

polymer communications

Effects of high hydrochloric acid concentration on aniline chemical polymerization

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The rate of aniline polymerization, measured by calorimetry, decreases when the hydrochloric acid concentration in the polymerization solution is increased from 2 to 6 M. The amount of chloride covalently bonded to the aromatic rings of the polymer backbone, estimated from the presence of new vibrational bands in the i.r. spectra, increases with an increment of hydrochloric acid concentration. The enlarged substitution on the polymer backbone is correlated with a decrease of the extension of the electronic conjugation, as shown by the shift towards higher energy of the broad band due to extended conjugation. The trend is related with a simultaneous decrease of the polymer d.c. conductivity. © 1997 Elsevier Science Ltd.

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Introduction

Polyaniline (PANI) is one of the most promising materials for applications in batteries, electrochromic displays, sensors, etc. The general method of synthesis of PANI is the oxidative polymerization of the monomer using a chemical oxidant or electrochemical methods. Different mechanisms have been proposed for the chemical and electrochemical polymerization of aniline¹. Tzou and Gregory² studied the kinetics of the chemical polymerization of aniline by measuring the decrease in aniline concentration. The results were explained assuming that two different rate constants exist, in the presence and absence of polymer^{3,4}. They observed that increasing the acid concentration (between 0.1 M and 1 M) increases the polymerization rate and suggested that the reaction between oxidized polymer and aniline involves proton transfer. On the other hand, Lux⁵ measured the polymerization of PANI at different sulfuric acid concentrations and found a significant decrease of yield at high acid concentrations. Different acids can be used as polymerization media, but aqueous hydrochloric acid is the most widely used media for aniline polymerization¹. Kang *et al.*⁶ have observed, using X.p.s., the formation of covalently bonded chloride when aniline is polymerized in this media.

We are interested in the optimization of aniline bulk polymerization towards polymer industrial production. An increase in polymerization rate will be advantageous for the industrial production because it shortens the reactor residence time and therefore, could prevent degradative side reactions. However, the changes of procedure should not lead to deterioration of the polymer properties. Therefore the effect of media conditions has to be explored carefully at bench top pilot plant scale before up-scaling the synthesis. In the

present communication, the effect of the hydrochloric acid concentrations on the polymerization kinetics and PANI properties is investigated.

Experimental

Aniline (Merck) was twice distilled under reduced (20 mm Hg) pressure and stored below 4°C under nitrogen atmosphere. All solutions were prepared with twice distilled water. All other reagents were of analytical quality.

Preparations were carried in a stirred 1 l, all glass reactor under thermostatization, obtained by immersing the reactor in an agitated ice–water bath. The design of the reactor assures reproducible control of the stirring and thermal conditions during polymerization. A thermistor probe was immersed in the solution to measure the temperature change during polymerization. The ratio of oxidant ($S_2O_8(NH_4)_2$) to monomer (aniline) was always 0.8/1. Between runs the reactor was cleaned by treatment, for at least 8 h, in a cleaning solution (1/1 mixture of concentrated sulfuric and nitric acid).

The copolymer of aniline and 2-chloroaniline was prepared by treating a 1 M HCl solution, 0.1 M both in aniline and 2-chloroaniline, with equimolar quantity of ammonium persulfate. The copolymer was further treated as the PANI samples.

The measurements of FTi.r. were performed on the polymer in its base state to obtain a clearer picture of the vibrational spectral structure. To achieve the conversion into base form, the polymer materials were stirred for 48 h in a 1 M NH_4OH solution. Next, it was dried under vacuum at ambient temperature for 48 h. The polymer was mixed with KBr and pellets for transmission measurements were prepared.

The conductivity measurements were made by the four point method on pressed pellets of pure material. All polymers were first converted to base form and later reprotonated by a 24 h equilibration with 1 M HCl solution, followed by drying at ambient temperature

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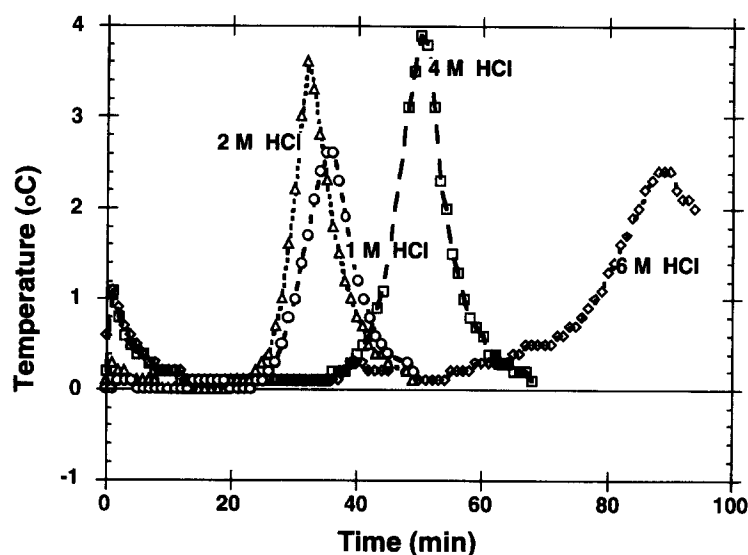


Figure 1 Calorimetric measurement of the aniline polymerization in electrolyte media with different HCl concentration. (○) 1 M HCl, (Δ) 2 M HCl, (□) 4 M HCl, (◇) 6 M HCl. Aniline concentration = 0.1 M. Persulfate concentration = 0.08 M. Time taken from the addition of oxidant

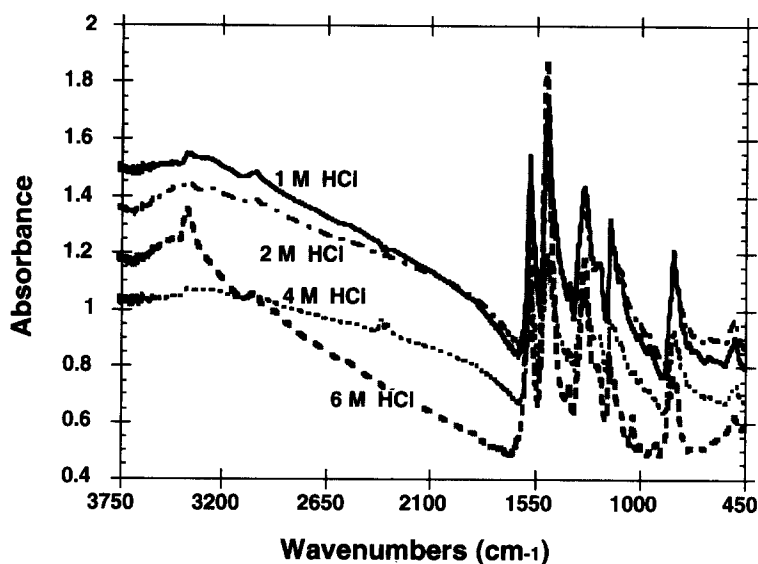


Figure 2 FTi.r. spectra of polyaniline produced in electrolyte media with different HCl concentrations: (— · — ·) 1 M HCl, (—) 2 M HCl, (· · · ·) 4 M HCl, (— — —) 6 M HCl. Pellet concentration = 1% w/w in KBr. Polymer in its emeraldine base state

Table 1 Dependence of the d.c. conductivity of PANI on the HCl concentration in the polymerization solution

HCl concentration (mol l ⁻¹)	D.c. conductivity (S cm ⁻¹)
1	10.2
2	4.1
4	1.7
6	0.29

under vacuum. The pellets were produced under *ca.* 10 000 kg cm⁻² of pressure.

Results and discussion

According to previous results², increasing the acid concentration in the range 0.1–1 M leads to a higher polymerization rate. We explore a higher acidity range (1–6 M). The results of calorimetric measurements for different acid concentration are shown in Figure 1. As the reactor is under constant thermal (cooling) flux,

when heat is produced a temperature increase occurs that decays as soon as the heat production has finished. In the polymerization of aniline, the heat production occurs at the end of the polymerization giving a measure of the total reaction time⁴. As can be seen in Figure 1, the reaction time decreases slightly between 1 M and 2 M HCl and increases significantly for higher concentrations. This indicates that the rate is slower at high acid concentrations. The trend between 1 M and 2 M would be in agreement with the one reported by Tzou and Gregory² while at higher concentrations it is reversed. The tendency at higher concentrations is more in agreement with that observed by Lux⁵.

The d.c. conductivity of PANI samples prepared in hydrochloric acid solutions of different concentrations is shown in Table 1. As can be seen, the conductivity decreases with increasing acid concentration. A possible reason of the conductivity change is an alteration of polymer structure. Therefore we investigated the structure using FTi.r. spectroscopy.

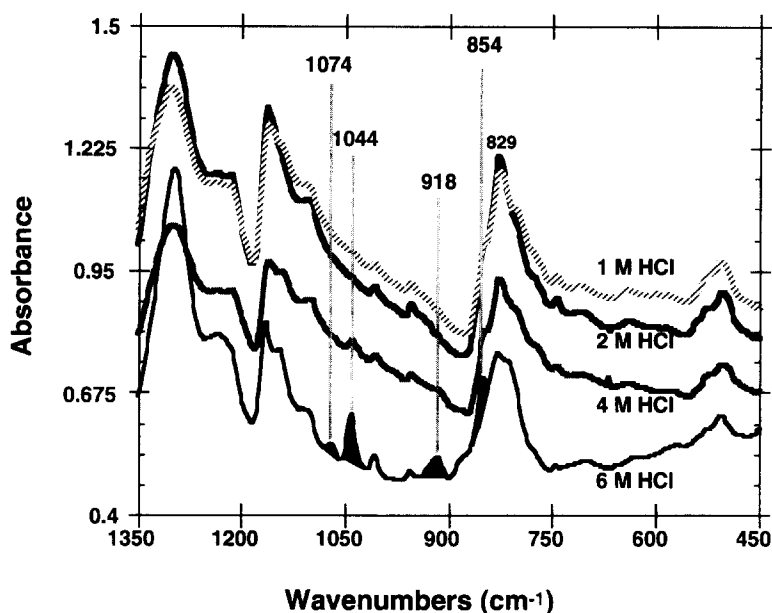


Figure 3 Expanded view of a region of the spectra shown in *Figure 2*. Marked are the bands occurring in Cl substituted PANI and the band at 829 cm^{-1}

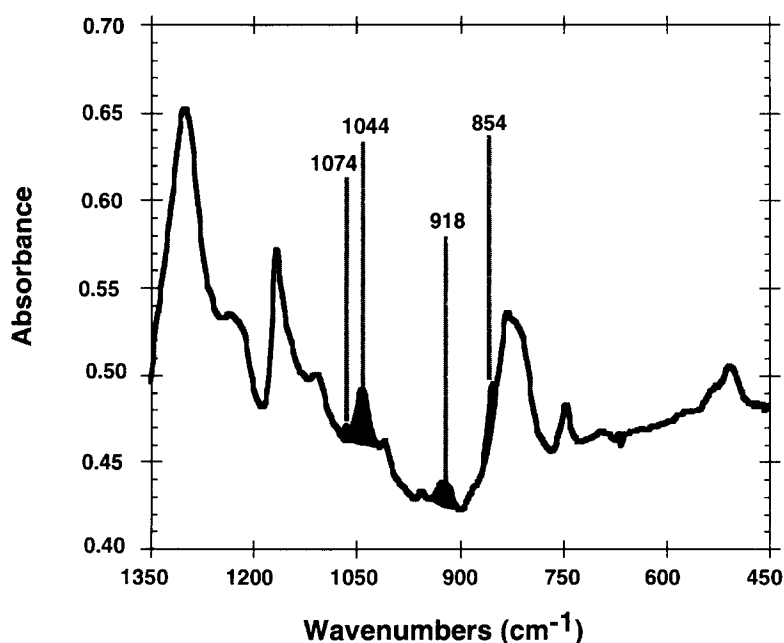


Figure 4 FTIR spectra of a copolymer of 2-chloroaniline and aniline produced in 1 M HCl. Pellet concentration = 1% w/w in KBr. Polymer in its emeraldine base state

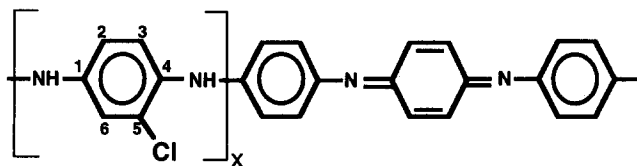
The FTIR spectra of PANI samples prepared in different HCl solutions are shown in *Figure 2*. The intensity of the broad band (at wave numbers $> 2000\text{ cm}^{-1}$), due to electronic extended conjugation, decreases when the HCl concentration in the polymerization solution increases. Accordingly, the position of the band shifts to higher energies (higher wavenumbers). The shift agrees with the observed decrease of the conductivity due to less extended electronic conjugation in the polymer chains⁷.

Additionally, changes are observed in the vibrational bands in region below 2000 cm^{-1} . An expanded view of the spectra (*Figure 2*) shows that, in addition to the bands already present in PANI, new bands appear at 1074 , 1044 , 918 and 854 cm^{-1} . Those bands are clearly

apparent in the PANI produced in 6 M HCl. The bands at 1074 and 1044 cm^{-1} are characteristic for skeletal vibrations of halogen substituted aromatic rings, the band at 1074 cm^{-1} being due to the *meta* substituted rings and the one at 1044 cm^{-1} due to *ortho* substituted rings⁸. The bands at 918 and 854 cm^{-1} can be assigned to the out-of-plane bending of C-H vibrations bonds on the aromatic rings in the backbone, the one at 854 cm^{-1} being due to 1,2,4 trisubstitution⁹ and the one at 918 cm^{-1} to an isolated aromatic hydrogen⁸. The intensity of the bands increase with an increase of HCl concentration in the polymerization media.

The bands suggests strongly that covalently bonded Cl is formed during polymerization in HCl media and that the substitution amount correlates with the HCl

concentration. The assignation corresponds to the polymer unit structure



where x denotes the degree of Cl substitution.

The Cl substituent is in position *ortho* to carbon 4 and *meta* to carbon 1, accounting for the skeletal vibration bands at 1074 and 1044 cm^{-1} . The band at 829 cm^{-1} due to 1,4 C–H aromatic bonds⁹ (present in unsubstituted PANI) is now accompanied by a band at 854 cm^{-1} due to the 1,2,4 trisubstituted C–H aromatic bond⁹. Moreover, the FTi.r. spectrum (Figure 4) of poly((2-chloroaniline)-*co*-aniline), prepared as described in the Experimental part, reveals additional (compared with PANI) bands at 1044, 1074, 918 and 854 cm^{-1} , confirming the assignment.

A seemingly simple way to check the increasing amounts of chlorine linked to the chain would be by elemental chemical analysis. However, in PANI it is necessary to eliminate the chloride present as dopant prior to the analysis as the chloride amount may change with small changes of polymer redox state. The elimination could be performed by deprotonation of the matrix. Elemental analysis of the polymer prepared in 6 M HCl solution, and converted into its base state, reveals up to 8% in weight of chlorine. However, the analysis of various samples show low reproducibility. The FTi.r. spectra of the same samples are quantitatively reproducible. As Cl^- ions are not i.r. active in the spectral region studied, it is likely that the variations in the chlorine content, observed in chemical analysis, are due to the presence of variable amounts of trapped Cl^- ions. Further studies will be carried out using X.p.s. which allow us to discriminate the contribution of covalent and ionic chlorine.

The presence of a significant amount of Cl bonded to aromatic rings in the polymer leads to a decrease in electronic conjugation (as evidenced in the FTi.r. spectra) and a decrease of the conductivity (Table 1). This is in agreement with the fact that poly(2-chloroaniline) has a lower conductivity ($10^{-3} \text{ S cm}^{-1}$)¹⁰ than polyaniline due to a combination of inductive (withdrawing of electrons by the Cl group) and steric effect (loss of planarity due to the size of the Cl substituent).

An open question remains the mechanism of chloride attack on the polymer backbone. Given the potential of $\text{S}_2\text{O}_8^{2-}/\text{SO}_4^{2-}$ (2.01 V/rhe) and Cl_2/Cl^- (1.36 V/rhe)¹¹ redox couples, chlorine formation in the media is thermodynamically favourable. However, it has to be kinetically

inhibited. An increase of chloride concentration could accelerate the reaction rate. Preliminary results indicate that polymerization of aniline in a 1 M HCl solution containing NaCl (saturated at 0°C, *ca.* 3 M) produces a polymer that shows i.r. bands similar to the one produced in 4 M HCl. Those results would suggest that a high chloride ion concentration and not a high proton concentration is necessary to promote the attack. In that sense, Kang *et al.*¹² proposed the existence of partial charge transfer between the chloride ion and the aromatic rings of polyaniline in the base of X.p.s. data. Such charge transfer complex could also act as an intermediate state of the substitution reaction. It would be important to detect the formation of chlorine during the reaction. Studies on this direction will be carried out.

Conclusions

The results presented here support the claim by Kang *et al.*⁶ that preparation of PANI by polymerization in aqueous HCl could lead to some amount of Cl covalently bonded to the polymer backbone. It has been shown, using FTi.r. spectroscopy, that the amount of Cl bonded increases when the HCl concentration present in the polymerization solution increases. The enlargement of Cl substitution leads to a decrease in the extent of electronic conjugation and therefore, the conductivity of the prepared polymer. The changes are correlated with a lower rate of polymerization. The results suggest that it is not advisable to produce pure PANI in HCl concentrations higher than 1 M. Further studies of the effect of acid concentration and other chloride ion salts, to try to elucidate the mechanism of attack, are underway in our laboratory.

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