Asian Journal of Chemistry; *Vol. 23, No. 10 (2011), 4573-4577*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Study on Electrochemical and Antiknock Properties of Toluidine

MING JIN[1,*] and ZHANGYU YU[2,*]

[1]School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, P.R. China
[2]Heze University, Heze 274015, P.R. China

*Corresponding authors: Fax: +86 530 5529585; Tel: +86 537 4458301; E-mail: jinming@mail.qfnu.edu.cn; zyu@mail.qfnu.edu.cn

(*Received*: 23 December 2010; *Accepted*: 27 June 2011) AJC-10102

Aromatic amine is an additive in gasoline, preventing gasoline from knocking combustion. Mechanism of toluidines function was studied on the basis of electrochemical properties of *o*-, *m*- and *p*-toluidines and their interaction with hydrogen peroxide. The electrochemical properties and the interaction were investigated by cyclic voltammetry and *in situ* UV-VIS spectroelectrochemistry. Experimental results indicated that low parent concentration and non-protonic solvent are in favour of producing dimers and/or short oligomers for the toluidines. Antiknock properties of the toluidines are related essentially to deprotonation existing in the formation of their dimers and to positioning of the ring substituent. The paper presents significant information on antiknock properties of toluidines using an electrochemical method.

Key Words: Toluidine, Hydrogen peroxide, Electrochemical properties, Antiknock properties.

INTRODUCTION

As an important gasoline additive, the use and development of antiknock agent will still be required in relatively far future. Study on antiknock mechanism is significant to improve antiknock effectiveness and develop new antiknock agent[1]. The mechanism of most of the antiknock agent, however, is not clear, in particular non-metallic antiknock agent, due to complexity of mechanism itself and difficulty of investigating directly the mechanism. It is known that toluidines have antiknock properties[2,3]. Antiknock mechanism of toluidines has also been reported[4], showing that antiknock action of an aniline derivative depends on its ability to destroy a chain-propagating free radical which is generated from the combustion of gasoline and can cause knocking combustion of gasoline. Nevertheless the suggested mechanism is little more than a hypothesis for lack of direct and sufficient evidence. Radical cation is an important intermediate in anodic oxidation of toluidines[5-8] and possibly has something to do with its antiknock properties. The present paper therefore tries to investigate the inherent relationship between the electrochemical properties and the antiknock properties of the toluidines.

Generation of the free radial is closely related to peroxide also generated from the combustion knockings of gasoline, removal of the peroxide therefore is a key procedure to alleviate detonation of gasoline[9,10]. Consequently, antiknock properties can be possibly assessed by the interaction of antiknocks with hydrogen peroxide. Hydrogen peroxide is the simplest peroxide in the detonation[9]. In the present work, the electrochemical properties of the toluidines in organic medium were studied, on the basis of which the interactions of the toluidines with hydrogen peroxide were analyzed and in turn their antiknock properties.

EXPERIMENTAL

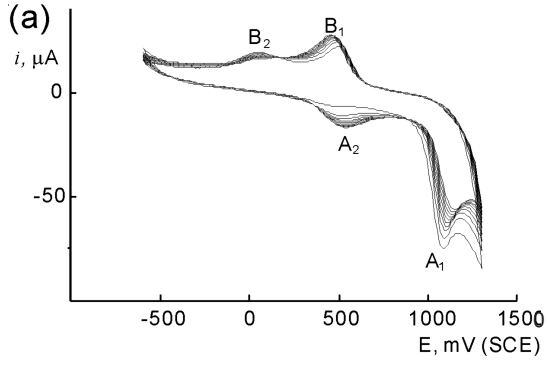
1,2-Dichloroethane, an auxiliary ingredient often used in antiknock agent, was employed as the solvent and dried over phosphorous pentoxide, then was distilled prior to use. The supporting electrolyte, tetrabutyl ammonium perchlorate (TBAP) and other reagents were of analytical grade and were used as received.

Cyclic voltammetry was performed on an EG and G PAR M398 electrochemical impedance system with a M283 potentiostat/galvanostat. The experiments were carried out in a conventional three-electrode cell. The auxiliary electrode was a platinum wire and the reference electrode was a saturated calomel electrode (SCE). All potentials were reported *versus* the SCE. Platinum circular electrode, 2 mm in diameter, was used as working electrode in cyclic voltammetry. Solutions were purged by bubbling with high purify nitrogen for 10 min and maintained in the nitrogen atmosphere. *In situ* UV-VIS measurements were made in a self-made long-optical-path thin-layer spectrum electrochemical cell (Loptlsec)[11] open to the air using Agilent8453 spectrophotometer combined with

an electrochemical workstation. The electrical-excited signal was single potential-step and a large platinum foil was used as the working electrode in the measurements. Each UV-VIS spectrum was obtained after a potential had been fixed for 5 min to assure the electrode reaching the stable state. All experimental measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Fig. 1a shows the progressive cyclic voltammograms of *m*-toluidine by repeated potential scanning between -0.7 and 1.4 V. The first cycle shows a well-defined peak marked A_1 at 1.09 V corresponding to *m*-toluidine oxidation. The peak decreased slowly and finally decayed away in the subsequent cycles. The redox peaks shown by A_2 and B_1, respectively, in the range between 0.25 and 0.75 V, in which peak A_2 began to appear from the second cycle, however were developed during the potential scanning. Moreover, the peak shifts of B_1 and A_2 occur in different directions, B_1 in a more negative direction and A_2 in a more positive direction. A thin layer film attaching to the electrode surface due to its low solubility was observed. After the electrode surface was retreated these observations can be repeated. Consequently this could be due to dimer and/or short oligomer formed upon the *m*-toluidine oxidation, which diffuse in or out slowly near the electrode surface and block *m*-toluidine molecules from diffusing toward the electrode. In addition a second cathodic peak marked B_2 showed up from the first cycle without corresponding anodic peak and was covered up gradually. Moreover, current of peak B_2 decreased proportionally with decrease of scan rate, which excludes the possibility of reduction of degradation products of the short oligomer. Similar cases also appeared actually in cyclic voltammograms of other aromatic amines such as aniline[12], *o*-toluidine, *p*-toluidine (will be shown below) under present experimental conditions, from which one can conclude that the peak is associated with deprotonation arising from the coupling process of cation radicals[13]. For the whole reaction *m*-toluidine undergoes chemically and electrochemically irreversible oxidation with no immediate cathodic current observed upon potential reversal, indicating that the immediate oxidation products (radical cations) undergo fast following reactions to the secondary products. The electrochemical behaviour of *m*-toluidine strongly resembles that of aniline[12]. On the fact above *m*-toluidine was not polymerized under the experimental conditions. The results are consistent with those reported earlier[14-16].



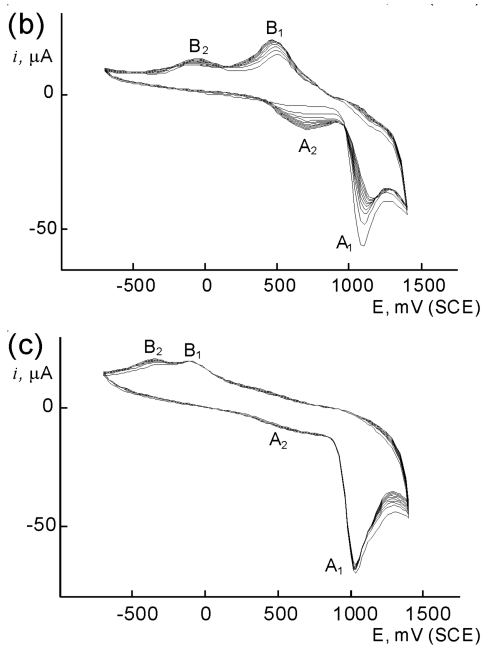


Fig. 1. Cyclic voltammograms of 2 mM *m*-toluidine (a), *o*-toluidine (b) and *p*-toluidine (c) in 1, 2-dichloroethane. Scan rate 200 mV/s

Under the certain experimental conditions, voltammetric behaviour of *o*-toluidine is similar to that of *m*-toluidine, which is in accordance with previous publications[17,18]. The differences were more quantitative than qualitative and the values of the corresponding peak potentials are shown in Table-1. The voltammetric behaviour of *m*- and *o*-toluidine in 1,2-dichloroethane is almost exactly identical with that of aniline indicates thereby that the oxidation mechanism involved in these compounds is exactly the same as suggested for aniline[12], *i.e.*, both the isomers yield tail-to-tail coupling products. Such a striking replication of behaviour of *m*- and *o*-toluidine with that of aniline lends otherwise unambiguous support to the mechanism suggested for the oxidation of aniline. The effect of the presence of electron-releasing methyl group in *m*- and/or *o*-position is also clearly visible. As expected, the potentials of peak A1 in *m*- and *o*-toluidine become slightly less positive than the corresponding values for aniline (Table-1). Introduction of a methyl group renders the electrooxidation easier, which can be explained by its +I-effect[19]. It is observed that the oxidation potential for dimer (peak A_2) of *m*-toluidine is lower than that of *o*-toluidine, indicating that electronic effect of methyl is more important than its steric effect in the formation of the tail-to-tail dimer.

TABLE-1
VALUE OF PEAK POTENTIAL (V *versus* SCE)

Aromatic amine	A_1	A_2	B_1	B_2
m-Toluidine	1.085	0.535	0.448	0.055
o-Toluidine	1.092	0.695	0.463	0.060
p-Toluidine	1.036	~ 0.621	-0.110	-0.350
Aniline*	1.150	0.698	0.474	-0.214

*Refer to earlier report[12].

Cyclic voltammogram of *p*-toluidine is shown in Fig. 1c. A comparison of Fig. 1c with Figs. 1a and 1b shows that the oxidative voltammetric behaviour of *p*-toluidine is considerably different from that of *m*- and *o*-toluidine. While we get a

growing well-defined reduction peak near 0.45 V during the first reverse (reduction) scan in the cases of *m*- and *o*-toluidine, we get an invariable and very subdued reduction peak at -0.11 V in the case of *p*-toluidine. In the followed scans there is a more subdued hump too (A_2). In all the cycles the potentials of the peaks stay constant. Thus, steric effect of ring substituted groups is more important in *p*- than in *m*- and/or *o*-. In the case of *p*-toluidine, since the *p*-position is occupied, it rules out the possibility of head-to-tail or tail-to-tail coupling. Only head-to-head coupling is permissible which results in the formation of *p*,*p*'-dimethylhydrazobenzene. This compound readily undergoes electrooxidation at the same potential forming *p*,*p*'-dimethylazobenzene as a stable product. During the reverse (reduction) scan, the *p*,*p*'-dimethylhydrazobenzene should have been reduced to hydrazobenzene analogue thus giving a well-defined peak. But this does not happen. The presence of electron-releasing methyl group at *p*-positions tend to increase the electron density at the -N=N- site thereby decreasing its tendency to gain electrons and thus get reduced. Consequently, during the reduction scan only a limited reduction of azo compound to hydrazobenzene analogue takes place. The formation of a similar smaller subdued oxidation hump during the second forward (oxidation) scan is then easily understandable. Thus the dimer cannot converge at the electrode surface and the current peak of *p*-toluidine monomer (A_1) stays constant.

For further confirmation of the results obtained above, *in situ* thin-layer UV-VIS spectra of the toluidine are recorded, with the potential under the control of an electrochemical workstation. Fig. 2 shows UV-VIS spectra of toluidines at various potentials selected according to the cyclic voltammograms. Under open circuit conditions the toluidines have no absorption clearly after 320 nm. At 1.4 V, where the toluidines are completely oxidized, two distinct absorption bands at 550 and 733 nm, respectively, are observed for *m*-toluidine, demonstrating that a large conjugated system is formed. The absorption at 733 nm is relevant to the exciton transition from benzene ring to quinone ring, corresponding to the oxidation state of the product. The product is in the structure of an imine quinone at the oxidation state, from which one can conclude that the absorption resulted from the tail-to-tail dimer forming larger conjugate system than other dimers. The other absorption at 550 nm is related to *p*-π conjugate between methyl of benzene ring and the conjugated system. The spectra for *o*-toluidine and *m*-toluidine are similar, which is in well agreement with their similarity in cyclic voltammogram. The difference was also more quantitative than qualitative, *i.e.*, the absorption at 550 nm is stronger for *m*-toluidine than for *o*-toluidine. If the potential was stepped to -0.7 V, these bands disappeared almost fully and a new weak but broad wave was observed at *ca.* 475 nm related to reduction state of the products. However, for *p*-toluidine the absorption band at 1.4 V shifts considerably to 507 nm. This indicates that there is no large conjugated system in the product. The dimer should be formed by the way of head-to-head. Moreover at -0.7 V the absorption is similar to *mata*- and *o*-toluidine. This is also in well agreement with its cyclic voltammogram behaviour. The dimerizations of the toluidine are suggested accordingly in **Schemes I** and **II**, respectively.

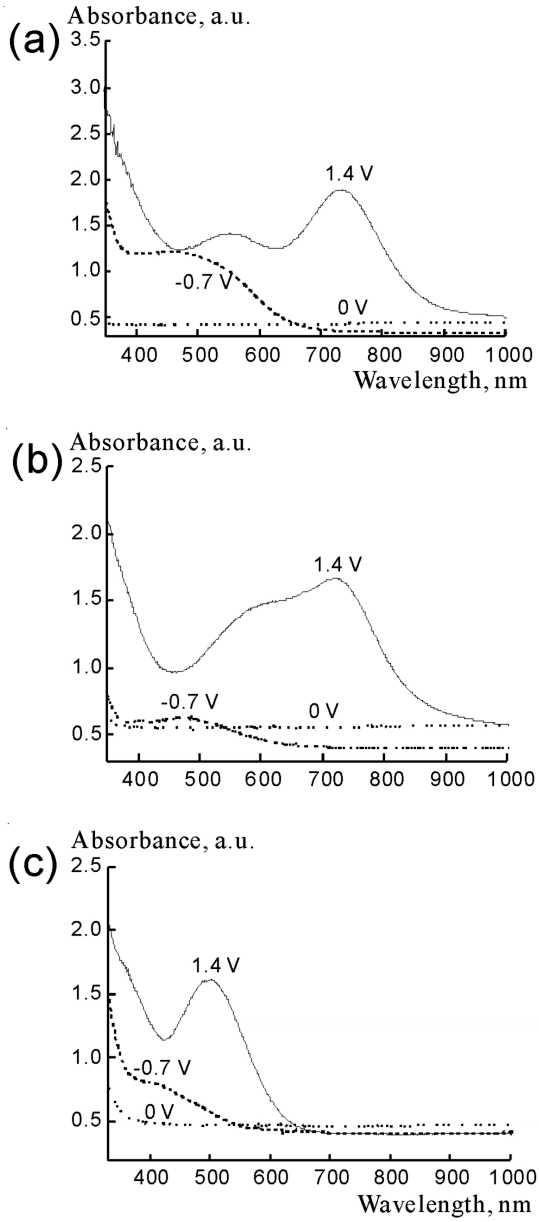
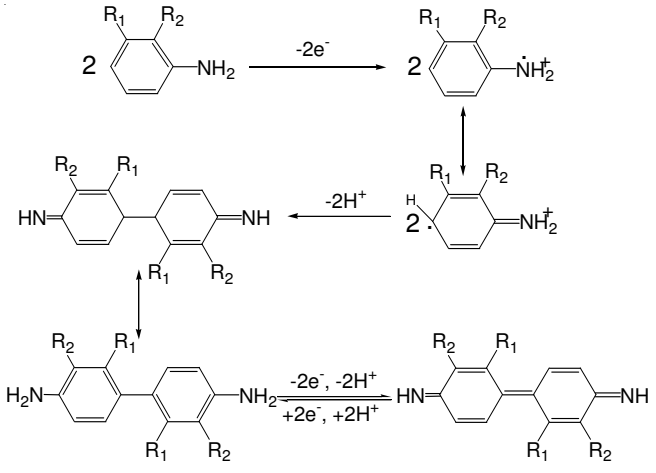
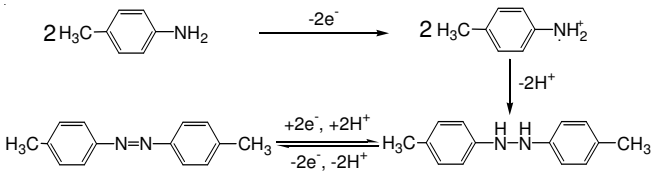


Fig. 2. UV-VIS absorption spectra of 2 mM *m*-toluidine (a), *o*-toluidine (b) and *p*-toluidine (c) in 1,2-dichloroethane at various potentials (*versus* SCE). Single potential-step is in the order 0, 1.4, -0.7 V



Scheme-I: Dimerization of *m*- and *o*-toluidine (R_1 = H, R_2 = CH_3, for *m*-toluidine; R_1 = CH_3, R_2 = H, for *o*-toluidine)



Scheme-II: Dimerization of *p*-toluidine

Fig. 3 shows cyclic voltammogram behaviour of toluidine after addition of hydrogen peroxide. As far as *m*- and *o*-toluidine are concerned, changes in cyclic voltammogram behaviour after addition of hydrogen peroxide are: (1) cathodic peak B_2 disappeared, (2) peak A_2 became more subdued and developed slowly and (3) the scanning cycles required forming a couple of redox peaks (A_2/B_1) decreased considerably and moreover, the cyclic voltammogram curve became flat soon. These changes are obviously relevant to hydrogen peroxide. Peak B_2 is associated with the deprotonation, its disappearance therefore can be interpreted by the following formula:

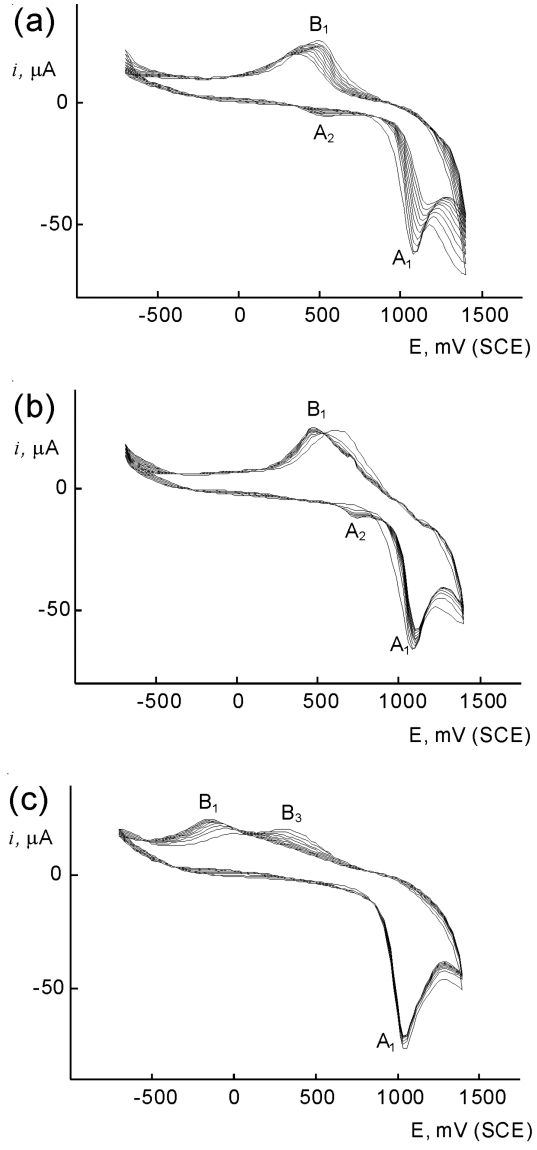


Fig. 3. Multicyclic voltammograms of a mixture of (a) 2 mM *m*-toluidine and 2 mM H_2O_2, (b) 2 mM *o*-toluidine and 2 mM H_2O_2 and (c) 2 mM *p*-toluidine and 2 mM H_2O_2. Scan rate 200 mV/s

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$

This interaction can lead apparently to decrease of protons. The deprotonation hereby was promoted and in turn the oxidation of the toluidines. At the same time reversibility of the redox of their dimers were aggravated. Peak A_2 arose from the oxidation of the dimers. The change in peak A_2 and the cyclic voltammogram curve showed that both the dimers and the monomers can interact with hydrogen peroxide. And the former does more easily than the latter. It is then expected that the antiknock effectiveness of the dimers should be higher than that of the monomers. As can be seen, the peak potentials of A_1 for *m*- and *o*-toluidine are less positive and that of B_2 more positive than those for anilne (Table-1). This indicates that the two toluidines are oxidated more easily and are easier for deprotonation than aniline. Thus the antiknock effectiveness of the toluidines should be higher than that of aniline. This is in excellent agreement with other experimental result reported[4].

For *p*-toluidine there were four changes worth of note in cyclic voltammogram behaviour arising from hydrogen peroxide. Firstly, a new clear cathodic peak (marked B_3) instead of peak B_2 in Fig. 1c appeared at *ca.* 0.310 V in the first cycle and however disappeared rapidly during the following scans. This is caused by reduction of an intermediate which needs further investigation. Secondly, the potential of peak B_1 shifted positively in the first reverse (reduction) scan and the current of the peak decreased slightly compared to that in Fig. 1c. Moreover, peak B_1 developed with the decline of peak B_3 during the following potential scans. Thus the two changes could assign causality. Thirdly, the subdued oxidation hump (marked A_2 in Fig. 1c) disappeared, which arose from the interaction of the dimer of *p*-toluidine with hydrogen peroxide. Last but not least is that peak B_2 also disappeared, which evidently resulted from the interaction of the protons with hydrogen peroxide. The interaction was the fundamental reason of the development of peak B_1 and the decline of peak B_3. These changes indicate that *p*-toluidine can interact with hydrogen peroxide and therefore also has antiknock properties. Because the peak potentials of A_1 for *p*-toluidine are less positive and that of B_2 more negative than those for anilne (Table-1), the former is therefore oxidated more easily and is more difficult for deprotonation than the latter. Thus the antiknock effectiveness of *p*-toluidine should be lower than that of *m*- and/or *o*-toluidine but higher than that of aniline.

Conclusion

Products of the electrochemical oxidation of *m*-, *o*- and *p*-toluidines are dominated by the dimers and/or the short oligomers by cation radical coupling in the condition of low parent concentration and non-protonic solvent. The toluidines can interact with hydrogen peroxide and then have antiknock properties. The interaction is essentially between proton released from the oxidation and hydrogen peroxide. The antiknock properties of toluidine thus are related to deprotonation depending on hydrogen bonded to nitrogen. Steric hindrance of substituent on the ring has influence on the antiknock effectiveness of aromatic amine. Antiknock effectiveness of *m*- and *o*-toluidine is close and slight higher than that of

p-toluidine. The dimers of the toluidines should have higher antiknock effectiveness than the monomers. Study on electrochemical behaviour of an antiknock agent with peroxide can present significant information on its antiknock properties.

ACKNOWLEDGEMENTS

The authors are grateful to Natural Science Fund of Shandong Province, China (Y2008E14) and China Postdoctoral Science Foundation funded project (200902558) and Initial Funding for Dr. Scientific Research of Qufu Normal University for financial support.

REFERENCES

1. V.A. Vinokurov and I.I. Vorob'ev, *Chem. Technol. Fuels Oil*, **37**, 101 (2001).
2. H. Alquist and L.K. Tower, Wartime Report (NACA), Memorandum Report E5H06 (MR No. E5H06).
3. V.N. Skobelev, V.M. Yablokov, V.V. Serdyuk and L.A. Ashkinazi, *Russ. J. Appl. Chem*., **80**, 1225 (2007).
4. J.E. Brown, F.X. Markley and H. Shapiro, *Ind. Eng. Chem*., **47**, 2141 (1995).
5. S. Bilal, A.H.A. Shah and R. Holze, *Electrochim. Acta*, **54**, 4851 (2009).
6. S.J. Su, M. Takeishi and N. Kuramoto, *Macromolecules*, **35**, 5752 (2002).
7. T. Kessler and A.M.C. Luna, *J. Appl. Electrochem*., **32**, 825 (2002).
8. F. Cases, F. Huerta, P. Garcés, E. Morallón and J.L. Vázquez, *J. Electroanal. Chem*., **501**, 186 (2001).
9. W.J. Pitz and C.K. Westbrook, *Combust. Flame*, **63**, 113 (1986).
10. K.C. Salooja, *Combus. Flame*, **9**, 211 (1965).
11. Z. Yu, T. Guo and M. Qin, *Anal. Chem*., **66**, 497 (1994).
12. M. Jin, Z. Yu and Y. Xia, *Russ. J. Electrochem*., **42**, 964 (2006).
13. L.R. Sharma, A.K. Manchanda, G. Singh and R.S. Verma, *Electrochim. Acta*, **27**, 223 (1982).
14. L. Duic, Z. Mandic and S. Kovac, *Electrochim. Acta*, **40**, 1681 (1995).
15. M. Matsushita, H. Kuramitz and S. Tanaka, *Environ. Sci. Technol*., **39**, 3805 (2005).
16. D. Sazou, *Synth. Met*., **118**, 133 (2001).
17. M. Leclerc, J. Guay and L.H. Dao, *J. Electroanal. Chem*., **251**, 21 (1988).
18. P.G. Desideri, L. Lepri and D. Heimler, *J. Electroanal. Chem*., **52**, 93 (1974).
19. M. Probst and R. Holze, *Macromol. Chem. Phys*., **198**, 1499 (1997).