Studies on the Electrochemical Parameters of Potentiodynamic Electrocopolymerization of Aniline

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To know more understanding on the parameters effecting electrocopolymerization of aniline, a theoretical study of electrochemical behaviour had been performed through cyclic voltammetry at the platinum electrode through controlled potential electrocopolymerization (CPE) in 0.01 M LiClO$_4$ solution at a scan rate of 50 mV s^{-1}. It is observed that parameters in the presence of additive (perchloric acid) and selective solvent-electrolyte pair parameters affect the morphology, stability and solubility of the copolymer matrix. The morphological structure analysis exhibits nano-structured polydispersity characterized by a scanning electron microscope.

Keywords: Electrocopolymerization, Aniline, Perchloric acid, Electroactivity, Cyclic voltammetry.

INTRODUCTION

Polyaniline (PANI), a conductive polymer of conjugated backbone drags the attention of many synthetic organic chemists due to their environmental stability, ease of preparation and exciting physio-chemical properties [1-9]. However, a conventional synthetic protocol had some demerits like insolubility, infusibility, incompatibility due to the rigid chain and modest environmental stability, which decreases its processability [10]. Thus to improve the processability of polyaniline with the perspective to develop greener route, electrochemical technology [11] represents the frontier of opportunity because environmentally and frugally challenging waste treatment can be discarded, largely since the electrons are free and not bound to a reagent, producing toxic wastes from consumed reagents [12].

Electroactivity is induced by protonation at the imine site of the PANI matrix using acidic dopant that enhances stability and conductivity. Catalysis by an electron that is tuned through doping is a chemical entity *i.e.* an intriguing aspect that depends upon addition or removal of the electron from conducting polymer. A simple explanation for this that electron is either extracted from highest occupied molecular orbital (HUMO) of valence band or added to lowest occupied molecular orbital (LUMO) of the conduction band. This redox behaviour *i.e.*

addition or removal creates a charge carrier in which charges are transferred. Charge carrier exists in the form of polaron named radical ions or bipolaron in polymers. Hence induction of electroactivity is a very important attribute during electro-copolymerization. It had been noticed that the conductivity of emeraldine salt of PANI is fluctuating in response to a pH change [13].

To achieve higher conductivity in conducting polymers, doping is one of the best methods. Generally, it has been seen that undoped polymers behave as insulator but after doping they may change their behavior from insulating to metallic behaviour [14]. This changing behaviour can be clearly understood with the help of a doping mechanism that takes place through the transference of charge carrier, which is called as polaron or bipolaron [14].

Thus, aiming at the developments of suitable protocols for the study of electrochemical performance, we focused on the copolymerization parameter condition that brings excellent copolymer film-forming attributes. Enhanced solubility and flexibility were observed, which was favoured by the level of LiClO$_4$/HClO$_4$/CH$_3$CN electrolytic system on oxidative copolymerization of aniline with substituted aniline monomers at equimolar concentration ratios at the platinum electrode. The copolymerization was studied by cyclic voltammetry and the

product (copolymer of polyaniline/substituted aniline) was characterized by UV-visible, FT-IR and SEM.

EXPERIMENTAL

The monomers like, aniline, *o*-anisidine, *o*-toluidine, and other solvents/chemicals *viz.* acetonitrile, perchloric acid and lithium perchlorate were obtained from Merck. All these chemicals were purified and distilled twice before use. Double distilled water was used in preparing the supporting electrolyte solution

General procedure: The electrochemical synthesis was performed in 50 mL three-electrode cell assembly with a platinum plate (flattened sheet with the dimension of 1.0 cm × 1.0 cm), a counter electrode, and saturated calomel electrode as a reference electrode. Cyclic voltammetry experiments were performed using the ALSCH instruments electrochemical analyzer Model 600A.

For controlled potential electrocopolymerization (CPE) at a platinum electrode, preparative electrolysis [15-20], aniline **1** (first monomer) and substituted aniline **2** (second monomer) in an equimolar ratio (1:1) in 50 mL acetonitrile was chosen as model substrate by using 0.01 M lithium perchlorate and few drop of 1.0 M perchloric acid as a doping agent. The reaction was monitored by passing optimal electricity that results in a corresponding and completed in 3-4 h (ohmic drop) until copolymer diffuse into the bulk. The product was extracted by simple solvent extraction method Progress of the reaction was monitored by TLC. All the products were coloured solid. After electrolysis, the supporting electrolyte was removed and products were isolated by silica gel column chromatography (CHCl₃:H₂O, 1:1 v/v). Controlled potential electrocopolymerization (CPE) exhibits superiority over cyclic voltammetry polymerization because it discards side reaction and yield copolymer with the highest electroactivity and purity.

Detection method: The UV-Visible spectral analysis was performed in DMSO using a UV-visible spectrophotometer Perkin-Elmer (L45). IR spectra (KBr) were recorded on a Shimadzu 8201 PC IR spectrophotometer. ^1H & ^{13}C NMR spectra were recorded on a Bruker, DRX 300 spectrometer (300 MHz) in CDCl₃ using TMS as an internal standard. The morphology and particle size were determined using a scanning electron microscope (SEM), JSM 5800, JEOL, Japan.

RESULTS AND DISCUSSION

Solvent parameters: Solvents selected for electrolytic reaction conditions should accompany by which easily they can facilitate the flow of current within the electrochemical cell without creating much ohmic resistance. In present work, acetonitrile is considered as a preferable solvent for reaction condition as it promptly dissolves both the electrolyte as well as the substrate which can be easily isolated through solvent extraction method after electrolysis. Secondly, the electrochemical window of acetonitrile is defined by LiClO₄ as acetonitrile is not electroactive at usual working electrode potential. Moreover direct activation of monomer, solvent acidity should below as it is not good proton donor, which can be calculated in terms of pK_a value. This has only occurred in CH₃CN since

its pK_a value is high (pK_a = 31.3 in DMSO) as compared to substrate aniline (pK_a = 30.6 in DMSO).

Electrolyte parameter: LiClO₄, a supporting electrolyte is our choice as it offers various advantages such as immensely solubility in various organic solvents, act a co-catalyst that can be easily recovered and reused in reaction.

Doping acid: An investigation was carried out at different acidic range by correlating acidity of doping acid with dissociation constant (pK_a) value. Table-1 shows the acidity range of different doping agent, thus perchloric acid were chosen as the dopant in present study, which introduces perchlorate of the emeraldine base of copolymer of aniline with substituted aniline. This can improve the charge transfer rate across the copolymer matrix and facilitate its redox processes. An addition of perchloric acid (pK_a value in water = 10.0) in CH₃CN (pK_a value in water/DMSO = 31.3) increases the acidity of reaction condition. Here, we correlate the acidity of additive with the help of pK_a value. Since, perchloric acid is more readily ionized in acetonitrile thus avoiding precipitation or coprecipitation as in the case of sulphuric acid or nitric acid thus forces the polymer to release more electrons. Hence, reactions proceed more effectively and affect the electrochemical performance of copolymer.

Entry	Doping agent	pKa in (H₂O) [16,17]	Potential (V)	Yield of **3** (%)	Time (h)
		TABLE-1 OPTIMIZATION OF GALVANIC POTENTIAL USING ACN/LiClO₄ PAIR			
1	NIL	–	2.10	82	4.0
2	HClO₄	10.0 (HClO₄)	1.54	92	3.0
3	H₂SO₄	3.0 (H₂SO₄)	1.30	68	4.0
4	H₃PO₄	2.21 (H₃PO₄)	1.20	54	4.5
5	HNO₃	1.3 (HNO₃)	1.10	48	5.0

Solvent-electrolyte pair parameter: For solvent-electrolyte pair (LiClO₄-CH₃CN) was selected to make the procedure more efficient and appropriate. The electrochemical behaviour of acetonitrile is defined by LiClO₄ as acetonitrile is not electroactive at usual working electrode potential. Moreover, indirect activation of monomer, solvent acidity should below as it is not good proton donor which can be calculated in terms of pK_a value. This has only occurred in CH₃CN since its pK_a value is high (pK_a = 31.3 in DMSO) as compared to substrate aniline (pK_a = 30.6 in DMSO).

Electroactivity modulation: When the reaction potential was 1.54 V, a Pt electrode surface (1 cm²) reaction was found to be optimal for the copolymerization and attributed to the highest yield of poly(PANI-*co*-ANI) using acetonitrile as solvent and LiClO₄ as an electrolyte (Table-1, entry 2). The yield of the reaction was low on a further increase of current density (Table-1, entries 3-5) in acetonitrile, which may be due to the acceleration of the undesired direct electrochemical process [21].

The electrochemistry of the redox couple corresponds to the transition of leuco-emeraldine (fully reduced form) and the polaronic emeraldine (radical cation) of copolymer are shown in Figs. 1 and 2, respectively. Initial current density
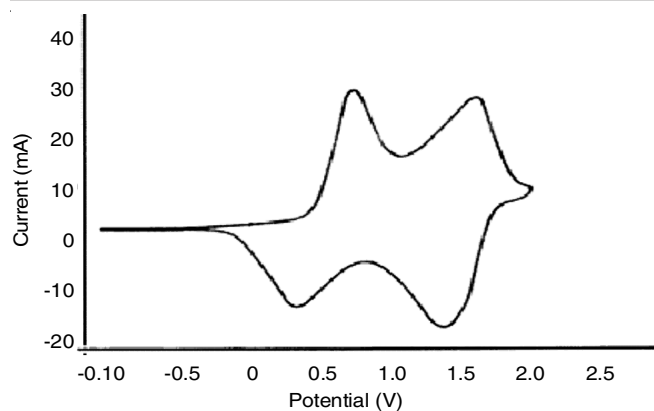
Fig. 1. Cyclic voltammogram of poly (aniline-*co-o*-anisidine) co-polymer 2 (i) in 0.01 M LiClO$_4$ with 1.0 M HClO$_4$ scanning rate: 50 mV/s
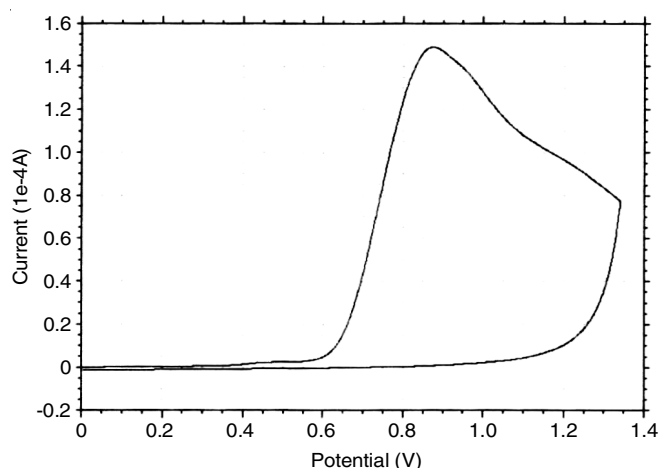

Fig. 2. Cyclic voltammogram of poly (aniline-*co-o*-toluidine) co-polymer 2 (ii) in 0.01 M LiClO$_4$ scanning rate: 50 mV/s

increase monotonically from 0.001 to 30 mA/cm^2 with increasing applied potential from 0.5 V to 2.0 V in poly (aniline-*co-o*-anisidine) and 0.7 V to 1.4 V in poly(aniline-*co-o*-toluidine).

Two electron transfer oxidation reactions examined through cyclic voltammetry at platinum electrode containing 0.01 M LiClO$_4$ and 1.0 M perchloric acid as a doping agent with successive two anodic peaks. The first peak corresponds to the oxidation of aniline indicating the generation of aniline radical cations and the second oxidation peak indicates further coupling of these radical cations to form a copolymer of aniline with *o*-anisidine. The electron transfer driven mechanism in oxidative copolymerization is shown in **Scheme-I**.

The tentative mechanism for poly(aniline-*co-o*-anisidine) copolymer shows that aniline and *o*-anisidine undergoes two-electron transfer oxidative driven reaction to form radical cation (1a,1b) and (2a,2b) followed by proton loss and form 3a, which undergoes chain propagation to final desired copolymer 2(i) as product.

Electroactivity studies: Electroactivity is enhanced due to the doping of perchloric acid present in the system which instantly ionized in acetonitrile medium and encouraged the copolymer to release more electrons to the cathode. This led to a decrease of the electrodic potential of 1.54 V in poly-(aniline-*co-o*-anisidine) and 1.30 V in poly(aniline-*co-o*-toluidine) measured through potentiostatic technique. This doping effect in combination with lithium perchlorate is favoured due to the formation of good conducting emeraldine salt (ES) phase of polymers.

Galvanic potential studies: The presence of -OCH$_3$ group in the benzene ring *i.e.* in *o*-anisidine and perchloric acid with lithium perchlorate creates a nominal current density, which

Scheme-I
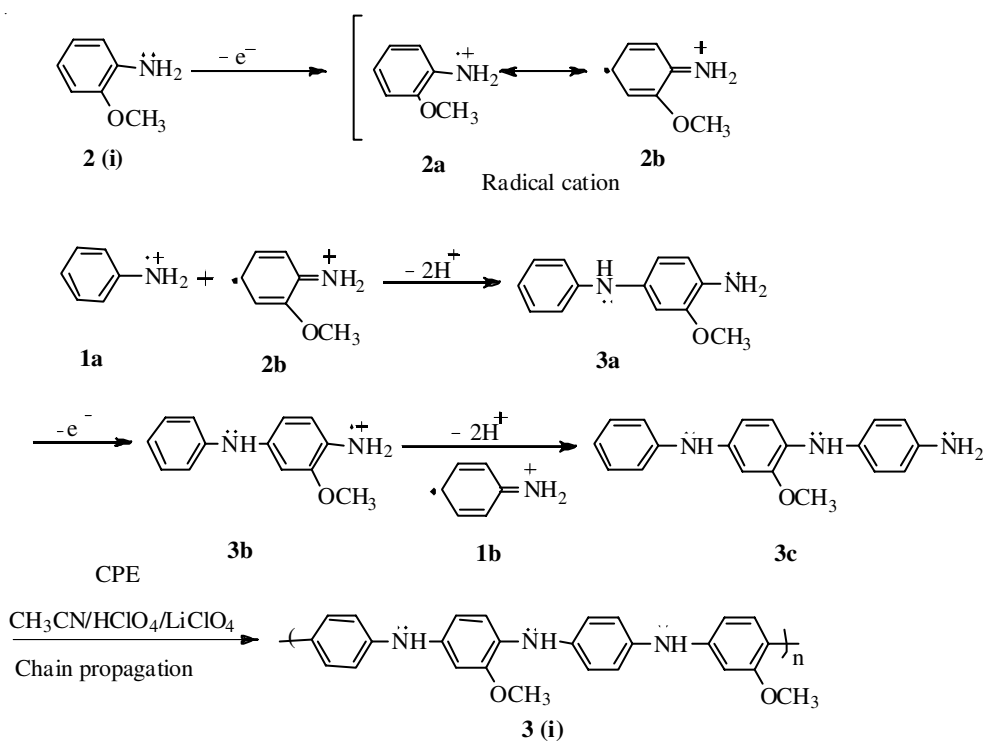
provokes the shift of leuco-emeraldine/emeraldine redox couple to a more oxidative positive potential and emeraldine/pernigr-aniline couple to less potential; hence two oxidative vertexes from 0.5 to 2.0 V were obtained. The shift of redox couple from vertex-1 to vertex-2 depends upon the chemical nature of dopant.

The variation in substituent, the oxidative potential also changes (Table-2), as the introduction of -CH₃ group in place of -OCH₃ group in the second monomer of aniline, the oxid-ative potential value decrease. Such change can be explained based on the inductive effect. Group -CH₃ shows (+I) effect so the electron is easily available to the platinum cathode to form *in situ* reactive intermediate. Hence the amount of charge being recorded *i.e.* only 1.30 V.

TABLE-2
VARIATION OF OXIDATIVE POTENTIAL CONCERNING
SUBSTITUENT VARIATION IN MONOMER 2

Monomer 2	Entry	R	Inductive effect	Oxidative potential (V)
o-Anisidine	2 (i)	-OCH₃	-I effect	1.54
o-Toludine	2 (ii)	-CH₃	+I effect	1.30

Above changes cause an increase in the processability of co-polymer in the following way.

Thus, this factor based modulation controls the electro-philicity of *in situ* generated radical cation or charge carrier named polaron and encourage the copolymer to release more electrons to the cathode. So reactions proceed more smoothly.

Stability: The entanglement origin of large size of perchlorate anion does not allow the perchlorate anion to exit the copolymer matrix during the copolymerization process. Such large counter ion interacts with the cationic copolymer chain resulted in the formation of the stable copolymer matrix. Therefore, it is necessary to use acidic macromolecules as elect-rolytes during PANI synthesis. Herein, lithium perchlorate is used as an electrolyte with perchloric acid having large perch-lorate anion as common in both in the copolymerization of aniline with *o*-anisidine. Although the effect of acidic electrolyte is not very remarkable, which can be speculated due to their molecular structure. The exchange of perchlorate anion is easier in the presence of the perchloric acid groups, and therefore the stability of the films may be increased.

Solubility: Usually, undoped copolymers have less solu-bility due to the presence of a strong intermolecular force of attraction which strongly depends on the high polarity and highly crystalline structure. But after doping, the solubility of the copolymer matrix had shown increment as compared to polyaniline (PANI). However, this reason depends upon the dopant size, where the greater the dopant size (length) lower will be the crystalline and greater will be the solubility. Thus, large dopant size is required as in this case due to the presence of large size of perchlorate anion, higher the *d*-spacing or inter-chain gap, and hence it becomes easier for any solvent mole-cule to penetrate the cluster of copolymer chain and solubilize it. The improved processability in the backbone of copolymer polyaniline was due to the introduction of nitrogen heteroatom incorporated between phenyl rings that provide chemical flexibility.

Effect of LiClO₄/HClO₄/CH₃CN electrolytic system: Perchloric acid is applied as a doping agent who instantly ionized in acetonitrile which initiate the polymer to release more and more electrons to the cathode. Doping anion (chlorate anion) fulfills the creteria of electroneutrality, and therefore their con-centration at the stoichiometric level has a strong influence on conductivity, surface morphology and electrochemical activity. Effect of perchloric acid on the inorganic electrolyte lithium perchlorate can be explained through the Le-Chatelier principle and found to be more suitable than the organic counterparts as they favour the formation of good conducting Emeraldine salt (ES) phase of polymers due to their easy solubility and mobility in the aqueous medium. Lithium perchlorate as dopant showed an enhanced conductivity phase of 0.0596 S/cm than PANI of 0.0591 S/cm, which is due to the smallest size of cation lithium.

Solubility: The solubility of poly(aniline-*co*-*o*-anisidine) was enhanced by introducing -OCH₃ group in aniline which exhibits a good solubility characteristics as compared to poly-aniline (PANI). This improved processability in the backbone of polyaniline is attributed due to the introduction of nitrogen heteroatom incorporated between phenyl a ring that provides chemical flexibility.

Morphology: The SEM images of poly(aniline-*co*-o-anisidine) and poly(aniline-*co*-*o*-toluidine) copolymers reveals that there is a homogenous composition containing some pore, Pa1 (205.7 nm) & Pa2 (402.9 nm) and Pa1 (200.5 nm) & Pa 2 (322.4 nm), respectively (Fig. 3). Formation of pores could be
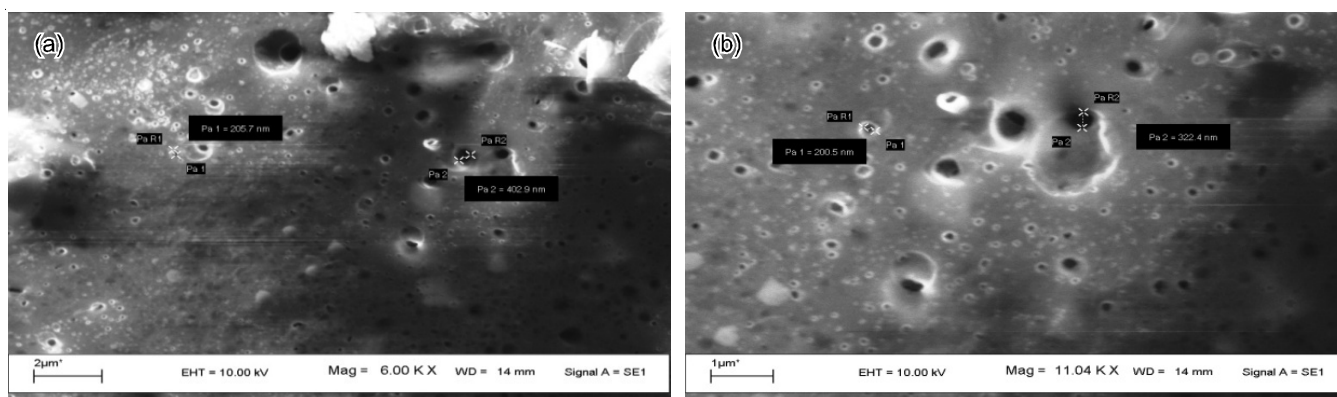

Fig. 3.   SEM images of poly(aniline-*co*-*o*-anisidine) (a) and poly(aniline-*co*-*o*-toluidine) (b) copolymers

explained with the help of interfacial nucleation mechanism (progressive nucleation occur at an early stage) which rely on the metal deposition theory [22]. Insertion of dopant anion with inorganic electrolyte (perchlorate anion common in both) results in the formation of a compact layer that depends on the mass transfer phenomenon controlled at an early stage, thus exert the corrosion resistant property in copolymer.

UV-Vis spectral studies: UV-visible spectra of poly-(aniline-*co-o*-anisidine) in DMSO (Fig. 4) accounted the π-π* bandgap around 280 to 380 nm, which is due to the electronic transition in the phenyl ring present in the backbone of polymer and the peak above 570 nm is due to interband charge transfer.
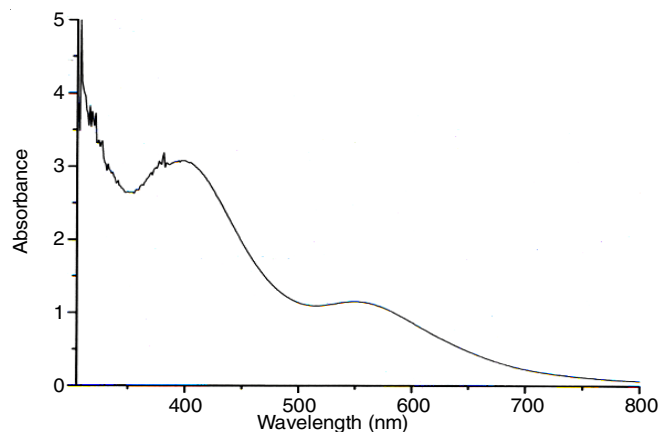

Fig. 4. UV-Visible absorption spectrum of poly(aniline-*co-o*-anisidine) copolymer

FTIR spectral studies: FTIR spectra of poly(aniline-*co-o*-anisidine) revealed a characteristic peak at 1683.4-1460.0 cm^{-1}, which accounts for the C=C stretching of benzenoid rings, while the bands at 1250.2-1222.9 and 3309.1 cm^{-1} are accounted to the C-N stretching and N-H stretching modes, respectively (Fig. 5).
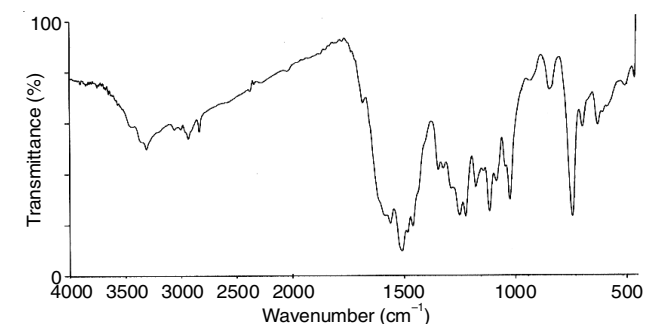

Fig. 5. FTIR spectrum of poly(aniline-*co-o*-anisidine) copolymer

Conclusion

In this work, various factors were evaluated during the controlled potential electrolysis of poly(aniline-cofunctionalized aniline) nanoporous material such as selective solvent electrolyte pair and presence of perchloric acid that affects the morphology, electroactivity and solubility and stability of copolymer. The cyclic voltammetric studies indicated the formation of electroactive poly(aniline-*co*-substituted aniline) copolymer (R = -OCH$_3$ or R = -CH$_3$) in one pot using stoichiometric amount of LiClO$_4$/HClO$_4$/CH$_3$CN electrolytic system. Renewable energy input assisted through this electrolytic system controlled the charged amount through CPE at the platinum electrode which effects the electrophilicity of *in situ* generated radical action and allow the copolymer to release more electrons to the cathode. The effect of perchloric acid on lithium perchlorate can be understood through the Le-Chatelier principle as they favour the formation of good conducting Emeraldine salt phase of polymers due to their easy solubility and mobility in the aqueous medium.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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