtained from other techniques such as u.v.-vis. absorption spectroscopy and X.p.s. The differences in the u.v.-vis. absorption spectra of the products at different reaction times in 0.01 M $HClO_4$ are illustrated in *Figure 3*. The u.v.-vis. absorption spectrum of product A (0°C, 45 min) shows two peaks at 280 and 370 nm (*Figure 3a*). For products obtained at increasing reaction times at this temperature, an increase in the absorbance between 450 and 700 nm is observed. The spectrum of the product obtained after 3 h 30 min at 0°C (product D) is similar to that of the product obtained after 45 min at 25°C (product F, *Figure 3b*), with a plateau in the 500–600 nm region. This plateau eventually evolves into an absorption band at 620 nm (*Figures 3c* and *3d*). It should be noted that the spectra in *Figures 3a*, *3b* and *3c* are those of the as-synthesized products, whereas for *Figure 3d* the base-treated product was used. When products E, F and G were treated with base, there was a slight dissolution of the products. However, the spectra of the insoluble fractions are similar to those in *Figures 3a*, *3b* and *3c* respectively. The as-synthesized products (salts) after 2 h at 25°C do not dissolve in NMP as readily as the base-treated samples, and hence the spectrum in *Figure 3d* was obtained using the base-treated sample. Furthermore, it has been established that $HClO_4$-protonated polyaniline undergoes deprotonation in excess NMP and hence its solution spectrum would also be that of the base.[18]

Previous spectroscopic studies of polyaniline base[19,20] have established that the π–π^* transition results in an absorption band at approximately 330 nm, while a charge-transfer exciton-like transition from the highest occupied level (centred on the benzenoid rings) to the lowest occupied energy level (centred on the quinoid rings) results in the band at 635 nm. A comparative study of the electronic spectra of aniline oligomers with that of polyaniline base shows that the π–π^* transition band shifts from 289 nm for aniline dimers to 309 nm for tetramers and to 326 nm for polyaniline base[21]. Thus the 280 nm band in *Figures 3a*, *3b* and *3c* and the 320 nm band in *Figure 3d* are assigned to the π–π^* transition, and the increase in chain length of the products as indicated by the red shift of this band is consistent with the i.r. absorption spectra presented earlier. Although the exciton band can be used as a measure of the oxidation state of polyaniline, its peak position and relative intensity to the π–π^* transition band are also dependent on the chain length[21]. The absence of this band in *Figure 3a* suggests that product A consists mainly of

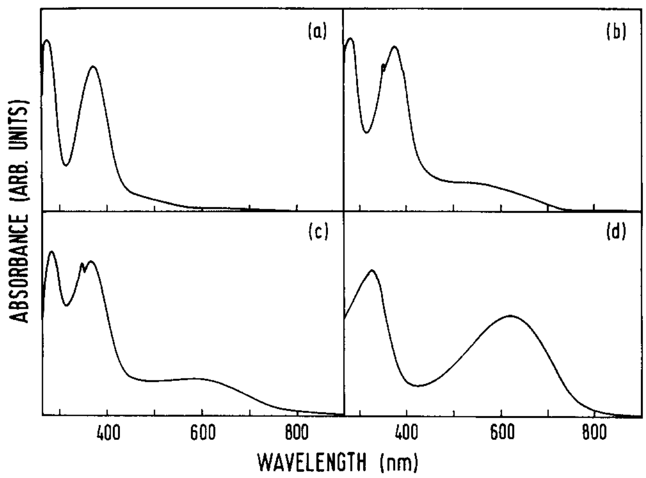

Figure 3 U.v.-vis. absorption spectra of products from aniline polymerization in 0.01 M $HClO_4$: (a) product A, (b) product F, (c) product G and (d) product H after base treatment. NMP is used as the solvent and reference

benzenoid units. However, the u.v.-vis. absorption spectra of the aromatic amines, *p*-aminodiphenylamine and *N,N'*-diphenyl-1,4-phenylenediamine, reveal only one band in the 300 nm region. The nature of the 370 nm band in *Figures 3a*, *3b* and *3c* is not known. It is also interesting to note that when $(NH_4)_2S_2O_8$ is added to a suspension of *p*-aminodiphenylamine in 0.01 M $HClO_4$ at 25°C, the reaction mixture turns purple immediately and a green precipitate is observed within 5 min. The much more rapid rate of reaction of *p*-aminodiphenylamine compared to aniline (see later section) is consistent with the lower oxidation potential of the former[22]. However, after 5 h, the polymer obtained from *p*-aminodiphenylamine has a lower degree of polymerization, as indicated by the *FT*i.r. absorption spectra (and t.g. scan indicates no substantial amount of monomer remaining in the product), than the corresponding product from aniline (product J). This is in agreement with the substantially lower molecular weight of electropolymerized poly(*p*-aminodiphenylamine) (determined by gel permeation chromatography) when compared to polyaniline, and this difference is attributed to the different reaction mechanisms during polymer growth[23]. Although the oxidation of aniline monomers to form the dimeric species has been demonstrated to be the rate-determining step in the polymerization process[3,8], those earlier experiments were performed with 1 M acid. The results obtained with 0.01 M acid show that the dimers and/or higher oligomers remain for substantial periods of time before the polymer is formed. With the 1 M acid (later section) the solid isolated soon after precipitation is clearly long-chain polyaniline salt.

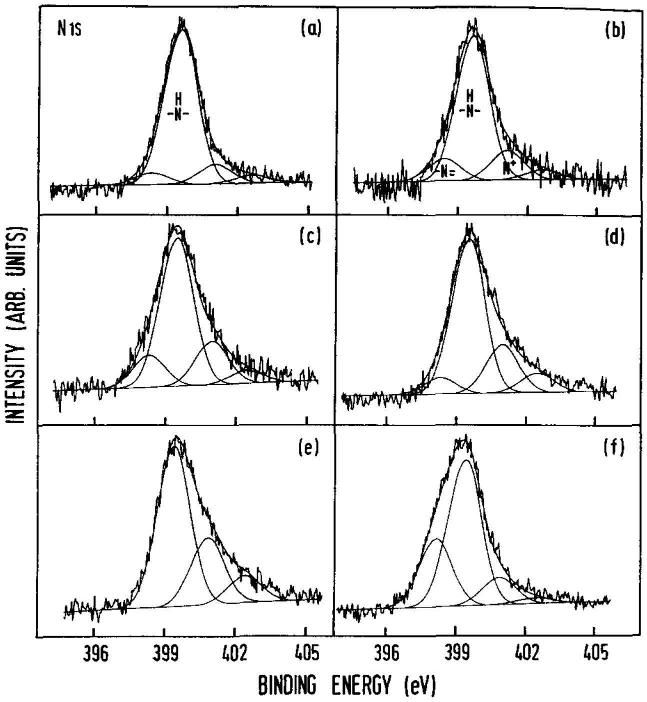

Figure 4 X.p.s. N(1s) core-level spectra of (a) product A, (b) product D, (c) product F, (d) product H, (e) product J and (f) product J after base treatment

X.p.s. measurements

The X.p.s. N(1s) core-level spectrum of product A (*Figure 4a*) confirms that the nitrogen is mainly in the form of amine units (predominant peak at a binding energy (*BE*) of 399.4±0.1 eV)[9]. At 0°C, the increase in reaction time results in the product having a N(1s) core-level spectrum that shows an increase in the intensities of the component peak at a *BE* of 1.2 eV lower than the amine peak and the high *BE* tail above 400 eV. This is illustrated by the N(1s) core-level spectrum of product D in *Figure 4b*. The spectra of products C and E are similar to that shown in *Figure 4b*. The lower *BE* component (at 398.2±0.1 eV) is attributed to the imine nitrogens, while the high *BE* tail, which has been deconvoluted as two component peaks at 1.5 and 3 eV from the amine peak using the fixed f.w.h.m. approach, is assigned to the positively charged nitrogens[9]. Comparing *Figures 4b* and *4c* the similarity in the spectra of the products D (0°C, 3 h 30 min) and F (25°C, 45 min) is consistent with the similarity in the u.v.-vis. absorption spectra, as mentioned earlier. The increase in the oxidation state of products D and F over that of product A is also consistent with the u.v.-vis. absorption spectra in *Figure 3*.

For the 25°C experiment, after the rapid increase in polymerization rate (~2 h), the amount of unprotonated imine units decreases and a concomitant increase in the proportion of positively charged nitrogens is observed (*Table 1*, *Figures 4d* and *4e*). The proportion of amine units remains constant for the five samples. Since $HClO_4$ is used as the protonic acid, the counterion in the polymer salt would be ClO_4^- anion, which has a characteristic *BE* in the 207 eV region in the Cl(2p) core-level spectrum[24]. From *Table 1*, it can be seen that the ClO_4^-/N and N^+/N ratios agree well at long reaction times but the former is substantially less than the latter in the initial stages. For charge neutrality to be maintained, the positive charges on the nitrogen have to be balanced by other anions. The X.p.s. results reveal the presence of a peak at 168.4 eV in the S(2p) core-level spectra, consistent with a sulfate environment[25]. The S/N ratio is about 0.1 for product F but decreases to about 0.05 for product J. When the polymerization was carried out at 0°C, the S/N ratio of the product after 5 h (product E) is close to 0.2. The sulfate anions are the result of the reduction

Table 1 X.p.s. results of reaction products from aniline polymerization in $HClO_4$ at 25°C

Sample	Reaction time	-N=/N[a]	-NH-/N	N^+/N	ClO_4^-/N[b]
F	45 min	0.13	0.63	0.24	0.11
G	1 h 30 min	0.13	0.64	0.23	0.14
H	2 h 15 min	0.07	0.65	0.28	0.30
I	3 h	0.06	0.65	0.29	0.26
J	5 h	0	0.63	0.37	0.30

[a] Neutral imine structure
[b] Based on the corrected chlorine to nitrogen core-level spectral area ratios

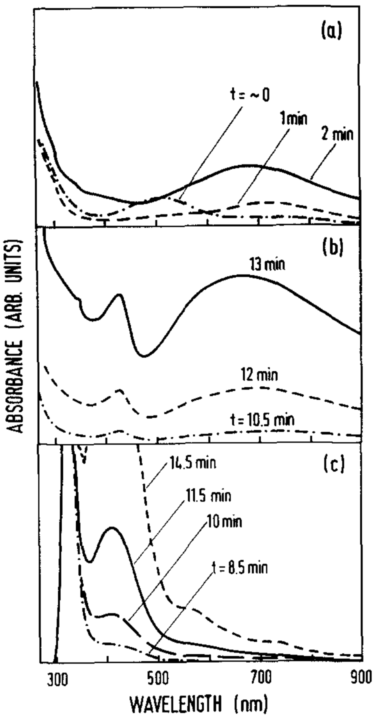

Figure 5 U.v.-vis. absorption spectra of reaction mixture of aniline and $(NH)_4S_2O_8$ in (a) 1 M HCl, (b) 1 M $HClO_4$ and (c) 0.01 M $HClO_4$, at 25°C. Reference: aniline in the respective acid. Time shown is the time from the addition of oxidant

of the oxidizing agent:

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$$

However, based on charge-neutrality considerations, it is likely that the counterions are the monovalent HSO_4^- rather than SO_4^{2-}. A similar conclusion was reached[26] for polyaniline synthesized in H_2SO_4. Using the general representation:

$$\{(\text{-B-NH-B-NH-})_{1-y}[(\text{-B-N=Q=N-})_{1-x}$$
$$(\text{-B-HN}^+\text{=Q=N}^+\text{H-})_x\ (2A^-)_x]_y\}_n$$

for the reaction products, the results obtained for polymerization in 0.01 M $HClO_4$ can be summarized as follows: For the initial reaction product, $y=0$ and n is of the order 1. As reaction time (or reaction temperature) increases, y, x and n increase, resulting in a polymer with both unprotonated and protonated imine units. At long reaction time, x approaches 1 and hence all the imine units are protonated. In the initial stages of polymerization, HSO_4^- anions may serve as the counterions, A^-, but as reaction time increases, this role is mostly taken over by the ClO_4^- anions.

Effect of pH

The reaction mixture, prior to the precipitation of solids, was observed to undergo colour changes, which varied with the type and concentration of acid used. The polymerization of aniline is frequently carried out in 1 M HCl[1,2,8] and under this condition, the reaction mixture first turns pink and then blue followed by precipitation. The u.v.-vis. absorption spectrum of the reaction mixture (*Figure 5a*) shows an absorption band in the 500 nm region for the pink solution, which is obtained immediately upon addition of oxidant. This is then replaced by another band in the 700 nm region as the solution turns blue. The latter increases in intensity and an absorption tail extending into the near-i.r. region is also present. The intermediate pink coloration is not observed when 1 M $HClO_4$ is used and the solution turns blue-green prior to precipitation (*Figure 5b*). Precipitation of solids occurs after a longer reaction time with $HClO_4$ than HCl, being after 13 min for the former compared to 3 min for the latter, at room temperature. In both cases, the solid is dark blue when it first forms and then it gradually turns dark green. When the concentration of the acid (either HCl or $HClO_4$) is lowered to 0.01 M or less, the solution first turns yellow followed by precipitation of a brownish solid (~20 min after addition of oxidant), which gradually darkens. The u.v.-vis. absorption spectra obtained with 0.01 M $HClO_4$ (*Figure 5c*) are very different from those in *Figures 5a* and *5b*.

The differences in the optical spectra of the reaction media of different acids and pH prior to solid precipitation suggest that the initial reaction pathway and intermediates may not be identical. The transient pink coloration observed when the reactions occur in 1 M HCl has been attributed to a radical cation of aniline[27]. Since this intermediate state is not observed when 1 M $HClO_4$ is used, it is possible that either the lifetime of this species is very short or it may not be present as an intermediate. In contrast, the 423 nm band is prominent in *Figure 5b* but not in *Figure 5a*. Absorbance spectra obtained during the electropolymerization of aniline show that the relative intensities of the 420 and 650 nm bands are dependent on the potential[28]. It has been proposed that at low oxidation potential the polyaniline formed results from the polymerization of the monomer radical cations ($C_6H_5N^{\bullet +}H_2$), whereas at higher potential the nitrenium cation ($C_6H_5NH^+$) is formed and this species contributes to the absorption at 420 nm[28]. Thus it is possible to envisage that with the different acids a preferential formation of the different cations also occurs. The much longer time required for precipitation to occur in 1 M $HClO_4$ as compared to 1 M HCl further attests to the differences in the nature and/or the stability of the intermediates in solution. When HCl or $HClO_4$ at low concentration ($\leqslant 0.01$ M) is used, the colour changes of the solution are similar to that obtained with deionized water. It can be expected that, in these solutions, the deprotonation of radical cations will be facilitated. Such a process, which gives rise to neutral free radicals and the subsequent coupling of these radicals with the parent molecules, has been proposed to account for the observed pH dependence of the proportions of the different dimeric species (e.g. *p*-aminodiphenylamine and benzidine) in the electropolymerization of aniline[5]. From *Figure 5c*, it can be seen that the growth of the band in the 700 nm region is slow (compared to the band at 410 nm). The increase in the intensity of the 700 nm band may be indicative of the protonation of the chain of increasing length. The entirely different nature of the solid products isolated soon after precipitation in 0.01 M and 1 M $HClO_4$ (see below) supports the u.v.-vis. absorption spectroscopy results.

The solid products isolated at vastly different polymerization times in 1 M $HClO_4$ do not show the large variation in structure that was described in the earlier sections for the case of 0.01 M $HClO_4$. Although the product yield/monomer ratios after reaction times of

45 min and 5 h in 1 M $HClO_4$ at 0°C are 0.17 and 0.92 respectively, the presence of a strong band at 820 cm^{-1} in the *FT*i.r. absorption spectrum of the precipitate at 45 min indicates that this sample already comprises predominantly *para*-disubstituted polymer chains. The features that are indicative of doped polyaniline (described in an earlier section) are present in both spectra. Similarly, for polymerization in 1 M HCl, the predominantly *para*-disubstituted nature of the chains is evident from the *FT*i.r. spectrum of the product obtained soon after precipitation is observed.

The X.p.s. N(1s) core-level spectrum of the product obtained after 45 min polymerization in 1 M $HClO_4$ is given in *Figure 6a* and the corresponding spectrum for the sample after base treatment is given in *Figure 6b*. For the salt sample, all the imine units are protonated and the N^+/N ratio is calculated to be 0.54. It is interesting to note that in this case the second N^+ component peak is now the larger peak and has shifted closer (2.45 eV) to the amine peak (compare *Figure 4e*). For polyaniline synthesized in 1 M $HClO_4$, the N^+/N rather than the ClO_4^-/N ratio is a better indication of the protonation level, since $HClO_4$ is a non-volatile acid and may remain on the surface of the sample after drying. Although the increase in reaction time from 45 min to 5 h in 1 M $HClO_4$ (at 0°C) results in a substantial increase in product yield, the protonation level is only slightly increased to 0.6. No sulfate peak is observed in the S(2p) core-level spectra of both samples. As expected, when the acid concentration is decreased, the protonation level also decreases (*Table 2*). With the decreasing availability of ClO_4^- anions, the role of sulfate anions as counterions becomes more prominent as illustrated by the increasing S/N ratio in *Table 2*. However, some of the imine units remain unprotonated. As mentioned earlier, when the polymerization is carried out in acid of low concentration (0.01 M or lower) at 0°C, the rate of polymerization is slow and hence the product yield after 5 h is very low compared to the case when 1 M acid is used. However, if the polymerization is carried out at 25°C and sufficient time (~5 h) is allowed for the completion of the reactions, the amount of polymer formed is not strongly dependent on the acid concentration (*Table 2*) In *Table 2*, the base polymer/monomer ratios have been calculated from the yield of the as-synthesized salts after correcting for the proportion of the counterions (as estimated from the X.p.s. data). The *FT*i.r. absorption spectra of these polymers obtained after 5 h show that the polymer chains are predominantly *para*-disubstituted.

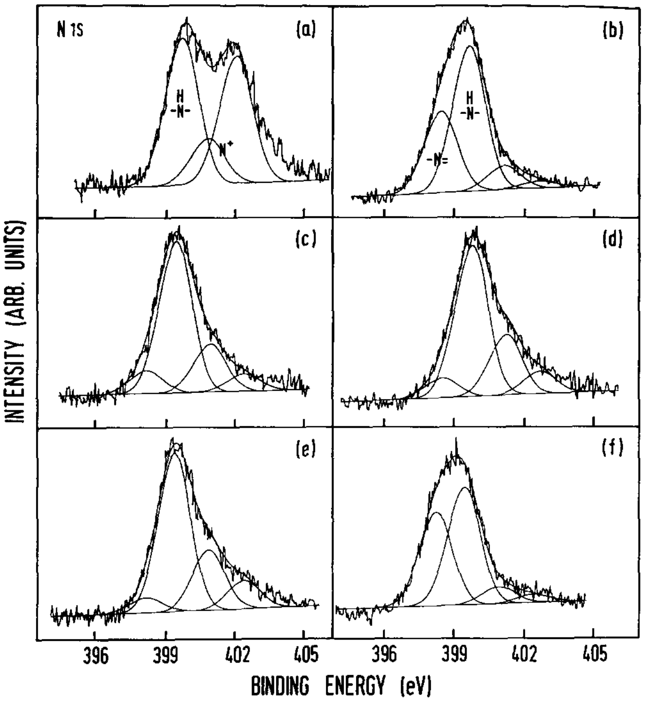

Figure 6 X.p.s. N (1s) core-level spectra of products from (a) 45 min polymerization in 1 M $HClO_4$ at 0°C, (b) base treatment of product in (a), (c) 5 h polymerization in 0.01 M HCl at 25°C, (d) 30 min polymerization in 1 M HCl at 0°C, (e) 5 h polymerization in 1 M HCl at 0°C and (f) base treatment of product in (e)

When HCl is used as the protonic acid in the polyaniline synthesis, the X.p.s. N(1s) core-level spectra of the products show the presence of a neutral imine peak regardless of the concentration of acid used (*Figures 6c, 6d* and *6e*). Although the N^+/N ratios of the salts obtained after 5 h in 0.01 and 1.0 M HCl (*Figures 6c* and *6e*) do not differ as greatly as those obtained with the corresponding concentrations of $HClO_4$, the salt from 0.01 M HCl contains substantial amounts of sulfate anions even after 5 h. The N^+/N ratios of the salts from 1 M HCl remain rather invariant from 0.30 to 0.35 (*Figures 6d* and *6e*) for reaction times ranging from 10 min to 5 h. These values are substantially lower than those obtained with 1 M $HClO_4$. Since HCl is volatile, the possible loss of this species in the high-vacuum environment during X.p.s. measurements will be consistent with the small amount of neutral imine species observed even for the salt from 1 M HCl (*Figures 6d* and *6e*). However, the higher amine content of the salt (*Figure 6e*, NH/N=0.61) as compared to the base (*Figure 6f*, NH/N=0.50) suggests that some of the species may be lost as chlorine as well. With 1 M HCl, the polymer obtained has a higher oxidation state (as indicated by the imine/amine ratio of the base polymer) than the corresponding polymer obtained with 1 M $HClO_4$ (comparing *Figures 6f* and *6b*).

Table 2 Effect of acid concentration on protonation behaviour of polyaniline

$HClO_4$ concentration	Salt					Base polymer
	-N=/N	-NH-/N	N^+/N	ClO_4^-/N	S/N	Monomer[c]
0.1 M[a]	0	0.49	0.51	0.59	~0	0.48
0.01 M[b]	0	0.63	0.37	0.30	0.05	0.40
0.002 M[b]	0.10	0.67	0.23	0.11	0.14	0.42
0 (deionized H_2O)[b]	0.11	0.66	0.23	0	0.19	0.36

[a] Polymerization at 0°C for 5 h
[b] Polymerization at 25°C for 5 h
[c] Weight ratio

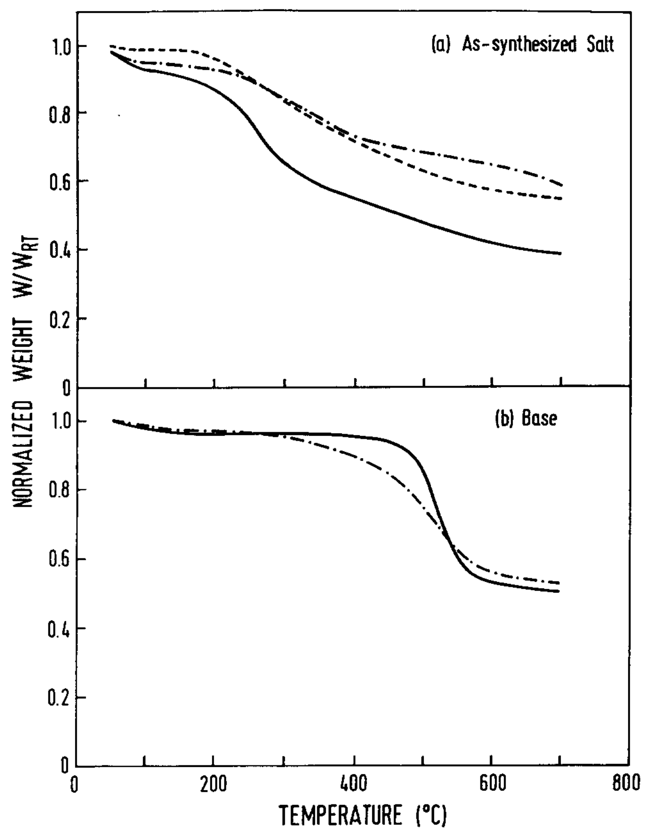

Figure 7 T.g. scans of (a) product G (– – –), product J (—·—) and as-synthesized salt from 5 h in 1 M $HClO_4$, 0°C (——), and (b) product J after base treatment (—·—) and salt from 1 M $HClO_4$ after base treatment (——). W_{RT} is the weight at room temperature

The thermal stability of the products synthesized in reaction media of different pH for varying periods of time can provide an indication of their structural variations. The t.g. scan of the salt synthesized in 1 M $HClO_4$ for 5 h shows a steady weight loss immediately upon heating above room temperature and the major weight loss occurs at about 200°C (*Figure 7a*). The initial weight loss is ascribed to absorbed water, which is bound by hydrogen bonds to the acidic protons, and the amount increases with the protonation level[29,30]. The major weight loss, which is exothermic in nature, is attributed to the decomposition of the ClO_4^- anions[31]. The smaller initial weight loss for products J and G (*Figure 7a*) is consistent with the smaller amount of water associated with the protons since the level of protonation is lower in these samples. However, since the thermal degradation behaviour of the as-synthesized salts is affected by the decomposition of the ClO_4^- anions and the subsequent reactions of the chlorine species with the polymer[32], the differences in the stability of the different polymers are not obvious from the t.g. scans of the salts. The t.g. scans of the bases obtained from the salt from 1 M $HClO_4$ (5 h) and product J are compared in *Figure 7b*. The former is stable to 425°C, whereas the latter starts to decompose at 300°C. However, the weights remaining at 700°C are similar for both base samples. The decomposition of the base sample obtained from polymerization in deionized water also commences at 300°C. A decrease in the decomposition temperature (by 75°C) is also observed for the base sample from polymerization in 1 M $HClO_4$ when the reaction time is shortened to 45 min. However, the polymerization in either 1 M $HClO_4$ or 1 M HCl for 5 h yields base samples with no substantial differences in thermal degradation behaviour. Thus the t.g. data indicate that structural differences exist among the base polymers obtained at different reaction times or pH even though these differences may not be apparent from the x.p.s. or *FT*i.r. absorption spectroscopy data. Conversely, the base polymers obtained after 5 h with 1 M acid show little differences in thermal stability even though the type of anions (Cl^- or ClO_4^-) and level of protonation of the salts may be different.

CONCLUSION

In summary, we have investigated the oxidative polymerization of aniline by $(NH_4)_2S_2O_8$ in $HClO_4$ and HCl of various concentrations. The polymerization rate decreases with decreasing acid concentration. Moreover, the u.v.-vis. absorption spectra of the reaction mixtures indicate that the initial reaction pathways and intermediates are dependent on the pH as well as the acid type. When the acid concentration is 0.01 M, the solid that is initially precipitated out consists of oligomer salts incorporating anions from the protonic acid and sulfate anions but a substantial proportion of the imine units in these salts are unprotonated. With 0.01 M $HClO_4$ at 25°C, it takes approximately 3 h for the polymerization to be completed, resulting in predominantly *para*-disubstituted chains, and after this time essentially all imine units are protonated and the anions are predominantly ClO_4^-. However, with decreasing acid concentration, the sulfate anions play an increasingly important role as counterions but some imine units remain unprotonated even after 5 h. In contrast, with 1 M $HClO_4$ or HCl the solid that is isolated soon after precipitation consists of *para*-disubstituted chains. In the former, complete protonation of the imine units by ClO_4^- anions is observed while a small amount of unprotonated imine units in the latter may be due to loss of HCl during X.p.s. measurements. The decrease in the thermal stability of the polymers when the concentration of the protonic acid is decreased from 1 to 0.01 M or lower suggests that a certain degree of structural variation exists among the polymers.

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