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Spectroscopic Investigation of the Chemical Polymerization of Aniline with $FeCl_3$ in Acetonitrile

SULTAN UZUN* and MUZAFFER CAN
Department of Chemistry, Gaziosmanpasa University, Campus of Tasliciftlik, Tokat-60250, Turkey
Fax: (90)(212)473 2634; Tel: (90)(212)4732600; E-mail: suzun707@hotmail.com

Chemical polymerization of aniline with anhydrous ferric chloride ($FeCl_3$) in non-acidic medium was investigated using experimental methods such as conductivity measurements, thermal analysis (TGA-DTG) UV-visible and FTIR spectroscopy. As well known, $FeCl_3$ is a Lewis acid, which can form complex with aniline. In the chemical polymerization, these properties of $FeCl_3$ are not taken into consideration. The studies indicate that $FeCl_3$ behaves as a Lewis acid, a substance, forming complex or oxidant material depending of the acidity of medium.

Key Words: Conducting polymers, Polyaniline, Chemical polymerization, Oxidant effect, $FeCl_3$.

INTRODUCTION

Polyaniline is one of the most promising conducting polymers due to its high conductivity, good redox reversibility and good stability in aqueous solutions and air. These properties provide favourable conditions for its potential applications in rechargeable batteries, corrosion prevention, electrocatalaysis, electrochromic devices and super capacitor. In addition, the research in the field of polyaniline nanostructures has also received a great deal of attention[1]. Polyaniline can occur in a number of well-defined oxidation states. The different states range from the fully reduced leucoemeraldine *via* protoemeraldine, emeraldine and nigraniline to the fully oxidized pernigraline. Unlike most other polyaromatics, the fully oxidized polyaniline is not conductive. Polyaniline becomes conducting when it is protonated to generate charge carries. This process is generally called protonic acid doping, which makes polyaniline so unique. In the case of the protonated emeraldine, a delocalized poly (semiquinone radical cation) is the polaronic carrier. The conductivity is affected by the water content. Completely dry samples are five times less conductive than samples containing some water[1].

The conducting polymers, such as polypyrrole, polyaniline and polythiophene are prepared either by chemical[2-7] or electrochemical[8-12] synthesis. Aniline and pyrrole[13] are most easily oxidized monomers and a variety of oxidizing agents are available for chemical preparation of polypyrrole and polyaniline[14]. In the chemical polymerization of aniline, $FeCl_3$ is usually used as oxidant reagent. $FeCl_3$ has some characters which are acid (Lewis acid), complex forming and oxidant. In the chemical polymerizations, these properties (acid and forming complex) do not take into consideration.

In this study, chemical polymerization of aniline monomer with the $FeCl_3$ was investigated using UV-vis spectroscopy, TGA and FTIR studies, conducting measurements.

EXPERIMENTAL

Aniline (97 % Aldrich) was distilled before use. Anhydrous acetonitrile (99.8 %, Aldrich), perchloric acid ($HClO_4$) (60-62 %, BDH), anhydrous aluminium chloride ($AlCl_3$) (99 %, Aldrich), anhydrous ferric chloride ($FeCl_3$) (99 %, Fuluka) were used as received. Tetrabutylammoniumperchlorate (TBAP) used as dopant material was prepared by reacting a 68 % aqueous solution of perchloric acid with a 40 % aqueous solution of tetrabutylammoniumhydroxide. It was recrystallized from ethanol and water mixture and dried under vacuum.

The UV-vis spectrum was recorded in the range of 300-1000 nm using Jasco V-530 UV-visible spectrometer. FT-IR spectrum of polymer-KBr pellet was obtained using Jasco FTIR-430 Fourier transform infrared spectrometer in the range from 2000 to 400 as transmission. The TGA and DTG curves were obtained using PRIS Diamond TGA/DTA (DSC) apparatus in a dynamic nitrogen atmosphere (heating rate of 10 ºC/min, platinum crucibles, mass *ca.* 10 mg and temperature range 35-600 ºC. The dry conductivity values were measured using a four-probe technique. At least 10 different current values were used in the measurement of the potential drop for each polymeric sample in pellet form.

Synthesis of polyaniline samples: In the synthesis of polyaniline using $FeCl_3$, 1.0 mmol monomer, 1.0 mmol oxidant and various amounts of $HClO_4$ (1.0, 3.0 and 6.0 mmol) acid were mixed and these mixtures were stirred and kept in the dark medium for 24 h at 5 ºC. The colloidal polymer samples were subjected to multiple rinsing procedures with acetonitrile to remove any residual oxidants, dopant material, soluble oligomers formed during polymerization and oxidative products and then dried under vacuum before FT-IR, TGA and dry conductivity measurements.

RESULTS AND DISCUSSION

UV-vis studies: Acetonitrile solutions containing aniline, $FeCl_3$ and aniline + $FeCl_3$ mixture (1:1) were prepared and examined using UV-vis spectrometer (Fig. 1a). Each $FeCl_3$ oxidant and aniline monomer has three bands at 238, 313, 360 nm and 207, 240 and 289 nm, respectively. As can be seen in Fig. 1a, some absorption bands of aniline (at 240 and 289 nm) and $FeCl_3$ (at 238 and 313 nm) overlap with each other. For this reason, it can not be seen clearly by spectroscopic means whether a reaction occurs between aniline and $FeCl_3$ or not.

Acetonitrile solutions containing aniline, aniline + increasing amount of $FeCl_3$ were prepared and each solution was examined to determine the oxidative effect of $FeCl_3$ on chemical polymerization of aniline. As can be seen in Fig. 1b, when increased amounts of $FeCl_3$ were added to the aniline solution, no shift in the positions of the bands was observed. In addition, there is no new absorption band above 400 nm belonging to polyaniline polymers or oligomers[15] when formed with the addition of $FeCl_3$. It does not mean that aniline and $FeCl_3$ do not react with aniline to form other products except polymer. In addition to the oxidative reaction of $FeCl_3$, it can also be expected that two reactions may occur between aniline and $FeCl_3$. One of them is an acid-base reaction because aniline is a base and $FeCl_3$ is a Lewis acid. The other is a complex formation reaction because aniline is ligand and Fe^{3+} is a transition metal ion, which can form a complex.

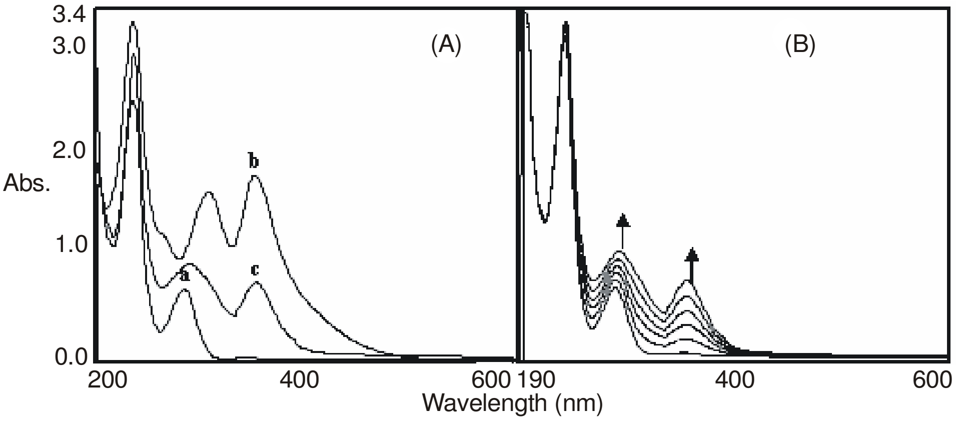

Fig. 1. UV-vis spectra of acetonitrile solutions contain aniline (1×10^{-3} M) A(a), $FeCl_3$ (1×10^{-3} M) A(b), aniline (1×10^{-3} M) and $FeCl_3$ (1×10^{-3} M) A(c); aniline and increasing amount of $FeCl_3$ (The concentration of aniline is 1×10^{-3} M)

To determine whether an interaction occurs between aniline and $FeCl_3$ or not, $AlCl_3$ was used instead of $FeCl_3$, because $AlCl_3$ is a Lewis acid like $FeCl_3$. $AlCl_3$ does not behave as an oxidant and has not absorption bands[16] between 200 and 1000 nm. The spectra were obtained from acetonitrile-aniline solutions to which increased amounts of $AlCl_3$ were added (Fig. 2a). The intensities of the absorption bands of aniline monomer at 238 and 289 nm decrease with addition of $AlCl_3$ into the aniline-acetonitrile solution. The results indicate that a reaction occurred between aniline and $AlCl_3$. The same type of interaction was observed between aniline and $HClO_4$ (Fig. 2b). As well known, these reactions occurring between aniline-$AlCl_3$ and aniline-$HClO_4$ are acid-base reactions. Increasing the intensity of the bands of $FeCl_3$ at 238 and 313 nm covers the change in the aniline absorption bands occurring with aniline-$FeCl_3$ reactions. So, the reaction occurring between aniline and $FeCl_3$ is not observed spectroscoplly. According to these experimental results, it can be suggest that similar acid-base reaction should occur between aniline and $FeCl_3$, because $FeCl_3$ is also a Lewis acid like $AlCl_3$.

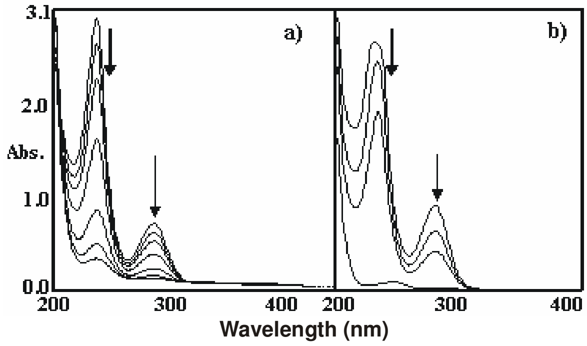

Fig. 2. UV-vis spectra of acetonitrile solutions contain (a) aniline (1×10^{-3} M) and increasing amounts of $AlCl_3$; (b) aniline (1×10^{-3} M) and increasing amounts of $HClO_4$

If equivalent amount of acid to the aniline is added into polymerization solution, the absorption bands of aniline at 238 and 289 nm disappear as mentioned above (Fig. 2b). When the $FeCl_3$ is gradually added to the acid-aniline mixture, the intensity of the band observed at 360 nm increases (Fig. 3). The increase in the band intensity continues until the ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:1. The intensity of band observed at 312 nm, which belongs to the $FeCl_3$, does not change. This behaviour is not observed in the non-acidic medium (Fig. 1b). It is probable that this new band observed at 360 nm belongs to a new product. It can be thought that this new product may be an aniline-$FeCl_3$ complex which occurs in acidic medium. When the excessive amount of the $FeCl_3$ was added to acid-aniline mixture, the bands of the soluble polyaniline were observed above 400 nm (Fig. 4). These bands are attributed to polaron/bipolaron transitions of polyaniline, as reported in the literature[17,18].

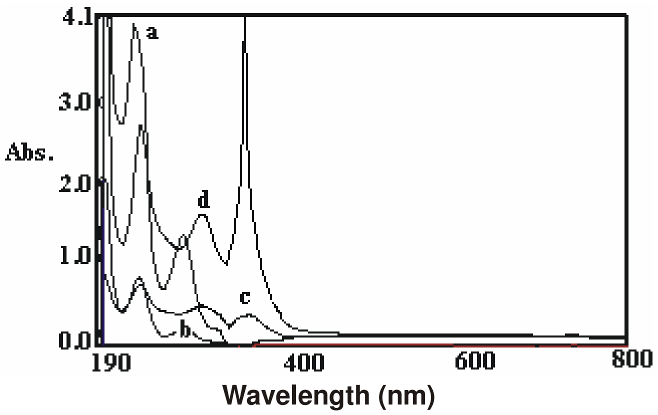

Fig. 3. UV-vis spectra of acetonitrile solutions contain (a) Aniline (1×10^{-3} M), (b) Aniline (1×10^{-3} M) and $HClO_4$ (1×10^{-3} M), (c) $FeCl_3$ (1×10^{-3} M), (d) Aniline (1×10^{-3} M), $HClO_4$ (1×10^{-3} M) and $FeCl_3$ (1×10^{-3} M)

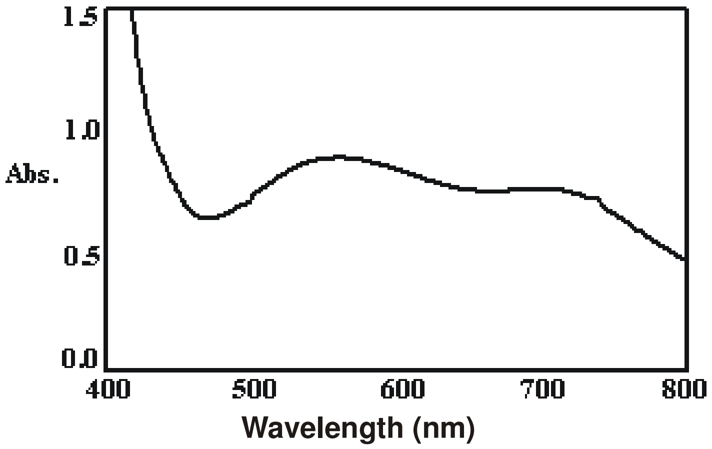

Fig. 4. UV-vis spectrum of acetonitrile solution containing aniline (1×10^{-3} M), $HClO_4$ (1×10^{-3} M) and $FeCl_3$ (5×10^{-3} M)

When excessive amounts of the $FeCl_3$ were added to the acetonitrile-aniline solution without acid and kept for 24 h, it was observed that colored and soluble polyaniline occurred in acetonitrile, not in a precipitate form. Polyaniline polymer as precipitate form was only synthesized in the acidic medium using $FeCl_3$ oxidant, because the acidic property of $FeCl_3$ can be avoided by forming anilinum salt. $FeCl_2 + H_2O_2$ mixture has also been used as oxidant in the chemical polymerization of aniline monomer in aqueous-HCl medium instead of $FeCl_3$ to produce $FeCl_3$[15]. It is probable that this formation prevents the acidity behaviours of the $FeCl_3$.

According to the results obtained, the behaviour of $FeCl_3$ can be summarized as follows: $FeCl_3$ behaves as an acid (Lewis acid) without protonic acidic media. When the ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:1, $FeCl_3$ can behave as a substance which forms a complex in acidic media. Only beyond this ratio, it behaves as an oxidant for the chemical polymerization of aniline.

FTIR Studies: Fig. 5 shows the FTIR spectra of polyaniline samples synthesized by using $FeCl_3$. Polyaniline samples had strong absorption peaks at 1699, 1621, 1540, 1294, 1240, 615and 460. The peaks at 1565 and 1164 cm^{-1} are assigned to the quinonoid units in polyaniline. The peak attributed to the benzenoid ring stretching is observed between 1500 and 1400 cm^{-1} [19]. As seen in Fig. 5a, when the ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:3, the peak at 1464 cm^{-1} attributed to the benzenoid unit for polyaniline was not observed in the spectrum of polyaniline synthesized. So, polyaniline synthesized by using $FeCl_3$ only contains quinonoid units which are not conductive.

If the ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:6, the peaks at 1565 and 1464 cm^{-1}, which belong to the benzenoid and quinonoid units of polyaniline, were not observed (Fig. 5b). The polyaniline synthesized in this medium was over oxidized by excessive $FeCl_3$.

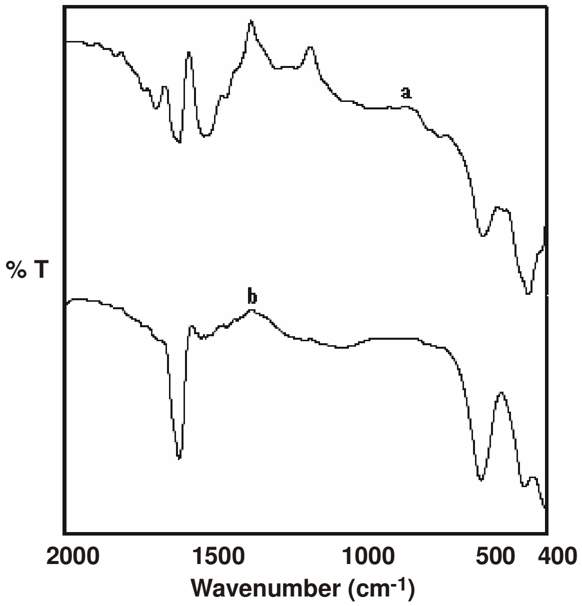

Fig. 5. FTIR spectra of polyaniline samples synthesized in the various ratios; (a) The synthesis ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:3, (b) The synthesis ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:6

Thermal studies: When the ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:3 there are two weight loss steps in the TGA and DTG curves of polyaniline (Fig. 6). The first weight loss may be due to the loss of the dopant above 250 °C, the second weight loss observed above 400 ºC may be due to loss of the decomposition of polyaniline. It was observed that the polyaniline in the ratio 1:1:6 had four weight loss steps which are above 200, 400, 700 and 900 ºC (Fig. 7). As mentioned above, the weight loss observed above 200 and 400 ºC results from loss of the dopant and decomposition of polyaniline, respectively. It is possible that the weight loss observed above 700 and 900 ºC results from the decomposition of polyaniline over oxidized by excessive $FeCl_3$.

Conductivity measurements: The conductivity values of the polyaniline synthesized using $FeCl_3$ oxidant was also measured for its characterization. As mentioned above, polyaniline was not synthesized using $FeCl_3$ non-acidic medium. Polyaniline polymer was prepared as precipitate by using $FeCl_3$ in the presence of acid and their conductive values were measured. When the ratios of acid-monomer-$FeCl_3$ are 1:1:1, 1:1:3 and 1:1:6, the conductivity values measured are 0.47, 21.7 and 6.80 S cm^{-1}, respectively. As seen in these values, the conductivity of polyaniline depends on both the amount of the $FeCl_3$ and acid used.

The conductivity value of polyaniline synthesized in the presence of higher amounts of $FeCl_3$ decreases because of the over oxidation of the polyaniline by $FeCl_3$.

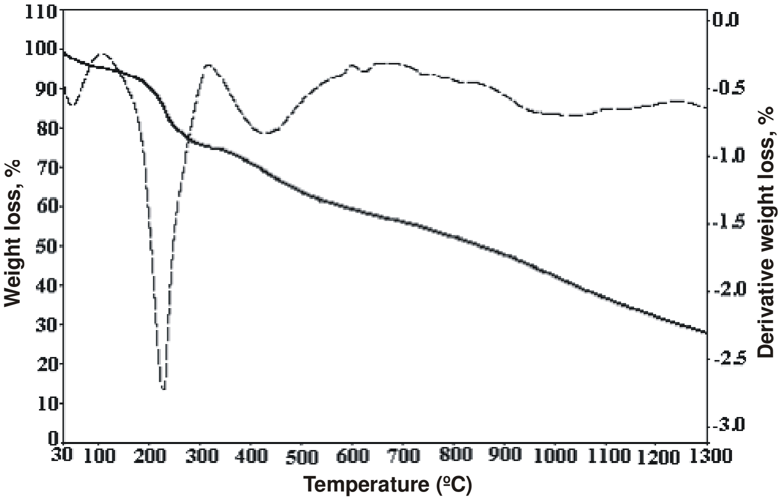

Fig. 6. TG-DTG curves of polyaniline sample synthesized (The synthesis ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:3) in nitrogen atmosphere at heating rate of 10 ºC/min

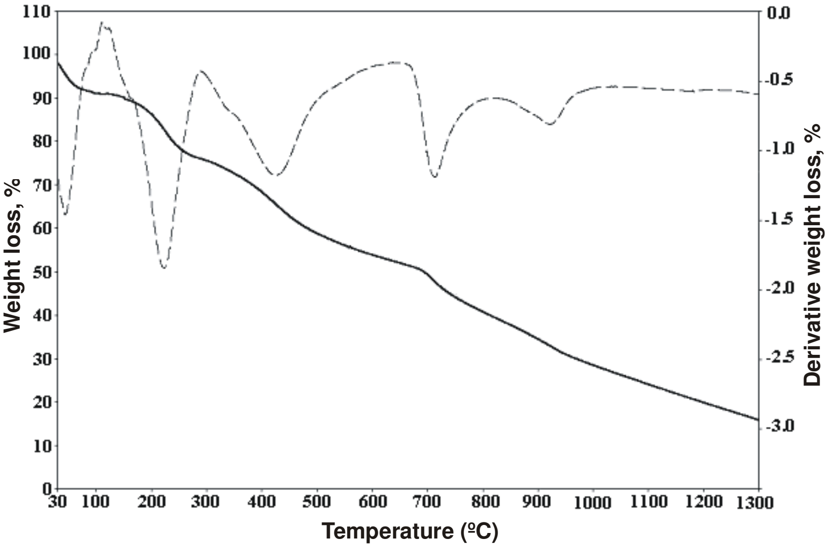

Fig. 7. TG-DTG curves of polyaniline sample synthesized (The synthesis ratio of aniline-$HClO_4$-$FeCl_3$ is 1:1:6) in nitrogen atmosphere at heating rate of 10 ºC/min

Conclusion

The effect of the oxidants on chemical polymerization of aniline monomers can be summarized as follows. When $FeCl_3$, is used as an oxidant in chemical polymerization of aniline in acetonitrile, either it reacts with the aniline, a base or behaves as a substance, forming a complex. Its oxidation capability is limited only to the formation of very low molecular weight oligomers.

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