Electrocopolymerization of poly(*o*-toludine-co-metanilic acid) on mild steel surfaces and their physico-electrochemical characterizations

P. Raja Kumar, D. Kalpana *, N.G. Renganathan, S. Pitchumani

Central Electrochemical Research Institute, Karaikudi 630006, India

Abstract

For the first time, poly(*o*-toludine-co-metanilic acid) (POM) layers have been deposited on mild steel (MS) substrate by galvanostatic (GS), potentiostatic (PS) and potentiodynamic (PD) methods. AC impedance of the electrodes has been analyzed. The shape and impedance parameters of galvanostatically prepared electrodes are similar to those of potentiostatically grown electrodes. The impedance spectra of potentiodynamically prepared electrode, however, are different. The redox behavior of POM copolymer has been studied using cyclicvoltammetric technique. Also, the copolymer prepared by potentiodynamic method has been characterized by UV–vis spectroscopy, Fourier Transform Infrared spectroscopy (FTIR) and Thermogravimetric analysis. It has been observed that polymerization of POM are greatly influenced by the method of preparation.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Conducting polymer; *o*-Toludine; Potentiodynamic; Cyclic voltammetry; Impedance spectroscopy

1. Introduction

Due to immense technological applications of conducting polymers as active electrode materials in energy storage devices [1], display services [2], opto-electronic devices [3] and as chemically modified electrodes [4], they have received a great deal of attention from chemists and physicists. Intrinsically, conducting polymers have attracted the attention of researchers around the world due to the possibilities of applications. A common example of this is the poly aniline (PANI) probably the most extensively studied conducting polymer [5–7]. PANI emerged as one of the best candidates because of its ease of preparation, environmental stability, cheap raw material and wide applicability.

PANI is particularly interesting because of the presence of chemically flexible NH-group in the polymer back bone, which will not take part in protonation and de-protonation, but contributes to π-bond formation [8], thus, ensuring greater environmental stability. However, the complete characterization of this polymer has been restricted largely due to its solubility in solvents and difficulties in processibility. Many research groups have tried to achieve solublization of this polymer so that it

becomes applicable in electronic devices and structural elucidation [9,10].

One of the methods used to carry out the changes in the properties of conducting polymers is copolymerization in which precursor solution contains a mixture of monomers. In this case, it is expected that the properties of the copolymer will be intermediary to those of the homopolymers [9,11]. Wei et al. [12,13] reported that aniline could be polymerized with *o*-toludine to give rise to a copolymer film, of which conductivity could be controlled in a broad range. Fahlman et al. [14] used emeraldine-based polyaniline undercoats for the application of corrosion protection for both the cold rolled steel and iron samples. They found that the degree of protection changes depending upon the thickness of the iron oxide layer at the polymer/metal interface as well as on the thickness of the top oxide layer. Implications of polyaniline with metal interfaces on corrosion protection of steel and aluminum alloys have also been studied [15,16]. Bergeron and Dao [17] reported copolymerization of aniline with *N*-butyl aniline. Dhawan and Trivedi [18] studied copolymerization of aniline and *o*-toludine by electrochemical and chemical methods. These reports suggest that the copolymerization could provide us a convenient synthetic method to prepare new conducting materials with desired properties. Although copolymerization attempts have been known with aniline and toludine [19–25], attempts of copolymerizing

----

* Corresponding author. Tel.: +91 4565 227 551; fax: +91 4565 227 651.
  E-mail address: dkalps@rediffmail.com (D. Kalpana).

with metanilic acid is known only for aniline but not for *o*-toludine. Moreover, the impedance analysis for the copolymer prepared by different techniques has not yet been discussed. Hence, an attempt has been made to copolymerize *o*-toludine with metanilic acid analogous to aniline copolymerization in this investigation. Based on these strengths, for the first time, it is intended to examine the copolymerization of *o*-toludine and metanilic acid via potentiodynamic (PD), potentiostatic (PS) and galvanostatic (GS) methods. The characterization of copolymer deposit on mild steel was characterized by using impedance spectra and cyclicvoltammogram.

2. Experimental

The monomer *o*-toludine was double distilled before use and the co-monomer metanilic acid (Aldrich) was used as received. The copolymer deposit of POM is synthesized electrochemically on mild steel surface under cyclicvoltammetric (potentiodynamic) conditions in a simple, one compartment glass cell. A mild steel (MS-304) foil was polished with emery, washed with detergent, acetone, rinsed with triple distilled water and air-dried. A three-electrode geometry was employed during the electrochemical polymerization using mild steel as working electrode of area $1\,cm^2$, platinum foil as counter electrode and SCE as reference electrode. The deposition of copolymer was carried out galvanostatically (GS) with various current densities, potentiostatically (PS) and potentiodynamically (PD). The optimization was performed by varying the upper switching potential, current density and ratio of poly(*o*-toludine) to metanilic acid and the H_2SO_4 concentration. In GS and PS techniques, the oxidation of *o*-toludine and metanilic acid to copolymer of required thickness was achieved by allowing electrolysis for 15 min duration. During the galvanostatic deposition, the electrode potential was nearly invariant about 0.8 V. In the potentiodynamic method, the electrode was subjected to cycling between −0.2 and 0.8 V and the growth of the copolymer deposit to the required thickness was achieved by cycling 100–200 sweep rates at 50 mV/s.

The POM deposits were electropolymerized in the solution containing 3:1 molar ratio (in order to get more electrodeposited polymer for corrosion studies, it was optimized for 3:1 ratio as polyaniline looses its electroactivity at higher pH, i.e., >4) of *o*-toludine and metanilic acid in 0.1 M sulphuric acid as electrolyte by applying sequential linear potential scan rate of 50 mV/s between −0.2 and 0.8 V versus SCE. The deposits of POM were deposited with 100–200 cycles for the polymerization.

Throughout the studies, anaerobic conditions were maintained with nitrogen gas atmosphere. The current density and the potential were fixed after a series of experiments wherein the deposits of POM was carried out by either galvanostatically with various current densities from 1 to $8\,mA/cm^2$ and potentiostatically from 0.7 to 1.2 V. In these two techniques, the oxidation of poly(*o*-toludine) of minimum thickness (or mass per unit area) was arrived and thus the values of $5\,mA/cm^2$ and 0.8 V were fixed for galvanostatic and potentiostatic experiments for consistent results.

The BAS 100B instrument was used for carrying out cyclicvoltammetric experiments and EG&G PAR electrochemical impedance analyzer (Model 6310) instrument was used to carryout the AC impedance measurements in the frequency range from 100 KHz to 10 MHz with an excitation signal of 5 mV. The copolymer was determined by FTIR spectroscopy using a Nexus FT-IR spectrometer 670 Model with DTGS detector and KBr pellets of solid samples. The electrodeposited copolymers were also dissolved in NMP whenever possible. The UV–vis spectra of polymer solutions were recorded on a Cary 1 UV–vis NIR Spectrometer. The TG/DTA curves were recorded on STA 1500 system.

3. Results and discussion

3.1. Electrochemical behavior of POM/MS electrode

Fig. 1 shows the electrochemical oxidation of *o*-toludine in aqueous acidic electrolyte which produces POM. Fig. 2 shows cyclicvoltammogram recorded during the synthesis of poly(*o*-toludine-co-metanilic acid) on mild steel. The formation and growth of the polymer film can be easily seen from the figure. The intensity of the two broad oxidation and reduction peaks of the film increase as the film grows. Fig. 3 shows the cyclicvoltammograms recorded after the synthesis of POM by potentiostatic (PS), galvanostatic (GS) and potentiodynamic (PD) methods in aqueous solutions of 0.1 M H_2SO_4 acid at room temperature. The CVs were recorded for various scan rates, namely 2, 5 and 10 mV/s, respectively, and the over all observations and results obtained from CVs are listed below.

(i) When the applied potential is cycled from −0.2 V to positive potential of 0.8 V versus SCE, the anodic current began to increase, showing that monomer dissolved in solution, oxidized at the surface of the electrode. At higher potential
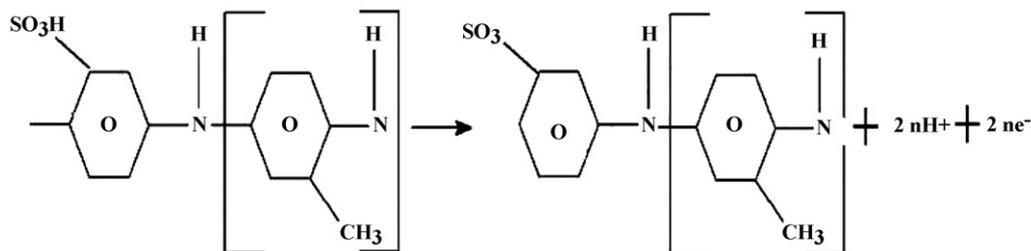
Fig. 1. Electrochemical oxidation of poly(*o*-toludine-co-metanilic acid).
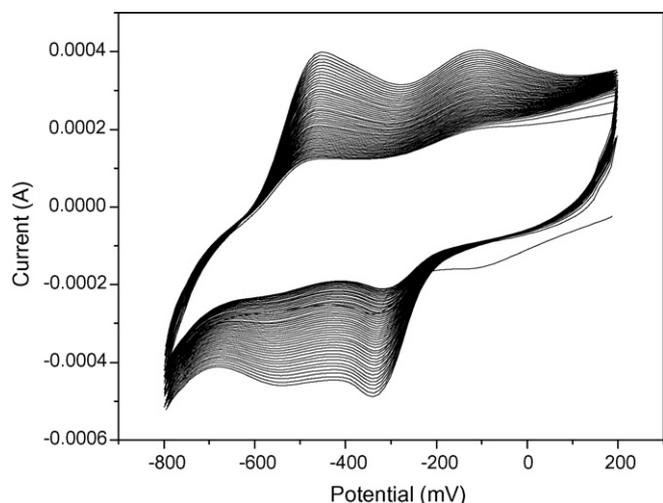
Fig. 2. Cyclicvoltammogram recorded during the synthesis of poly(*o*-toludine-co-metanilic acid) on mild steel.

Table 1
CV parameters obtained for electrochemical copolymerization of POM at the scan rate 10 mV/s

Method of preparation	Peak potential (mV)			Peak current (mA)	
	Anodic (E_p^a)	Cathodic (E_p^c)	ΔE_P	Anodic (i_p^a)	Cathodic I_p^c
PD	325	410	85	27.0	28.3
PS	200	340	140	7.0	6.5
GS	220	385	165	2.78	2.4

(0.8 V) oxidation takes place, and therefore, high anodic current (14.5 mA) flows for the PD method.

(ii) The CV curves grow with number of cycles indicating the formation of conducting polymer. It signifies that oxidation potential of the monomer is dependent on size and type of the anion present [26–28].

(iii) There is only one redox peak observed in 0.1 M H_2SO_4 for each preparation technique which indicates that POM film prepared with each technique is electroactive. The anodic peak of electrocopolymerization ranges from 200 to 325 mV and cathodic peak from 340 to 410 mV. The different redox peaks and their corresponding current values obtained for all the techniques indicate that the electrochemical behavior of POM depends upon the preparation conditions.

(iv) The redox potentials and the corresponding peak current are presented in Table 1. The highest anodic current of 27 mA corresponding to the peak potential of 325 mV obtained for the PD method at 10 mV/s scan rate shows the formation of polymerization of POM. The anodic peak is assigned to the oxidation of polymer deposited on the electrode surface,
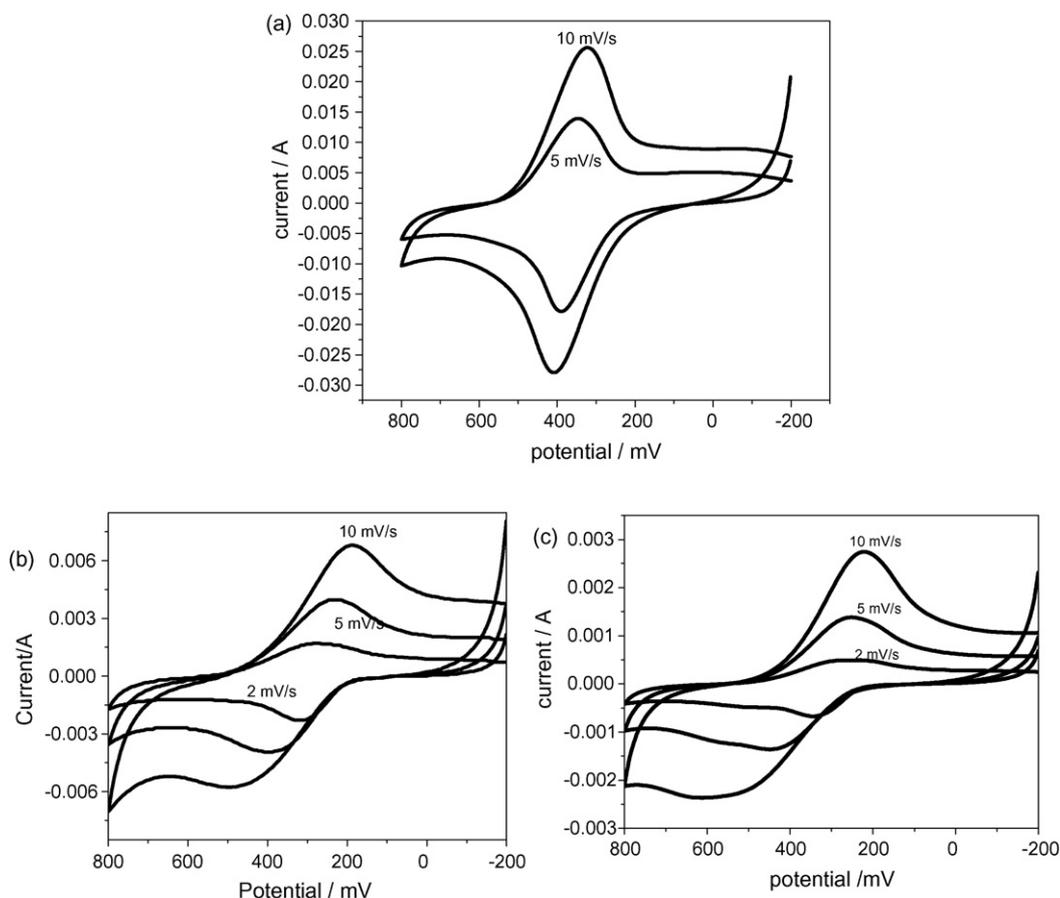
Fig. 3. Cyclicvoltammograms of POM/MS electrodes in 0.1 M H_2SO_4 at 2, 5 and 10 mV/s scan rates. POM/MS electrodes prepared by (a) potentiodynamic (b) potentiostatic and (c) galvanostatic.

which corresponds to the conversion of amine units into radical anions [29].

(v) For all techniques, the voltammograms are fairly broad and there is an increase in current with increase of sweep rate. This increase may be directly proportional to capacitance and hence there will be a linear relationship between I and V which is indicative of the fact that the voltammetric current is essentially due to capacitance.

Thus, the CVs clearly reveal the formation of electroactive conducting polymer deposits in all the three methods. The appearance and intensity of the peak is highly dependent on the preparation conditions. CV of the POM copolymer prepared by PD method (Fig. 3a) is different from that of the copolymer deposits obtained from other methods (Fig. 3b and c). This clearly supports the formation of the POM copolymer which is dependent on the preparation conditions.

I–t curves traced under potentiostatic polymerization condition is given in Fig. 4. As shown in the figure, the current decays as the electrolysis proceed to deplete the solution near the electrode of electroactive species. The mechanism of electrochemical polymerization of monomer is believed to proceed via a radical cation which reacts with a second radical cation to give a dimer. This reacts further with the radical cation of the monomer to build up the polymer chain. In case of copolymerization, a chain might be built up by formation through conjugation of radicals of two different monomers followed by propagation [30,31]. From Table 1, it is clearly seen from ΔE_P values that
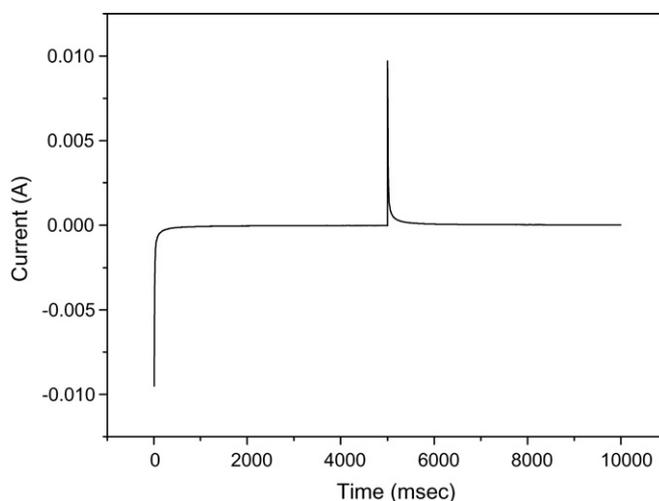
Fig. 4. *I–t* curves traced under potentiostatic polymerization condition.

POM formed by PD method shows higher reversibility indicative of polymer redox activity.

3.2. AC impedance spectroscopy characteristics of POM/MS prepared by PD, PS and GS techniques

The Nyquist impedance spectra of POM/MS electrodes prepared by PD, PS and GS methods are shown in Fig. 5a–c for 0.0, 0.2 and 0.4 V potentials. The spectrum is characterized by a high frequency intercept on the real axis due to solution resistance
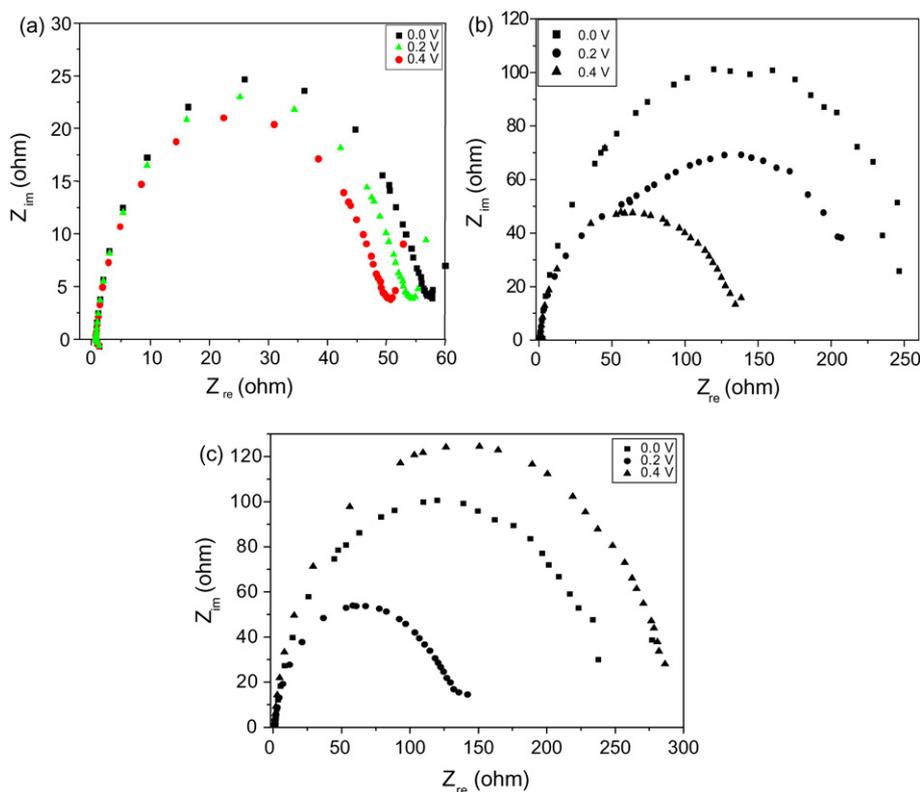
Fig. 5. Nyquist impedance spectra of POM/MS electrodes in 0.1 M H$_2$SO$_4$ at 0.0, 0.2 and 0.4 V vs. SCE. POM/MS electrode was prepared by (a) potentiodynamic (b) potentiostatic and (c) galvanostatic method.

(R_s), a semicircle due to polymer resistance (R_p) in parallel with the capacitance C and a linear Warburg part at low frequency range. The variations of impedance parameters with various applied potential are shown in Fig. 5b and c for potentiostatically and galvanostatically prepared electrodes, respectively. It is seen that there is a decrease in R_s, and R_p with an increase in applied potential. The solution resistance R_s for the GS technique is $1.138\,\Omega$ at $0.0\,V$ potential. It decreases to $0.726\,\Omega$ as the applied potential increases from 0.0 to 0.4 mV. This is contributed from the electrolyte between the working and reference electrodes, as well as from the electrolyte trapped inside the polymer. In the case of PS technique, the increase in R_s is also contributed essentially by the electrolyte trapped within the polymer layer. Due to the entry of anion into the polymer layer, the electrolyte resistance increases. It is interesting to observe that there is an increase in capacitive element (162 to $280\,\mu F$) in both the cases (GS and PS techniques) with an increase in solution resistance, due to the increase in thickness of the copolymer.

3.2.1. Impedance of POM/MS electrode prepared by potentiodynamic method

The impedance spectrum of POM/MS electrode at 0.0, 0.2 and 0.4 mV is shown in Fig. 5a and the impedance parameters are given in Table 2. The electrode was prepared by potentiodynamic method at a sweep rate of 50 mV/s. The spectrum differs from those shown in Fig. 5b and c (PS and GS) in intermediate frequency range, as it contains the 45° linear part. The semicircle at high frequency intercept on real axis is common for all the three systems. However, there is a small capacitive spike appears immediately after the formation of semicircle in Fig. 5a. It is noted that R_p of potentiodynamically deposited electrode is much smaller ($51\,\Omega$) than that of potentiostatically/galvanostatically deposited electrode.

In the PD method, the growth of deposit takes place layer by layer. However, similar activation of the polymer does not exist in the case of continuous growth under galvanostatic and potentiostatic conditions. Since the polymerization is uninterrupted, it is possible for the formation of branched POM chain under galvanostatic/potentiostatic conditions. On the other hand, this possibility is less under potentiodynamic conditions due to the interruption of polymerization between consecutive sweeps. During PS/GS methods of POM deposition, the intermediates could be trapped within the POM deposit because of continuous growth. On the other hand, the intermediates could be released or dissolved into the electrolyte during interruption period of POM deposition of PD method.

Fig. 6. TG/DTA curves of POM prepared by potentiodynamic method.

3.3. Thermogravimetric analysis

TG/DTA and DTG curves of POM prepared by PD method are shown in Fig. 6. The degradation can be roughly divided into three main weight loss steps. The thermal degradation of POM commences with a weight loss of typically at 80 °C extending from room temperature up to 245 °C. It can be seen that a straight-line plot was obtained for the weight loss steps. The first weight loss step is mainly due to the expulsion of water molecules from the polymer matrix. The second weight loss step occurring typically between 245 and 449 °C is due to the loss of 50% bound to the POM chain. Based on the TG results, the third weight loss from 449 to 541 °C is due to the degradation of skeleted PANI backbone chain structure.

3.4. UV–vis analysis

The UV–vis spectrum of copolymer solutions prepared by PD method in NMP is shown in Fig. 7. The spectrum is dominated

Table 2
Nyquist impedance parameters for a electrocopolymerization of POM prepared by PD method

Applied potential (V)	Polymer resistance R_p (Ω)	Capacitance C (μF)	Solution resistance R_s (mΩ)
0.0	55.4	162.0	712
0.2	51.6	174.1	706
0.4	48.6	190.3	700
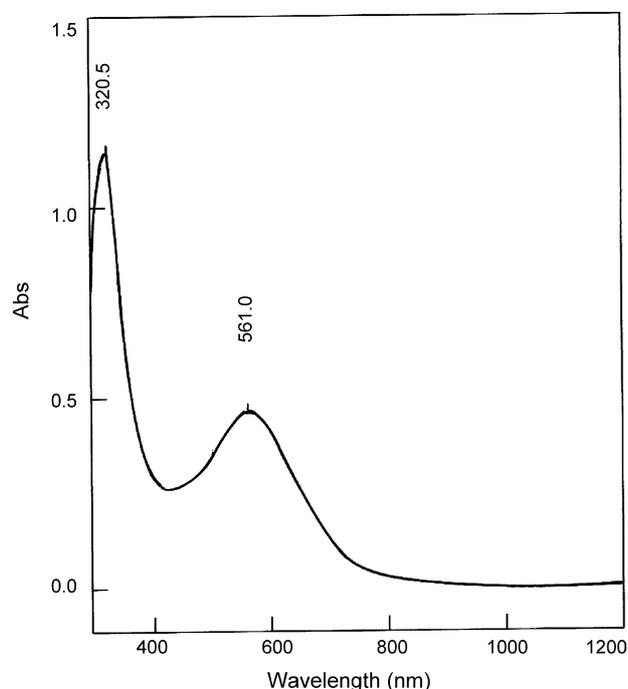
Fig. 7. UV–vis spectrum of POM in NMP solution prepared by potentiodynamic method.
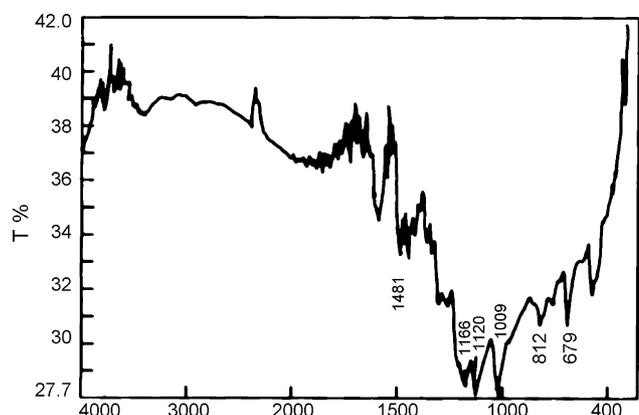
Fig. 8. FTIR spectrum of the POM (in KBr pressed pellet) obtained by potentiodynamic method.

by two broad absorption bands at 320 and 561 nm. The peak at 320 nm can be attributed to π–π* transition in the benzenoid ring of reduced leucoemeraldine [31–32] and the peak at 561 nm attributed to n–π* transition [33–35].

3.5. FTIR analysis

The FTIR spectra of the copolymer show the various characteristic peaks in Fig. 8. The absorption peaks at 1120 and 1166 cm^{-1} are characteristic peaks due to the charge delocalization in polymer matrix. The absorption peak at 1166 cm^{-1} may be assigned to the characteristic mode of –N=Q=N (imine) or B–NH–B (where B denotes benzenoid and Q denotes quinoid ring). The presence of sulphonate functional group was inferred from the S=O stretching mode at 1009 cm^{-1} and peak at 679 cm^{-1} as an identification for the sulphonate group. The peak at 812 cm^{-1} is characteristic of para disubstituted aromatic rings in the polymer. The peak at 1481 cm^{-1} (C–C stretching) indicating the existence of methyl group in the copolymer [36].

4. Conclusion

Following conclusions have been drawn from the present POM copolymerization process.

1. The cyclicvoltammetric investigation clearly indicates the formation of electroactive POM copolymer in 0.1 M H$_2$SO$_4$ electrolyte on mild steel surface.
2. It is observed that the anodic current densities of polymerization of POM are greatly influenced by method of preparation.
3. AC impedance studies clearly indicate that the electroactive POM copolymer can be deposited on mild steel by all the methods of synthetic routes. But, it has been observed that the potentiodynamic method is the best instrument to synthesize the POM copolymer.

4. FTIR and UV–vis results confirm the formation of POM. The application of POM as corrosion inhibitor is under progress.

References

[1] A.G. Mac Diarmid, S.L. Mu, N.L.D. Somasiri, W. Wu, Mol. Cryst. Liq. Cryst. 125 (1985) 187.
[2] A. Kitani, J. Yano, K. Sasaki, J. Electronal. Chem. 209 (1986) 227.
[3] E.W. Paul, A.J. Ricco, M.S. Wrighton, J. Phys. Chem. 89 (1985) 1441.
[4] S.K. Dhawan, D.C. Trivedi, Bull. Mater. Sci. 12 (1989) 153.
[5] B. Wessling, Synth. Met. 93 (1998) 143.
[6] D. Cottevieille, A. Le Mechaute, C. Challioui, J. Chim. Phys. 95 (1998) 1502.
[7] J.R. Santos Jr., J.A. Malmonge, A.J.G.C. Silva, A.J. Motheo, Y.P. Mascarenhas, L.H.C. Mattoso, Synth. Met. 69 (1995) 141.
[8] A.F. Diaz, J.A. Logan, J. Electroanal. Chem. 111 (1980) 111.
[9] S.Ye. Besner, L.H. Dao, A.J. Vijh, J. Electroanal. Chem. 381 (1995) 71.
[10] S.W. Byun, S.S. Im, Polymer 39 (1998) 485.
[11] H. Tang, A. Kitani, S. Ito, Electrochim. Acta 42 (1997) 3421.
[12] Y. Wei, W.W. Focke, G.E. Wrek, A. Ray, A.G. MacDiarmid, J. Phys. Chem. 93 (1989) 495.
[13] Y. Wei, R. Hariharan, S.A. Patel, Macromolecules 23 (1990) 764.
[14] M. Fahlman, S. Jasty, A.J. Epstein, Synth. Met. 85 (1997) 1323.
[15] M. Fahlman, X. Crispin, H. Guan, S. Li, J.A.O. Smallfield, Y. Wei, A.J. Epstein, Polymer Preprints 41 (2) (2000) 1753.
[16] M. Fahlman, X. Crispin, J.A.O. Smallfield, R. Lazzaroni, J.L. Bredas, S. Li, Y. Wei, A.J. Epstein, Am. Chem. Soc. Symp. Ser. 843 (2003).
[17] J.Y. Bergeron, L.H. Dao, Polym. Commun. 32 (1991) 403.
[18] S.K. Dhawan, D.C. Trivedi, Synth. Met. 60 (1993) 63.
[19] R. Cordova, M.A. Del valle, A. Arratia, H. Gomez, R. Schrebler, J. Electroanal. Chem. 377 (1994) 75.
[20] W.S. Huang, B.D. Humphrey, A.G. Mac Diarmid, J. Chem. Soc., Faraday Trans. 82 (1986) 385.
[21] T. Inoue, T. Yamase, Bull. Chem. Soc., Jpn. 56 (1983) 985.
[22] J.Y. Lee, C.Q. Cui, X.H. Su, M.S. Zhou, J. Electroanal. Chem. 369 (1993) 177.
[23] J.Y. Lee, X.H. Su, C.Q. Cui, J. Electroanal. Chem. 367 (1994) 71.
[24] D.D. Borole, U.R. Kapadi, P.P. Mahulikar, D.G. Hundiwale, Mater. Lett. 60 (2006) 2447.
[25] C.Q. Cui, L.H. Ong, T.C. Tan, J.Y. Lee, J. Electroanal. Chem. 346 (1993) 477.
[26] Y. Wei, C.C. Chan, J. Tian, G.W. Jang, K.F. Hsuch, Chem. Mater. 3 (1991) 888.
[27] T.P. Mc Andrew, S.A. Miller, A.G. Gilicinski, L.M. Robeson, ACS Symp. Ser. 689 (1998) 396.
[28] J.Y. Lee, C.Q. Cui, X.H. Su, M.S. Zhou, J. Electroanal. Chem. 367 (1994) 71.
[29] J. Yue, Z.H. Wang, K.R. Kromack, A.J. Epstein, A.G. MacDiarmid, J. Am. Chem. Soc. 113 (1991) 2665.
[30] A.D. Borkar, S.S. Umare, M.C. Gupta, Prog. Cryst. Growth Character. Mater. 44 (2002) 201.
[31] N. Pekmez, K. Pekmez, R. Holze, A. Yidiz, J. Appl. Polym. Sci. 90 (2003) 3417.
[32] A. Zagorska, A. Pron, S. Leftrant, in: H.S. Nalwa (Ed.), Handbook of Organic Conductive Molecules and Polymers, vol. 3, Wiley, New York, 1997, p. 183.
[33] S.S. Pandey, S. Annapoorni, B.D. Malhotra, Macromolecules 26 (1993) 3190.
[34] M.K. Ram, E. Maccioni, C. Nicolini, Thin Solid Films 303 (1997) 27.
[35] A.J. Motheo, M.F. Pantoja, E.C. Venancio, Solid State Ion. 171 (2004) 91.
[36] J.W. Chevalier, J.Y. Bergeron, L.H. Dao, Macromolecules 25 (1992) 3325.