

## Oxidizing Effect of the $\text{Cu}(\text{ClO}_4)_2$ on Chemical Polymerization of Aniline in Anhydrous Media

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The oxidative effect of copper(II) perchlorate [ $\text{Cu}(\text{ClO}_4)_2$ ] on chemical polymerization of aniline was elucidated by using experimental methods such as conductivity measurements, thermogravimetric analysis, UV-visible and FTIR spectroscopy. Experimental studies indicate that copper(II) perchlorate can be used as oxidant in the chemical polymerization of aniline at the ratio of aniline- $\text{Cu}(\text{ClO}_4)_2$  is 1:1.

**Key Words: Conducting polymers, Polyaniline, Chemical polymerization, Oxidant effect, Copper(II) perchlorate.**

### 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, electrocatalysis, electrochromic devices and super capacitor. In addition, the research in the field of polyaniline nanostructures has also received a great deal of attention<sup>1</sup>. 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 pernigraniline. Unlike other polyaromatics, the fully oxidized state of polyaniline is not conducting. Polyaniline becomes conducting at the moderately oxidized states, in particular the emeraldine base, are protonated and charge carriers are generated.

It is a process, 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<sup>1</sup>.

The conducting polymers, such as polypyrrole, polyaniline and polythiophene are prepared either by chemical<sup>2-7</sup> or electrochemical<sup>8-12</sup> synthesis. Aniline and pyrrole<sup>13</sup> are most easily oxidized monomers and a variety of oxidizing agents are available for chemical preparation of polypyrrole and polyaniline<sup>14</sup>. In the chemical polymerization of aniline, copper(II) perchlorate is usually used as oxidant reagent. However, there are some important unexplained points in chemical polymerization of aniline by copper(II) perchlorate.

In this study, copper(II) perchlorate oxidant which has both complex formation character and oxidant was used to determine the oxidant effect on the chemical polymerization of aniline monomer in non-aqueous medium. The interactions between monomer and oxidant were investigated by using UV-vis spectroscopy. Considering the results obtained from UV-vis spectroscopy, polyaniline polymers were synthesized and characterized.

## EXPERIMENTAL

Aniline (97 % Aldrich) was distilled before use. Anhydrous acetonitrile (99.8 %, Aldrich), perchloric acid ( $\text{HClO}_4$ ) (60-62 %, BDH), copper(II) perchlorate hexahydrate ( $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ ) (98 %, Aldrich) were used as received. Tetrabutylammonium perchlorate (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 by using Jasco V-530 UV-visible spectrometer. FT-IR spectrum of polymer-KBr pellet was obtained by 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 TG/DTA (DSC) apparatus in a dynamic nitrogen atmosphere (heating rate of 10 °C/min, platinum crucibles, mass *ca.* 10 mg and temperature range 35-600 °C. 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  $\text{Cu}(\text{ClO}_4)_2$ , 2.0 mmol *tert*-butylammonium perchlorate (TBAP) which was used as dopant, 1.0 mmol monomer and 1.0 mmol oxidant were mixed and these mixtures were stirred and kept in the dark medium for 24 h at 5 °C. The colloidal polymer samples were subjected to multiple rinsing procedures with acetonitrile or acetonitrile-water mixture to remove any residual oxidants, dopant material, soluble oligomers formed during polymerization and oxidative products and then dried under vacuum before FT-IR, TGA/DTG and dry conductivity measurements.

## RESULTS AND DISCUSSION

**UV-vis studies:** In order to investigate the oxidative effect of copper(II) perchlorate on chemical polymerization of aniline, the UV-vis spectra of acetonitrile solutions consisting of aniline and aniline + copper(II) perchlorate mixture (1:1) and aniline + excessive amount copper(II) perchlorate mixtures were obtained (Fig. 1a). The absorption band (polaron band) of the soluble forms of polyaniline was observed above 552 nm with addition of copper(II) perchlorate to the aniline-acetonitrile mixture<sup>15-17</sup>.

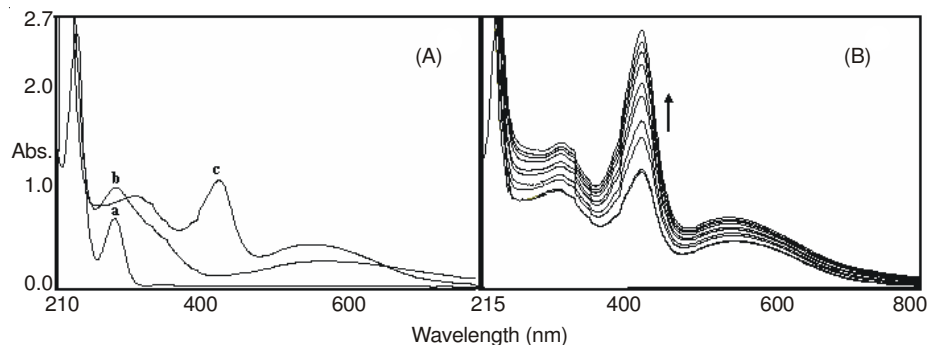


Fig. 1. UV-vis spectra of acetonitrile solutions containing (A); (a) aniline ( $1 \times 10^{-3}$  M), (b) aniline ( $1 \times 10^{-3}$  M) and  $\text{Cu}(\text{ClO}_4)_2$  ( $1 \times 10^{-3}$  M), (c) aniline ( $1 \times 10^{-3}$  M) and  $\text{Cu}(\text{ClO}_4)_2$  ( $3 \times 10^{-3}$  M), (B) aniline and increasing amounts of  $\text{Cu}(\text{ClO}_4)_2$

When the amount of copper(II) perchlorate added is higher than the amount of aniline, a new absorption band is observed at 429 nm (Fig. 2). The intensity of this new band increases with the addition of copper(II) perchlorate. The intensity of bipolaron band observed at 552 nm does not increase further with the addition of copper(II) perchlorate. This indicates that the amount of the polyaniline formed by copper(II) perchlorate does not increase with the addition of copper(II) perchlorate. It is probably that the band observed at 429 nm belongs to polyaniline (or oligomers)-Cu complex. It has been proposed that polyaniline and  $\text{Cu}^{2+}$  forms complex and the band belonging to soluble polyaniline shift to the lower wavelengths (below 600 nm)<sup>18</sup>.  $\text{Cu}^{2+}$  formed by dissolving of copper(II) perchlorate reacts with polyaniline or oligomers to produce a complex because of having complex formation property<sup>16</sup>.

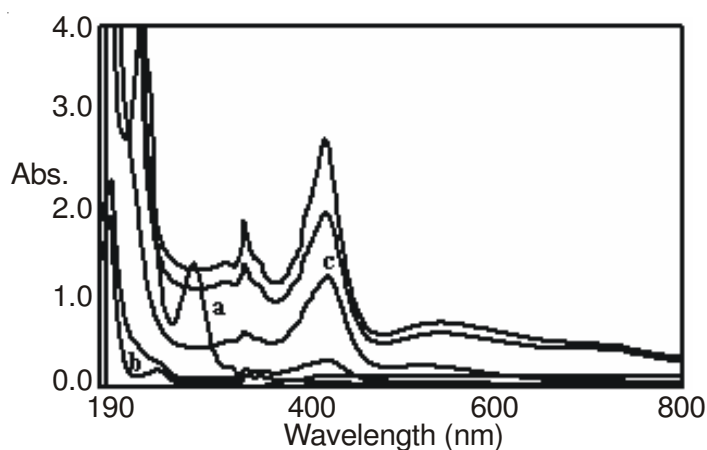


Fig. 2. UV-vis spectrum of acetonitrile solutions containing a) aniline ( $1 \times 10^{-3}$  M), (b) aniline ( $1 \times 10^{-3}$  M) and  $\text{HClO}_4$  ( $1 \times 10^{-3}$  M), (c) aniline ( $1 \times 10^{-3}$  M),  $\text{HClO}_4$  ( $1 \times 10^{-3}$  M) and  $\text{Cu}(\text{ClO}_4)_2$  ( $5 \times 10^{-3}$  M)

When copper(II) perchlorate was added to the acetonitrile solution that consists of equivalent amounts of acid and aniline, the absorption band at 429 nm attributed to the aniline (polyaniline)-Cu complex was observed (Fig. 2). This case also indicates that aniline (polyaniline)-Cu complex occurs in acidic media.

All results obtained from experimental studies indicate that copper(II) perchlorate can be used as an oxidant in the chemical polymerization of aniline until the ratio of aniline-copper(II) perchlorate is 1:1, but not higher than this value.

**FTIR studies:** Fig. 3 shows the FTIR spectra of polyaniline synthesized using  $\text{Cu}(\text{ClO}_4)_2$ . Polyaniline samples synthesized by using copper(II) perchlorate had strong absorption peaks at 1564, 1465, 1298, 1074, 802, 605 and 500. The peaks at 1565-1164  $\text{cm}^{-1}$  are assigned to the quinonoid units in polyaniline. The peak attributed to the benzenoid ring stretching is observed between 1500-1400  $\text{cm}^{-1}$ <sup>18</sup>. In the spectrum of polyaniline synthesized by copper(II) perchlorate, the intensity of the peak at 1464  $\text{cm}^{-1}$  due to the benzenoid units is greater than that of the peak at 1565  $\text{cm}^{-1}$  due to the quinonoid units. This case shows that polyaniline synthesized by copper(II) perchlorate contains dominantly benzenoid units.

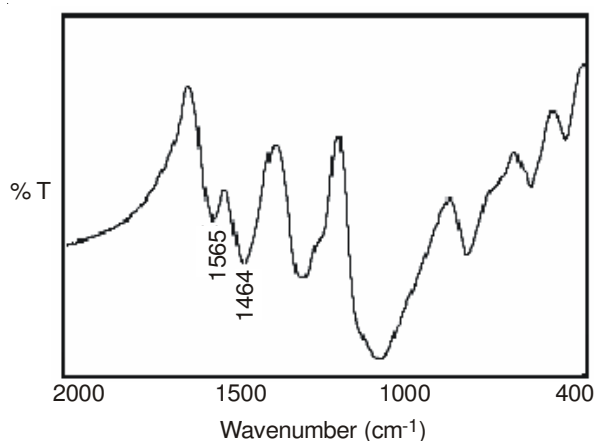


Fig. 3. FTIR spectra of polyaniline

**Thermal studies:** Fig. 4 shows TGA-DTG curves of polyaniline in nitrogen at heating rate of 10 °C /min. In the TGA curve, the first weight loss may be due to the loss of moisture, the second weight loss observed above 250 °C may be due to loss of dopant ( $\text{ClO}_4^-$ ). The decomposition temperature of polyaniline is about 400 °C.

**Conductivity measurements:** The conductivity values of the polyaniline were also measured for its characterization. The polyaniline obtained using copper(II) perchlorate ( $\text{Cu}(\text{ClO}_4)_2$ -aniline) in 1:1 ratio gave a conductivity value of 1.90  $\text{S cm}^{-1}$ . When excessive amount of copper(II) perchlorate was added to the acetonitrile-aniline solution, the white precipitate, which is in crystal form, occurred together with black polymer. It is probable that the crystal form is an anilinium perchlorate due to formation of the proton during the polymerization. So, the conductivity of

the polyaniline sample synthesized using excessive amount of copper(II) perchlorate was not measured. If this polymer synthesized is washed with water and water +  $\text{HClO}_4$  mixture, its conductivity value can be measured. The conductivity value measured is  $1.90 \text{ S cm}^{-1}$ .

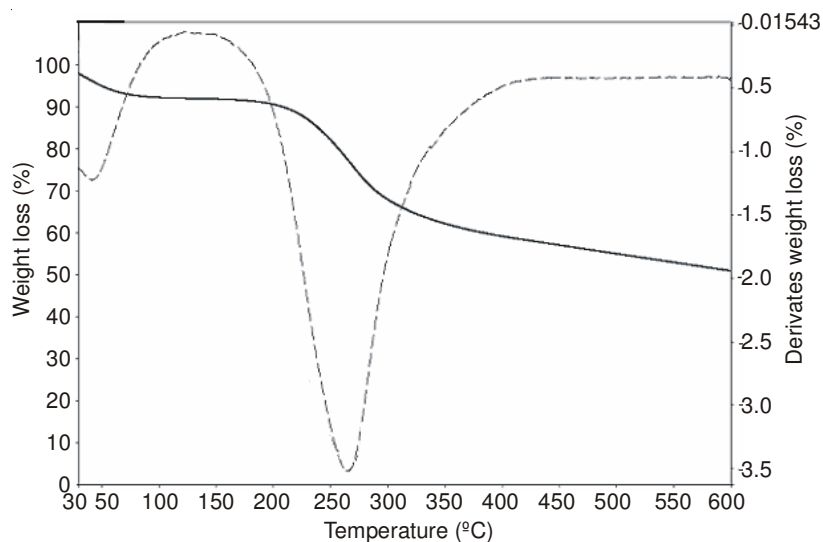


Fig. 4. TG-DTG curves of synthesized polyaniline in nitrogen at heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$

### Conclusion

When copper(II) perchlorate is used as an oxidant, it functions as an oxidant until the monomer-oxidant ratio is 1:1, producing higher molecular weight oligomers and polymer. If this ratio is higher than 1:1, it reacts with aniline to produce copper-aniline complexes.

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