A. Bilici / Hacettepe J. Biol. & Chem., 2017, 45 (4), 563-571

Chemical Oxidation of 5-Amino Quinoline with $(NH_4)_2S_2O_8$: Synthesis and Characterization

5-Amino Kinolinin $(NH_4)_2S_2O_8$ ile Kimyasal Oksidasyonu: Sentez ve Karakterizasyon

Research Article

Ali Bilici
Çanakkale Onsekiz Mart University, Fen Edebiyat Fakültesi, Kimya Bölümü, Çanakkale, Turkiye.

ABSTRACT

5-amino quinoline (AQ) was chemically oxidized in $(NH_4)_2S_2O_8$/HCl system, whose structure was identified by UV-vis, FTIR, ^{1}HNMR and ^{13}CNMR analysis. Spectral analysis results indicated the formation of phenazine like units in the oxidation product and C3, C6, C8 positions of quinoline ring were suggested as a possible polymerization sites. Size exclusion chromatography indicated the oxidation product (OAQ) consisted of oligomeric units (1200 g/mol). OAQ was thermally stable and half of its mass was decomposed at 1000ºC.

Key Words
Oxidative polymerization, 5-amino quinoline, thermal stability, fluorescent.

ÖZ

5-amino kinolin monomeri $(NH_4)_2S_2O_8$/HCl varlığında kimyasal olarak yükseltgendi. Elde edilen oksidasyon ürününün (OAQ) yapısı, UV-vis, FTIR, ^{1}HNMR ve ^{13}CNMR analizleri ile aydınlatıldı. Spektral analizler sonucunda oksidasyon ürünün yapısında fenazin birimlerinin bulunduğu ve momomerik birimlerin birbirleri ile 3,6 ve 8 pozisyonları ile birleştiği belirlendi. Büyüklükçe ayırma tekniği, ürünün oligomerik birimlerden oluştuğunu gösterdi. OAQ ısısal bozunmaya karşı dayanıklıdır. Yarı bozunma sıcaklığının 1000ºC olduğu belirlendi

Anahtar Kelimeler
Oksidatif polimerizasyon, 5 –amino kinolin, termal dayanıklılık, floresans.

Article History: Received: Mar 21, 2017; Revised: Apr 25, 2017; Accepted: Aug 10, 2017; Available Online: Dec 25, 2017.

DOI: 10.15671/HJBC.2018.198

Correspondence to: A. Bilici, Çanakkale Onsekiz Mart University, Faculty of Sciences and Arts, Dep. Chemistry, Çanakkale, Turkey

Tel: +90 286 218 00 Fax: +90 286 218 05 33 E-Mail: alibilici@comu.edu.tr

INTRODUCTION

The extensive works have been devoted to synthesis of aromatic polymers. The optical, electrical and mechanical properties of polyaromatics provide a potential use in optical and electronic device application [1]. Polytiophenes, polyanilines, polycarbazoles, polypyrolles, polyfluorenes and their derivates are among the most studied aromatic polymers [2]. Polyquinolines form another important class of these polymers [3]. They exhibit high thermal and oxidative stability, outstanding mechanical property [4]. Their electroluminescent, nonlinear optical and conductive properti have been also widely studied [4,5].

Polyquinolines were synthesized in the 1970s. In general, they are prepared by Friedlander condensation [6]. The oxidative polymerization [7], electrochemical polymerization [8,9], plasma polymerization [10], and recently, Aza-Diels–Alder routes [11] were the other methods to produce these polymers.

The oxidative polymerization is inexpensive and environmentally friendly method and gram-scale product can be synthesized in one step [12] but its weakness is the formation of undesirable linkages in polymer chains (region-random polymerization).

The oxidation of various hydroxyl and amine functionalised quinoline monomers, 4- hydroxy quinoline [13], 5- hydroxy quinoline [14], 6- hydroxy quinoline [15], 8-hydroxy quinolone [16] and 5-aminoquinoline [17,18], 6-aminoquinoline [19], 8-aminoquinoline [20], were studied in various polymerization medium. The majority of polymerization products were oligomers. The some physical properties of the oxidation products were investigated. The oxidative polymerization of 8-hydroxy quinoline was studied by Ragimov and co-workers [20]. In that study, electrical and antibacterials properties of 8-hydroxy quinoline polymer was presented. The enzymatic polymerization of 8-hydroxy quinoline was also studied by Yomamato and co-workers in catalytic reaction medium [21]. It was reported that the regio-regular (C2-C7 linked) quinoline homopolymer was obtained. Hydroxyl- functionalised quinolone monomer, 2-methyl quinoline-8-ol was oxidized by NaOCl (oxidant) in alkaline medium. The metal complexes of this polymer were also prepared [22].

The oxidation of 5-aminoquinoline were accomplished by gold solution [17]. The nanocomposite obtained exhibited high thermal stability: 5% of its mass was decomposed at 643°C. This composite was also characterized by high crystalline structure and its green light emitting nature.

In our previous work, it was reported the first enzyme-catalyzed oxidation reaction of 5-amino quinoline [18]. Horse radish peroxidase and H_2O_2 were used as catalyst and oxidant, respectively and the polymerization products with the low regio-regularity were obtained.

In here, we present the chemical oxidative polymerization of amine functionalized quinoline monomer, 5-amino quinoline, in acidic medium, for the first time. The structure and properties of oxidation product (OAQ) given here are completely different from reported ones [17,18]. In the present study, monomer units are linked to each other at C3, C6, C8 positions and the formation of phenazine type structures are suggested. The product obtained was characterized with the different analytical techniques.

EXPERIMENTAL

Materials

The chemicals and all solvents were commercially obtained (Merck) and used as received.

Characterization Techniques

The solubilitiy tests of OAQ were conducted in various solvents using 1mg sample and 5 ml solvent. The infrared and ultraviolet–visible (UV–vis) spectra were measured by Perkin Elmer FT-IR Spectrum One and PerkinElmer Lambda 25, respectively. ^{1}HNMR spectra were recorded at 25°C using deuterated DMSO as solvent. Tetramethylsilane (TMS) was used as internal standard. The number average molecular weight (Mn) was determined by size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm column was used; eluent: DMF (0.4 mL/min), polystyrene standards. A refractive index detector (RID) and UV detector were used to analyse the products at 25°C. Thermal data were obtained using a Perkin Elmer

Diamond Thermal Analysis. The TG-DTA measurements were made between 15 and 1000 °C (in N_2, rate 10°C min^{-1}). The surface morphology of polymer was evaluated by scanning electron microscopy (SEM), using a Philips XL 30S FEG apparatus. Cyclic voltammetry measurements were conducted by a CHI 660 C Electrochemical Analyzer (CH Instruments, Texas, USA). All the experiments were performed in a dry box filled with argon at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc+) couple. The half-wave potential ($E_{1/2}$) of (Fc/Fc+) was measured in acetonitrile solution of 0.1 mol tetrabutylammonium hexafluorophosphate (TBAPF6) and was 0.39 V with respect to Ag wire. The voltammetric measurements were carried out in acetonitrile/ DMSO mixture (v/v: 5/1) Scanning electrone microscope analysis (SEM) were conducted by using JEOL JSM-7100F instrument. Fluorescence analyses were performed using a Shimadzu RF-5301PC spectrofluorophotometer. Slit width in all measurements was 5 nm.

Polymerization

The oxidation of AQ was performed using previous described method. The procedure for the preparation of OAQ is given below [7]: HCl solution (1.0 M, 25 mL) and AQ (0.01 mol, 1.45 g) were stirred for half an hour in 100 mL glass flask. The ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, (0.01 mmol, 2.28 g), was dissolved in HCl (1.0 M, 25 mL). Then, oxidant solution was added into the solution prepared above, drop by drop, at 25°C for 30 min. The reaction mixture was further stirred for 48 h. The resulting product was precipitated from the reaction mixture by centrifugation. It was washed with distilled water to eleminate the oxidant. The product was also washed with ethanol several times for removal of residue monomer.

RESULTS and DISCUSSION

Treatment of AQ with ammonium persulphate solution produced a black precipitate, which was isolated by filtration. During polymerization reaction, the colour of solution changed from opaque to brown, and finally to black. The solubility of OAQ was very poor in ethanol, methanol and chloroform but it was dissolved in THF, DMSO and NMP. Molecular weight determined by GPC analysis was 1200 g/mol.

The UV-Vis spectrum of the monomer in DMSO solution exhibited one absorption maximum at 360 nm (Figure 1).

As expected, absorption band of the OAQ was much broader. A broader absorption indicates a successful polymerization reaction [21]. AQ has aniline like structure and therefore it is conceivable to supposed that AQ with ammonium persulphate proceeds through a cation-radical mechanism [22,23] and in the course of oxidation, radical cation is formed in several resonance forms (R_1,R_3, R_5 and R_6) given in Figure 2.

These radicalic forms are take into account to establish possible coupling sites between monomer units. The FTIR spectra of monomer and oxidation product were given in Figure 3. The strong peaks at 3328 and 3189 cm^{-1} observed in the spectrum of AQ were the characteristic absorption of the N–H stretching vibration, which was broader and shifted to 3600 cm^{-1} in the spectrum of the OAQ [24]. A shoulder like band at 3200 cm^{-1} was attributed to the hydrogen-bonded -N-H vibration [25]. A weak shoulder like peak at about 3060 cm^{-1} was due to C-H stretching on aromatic phenazine rings [25,26]. The two sharp IR adsorptions at 1491 and 1637 cm^{-1} were also associated with aromatic ring stretching. The peaks at 1637 cm^{-1} and 1474 cm^{-1} were assigned to the quinoid and benzenoid ring vibrations, respectively [27]. A peak at 1355 cm^{-1} was assignable to the C-N stretching vibration in quinoid imine units [26].

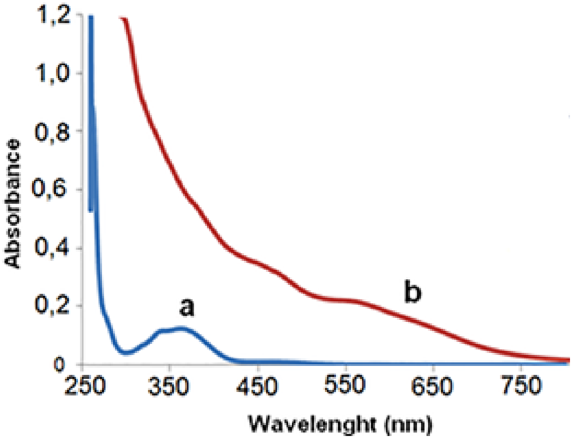

Figure 1. UV-vis spectra of AQ (a) and OAQ (b) solutions (in DMSO).

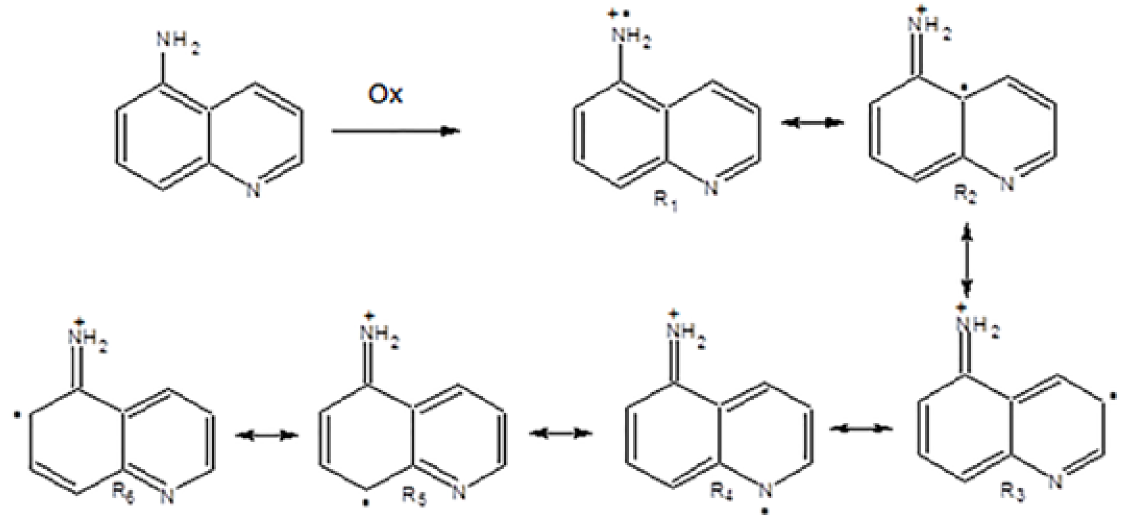

Figure 2. Resonance forms of AQ.

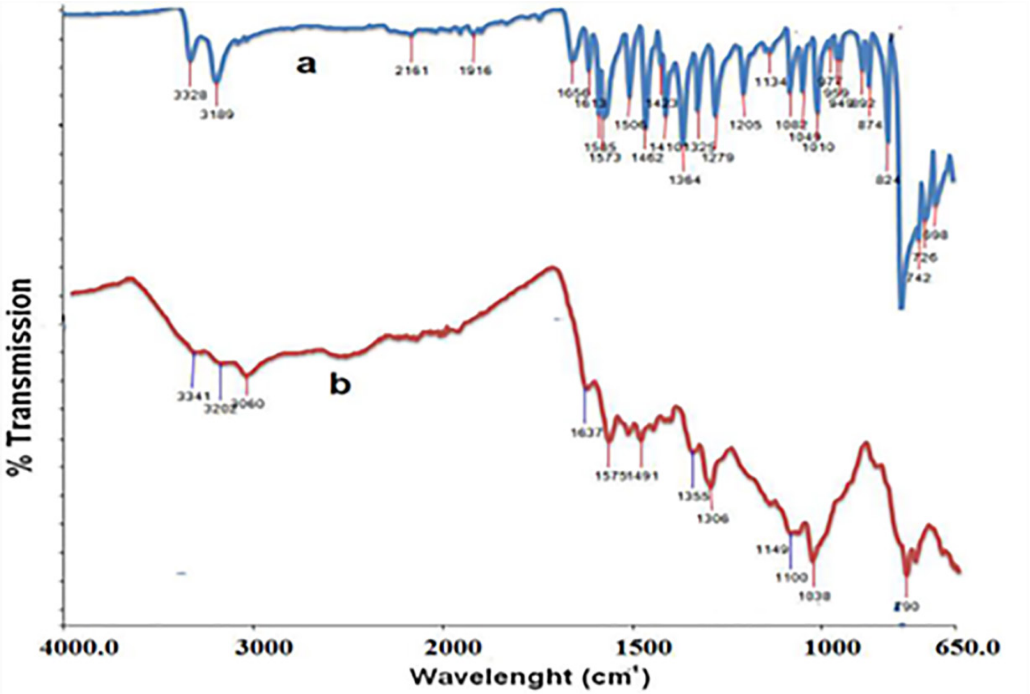

Figure 3. FTIR spectra of AQ (a) and OAQ (b).

The valuable structural information was obtained by NMR analysis. As known, oxidation of phenol and aniline like aromatic compounds often produce regio-random polymerization products [18,28] and therefore, these polymers are characterized by broad NMR signals. This case limits their characterization. ^{1}H-NMR spectrum of the OAQ is characterized by three main signals (Figure 4).

This simple spectrum assigned the presence of regio-regular polymer chains. These signals should correspond to the three types of protons on the OAQ chains, as shown in Figure 5. The peaks centered at 6.95, 7.10 and 7.25 ppm (high-field area of spectrum) were attributed to NH- and NH_2 groups of phenazine unit. The other signals between 8-9.30 ppm (low-field area of spectrum) ascribed to aromatic protons on quinoline units. Aniline derivate aromatic monomers were also oxidized in similar experimental conditions and the similar spectra were obtained [29].

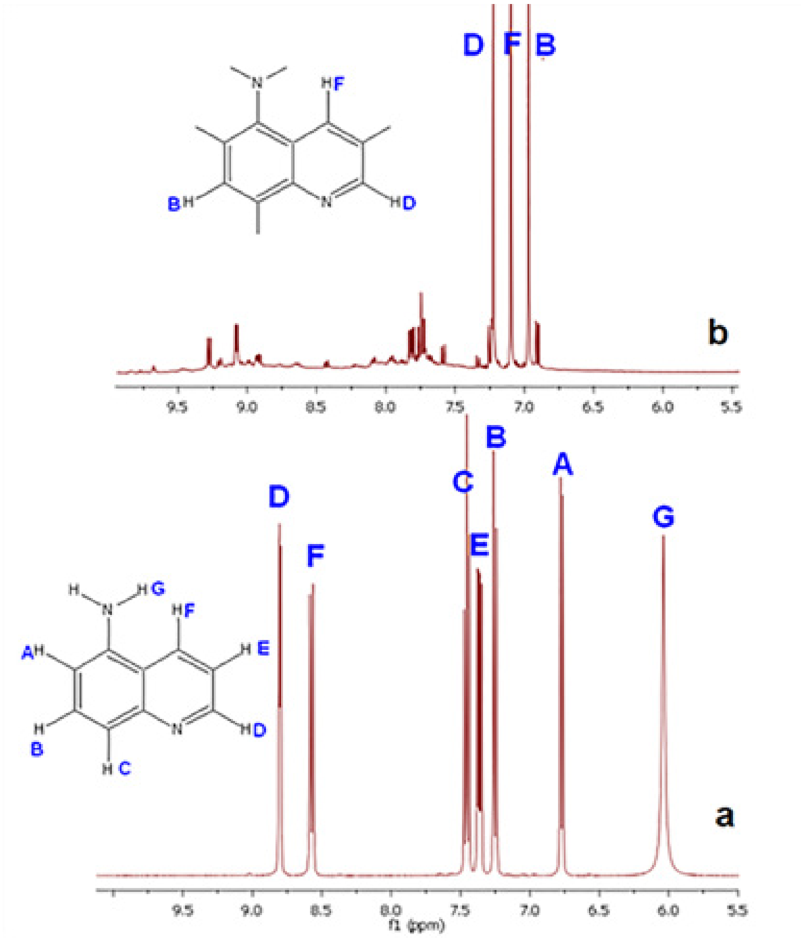

Figure 4. ^{1}H-NMR spectra of AQ (a) and QAQ (b).

Figure 5 belongs to ^{13}C-NMR spectra of AQ and QAQ. The peak assignments of AQ and QAQ were also given in this Figure. Both AQ and QAQ exhibited ten carbon signals. The absence of additional carbon peaks in the QAQ spectrum assigned the regio-regular oligomer formation. The most of carbon signals of OAQ shifted to low field area of spectrum due to formation of conjugated structure.

It is known that aromatic C-C couplings signals are observed between ca.110-130 ppm. On the other hand C-N couplings are expected to be seen in the low field area of spectrum (between 135-150 ppm). The only three carbon signals were observed low field area of spectrum for monomer. However, five carbon signals were observed for oligomer between 135-150 ppm. This assigned monomer units come together via C-N couplings but not C-C couplings.

In this case, it is suggested that the couplings between monomer units should be via amine nitrogen and 3,6 and 8 carbons of AQ. The possible structure should be as given in Figure 6.

TG/DTG analyses were conducted for thermal characterization of OAQ (Figure 7).

DTG curve showed the thermal decomposition of OAQ occured two main steps. The first mass loss was between 134-533ºC and corresponds to a mass loss of 18%. The mass loss was observed between 533-1000 ºC and this corresponds to a mass loss of 25%. The maximum decomposition temperatures were determined as 290 and 719ºC. The onset decomposition temperature was found to be 231 ºC. OAQ exhibited high char residue. 20 and 50% decomposition temperatures were determined as 440 ve 1000 ºC.

Aniline like oligomers and polymers are often characterized by electrochemical methods [30]. Figure 8a belongs to the cyclic voltammograms of OAQ recorded at different scan rates.

The experiments were conducted between -2V and 1.6 V and CH_3CN/DMSO (v:v, 1/5) mixture con-

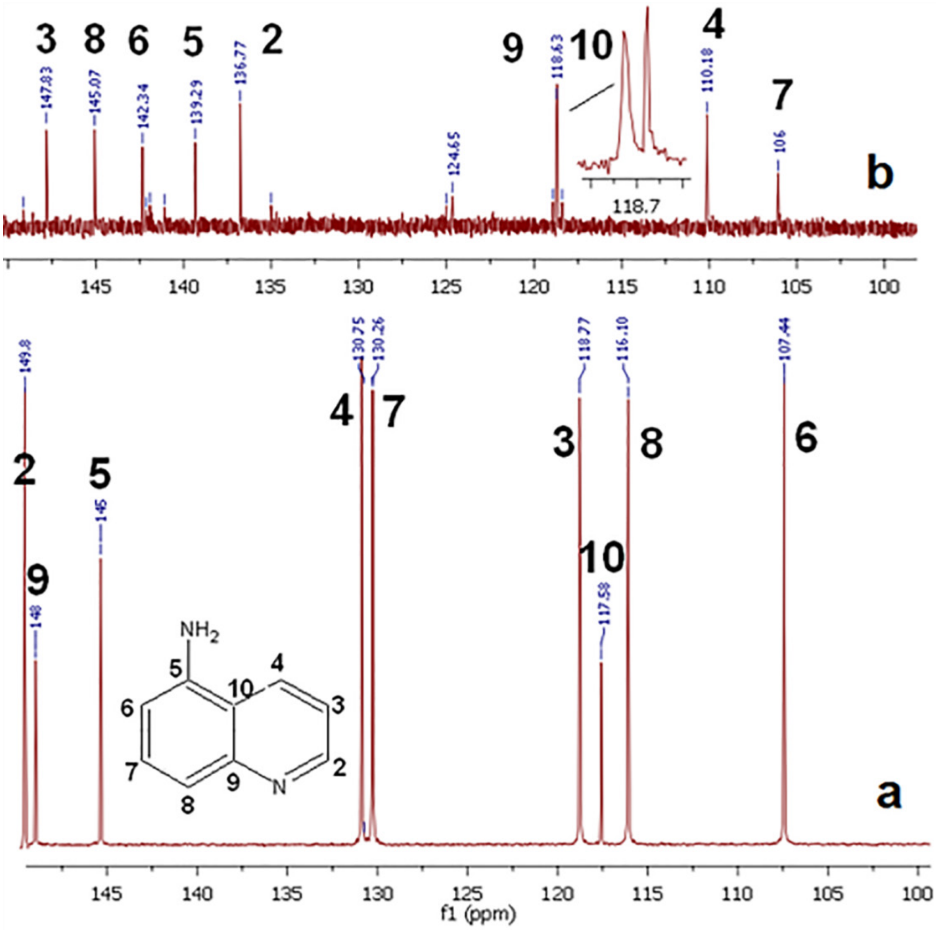

Figure 5. ^{13}C-NMR spectra of AQ (a) and OAQ (b).

taining 0.1 M $LiClO_4$ were used as solvent. In this figure, an anodic peak (1.116 V) and two cathodic peaks (–0.743 ve –1.41 V) were observed at 100 mv/s scan rate. The peak at 1.116 V was attributed to oxidation of NH groups to form radicalic cation species [19] and the cathodic peaks observed were attributed to re-reduction of oxidized structures [30]. Figure 8 b shows the plot of anodic and cathodic peak currents vs scan rates. These plots showed a linear relationship between peak currents and scan rate applied, suggesting the reversibility and diffusion control of the redox process [31].

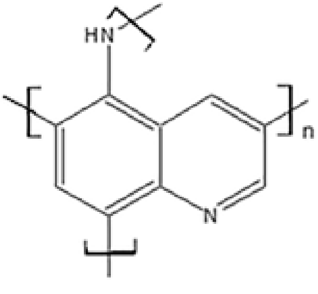

Figure 6. Proposed structure for OAQ.

Figure 9 belongs to SEM image of OAQ. This photograph assigned the presence of micro-scale, distorted- ring like structures. The observed structures were intensive-stacked and heterogeneous.

The quinoline monomer, homopolymers, copolymers and blends have interesting optical properties. Therefore, in here, the fluorescence characteristics of oxidation product were also studied. In solution, OAQ is a typically green light emitter (Figure 10).

Figure 10a shows emission of OAQ solution excited at 365 nm. However, It was non-fluorescent in solid state. It was observed that the fluorescent behaviours of OAQ were highly excitation-dependent. In other word, the emission maxima of OAQ were red shifted as the excitation wavelength of source was increased. Figure 10b, c and d belong to photographs of OAQ solution excited at different wavelengths. OAQ solution excited at 380, 420 and

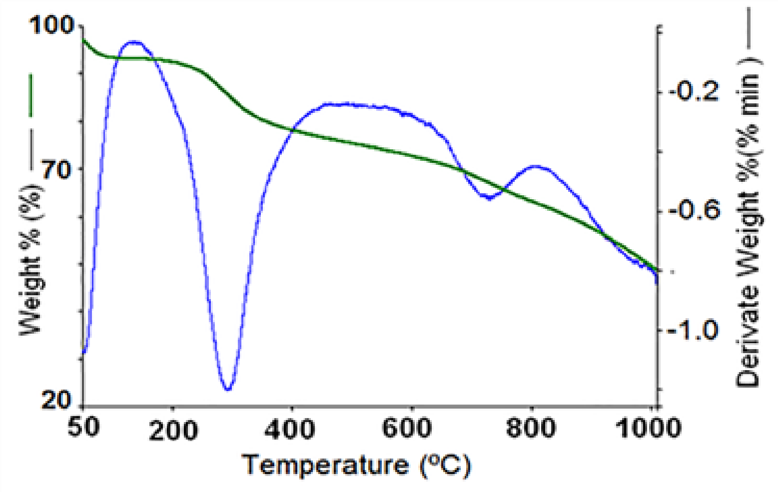

Figure 7. TG/DTG curves of OAQ.

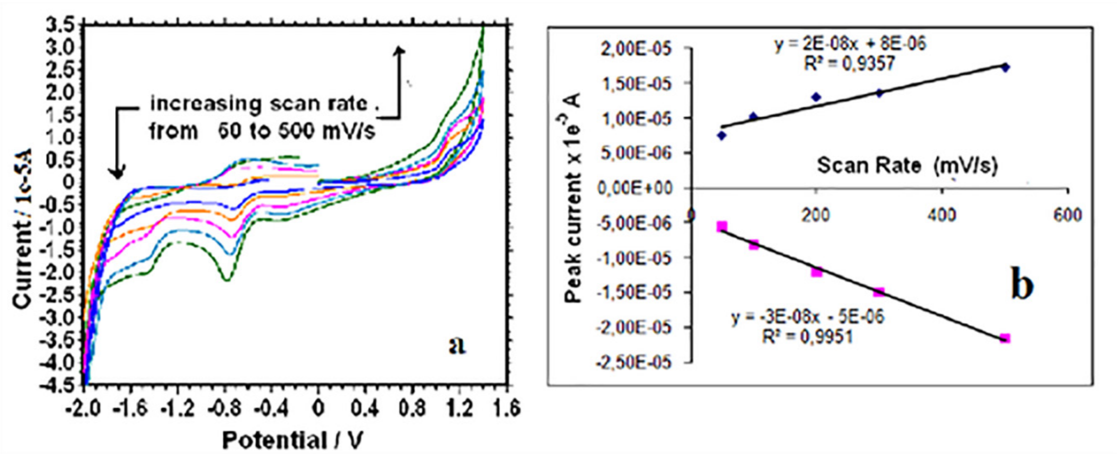

Figure 8. Cyclic voltammograms of OAQ.

520 nm exhibited green, yellow and orange emission colours. This emission phenomenon was also reported in the other aromatic oligomers and polymers including 4-hydroxyquinoline oligomers [13], oligopyrene nanowires [32], poliamidoamine particules [33], nitro substutiye pyrene oligomers [34], poly(8-amino-2 naphtol) [35,36].

Different theses have been proposed to explain the multicolour emission of these polymeric systems.

The cause of this phenomenon is ambiguous at present and requires extensive researches. It was noted that the 5-amino quinoline oxidation was also studied by two different pathways before: gold (III) chloride catalyzed [17] and Horse radish peroxidase/H_2O_2-catalyzed polymerization reactions [18]. Each oxidation product was oligomers and green light emitters like OAQ obtained by acidic medium. However, only OAQ obtained by ammonium persulphate exhibited multicolour emission behaviour. This indicated fluorescence nature of oxidation products was profoundly affected by the kind of oxidant used.

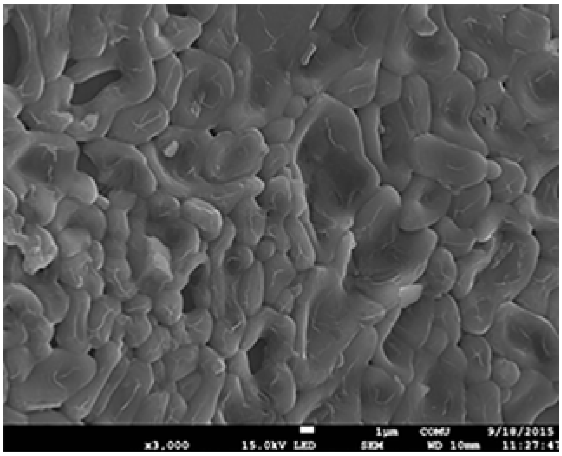

Figure 9. SEM image of OAQ.

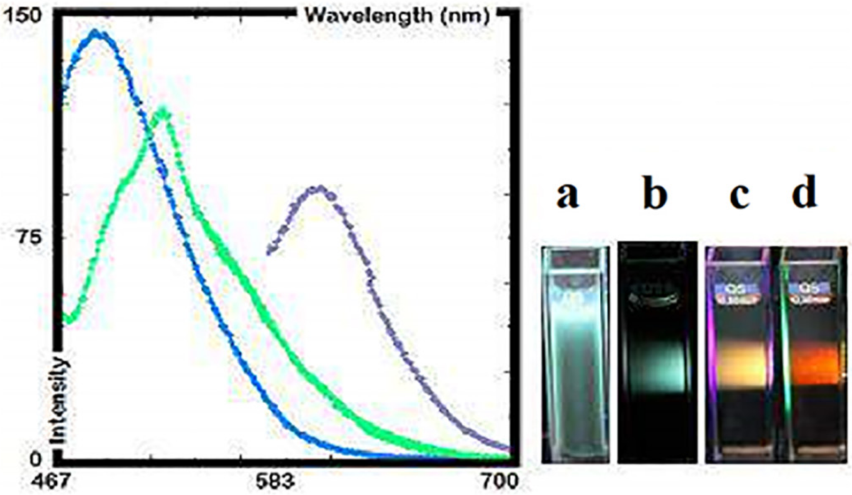

Figure 10. The photographs of OAQ solution excited at 365 nm (a) and OAQ solution excited at different wavelengths ; 380(b) , 420 (c) and 520 nm (d), respectively.

CONCLUSION

The oxidative oligomerization of AQ was accomplished in acidic medium using ammonium persulphate as oxidant. GPC analysis assigned that oligomeric structures were formed during polymerization. Spectral analysis indicated that monomer units were coupled with each other at 3.6 and 8 positions. TG-DTG analysis showed that OAQ was thermally stable and it yielded 50% char residue at 1000 C. SEM images showed the presence of intensive-stacked and distorted-ring like structures. OAQ exhibited multicolour emission and it showed green, yellow and orange colours as excited at 380, 420 and 520 nm, respectively.

ACKNOWLEDGEMENT
This work is financially supported by TUBİTAK Grants Commission (Project no: TBAG-113Z265). The author thanks to Prof Dr İsmet Kaya for support about some measurements.

References

1. A. Moliton, R.C. Hiorns, Review of electronic and optical properties of semiconducting π-conjugated polymers: applications in optoelectronics, Polym. Int., 53 (2004) 1397–1412
2. A. Bilici, F. Doğan, M. Yıldırım, İ. Kaya, Facile synthesis of self-stabilized polyphenol nanoparticles, Mater. Chem. Phys., 140 (2013) 66-74.
3. A. Kimyonok, XY. Wang, M. Weck, Electroluminescent poly(quinoline)s and metalloquinolates, J. Macromol. Sci., Polym. Rev., 46 (2006) 47–77.
4. J.L. Kim, J.K. Kim, H.N. Cho, D.Y. Kim, C.Y. Kim, and S.I. Hong, New polyquinoline copolymers: synthesis, optical, luminescent, and hole-blocking/electron-transporting properties, Macromolecules, 33 (2000) 5880-5885.
5. A.K. Agrawal, S.A. Jenekhe, H. Vanherzeele, J.S. Meth, Third-order nonlinear optical properties of conjugated rigid-rod polyquinolines, J. Phys. Chem., 96 (1992) 2837-2843.
6. J.K. Stille, Poly quinolines, Macromolecules, 14 (1981) 870-880.
7. X.G. Li ,M.R. Huang, Y.M. Hua, M.F Zhu, Q. Chen, Facile synthesis of oxidative copolymers from aminoquinoline and anisidine, Polymer, 45 (2004) 4693–4704.
8. H. An, M. Seki, K. Sato, K. Kadoi, R. Yosomiya, Electrochemical polymerization of methyl-substituted quinolines, Polymer, 30 (1989) 1076-1078.
9. N.Saito, T. Kanbara, Y. Nakamura, T. Yamamoto, K. Kubota, Electrochemical and chemical preparation of linear .pi.-conjugated poly(quinoline-2,6-diyl) using nickel complexes and electrochemical properties of the polymer, Macromolecules, 27 (1994) 756–761
10. Z.X. Yan, Synthesis and characterization of a Polyquinoline derivative thin film with a low dielectric constant, Acta Phys. Chim. Sin., 26 (2010) 1164-1170
11. D.J. Dibble, M.J. Umerani, A. Mazaheripour, Y.S. Park, J.W. Ziller, and A.A. Gorodetsky, An aza-diels-alder route to polyquinolines, Macromolecules, 48 (2015) 557–561.
12. A. Bilici, I. Kaya, M.Yıldırım, Biosynthesis and characterization of organosoluble conjugated poly(2-aminofluorene) with the pyrazine bridged, Biomacromolecules, 11 (2010), 2593–2601.
13. A. Bilici, F. Doğan, M. Yildirim, İ. Kaya, Tunable multicolor emission in oligo(4-hydroxyquinoline), J. Phys. Chem. C, 116 (2012) 19934-19940.
14. A. Bilici, F. Doğan, M. Yildirim, İ. Kaya, Facile and regioselective synthesis of poly(5-hydroxyquinoline), React. Funct. Polym., 71, (2011) 675-683.
15. F. Doğan, A. Bilici, M. Yıldırım, İ. Kaya, 6-Hydroxyquinoline oligomers emit white ligh, Sci. Adv. Mater., 6 (2014) 1957-1964.
16. S. Ncanana, S. Burton, Oxidation of 8-hydroxyquinoline catalyzed by laccase from Trametes pubescens yields an antioxidant aromatic polymer, J. Mol. Catal. B. Enzym, 44 (2007) 66-71.
17. A. Bilici, B. Ayten, İ. Kaya, Facile Preparation of gold nanoparticles on the polyquinoline matrix: catalytic performance toward 4-nitrophenol reduction, Synt. Met, 201 (2015) 11-17.

18. A. Bilici, İ.H. Gecibesler, İ.Kaya, Enzymatic synthesis of 5-amino quinoline oligomers and evaluation of their free radical scavenging activity, Can. J. Chem., 95 (2017) 7-11.
19. M.C. Stevic, G.C. Marjanovic, B. Marjanovic, L.M. Ignjatovi, D. Manojlovic, The electrochemical oxidation of 6-aminoquinoline: computational and voltammetric study, J. Electrochem. Soc., 159 (2012) G151-G159.
20. X.G. Li, M.R. Huang, Y.M. Hua, Facile synthesis of processible aminoquinoline/phenetidine copolymers and their pure semiconducting nanoparticles, Macromolecules 38 (2005) 4211-4219.
21. B. Lu, L. Zeng, J. Xu, Z. Le, H. Rao, Electrosynthesis of highly conducting poly(1,5-dihydroxynaphthalene) in BF3·Et2O, Eur. Polym. J., 45 (2009) 2279–2287
22. C. Heichert, H. Hartmann, on the formation of mauvein: Mechanistic considerations and preparative results, Z. Naturforsch. B, 64 (2009) 747-755.
23. I. Sapurina, A.V. Tenkovtsev, J. Stejskal, Conjugated polyaniline as a result of the benzidine rearrangement, Polym Int., 64 (2015) 453–465.
24. X.G. Li, H. Feng, M.R. Huang, Redox sorption and recovery of silver ions as silver nanocrystals on poly(aniline-co-5-sulfo-2-anisidine) nanosorbents, Chem. Eur. J., 16 (2010), 10113-10123.
25. A. Kellenberger, E. Dmitrieva, L. Dunsch, The stabilization of charged states at phenazine-like units in polyaniline under p-doping: an in situ, ATR-FTIR spectroelectrochemical study, Phys. Chem. Chem. Phys., 13 (2011) 3411-3420.
26. C. Stammer, A. Taurins, Infrared spectra of phenazines, Spectrochim. Acta, 19 (1963) 1625–1653.
27. R. U. Islam, S.K. Mahato, S.K. Shukla, M.J. Witcomb, K. Mallick, Palladium–poly(3-aminoquinoline) hollow-sphere composite: application in sonogashira coupling reactions, Chem. Cat. Chem., 5 (2013) 2453–2461.
28. J. Shan, L. Han, F. Bai, S. Cao, Enzymatic polymerization of aniline and phenol derivatives catalyzed by horseradish peroxidase in dioxane (II), Polym. Adv. Technol., 14, (2003) 330-336.
29. M.R. Huang, X.G. Li, Y. Yang, Oxidative polymerization of o-phenylenediamine and pyrimidylamine, Polym. Degrad. Stab., 71 (2001) 31-38.
30. G. Xu, W. Wang, X. Qu, Y. Yin, L. Chu, B. He, H. Wu, J. Fang, Y. Bao, L. Liang, Electrochemical properties of polyaniline in p-toluene sulfonic acid solution, Eur. Polym. J., 45 (2009) 92701-92707.
31. A. Bilici, R.N. Tezel, İ. Kaya, Facile chemical route to copper/polymer composite: simultaneous reduction and polymerization, Coll. Surf. Physicochem. Eng. Asp., 459 (2014) 254-260.
32. S. Dubey, D. Singh, R.A. Misra, Enzymatic synthesis and various properties of poly(catechol) Enzyme Microb. Technol., 23 (1998), 432–437.
33. L. Qu, G. Shi, Crystalline oligopyrene nanowires with multicolored emission, Chem. Commun., 24 (2004) 2800–2801.
34. W. Yang, C.Y. Pan, M.D. Luo, H.B. Zhang, Multiple functional hyperbranched poly(amido amine) nanoparticles: synthesis and application in cell imaging, Biomacromolecules, 12 (2011) 1523–1531.
35. B.Lu, J. Xu, C. Fan, F. Jiang, H. Miao, Facile electrosynthesis of nitro-group-substituted oligopyrene with bicolored emission, Electrochim. Acta, 54 (2008) 334-340.
36. F. Doğan, İ. Kaya, A. Bilici, M. Yıldırım, Chemical oxidative polymerization, optical, electrochemical and kinetic studies of 8-amino-2-naphthol, J. Polym. Res., 22 (2015) 104-110.