

Synthesis and Characterization of Benzealkonium chloride cationic surfactant doped nanosize poly (o-toluidine)

B. Mahalakshmi¹ and C. Vedhi²

^{1,2}Department of Chemistry, V.O. Chidambaram College, Thoothukudi-8, Tamil Nadu, India

Abstract

Nano-sized POT-BAC particles were synthesized (pH=7.80) by chemical method. The doping of BAC in the polymer network of POT was suggested using UV-Vis, FT-IR, XRD, SEM, and TEM. POT-BAC was completely soluble in DMSO and DMF. The analyses of UV visible and FTIR spectroscopy demonstrated that o-Toluidine has been polymerized to POT in its conducting emeraldine form. The FT-IR spectra showed that amine peak at 1598 cm^{-1} was shifted to 1589 cm^{-1} . This indicates the interaction of polymer with the surfactant. From the SEM micrographs it was observed that each polymer have different morphology. The variation in morphology of the doped POT was predominantly dependent on the concentration of the surfactant. The chemical composition of polymer was confirmed by EDAX. The X-ray diffraction studies revealed the formation of nanosized (29nm) polymer. The electrochemical behaviors of the polymers were studied by cyclic voltammogram. It shows one oxidation peak at 252.2 mV and one reduction peak at 82.6 mV. Increases in peak current and enhanced broadening were observed due to fast redox process in POT-BAC matrix. Electrical conductivity of BAC doped POT were studied by impedance spectroscopy. The thermal behavior of the polymer was studied by TGA/DTA. It shows that the surfactant doped POT has higher thermal stability than undoped POT. Nano sized particles were confirmed by TEM.

Keywords: Poly(o-toluidine), Benzalkonium chloride, Cyclic Voltammetry, XRD, morphology.

1. Introduction:

Over last few decades polyaniline and its derivatives like poly(o-toluidine) have become the polymer of great scientific and industrial importance as a result of their remarkable properties. These materials have the good environmental stability, high thermal stability and they are relatively easy in preparation. Their

conductivity can be reversible controlled either electrochemically or chemically [1-4]. Mac Diarmid et al. [5] investigated poly (o-toluidine) as an electrically conducting polymer, which is emerging as a promising synthetic metal. The processibility of synthesizing and doping of poly (o-toluidine) with dopants containing different types of counterions is one of the key factors responsible for the versatility of this class of polymers.

The surfactants have special properties like lowering of the surface tension of solutions and association tendency. Surfactants have been used as an additive in the polymerization reactions for it affects the inverse emulsion pathways and it improves the properties of the polymers with respect to conductivity, stability, solubility in organic solvents, and processibility. The size and type of the dopant (anion) affect the morphology, size and electrical conductivity of resulting polymers [6, 7]. Surfactants have been used as an additive in the polymerization of aniline and pyrrole and their electrical and thermal properties have been compared [8]. Mahasweta Nandi et. al., have prepared mesoporous poly (p-phenylenediamine) with anionic surfactant Sodium Dodecyl Sulphate (SDS) as a template and their porosity and magnetic property was studied [9]. D. Ichinohe et al prepared o, m, p-phenylenediamines using hydrogen peroxide as an oxidizing agent in reversed micellar systems consisting of an anionic surfactant sodium di (2-ethylhexyl)sulfosuccinate and their magnetic property has been studied [10]. The surfactants influence the physical properties (morphology, solubility) of the resultant polymer [11]. The presence of surfactants improves the colloidal solubility of conducting polymers in organic solvents [12-14] and consequently, the processability [15, 16]. In this study, we are reporting the study of the effect of varying the molar ratio of cationic surfactant (BAC) with poly (o-toluidine) and to study the structural, electrochemical and thermal behavior of the synthesized polymers.

2. Materials and Methods

2.1. Materials

Benzalkonium chloride (BAC, Cationic surfactant), (Merck AR grade), Potassium perdisulphate (E Merck) were used as such without further purification. O-toluidine was distilled under vacuum prior to use.

2.2. Chemical preparation of Poly(o-toluidine) with and without BAC

Aqueous micellar dispersion was prepared by chemical oxidation method. BAC doped polymer were synthesized by keeping the concentration of the monomer (0.1 M) and oxidant (0.1M) constant and varying the molar ratio of the surfactant (below cmc). Table 1 describes the synthetic conditions of the respective samples. Polymerization was performed by the addition of potassium peroxydisulfate (0.1M) in the micelle solution and stirred for 5 hrs. The colour of polymerization solution changed with polymerization step. In the initial stage, o-toluidine/surfactant/KPS solution was colorless with high transparency. As the polymerization proceeded, the color of the solution changed to white through yellow, brown and finally to green, which indicates the formation of POT emeraldine salt (ES). The precipitated particles were collected after filtering and washing with distilled water and then dried at room temperature.

Table 1. Synthetic conditions of doped and undoped POT

Sample	o-toluidine(M)	KPS(M)	BAC(M)
POT	0.1	0.1	-
POT 1	0.1	0.1	2×10^{-2}
POT 2	0.1	0.1	1×10^{-2}
POT 3	0.1	0.1	1×10^{-3}
POT 4	0.1	0.1	1×10^{-4}
POT 5	0.1	0.1	1×10^{-5}

2.3. Instrumentation

FT-IR spectra of the polymers were recorded using a SHIMADZU instrument in the frequency range of 400 to 4000 cm^{-1} . UV-Vis spectra of the samples, which were dispersed in DMSO, were recorded on a JASCOV530 UV-Vis spectrophotometer in the wavelength region 200 to

1100nm. X-ray diffraction patterns of the coatings were obtained by employing XPERT-PRO diffractometer using $\text{CuK}\alpha$ ($k\alpha = 1.54060$) radiation. The diffractometer was operated at 40Kv and 30mA. Powder X-ray diffraction pattern was recorded. Morphology study of the polymers was carried out using scanning electron microscope (SEM Model: JEOL JSM 6360) operating at 25kV. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed using Perkin Elmer instruments. Electrochemical workstation CHI 650C (CH Instruments, USA) was employed for performing Cyclic voltammetry and impedance studies. TEM were taken using PHILIPS Model CM200 operating at voltages 20-200kv and with a resolution of 2.4 \AA . The percentage solubility of the polymers were determined by weight loss method (W/V %). The conductances (κ) of the surfactant solution were measured using ELICO CM180 conductivity meter.

3. RESULTS AND DISCUSSION

3.1. Solubility

The solubility of POT-BAC was studied in various solvents. The solubility percentages of BAC doped polymers are presented in the table 2. The percentage of solubility increases with increasing the concentration of the surfactants. This behavior was more advantageous for further processing of doped POT.

Table 2. The range of percentage solubility of BAC doped POT (POT 1 – POT 5) in various solvents

Solvent	% solubility
DMSO	100
DMF	100
Acetone	85-98
Aceticacid	80-89
Dichloromethane	75-79
THF	85-90
Water	42-49
Toluene	50-55
Xylene	42-47

3.2. IR spectra

Fig.1 shows the FTIR spectrum of POT and surfactants doped POT. The skeletal vibrations of the aromatic rings show two bands at 1598 and

1498 cm^{-1} , which are attributed to C=C stretching vibrations of quinoid and benzenoid ring, respectively [17, 18]. The intensity of quinoid ring stretching vibrations relative to the intensity of benzenoid ring stretching vibrations is considered to be a measure of the degree of oxidation of the polymer [19]. The intensity of the band at 1598 cm^{-1} is higher than that of the band at 1498 cm^{-1} indicating the presence of predominantly quinoid rings in POT (the polymer exist in its completely oxidized state) [19-21]. The shoulder at 1330 cm^{-1} and a weak peak at 1265 cm^{-1} are assigned to C-N stretching vibrations of quinoid and benzenoid rings, respectively, as reported [22, 23]. The peak at 1265 cm^{-1} originates from the C-N stretching vibrations associated with the oxidation or protonation (doped) states in POT. The signal due to C-H in plane bending vibrations is observed at 1114 cm^{-1} . The peak at 879 cm^{-1} has been assigned to 1, 2, 4-trisubstituted aromatic rings indicating polymer formation [24]. The signal at 605 cm^{-1} is due to C-H out of plane bending vibrations. The new band appears at 1197 cm^{-1} which could be attributed to the $-\text{CH}_3$ rocking mode. The IR bands for all doped samples of poly (o-toluidine) with different dopant concentrations show significant as well as moderate changes in the wavelength. The peaks at 1660, 1598, 1330, 1265, 1114, 879, 605 and 1197 cm^{-1} are shifted to 1666, 1589, 1334, 1251, 1112, 883, 607 and 1195 cm^{-1} , respectively. The peaks at 1483 and 1456 cm^{-1} are assigned to CH_3 stretching and deformations of the n-alkyl tail of BAC, are observed also in the spectra of POT-BAC [25]. The relative intensity of these bands increases with increase in the surfactant content in the polymer. The change in number and intensity of IR vibrational bands confirms the dopant interaction with poly (o-toluidine).

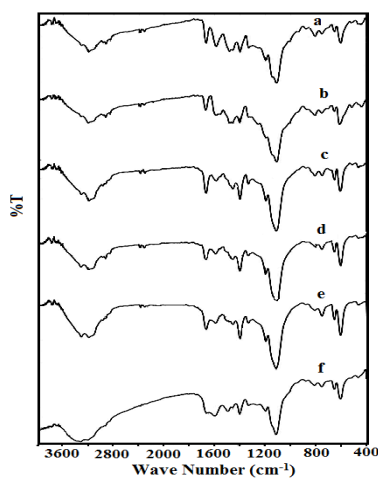


Fig.1. FT-IR spectra of a) POT 1 b) POT 2 c) POT 3 d) POT 4 e) POT 5 f) POT (undoped)

3.3. UV spectra

The UV-VIS spectra of POT and POT-BAC are shown in Fig.2. The polymers were dissolved in DMSO and used to study spectral behavior. The band observed at 313nm corresponds to $\pi-\pi^*$ transition. The band observed at 343 nm assigned to the $\pi-\pi^*$ transition of the benzenoid ring based on the earlier studies on poly (o-toluidine) [26-28]. It is related to the extent of conjugation between the phenyl rings along the polymeric chain. The absorption at 601nm is assigned to the "exciton" transition from HOMO of benzenoid to LUMO of quinoid ring. It is sensitive to the overall oxidation state of the polymer. The absorbance band appears in the region of 805-817nm assigned to polaron form (surfactant doped POT) are not so high. The peak in the visible range also confirms the presence of the doped state of conducting polymer. The band at around 343nm is considerably blue shifted which indicates the interaction between POT and the surfactant. The intensity of absorption band increases with the increasing BAC content.

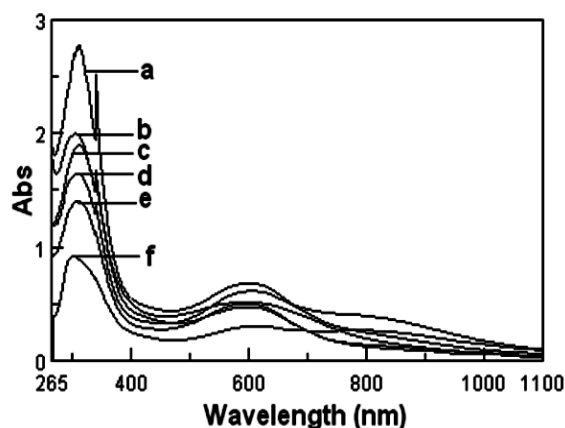


Fig.2. UV-Vis spectra of a) POT 1 b) POT 2 c) POT 3 d) POT 4 e) POT 5 f) POT (undoped)

3.4. SEM analysis

Fig.3 shows the surface morphology of doped and undoped POT. Pure POT (fig.3 (a)) exhibits a granular structure [29] and the granular are not entirely uniform. The addition of surfactant increases the number of porous structures on the polymer. The morphology of POT 1 shows the irregular flake like morphology and POT 2 display petals like morphology. POT 3 depicts the irregular shape with more aggregation and POT 4 shows granular with more pores in the polymer. POT 5 exhibits a globular structure. The variation in morphology of the doped POT predominantly is dependent on the concentration of the surfactant. Fig.4 shows the EDX spectroscopy for the undoped and BAC doped POT. It can be seen from line a, that for the undoped POT, only peaks corresponding to C and N elements were displayed.

While for the BAC doped POT, besides above peaks, peaks corresponding to Cl were also clearly observed, suggesting that Cl element originated from BAC was doped into the polymer.

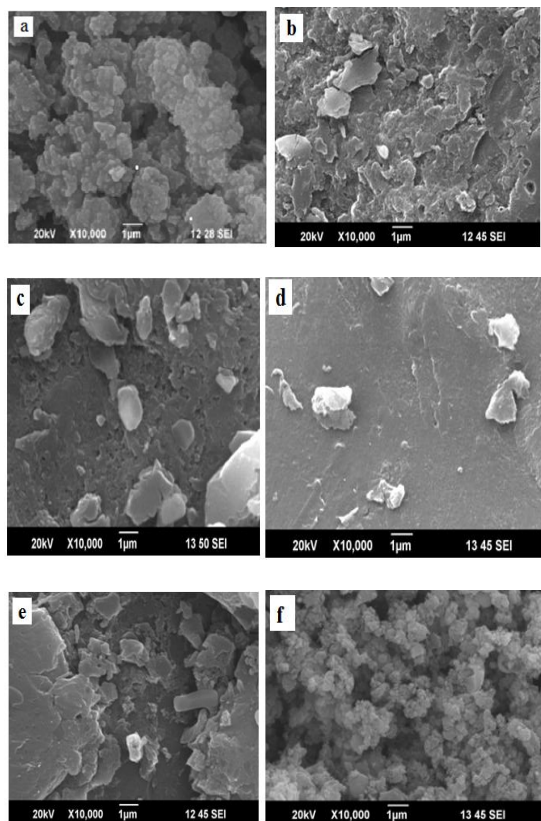


Fig.3. SEM photographs of a) POT (undoped) b) POT 1c) POT 2 d) POT 3 e) POT 4 f) POT 5

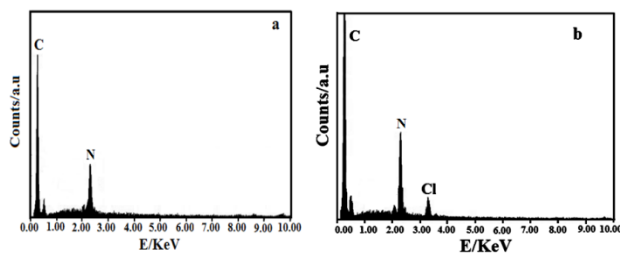


Fig.4. EDAX behaviour of a) POT (undoped) b) POT 1

3.5. XRD analysis

The XRD patterns of surfactant doped and surfactant free POT are shown in Fig.5 (a-f). Surfactant free POT shows only one broad peak around 24° , and 17° for surfactant doped POT1. It indicates that the intermolecular stacking structure and amorphous packing of the prepared poly (o-toluidine) [30, 31]. The intensity of the peak increases with the increase in the concentration of the surfactants when compared with surfactant free POT which elucidates the degree of crystallinity of

the samples increased due to the presence of surfactants. It confirms that the surfactant may reduce the agglomeration of the polymers. The crystallites size of the sample is estimated from the peak width (FWHM) using Scherrer's formula: $D = K\lambda / \beta \cos\theta$ where, λ is the X-ray wavelength, β is full width at maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer's constant of the order of unity for usual crystals (here $K=0.9$). XRD pattern of undoped POT sample shows semi crystals around 24° and the particle size is 53nm. The particle size varied gradually from 29nm for POT 1 to 82nm for POT 5 indicating that the concentration of the surfactant highly influenced the size of the particles. Particle size can be decreased by increasing the concentration of surfactant. The variation in diffraction intensity with dopant concentration exhibits the interaction of BAC in POT network.

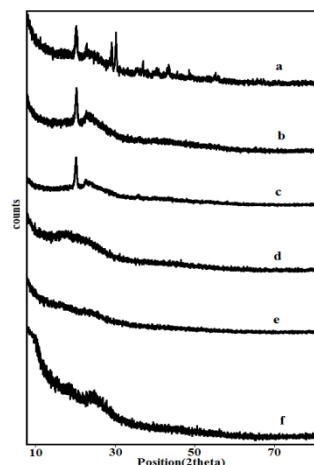


Fig.5. XRD of a) POT 1 b) POT 2 c) POT 3 d) POT 4 e) POT 5 f) POT (undoped)

3.6. Cyclic voltammogram

Electrochemical studies of BAC doped and undoped POT were done using cyclic voltammetry (Fig.6). The surfactant free POT exhibits three oxidation peaks. The peak at 992.2 mV corresponds to the oxidation of the monomer. The peak 279.4 mV was attributed to the transformation of POT from the reduced leuco emeraldine (LE) state to the partially oxidized emeraldine state (ES) of POT. The peak at 610.6 mV was due to the presence of quinone / hydroquinone [32-34]. The surfactant doped POT shows one redox peak around 252.2/82.6mV. The shape of undoped POT voltammogram, change from that of BAC doped POT, indicating that the presence of BAC, plays an important role in the electrochemical response of the POT matrix. The currents of BAC doped POT increase with increasing the concentration of the surfactant. As the scan rate increases, the peak

current of polymer also increased linearly, thus indicating an adherent film on the glassy carbon electrode, this was further confirmed by a straight line graph obtained by plotting peak current Vs scan rate as shown in Fig.7.

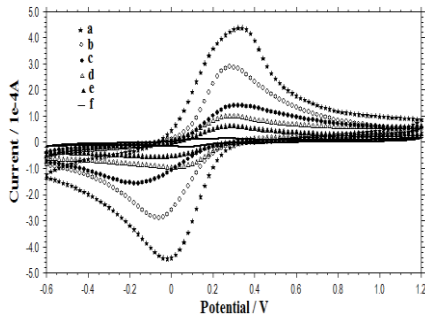


Fig.6. Cyclic voltammogram of a) POT 1 b) POT 2 c) POT 3 d) POT 4 e) POT 5 f) POT (undoped)

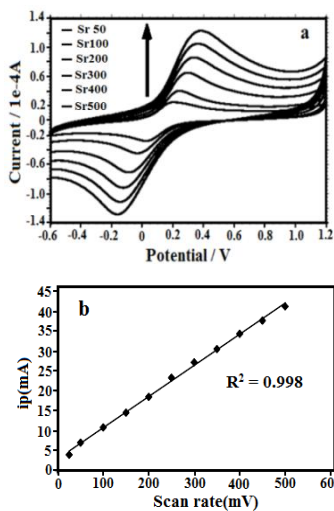


Fig.7. a) CV taken at various scan rates for POT 1 b) Plot of anodic current Vs scan rate for POT 1

3.7. Impedance spectra

The Nyquist plots of BAC doped and undoped POT in 0.1M H₂SO₄ are shown in fig.8. The diameter of the semi-circle gives an approximate value of the charge transfer resistance (R_{ct}) of the POT/electrolyte interface. The charge transfer resistances (R_{ct}) and Cdl values are presented in table 3. It can be observed that R_{ct} value increased with a decrease in surfactant concentration. The polymer doped with maximum BAC (POT 1) gives maximum conductivity.

Table 3. Impedance parameters of BAC doped and undoped POT

polymer	R _{ct} (Ωcm ²)	C _{dl} (μFcm ⁻²)
POT(pure)	2297.8	0.0606
POT 1	310.4	3.0355
POT 2	680.8	0.6835
POT 3	1191.7	0.2198
POT 4	1406.8	0.1630
POT 5	1731.6	0.1066

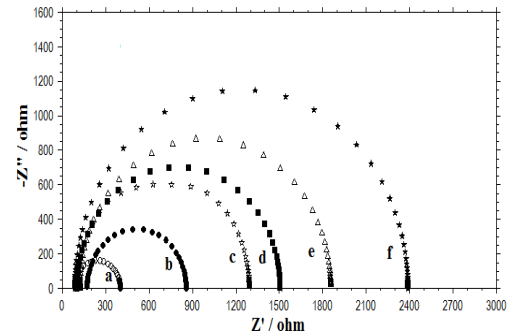


Fig.8. Impedance spectra of a) POT 1 b) POT 2 c) POT 3 d) POT 4 e) POT 5 f) POT (undoped)

3.8. TGA/DTA

The Thermo gravimetric analysis of POT and surfactants doped POT are shown in Fig.9. It is generally known that three weight loss steps are observed in the TGA measurements for poly (o-toluidine) and surfactants doped POT. The thermo gravimetric analysis exhibits a three step loss in the range of 36^oC-702^oC for POT. The first weight loss starts from room temperature to 315^oC corresponding to the loss of water molecule/moisture and dopant (HCl) present in the polymer matrix. The TGA curve does not show appreciable change in weight of sample up to 315^oC. The weight loss after 461.17^oC corresponds to degradation of the polymer backbone [35]. In the case of POT 1, it shows 4.2% weight loss upto 82^oC due to the loss of water molecule. 17.5% weight loss is observed upto 282.21^oC corresponds to loss loosely bounded surfactant molecules in the polymer matrix. The weight loss after 479.40^oC corresponds to degradation of the polymer backbone.

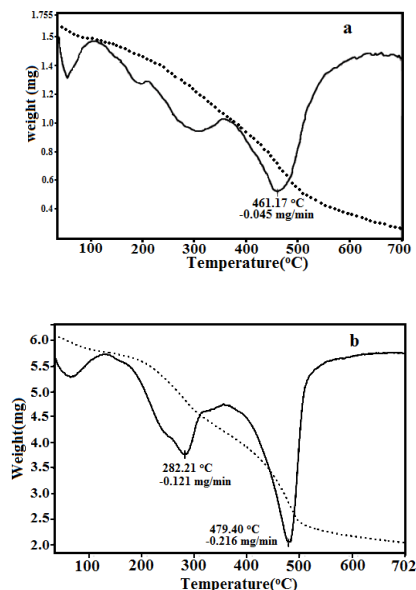


Fig.9. TGA/DTA images of a) POT (undoped) b) POT 1

3.9. TEM analysis

TEM micrograph is taken for POT 1 and shown in the fig.10. The figure shows that it is nearly spherical in shape and the particles are found to be in nano range. In the image, the dark portion which is spherical in nature is the surfactant and the grey areas are showing the polymer chain. Hence it is clear from the micrograph that the surfactant molecules are incorporate into the polymer.

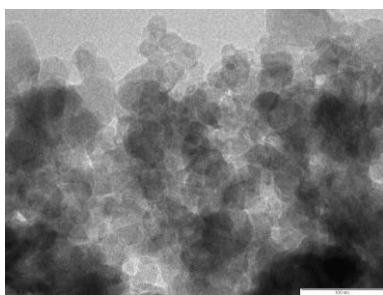


Fig.10. TEM image of POT 1

4. Conclusion

The POT and POT-BAC was prepared and the polymers were characterized using FT-IR, UV-Vis spectra, SEM, TEM, TGA, cyclic voltammetry and impedance spectra. UV-Vis spectra show the absorbance in the region of 805-817 nm is assigned to doped state of poly (o-toluidine). The

FT-IR spectra show the amine peak at 1598 cm^{-1} is shifted to 1589 cm^{-1} . This indicates the interaction of polymer with the surfactant. From the SEM micrographs it was observed that each polymer have different morphology. XRD results exhibit the particle size varied from 29nm in the case of POT 1 to 82 nm in the case of POT 5. Cyclic Voltammogram studies of the polymers show good adherent behavior on electrode surface. The polymer with maximum concentration of BAC (POT 1) shows maximum conductivity, which is confirmed by impedance spectra. The thermal behavior of the polymer was studied by TGA/DTA. It shows that the surfactant doped POT has higher thermal stability than undoped POT. Nano sized particles were confirmed by TEM image.

5. Acknowledgments

The authors were extremely grateful to DST (FAST TRACK and FIST) New Delhi, INDIA for using CHI Electrochemical workstation and JASCO UV-VIS spectrophotometer (UGC New Delhi) at V. O.Chidambaram College Tuticorin.

References:

- [1] B. Inganas, G. Gustafsson and J. Gustafsson-Carlberg et. al., Nature, vol. 372, pp. 444, (1994).
- [2] E. Genies and M. Lapkowski, Synth. Met., vol. 24, pp. 61, (1988).
- [3] S. Chen and W. Fang, Macromolecules, vol. 24, pp.1242, (1991).
- [4] H. Dao Le, T. Nguyen and R. Paynter, Synth. Met., vol. 41-43, pp. 649, (1991).
- [5] A. G. Macdiarmid, R. I. Mammone, J. R. Krawczyk and S. J. Porter, Molecular Crystals and Liquid Crystals, Vol. 105, pp. 89, (1984).
- [6] S. Hayashi, S. Takeda, K. Kaneto, K. Yoshino and T. Matsuyama, Synthetic Metals, vol. 18, pp. 591, (1987).
- [7] M. Tang, T. Y. Wen, T. B. Du and Y. P. Chen, European Polymer Journal, vol. 39, pp. 143, (2003).

- [8] Jaroslav Stejskal, Ma'ria Omastova', Svetlana Fedorova, Jan Prokes and Miroslava Trchova, *Polymer*, vol. 44, pp. 1353, (2003).
- [9] Mahasweta Nandi, Swapan Kumar Das, Saurav Giri and Asim Bhaumik, *Microporous and Mesoporous Materials*, vol. 142, pp. 557, (2011).
- [10] D. Ichinohe, K. Akagi and H. Kise, *Synthetic Metals*, vol. 85, pp. 1671, (1997).
- [11] B. Sun, J.J. Jones, R.P. Burford and M. Skyllas-Kazacos, *J. Mater. Sci.*, vol. 24,(11), pp.4024, (1989).
- [12] P.J. Kinlen, B. G. Frushour, Y. Ding and V.Menon, *Synth. Met.*, vol. 101, pp.758, (1999).
- [13] M. Wan, J. Huang and Y. Shen, *Synth. Met.*, vol. 101, pp. 708, (1999).
- [14] A.J. Dominis, G. M. Spinks, L. A. P. Kane-Maguire and G. G. Wallace, *Synth. Met.*, vol. 129, pp. 165, (2002).
- [15] D. Ichinohe, T. Arai, and H. Kise, *Synth. Met.*, vol.84, pp.75, (1997).
- [16] E. J. Oh, K. S. Jang and A. G. MacDiarmid, *Synth. Met.*, vol. 125, pp. 267, (2002).
- [17] J. Tang, X. Jing, B. Wang and F. Wang, *Synth. Met.*, vol.24, pp. 231, (1988).
- [18] Z. Ping, H. Neugebauer and A. Neckel, *Electrochim. Acta*, vol. 41, pp.767, (1996).
- [19] N. S. Sariciftci, H. Kuzmany, H. Neugebauer and A. Neckel, *J. Chem. Phys.*, vol. 92, pp. 4530, (1990).
- [20] Z. Ping, *J. Chem. Soc. Faraday Trans.*, vol. 92, pp. 3063, (1996).
- [21] N. Chandrakanthi and M. A. Careem, *Polym. Bull.*, vol. 45, pp. 113, (2000).
- [22] D. Shan and S. Mu, *Synth. Met.*, vol. 126, pp. 225, (2002).
- [23] T. C. Wen, L. M. Huang and A. Gopalan, *Synth. Met.*, vol. 123, pp. 451, (2001).
- [24] M. S. Wu, T. C. Wen and A. Gopalan, *Mater. Chem. Phys.*, vol. 74, pp. 58, (2002).
- [25] D. Krajisnik, A. Dakovic, A. Malenovic, M. Milojevic, V. Dondur and J. Milic, *Proceedings of the 3rd Croatian-Slovenian Symposium on Zeolites, Trogir, Croatia*, pp. 23, (2010).
- [26] J. Anand, S. Palaniappan and D. N. Sathyanarayana, *Synth. Met.*, vol. 66, pp. 129, (1994).
- [27] D.P. Kang and M. S. Yun, *Synth. Met.*, vol. 29, pp. 343, (1989).
- [28] D.C. Trivedi, in *Handbook of Organic Conductive Molecules and Polymers*, H. S. Nalwa, John Wiley, Chichester, vol. 2, pp. 505, (1993).
- [29] C.H. Wang and T. C. Wen, *Electrochem. Soc.*, vol. 141, pp. 2624, (1994).
- [30] J. Mardalen, E. J. Samuelsen, O. R. Gautun and P. H. Carlsen, *Synth. Met.*, vol. 48, pp. 363, (1992).
- [31] Y.N. Li, G. Vamvounis and S. Holdcroft, *Macromolecules*, vol. 35, pp. 6900, (2002).

- [32] D.D. Borole, U. R. Kapadi, P.P Mahulikar and D. G. Hundiwale, J. Appl. Poly. Sci., vol. 90, pp. 2634, (2003).
- [33] D.E. Stilwell and S. M. Park, J. Electrochem. Soc., vol. 135, pp. 2254, (1988).
- [34] B.J. Johnson and S. M. Park, J. Electrochem. Soc., vol. 143, pp. 1277, (1996).
- [35] S.H. M. Ebrahim and A. Gad Morsy, Synth. Met., vol. 160, pp. 2658, (2010).