

Oxidizing Effect on Chemical Polymerization of Pyrrole Monomer in Anhydrous Media

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

The chemical polymerization of pyrrole monomer with ferric chloride (FeCl_3), copper(II) perchlorate [$\text{Cu}(\text{ClO}_4)_2$], ammonium peroxodisulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$] and periodic acid (H_5IO_6) in anhydrous medium was investigated by using conductivity measurements, thermal analysis methods (TG, DTA), UV-vis and FTIR spectroscopies. The results indicated that the best oxidation reagent for chemical polymerization of pyrrole in anhydrous medium was $\text{Cu}(\text{ClO}_4)_2$. It was also determined that FeCl_3 , which is both a Lewis acid and oxidant for chemical polymerization, adds to polymer chain such as proton.

Key Words: Conducting polymers, Polypyrrole, UV-vis spectroscopy, Oxidant effect, Chemical polymerization.

INTRODUCTION

Since the discovery of the conducting polymers more than 20 years ago, conducting polymers are finding an increasing use in various branches of technology, such as metallization of dielectrics, primary and secondary batteries, antistatic coatings, electromagnetic shielding, electrochromic systems, *etc.* Polypyrrole is one of the most extensively used conducting polymers in design of bioanalytical sensors, nanotechnology as well as for other purposes. Most of these properties depend on the synthesis procedure as well as on the dopant nature¹. Polypyrrole has been categorized as insoluble material like most of other conducting polymers.

The conducting polymers such as polypyrrole, polyaniline and polythiophene are prepared either by chemical²⁻⁶ or by electrochemical⁷⁻¹¹ synthesis. Aniline and pyrrole¹² are most easily oxidized monomers and a variety of oxidizing agents are available for chemical preparation of polypyrrole and polyaniline¹³. Polymerization of conducting polymers is usually carried out in aqueous solutions.

The major disadvantage of these media is the decomposition of polymer. In chemical and electrochemical polymerization of pyrrole monomer, the influence of several parameters such as nature of the electrolyte, solvent, pH and temperature on polymerization and conductivity values have been investigated¹⁴⁻¹⁹. But there is not a detailed study related to the comparison of the oxidants used in chemical polymerization of pyrrole.

In this study, four oxidants, which have various properties such as Lewis acid character (FeCl_3), proton acid character (H_5IO_6), complex formation character [$\text{Cu}(\text{ClO}_4)_2$] and much more higher oxidative character [$(\text{NH}_4)_2\text{S}_2\text{O}_8$], were used to compare and to make a generalization among their oxidizing effect on chemical polymerization of pyrrole in acetonitrile. The interactions between monomer and oxidants were investigated by using UV-vis spectroscopy. Considering the results obtained from UV-vis spectroscopy, polypyrrole was synthesized and characterized by using FTIR spectroscopy, conductivity measurement and thermal analysis methods (TGA, DTG).

EXPERIMENTAL

Pyrrole (97 % Aldrich) was distilled before use. Anhydrous acetonitrile (99.8 %, Aldrich), perchloric acid (HClO_4) (60-62 %, BDH), anhydrous ferric chloride (FeCl_3) (99 %, Fluka), copper(II) perchlorate hexahydrate [$\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$] (98 %, Aldrich), periodic acid (H_5IO_6) (99 %, Sigma-Aldrich) and ammonium peroxodisulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$] (98 %, Merck) were used as received. Tetrabutylammonium perchlorate (TBAP) was prepared by reacting a 68 % aqueous solution of perchloric acid with a 40 % aqueous solution of tetrabutylammoniumhydroxide. It was recrystallized from ethanol + water mixture and dried under vacuum.

The UV-vis spectra were recorded in the range of 190-1100 nm with a homogeneous pyrrole-acetonitrile solution and polypyrrole which is soluble form-acetonitrile solutions by using Jasco V-530 UV-visible spectrometer. FT-IR spectra of polypyrrole-KBr pellet were obtained by using Jasco FTIR-430 fourier transform infrared spectrometer in the range from 2000 to 400 cm^{-1} 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 $^\circ\text{C}/\text{min}$, platinum crucibles, mass *ca.* 10 mg and temperature range 35-600 $^\circ\text{C}$). 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 polypyrrole samples: In the synthesis of polypyrrole using $\text{Cu}(\text{ClO}_4)_2$ and FeCl_3 oxidants, 2.0 mmol *tert*-butylammonium perchlorate 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 $^\circ\text{C}$. In the synthesis of polypyrrole by using H_5IO_6 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidants, 1.0 mmol monomer, 1.0 mmol oxidant and 1.0 mmol HClO_4 acid were mixed and these mixtures were also stirred and kept in the dark medium for 24 h at 5 $^\circ\text{C}$. The reason for using acid in these polymerizations is that H_5IO_6 and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidants behave only in acidic media as oxidant. In the polymerization performed in acidic media, dopant material was not used, because HClO_4 acid contains ClO_4^- anion, a dopant material. The resulting black polymers were filtered. The colloidal polymer samples were subjected to multiple rinsing procedures with acetonitrile to remove any residual oxidant and oxidative products and then dried under vacuum and pelleted.

RESULTS AND DISCUSSION

UV-Vis studies of pyrrole-FeCl₃ mixture: The chemical polymerizations of pyrrole monomer in acidic media are not preferred because the electrical conductivity of the polymer synthesized in this media is very low compared to the polymer obtained in the neutral and basic media. The reason of this is that both Lewis acid and proton adds to the polymer backbone²⁰. Upon this addition, the conjugation in the presence of polymer chain is apparently broken (Fig. 1). The intensity of the broad absorption band observed at approximately 800 nm attributed to bipolaron in polypyrrole chains²¹ increases up to the equivalent amount of the FeCl₃ added. When the amount of the FeCl₃ added is more than that of pyrrole monomer (the ratio of FeCl₃-pyrrole is more than 1:1), the intensity of this band diminishes while the intensity of absorption band observed at 672 nm increases at the same time. These changes were interpreted as addition of FeCl₃ to the polypyrrole backbone²⁰. The reaction occurring between pyrrole and FeCl₃ may not be observed spectroscopically, because it has oxidant character in addition to its Lewis acidic character. So, in our previous study²⁰, AlCl₃, which has only Lewis acid character, was used instead of FeCl₃ to determine whether the interaction occurs between pyrrole and FeCl₃ or not spectroscopically. In this study, it was determined that AlCl₃ reacts with the pyrrole such as protonic acid and it produces the chemical polymerization of pyrrole in acetonitrile media without protonic acid and oxidant²⁰. The amount of the FeCl₃ added to the polymer backbone has been determined. The amount of FeCl₃ in the polypyrrole polymer synthesized in pyrrole-FeCl₃ (1:1) and pyrrole-FeCl₃ (1:3) mixtures are 4.8 % (correspondence to 14.0 % FeCl₃) and 13.5 % (correspondence to 39.2 % FeCl₃), respectively. The additions of FeCl₃ leading to a lower degree of conjugation along the polymer backbone result in a decrease in conductivity value. Thieblemont *et al.*²² have proposed that excessive amount of FeCl₃ causes the over oxidation of polypyrrole. It is probable that over oxidation performs addition of FeCl₃ to the polymer chains.

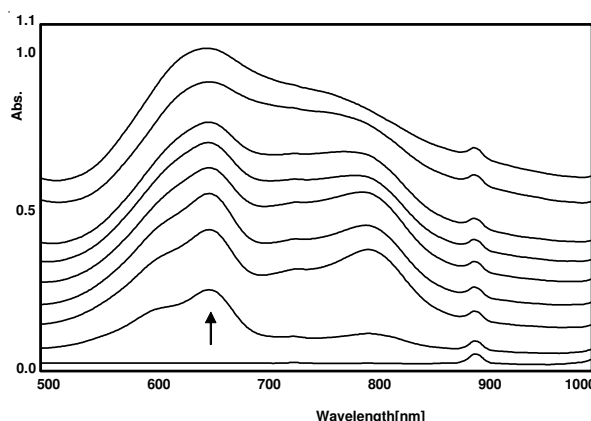


Fig. 1. UV-vis spectra of acetonitrile solutions containing pyrrole (1×10^{-3} M) and increasing amounts of FeCl₃

UV-Vis studies of pyrrole- $\text{Cu}(\text{ClO}_4)_2$ mixture: In order to investigate the oxidizing effect of $\text{Cu}(\text{ClO}_4)_2$ on chemical polymerization of pyrrole, the UV-vis. spectra of acetonitrile solutions consisting of $\text{Cu}(\text{ClO}_4)_2$ (Fig. 2a), pyrrole (Fig. 2b), pyrrole and increasing amount of $\text{Cu}(\text{ClO}_4)_2$ were taken (Fig. 2). As seen in Fig. 2, when the amount of $\text{Cu}(\text{ClO}_4)_2$ in the polymerization solution is increased, the formation of polypyrrole also increases.

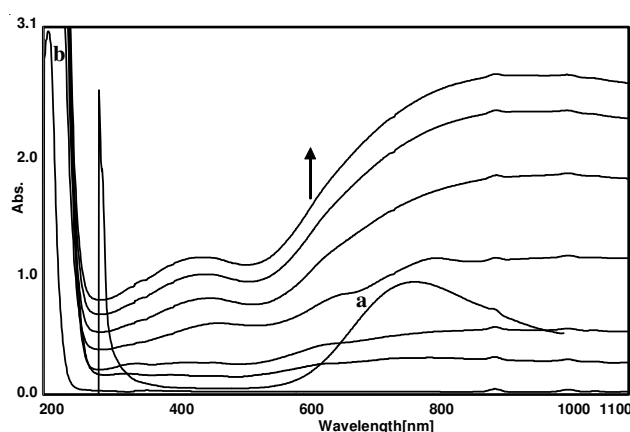


Fig. 2. UV-Vis spectra of acetonitrile solutions containing pyrrole (1×10^{-3} M) and increasing amounts of $\text{Cu}(\text{ClO}_4)_2$

The wavelength belonging to soluble polypyrrole polymers is above 800 nm. This value is very high in accordance with the polypyrrole synthesized by FeCl_3 . This case indicates that polymer synthesized by using $\text{Cu}(\text{ClO}_4)_2$ has longer conjugation than that of the polymer synthesized by using other oxidants. Moreover, it was observed experimentally that the polymerization solution was very clear at the end of the polymerization. It is probable that pyrrole monomers and all oligomers present in the polymerization solution were converted to the polypyrrole with long conjugation. Since residual $\text{Cu}(\text{ClO}_4)_2$ and its reduction products could be removed by washing with acetonitrile solution, it was not determined the existence of Cu in polymer matrix by atomic absorption spectroscopy. These studies indicated that Cu does not add to the polymer backbone as in Lewis or protonic acid and not react with the pyrrole to produce Cu-pyrrole complex.

UV-vis studies of pyrrole- $(\text{NH}_4)_2\text{S}_2\text{O}_8$ mixture: Fig. 3 shows the oxidative effect of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ on chemical polymerization of pyrrole monomer. According to this figure, it can be said that $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is a suitable oxidant for chemical polymerization of pyrrole because the wavelength belonging to pyrrole oligomers is above 600 nm as in $\text{Cu}(\text{ClO}_4)_2$. But, the same things can not be said in terms of conductivity of polypyrrole synthesized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The conductivity of polypyrrole synthesized by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is measured as very low due to some reasons. First reason is that the polymerization medium is acidic, because $(\text{NH}_4)_2\text{S}_2\text{O}_8$

only behaves as oxidant in acidic medium. As reported above, the acidic medium is not appropriate for synthesis of conducting polypyrrole. The second reason is that polypyrrole may be over oxidized by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ because it has the strongest oxidizing property among the other oxidizing agents used. The last one is that the residual $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the $(\text{NH}_4)_2\text{SO}_4$ which is salt, by-product of the reaction could not be removed from polymer matrix completely. The presence of residual like these species in the polymer matrix prevents the conductivity of polymer.

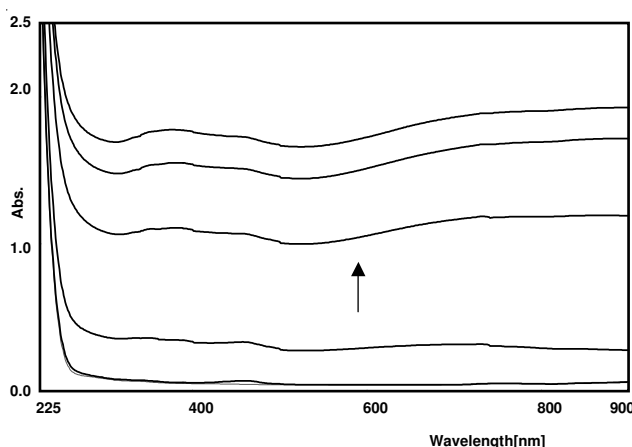
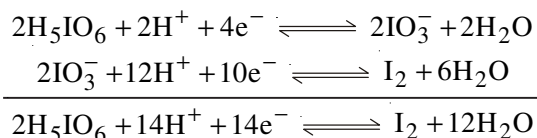


Fig. 3. UV-vis spectra of acetonitrile solutions containing pyrrole (1×10^{-3} M) and increasing amounts of $(\text{NH}_4)_2\text{S}_2\text{O}_8$

UV-Vis studies of pyrrole- H_5IO_6 mixture: It is the first time that H_5IO_6 was used as oxidizing agent in the chemical synthesis of polypyrrole in acetonitrile. H_5IO_6 has moderate oxidizing property among oxidants used chemical polymerization. As can be seen from the following half reactions, H_5IO_6 requires seven electrons per its mole when there are adequate amounts of acid in the medium. According to these reactions, the amount of the oxidizing agent used in chemical polymerization of monomers diminishes in the ratio of 1:7 when H_5IO_6 is used as oxidizing agent.



The reaction products of H_5IO_6 are IO_3^- and I_2 . IO_3^- is also used as oxidant in the chemical polymerization of conducting polymers¹³ and I_2 is used as a dopant material in the chemical polymerizations²³. Fig. 4 shows the absorption band of soluble pyrrole oligomers in polymerization solution. As can be seen in this figure, pyrrole oligomers have a long conjugation, because its absorption band is above 600 nm. Since H_5IO_6 also shows oxidizing property in acidic medium, the conductivity value of polypyrrole synthesized in this media is very low.

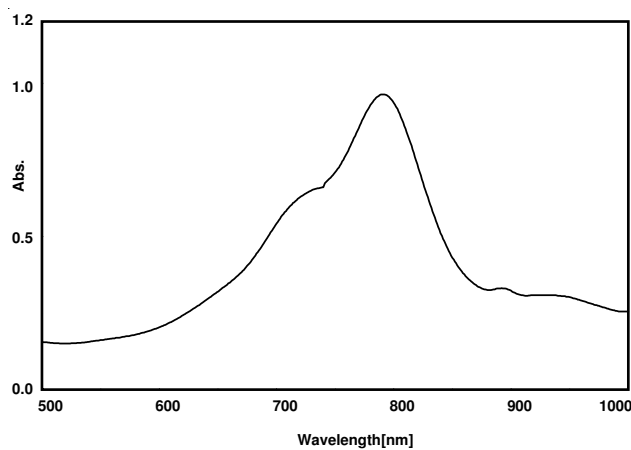


Fig. 4. UV-vis spectrum of acetonitrile solution containing pyrrole (1×10^{-3} M) and H_5IO_6 (1×10^{-3} M)

FTIR Studies: FTIR spectra of polypyrrole samples synthesized using $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{Cu}(\text{ClO}_4)_2$, FeCl_3 and H_5IO_6 are given in Fig. 5 and Fig. 6.

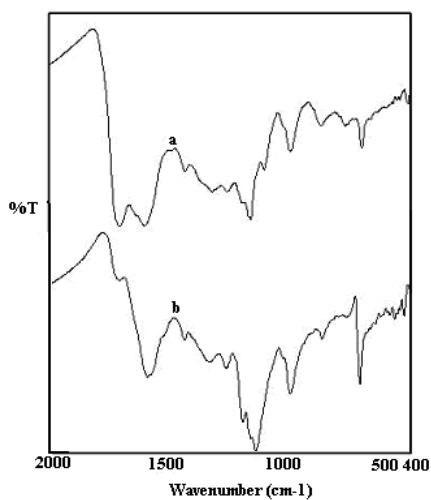


Fig. 5. FTIR spectra of polypyrrole polymers synthesized by using (a) $(\text{NH}_4)_2\text{S}_2\text{O}_8$, (b) H_5IO_6 , (the concentration of all species used synthesis of polypyrrole polymer is 1×10^{-3} M)

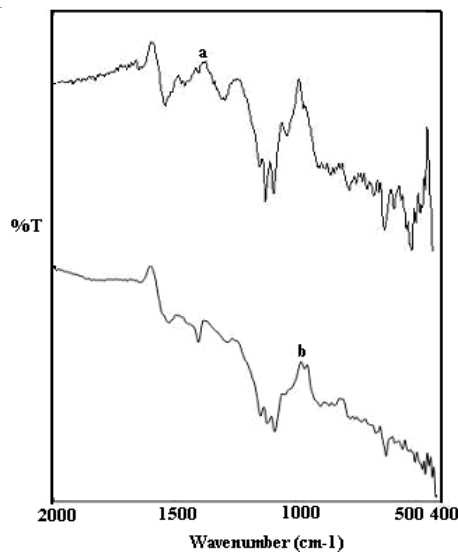


Fig. 6. FTIR spectra of polypyrrole polymers synthesized by using (a) $\text{Cu}(\text{ClO}_4)_2$, (b) FeCl_3 oxidants, (the concentration of all species used synthesis of polypyrrole polymer is 1×10^{-3} M)

The characteristic bands observed in polypyrrole synthesized by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and H_5IO_6 oxidant are at *ca.* 1691, 1577, 1400, 1279, 1215, 1147, 1120, 1109, 1051, 937, 796, 692, 617 cm^{-1} (Fig. 5a); 1684, 1560, 1398, 1290, 1214, 1142,

1107, 1088, 937, 872, 791 and 625 cm^{-1} (Fig. 5b), respectively. The characteristic bands observed in polypyrrole synthesized using $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and FeCl_3 oxidants are at about 1648, 1535, 1454, 1288, 1145, 1120, 1085, 1033, 771, 626, 512 cm^{-1} (Fig. 6a); 1522, 1506, 1402, 1144, 1120, 1088 and 625 cm^{-1} (Fig. 6b), respectively. The peaks at about 1542 cm^{-1} are attributed to C=C stretching vibration of pyrrole. The peaks at 1690 and 1360 cm^{-1} indicate the presence of C=N and C-N vibrations in polypyrrole. The characteristic C-H out-of-plane bending vibration is observed at about 640 cm^{-1} and this band may also overlap with that of the ClO_4^- ion. The band at about 625 cm^{-1} was assigned to the presence of ClO_4^- , which is the doping anion. Other bands were also attributed to the different groups in polypyrrole polymer^{24,25}. As can be seen in these spectra, there are differences in spectrum of each polypyrrole. It is probable that these differences also stem from addition of proton and FeCl_3 , a Lewis acid, to the polymer backbone, not removing residual $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and its reaction products, $(\text{NH}_4)_2\text{SO}_4$, from polymer matrix.

Thermal analysis: The thermal characteristics of polypyrrole films were obtained in the range from 35 to 600 °C under nitrogen (100 cc/min) atmosphere. Fig. 7 shows the TGA results for polypyrrole films synthesized by all oxidizing agents used in this study. Figures show clearly that the temperatures of weight loss are different each other. While the weight loss of the polypyrrole synthesized by using FeCl_3 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and H_5IO_6 carry out three steps which are between 37-141 (7.06 %), 141-245 (8.67 %), 245-600 °C (23.33 %); 39-112 (2.13 %), 113-156 (1.30 %), 156-441 °C (79.64 %); 38-135 (6.14 %), 135-393, (33.03 %), 393-600 (9.58 %) °C (Fig. 7a,b,d), respectively, that of the polypyrrole synthesized by using $\text{Cu}(\text{ClO}_4)_2$ performed two steps which are 35-126 (6.56 %) and 126-350 °C (45.63 %) (Fig. 7c). The weight loss observed below 100 °C and between 250-350 °C belong to losing water (adsorbing to the polymer) and decomposition of the dopant ion, ClO_4^- , respectively²⁴. It was proposed that the weight loss observed above 350 °C belong to decomposition of the polypyrrole polymer²⁴. The amount of the weight loss of polypyrrole synthesized with FeCl_3 also shows that FeCl_3 adds polymer backbone, because its total weight loss is very low in accordance with the other polymers synthesized using H_5IO_6 , $\text{Cu}(\text{ClO}_4)_2$ and $(\text{NH}_4)_2\text{S}_2\text{O}_8$. In addition, the weight loss is very high the polypyrrole synthesized with $(\text{NH}_4)_2\text{S}_2\text{O}_8$. This behaviour shows that it was not removed the residual oxidant, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and its reaction products (NH_4^+ , SO_4^{2-}) by washing with acetonitrile.

Conductivity measurement: The conjugation in the presence of polymer chain is apparently broken by the addition of FeCl_3 . The additions of FeCl_3 leading to a lower degree of conjugation along the polymer backbone result in a decrease in conductivity value. The conductivity value of polypyrrole synthesized by using anhydrous FeCl_3 in acetonitrile is 4.2 S cm^{-1} (Table-1).

The conductivity value measured for polypyrrole synthesized by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is very low (Table-1). As implied above, there are some reasons for this. (i) Since $(\text{NH}_4)_2\text{S}_2\text{O}_8$ behaves only as oxidant in acidic medium, the polymer-

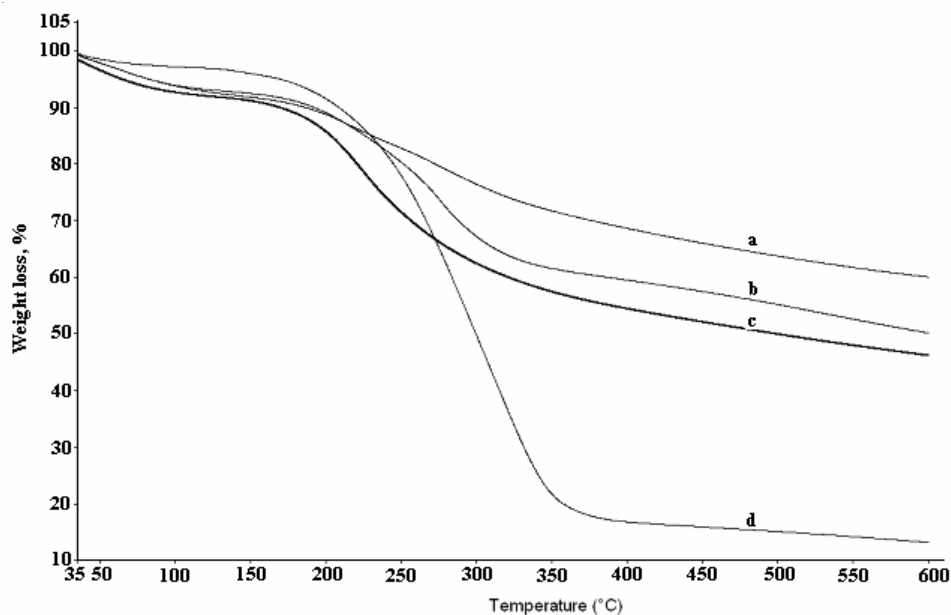


Fig. 7. TGA results of the polypyrrole synthesized by using (a) FeCl_3 , (b) H_5IO_6 , (c) $\text{Cu}(\text{ClO}_4)_2$, (d) $(\text{NH}_4)_2\text{S}_2\text{O}_8$ oxidants

TABLE-1
CONDUCTIVITY VALUES OF POLYPYRROLE POLYMERS
SYNTHESIZED USING VARIOUS OXIDANTS

Oxidant	Conductivity (S cm^{-1})
FeCl_3	4.2
H_5IO_6	3.8×10^{-4}
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	1.1×10^{-4}
$\text{Cu}(\text{ClO}_4)_2$	1.6×10^2

ization medium is acidic. As reported above, the acidic medium is not appropriate for synthesis of conducting polypyrrole due to addition of proton to the polymer backbone. (ii) The polypyrrole polymer is over oxidized by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ because it has the strongest oxidant property among the other oxidants. (iii) The residual $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and the $(\text{NH}_4)_2\text{SO}_4$ could not be removed from polymer matrix completely in anhydrous media. The presence of these species in the polymer matrix decreases or prevents the conductivity of polymer. The conductivity value measured is $1.2 \times 10^{-4} \text{ S cm}^{-1}$ (Table-1).

H_5IO_6 only shows oxidative property in acidic medium. As reported above, the conductivity of polypyrrole synthesized in acidic media is very low or not measured. In this study, the conductivity of polypyrrole synthesized using H_5IO_6 was measured as $3.8 \times 10^{-4} \text{ S cm}^{-1}$ (Table-1). When the polypyrrole was washed with water, this value increased up to $5.8 \times 10^{-1} \text{ S cm}^{-1}$.

The conductivity value of polypyrrole synthesized by using $\text{Cu}(\text{ClO}_4)_2$ as oxidant was very high compared to polymer obtained by using other oxidants in this study. The value measured was $1.6 \times 10^2 \text{ S cm}^{-1}$ (Table-1).

Conclusion

The effect of oxidants on chemical polymerization of pyrrole monomer can be summarized as follows. Since FeCl_3 adds to the polymer backbone, this additions leading to a lower degree of conjugation along the polymer backbone result in a decrease in conductivity value. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is not a good oxidant for chemical polymerization of pyrrole, because the polymer obtained using this oxidant produces non-conducting samples due to its high oxidation power, failure in removing the residuals in polymer matrix and the fact that it only behaves as oxidant in acidic medium. H_5IO_6 is also not good oxidant for chemical polymerization of pyrrole, because as implied above, acidic media are not a suitable medium for chemical polymerization of pyrrole. All experimental results show that $\text{Cu}(\text{ClO}_4)_2$ is the best oxidant for chemical polymerization of pyrrole. The conductivity value of the polymer obtained using this oxidant ($1.6 \times 10^2 \text{ S cm}^{-1}$) is higher than that of polypyrrole samples obtained by using $(\text{NH}_4)_2\text{S}_2\text{O}_8$, FeCl_3 and H_5IO_6 .

ACKNOWLEDGEMENT

The authors are indebted to the Department of Chemistry, Gaziosmanpasa University for financial support for this study (Grant No. 2005/08 University Research Fund).

REFERENCES

1. A. Ramanavicius, A. Ramanaviciene and A. Malinauskas, *Electrochim. Acta*, **51**, 6025 (2006).
2. S. Machida, S. Miyata and T. Techagumpuch, *Synth. Metals*, **31**, 311 (1989).
3. S. Rapi, V. Bocchi and G.P. Gardini, *Synth. Metals*, **24**, 217 (1988).
4. Y.A. Dubitsky, B.A. Zhubanov and G.G. Maresch, *Synth. Metals*, **41**, 373 (1991).
5. K.G. Neoh, T.C. Tan and E.T. Kang, *Polymer*, **29**, 553 (1988).
6. M. Kobayashi, J. Chen, T.C. Chung, F. Moraes, A. J. Heeger and F. Wudl, *Synth. Metals*, **9**, 77 (1984).
7. M. Arca, E. Arca, O. Guven and A. Yildiz, *J. Mater. Sci. Lett.*, **6**, 1013 (1987).
8. T.F. Otero and J.M. Sarasola, *J. Electroanal. Chem.*, **256**, 433 (1988).
9. T.F. Otero and I. Cantero, *J. Electroanal. Chem.*, **395**, 75 (1995).
10. S. Dong and W. Zhang, *Synth. Metals*, **30**, 359 (1989).
11. G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).
12. J.W. Loveland and G.R. Dimeler, *Anal. Chem.*, **33**, 1196 (1961).
13. N. Toshima and S. Hara, *Prog. Polym. Sci.*, **20**, 155 (1995).
14. P.A. Calvo, J. Rodriguez, H. Grande, D. Mecerreyes and J.A. Pomposo, *Synth. Metals*, **126**, 111 (2002).
15. G. Appel, D. Schmeier, J. Bauer, M. Bauer, H.J. Egelhaaf and D. Oelkrug, *Synth. Metals*, **99**, 69 (1999).
16. S.B. Saidman, *Electrochim. Acta*, **48**, 1719 (2003).
17. M.C. Henry, Chen-Chan Hsueh, B.P. Timko and M.S. Freund, *J. Electrochem. Soc.*, **148**, D155 (2001).

18. M. Zhou and J. Heinze, *J. Phys. Chem. B*, **103**, 8443 (1999).
19. S. Shimoda and E. Smela, *Electrochim. Acta*, **44**, 219 (1998).
20. M. Can, H. Ozaslan, O. Isildak, N.O. Pekmez and A. Yildiz, *Polymer*, **45**, 7011 (2004).
21. M. Zagorska, A. Pron and S. Lefrant, In: H.S. Nalwa (Ed), *Handbook of Organic Conductive Molecules and Polymers*, Wiley, New York, Vol. 3, pp. 183-190 (1997).
22. J.C. Thieblemont, J.I. Gabelle and M.F. Planche, *Synth. Metals*, **66**, 243 (1994).
23. J. Stejskal, M. Trchova, N.V. Blinova, E.N. Konyushenko, S. Reynaud and J. Prokes, *Polymer*, **49**, 180 (2008).
24. A.J. Ran, G.J. Lee, H.S. Kim, A. Kyungsoo, L. Kwanghee and K.H. Kim, *Synth. Metals*, **98**, 9 (1998).
25. E.T. Kang, T.C. Tan, K.G. Neoh and Y.K. Ong, *Polymer*, **27**, 1958 (1986).

(Received: 11 April 2009; Accepted: 24 October 2009) AJC-7987