A Novel Electro-Organic Synthesis of Aniline-Based Copolymers at Platinum Electrodes

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ABSTRACT: A novel, efficient, and ecocompatible electro copolymerization of anilines at platinum electrode using acetonitrile as non-aqueous solvent and lithiumperchlorate as supporting electrolyte was carried and described here. The progress and mechanistic study of copolymerization was done using cyclic voltammetry. The reaction proceeded smoothly and quantitatively at ambient temperature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1479–1485, 2012

Key words: copolymerization; conducting polymers; electrochemistry; controlled potential electrolysis; supporting electrolyte; ecofriendly

INTRODUCTION

Polyaniline, first synthesized in 1862, has been widely recognized as an interesting and unusual member of conducting polymers.[1–4] It has been extensively studied as conducting polymer[5,6] since 1980. Polyaniline has received great attention due to its salient characteristics such as environmental stability,[7,8] ease of preparation, and exciting electrochemical, optical, and electrical properties. These polymers find applications[9,10] including electrochromic display devices,[11] lightweight rechargeable batteries,[12] microelectronic devices,[13] biosensors[14,15] protective coatings, and chemical sensors.

However, the common usage of this material has been restricted because of its insolubility; infusibility, modest environmental stability, and incompatibility with common polymers due to its rigid chain that originated from an extended conjugate double bonds which rendering it unprocessable.[16] To improve the processability of polyaniline, various approaches have been developed. One of them is electrocopolymerization, which results in better conductivity and useful mechanical properties.

Copolymerization is one of the widely accepted methods of modifying polymer to meet specific requirements.[17,18] Electrochemical polymerization has advantages. It can be performed at room temperature and use of oxidizing chemicals can be avoided. Application of electricity as a non-conventional energy source for activation of reactants in suitable solvents has now gained popularity over the usual homogeneous and heterogeneous reactions. It provides processes with special attributes such as enhanced reaction rate, higher yield of pure products, better selectivity, and several ecofriendly advantages.

In the present study, copolymer of polyaniline have been prepared by electropolymerization of equimolar amounts of aniline and substituted aniline monomers. This has been done in the presence of lithium perchlorate as a supporting electrolyte and acetonitrile as a solvent. The copolymerization was studied by a cyclic voltammeter and the products (copolymer of polyaniline) were characterized by UV–Visible, FTIR, ^{1}H-NMR, ^{13}C-NMR spectroscopy, and the Scanning Electron Microscope.

EXPERIMENTAL

Chemicals

The monomers Aniline, *o*-Anisidine, *o*-Toludine, *N*-Methylaniline, *N*-Ethylaniline, *N*-Propyl aniline, and *o*-Phenylenediamine were obtained from Merck, whereas *o*-Chloroaniline, *o*-Nitroaniline, *o*-Aminophenol, acetonitrile, perchloric acid, and lithium perchlorate were obtained from Loba. These chemicals were all purified and distilled twice before use. Double-distilled water was used to prepare the supporting electrolyte solution. The copolymers were synthesized electrochemically on platinum plate under cyclic voltammetric conditions in undivided cells.

Reaction mixture

A reaction mixture for controlled potential electrolysis was prepared by dissolving a sufficient amount of monomers, supporting electrolytes in acetonitrile.

TABLE I
Current-Potential Data and % Yield of Electropolymerization Reaction

S. No.	Entry	Monomer 1 (Aniline)	Monomer 2 (Substituted aniline)	Time (h)	Potential (V)	Current (mA)	% Yield
1	3a	$C_6H_5NH_2$	o—OCH_3—$C_6H_5NH_2$	3	1.54	30	92
2	3b	$C_6H_5NH_2$	o—CH_3—$C_6H_5NH_2$	3	1.30	30	85
3	3c	$C_6H_5NH_2$	o—NO_2—$C_6H_5NH_2$	4	1.40	31	88
4	3d	$C_6H_5NH_2$	o—Cl—$C_6H_5NH_2$	5	1.75	29	78
5	3e	$C_6H_5NH_2$	o—OH—$C_6H_5NH_2$	4	1.23	23	80
6	3f	$C_6H_5NH_2$	o—$NH_2C_6H_5NH_2$	3	1.32	40	75
7	3g	$C_6H_5NH_2$	N—C_2H_5—$C_6H_5NH_2$	4	1.10	24	72
8	3h	$C_6H_5NH_2$	N—C_3H_7—$C_6H_5NH_2$	5	0.99	21	70
9	3i	$C_6H_5NH_2$	N—CH_3—$C_6H_5NH_2$	3	1.04	37	85

Preparation of reaction mixture for electropolymerization

The monomer **1** (Aniline) and the monomer **2** (Substituted Aniline) were taken in 1:1 ratio in 50 mL of acetonitrile: lithium perchlorate (0.08 g) was dissolved in the above solution to maintain the strength of the supporting electrolyte (0.01M). A few drops of 1.0M perchloric acid were added to the above reaction mixture. The inorganic supporting electrolytes are found to be more suitable than organic ones as they favor the formation of the good-conducting ES phase of polymers because of their easy solubility and mobility in the aqueous medium.

Electrolysis

The electrochemical polymerizations was performed in a 100 mL three-electrode cell assembly with a platinum plate (a flattened sheet with dimensions of 1.0 cm × 0.5 cm), a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode.[19–21] The reference electrode was kept in close proximity to the working electrode to minimize the ohmic drop. A magnetic stirrer was used for the proper mixing of the reaction mixture.

The electropolymerization was carried out at the corresponding potentials of the monomers and was completed in 3–4 h until the solid and colored product was seen to be present in the bulk. The current potential data was recorded at interval of 15 min and is shown in Table I.

Extraction

The product was extracted from acetonitrile solution by shaking with chloroform in a separatory funnel. After removing the chloroform layer, it was left over night and products were obtained in excellent purity and good yield. The progress of reaction was monitored by TLC. All of the products were solid, colored, and totally different from monomers. After electrolysis, the supporting electrolyte was removed and the products were purified by silica gel column chromatography ($CHCl_3$:H_2O, 1:1 v/v).

Instrumentation

The molecular structures of the copolymers were measured by spectroscopy. The UV–visible spectra were recorded on Perkin–Elmer-(L45) UV–visible spectrophotometer. Analysis of soluble portion of polymer in DMSO was also done. The IR spectra were recorded on a Perkin–Elmer 783 spectrophotometer KBr pellets. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DRX 300 (300 MHz) FT spectrometer in $CDCl_3$ using TMS as an internal reference. Chemical shifts are reported in ppm downfield from TMS as an internal reference. Cyclic voltammetry was performed at 25°C using VersaSTAT 3-200. The morphology and particle size were determined using a scanning electron microscope (SEM), JSM 5800, Jeol, Tokyo, Japan.

RESULTS AND DISCUSSIONS

Literature survey has revealed that copolymerization has emerged as a very strong, attractive, and challenging discipline in chemical research,[22–31] however, traditional polymerization[32–35] of aniline involves some oxidizing agents such as Ammonium Persulfate, $K_2Cr_2O_7$, $FeCl_3$, $KMnO_4$, BrO_3, $KClO_3$, Tetrabutylammonium persulfate (TABP), H_2O_2, etc., and results in the formation of insoluble and infusible polymer along with used oxidant by-products which are difficult to separate. These methodologies suffer from drawbacks like removal of by-products, wide range of polymer molecular weight, long reaction time, high temperature requirement, negative impact of oxidants on the environment and toxic effect on human beings.

The objective of our research program is to find out simple, ecocompatible, and efficient synthetic-methodology[36–41] for important organic compounds in which the use of toxic reagents could be minimized or eliminated. To fulfill our objective, an

$R = -OCH_3, -CH_3, -NO_2, -Cl, -NHC_2H_5, -NHCH_3, -NHC_3H_7, -OH, -NH_2$
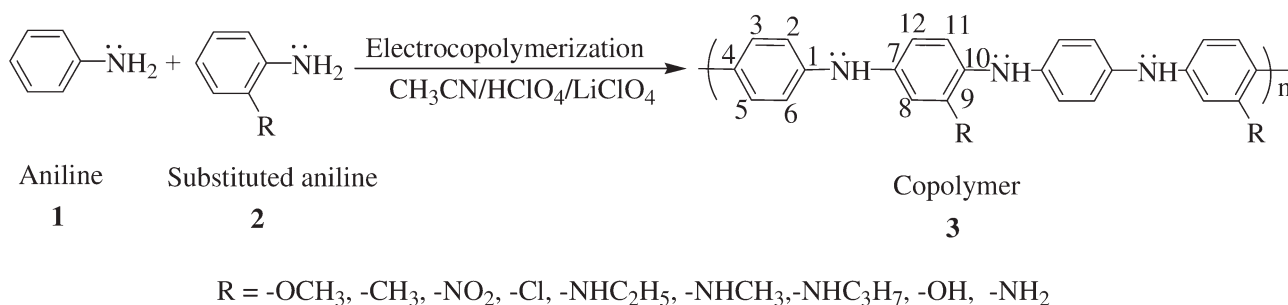
Scheme 1 Preparation of aniline-based copolymer.

effort was made as a trial for the electrochemical copolymerization of aniline and substituted aniline in which acetonitrile was used as non-aqueous solvent, perchloric acid as proton donor, and lithium perchlorate (LiClO$_4$) as supporting electrolyte. To our surprise, reaction proceeded smoothly and quantitatively and finally an apparent current density of 4.5–6.0 F/Mol was optimized for maximum yield of copolymer (Scheme 1).

It was found that the reaction proceeded smoothly and quantitatively at an apparent current density of 4 F/mol although the time required for the reaction was about 5–10 h. By adding the supporting electrolyte LiClO$_4$, however, the reactants were transformed into a product in 3–5 h. Thus, the electrocopolymerization was carried out in acetonitrile at an apparent current density of 4.5–6.0 F/mol using LiClO$_4$ as a supporting electrolyte, which is very small in comparison to the amount of energy used in other conventional methods.

It was observed that during controlled potential electrolysis, the redox potential varied as the substituents varied and was found that presence of electron releasing groups like —OCH$_3$ on monomer **2** facilitated the electron availability to form radical cation readily so polymerization was possible at lower potential but due to presence of electron withdrawing groups like —Cl higher potential was needed.

On the basis of general mechanism (Scheme 2) given by Mohilner et al.,[42] we proposed a mechanism for the electrocopolymerization. Monomer **1** and monomer **2** undergo one electron oxidation to form a radical cation **1a** and **2a**. The radical cation **2b** attacks on radical cation **1a**, followed by two pro-

ton loss to afford intermediate **3a**. The intermediate **3a** after one electron oxidation evolves a cation radical **3b** which attacks on radical cation **1b** and converted into intermediate **3c** by losing two protons. The intermediate **3c** undergoes a chain propagation to form copolymer **3** (Scheme 3). Perchloric acid is more rapidly ionized in acetonitrile and forces the polymer to release more and more electron to the cathode.

Cyclic voltammetry

Figure 1 presents the cyclic voltammogram obtained from electrochemical synthesis of poly_(aniline-*co-o*-anisidine) **3a** on a platinum electrode in acetonitrile containing 0.01M LiClO$_4$ and 1.0M perchloric acid. The corresponding voltagram exhibits two anodic peaks between 0.50 and 2.00 V. First peak corresponds to the oxidation of monomer indicating the generation of monomer radical cations and the second oxidation peak indicates further coupling of these radical cations to form copolymer.

UV–vis analysis

UV–vis absorption spectra of the poly_(aniline-*co-o*-anisidine) **3a** in DMSO is presented in Figure 2, respectively. The band around 280–380 nm is assigned to the π–π* (band gap) electronic transition in the phenyl ring in the polymer backbone and the peak above 570 nm is due to inter band charge transfer associated with excitation of the benzenoid to quinonoid moieties.

FTIR analysis

Figure 3 shows the FTIR spectra of copolymer **3a**. The bands changed between following data were observed: N—H stretching, 3309.1; aromatic C—H stretching, 2932.0 cm^{-1}; C=C stretching (in quinoid diamine ring), 1683.4 cm^{-1}; C=C stretching (in benzenoid diamine ring), 1510.5 cm^{-1}; and C—N stretching 1250.0 cm^{-1} (Table II). From the 842.7 cm^{-1} peak characteristic of an *ortho*, *para*-substituted aromatic ring.
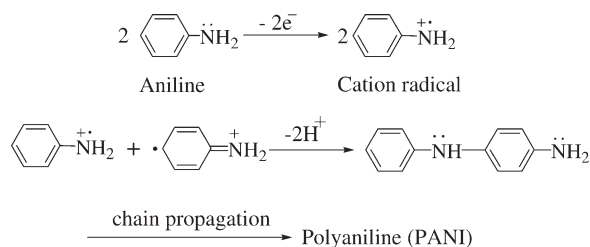
Scheme 2 General mechanism of aniline polymerization.
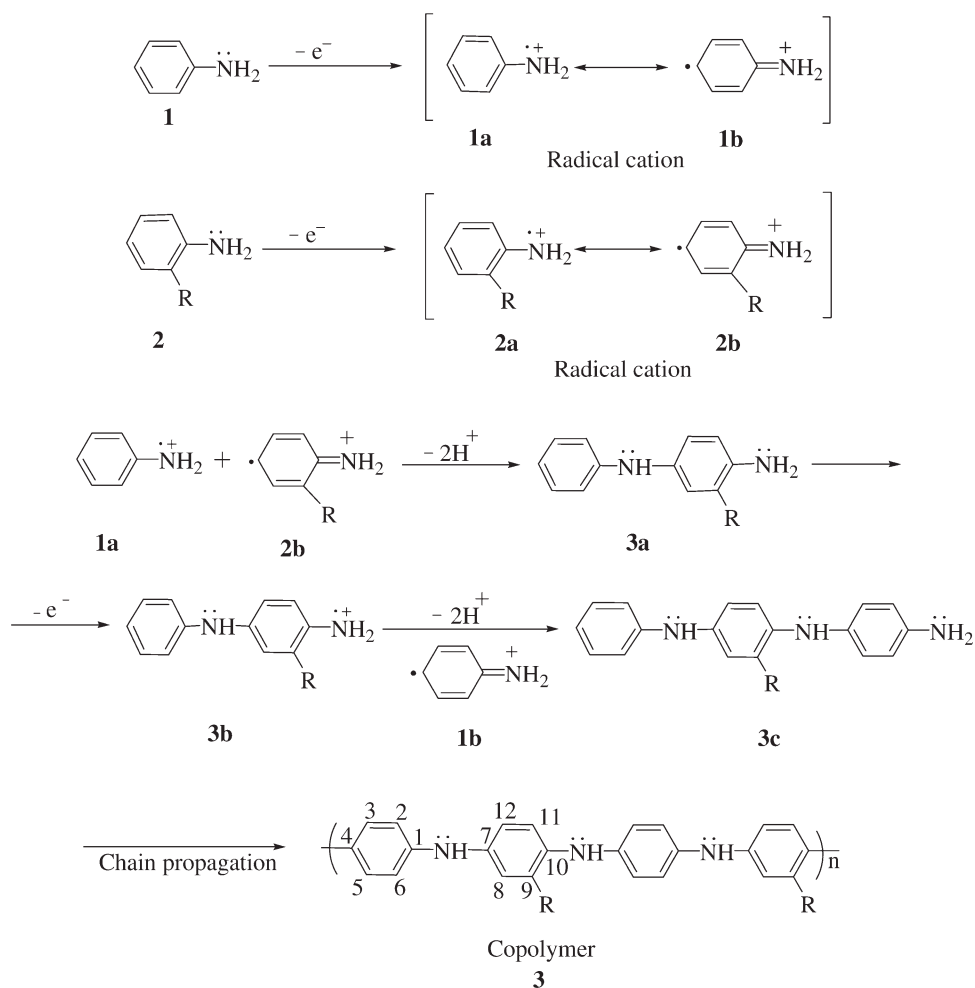
Scheme 3 Reaction scheme for the formation of aniline-based copolymer.

Copolymer solubility

Solubility of the copolymer was increased by an increment of the methoxy content. Consequently, the copolymer exhibits good solubility characteristics as compared to polyaniline. The copolymer **3a** is found to be partially soluble in chloroform but found to be highly soluble in CH_3CN and DMSO. The nitrogen heteroatom incorporated between phenyl rings in
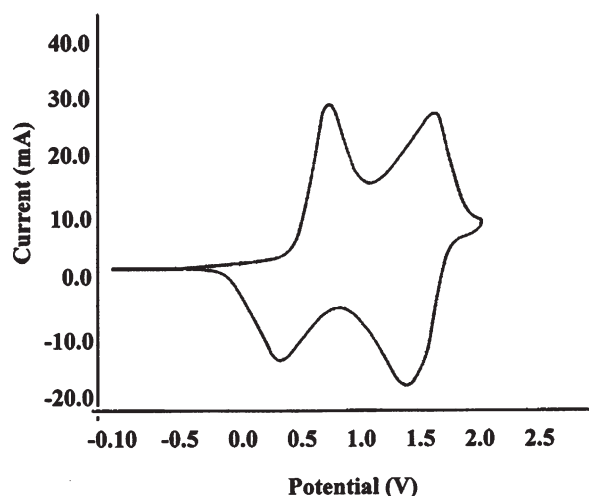

Figure 1 Cyclic voltammogram of poly_(aniline-*co-o*-anisidine) **3a** in $0.01M$ $LiClO_4$ scanning rate: 50 mV/s.
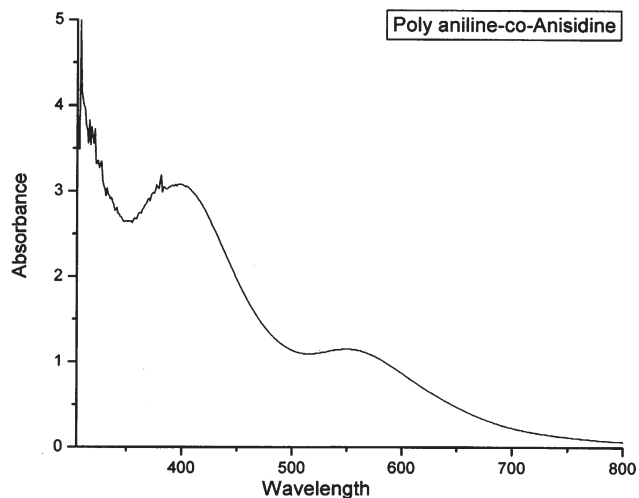

Figure 2 UV–visible absorption spectra of poly_(aniline-*co-o*-anisidine) **3a** copolymer.
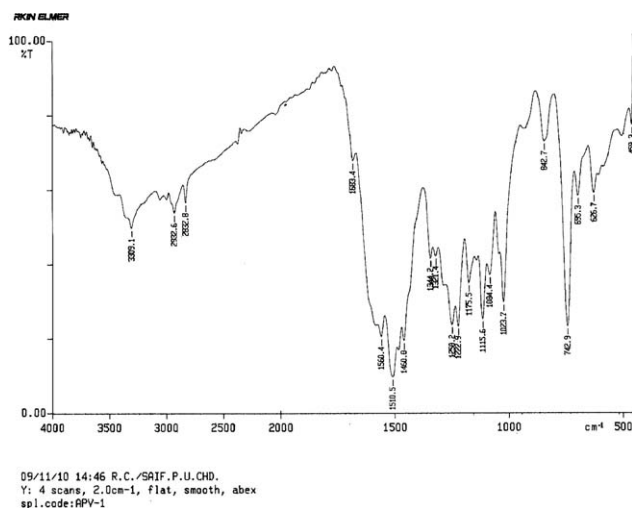
Figure 3 FTIR spectra of the poly_(aniline-*co-o*-anisidine) **3a** copolymer.

the backbone of polyaniline provides the chemical flexibility.

SEM analysis

The surface morphology of the copolymer coating synthesized at Pt plate was studied by scanning electron microscope (SEM). The SEM image of the copolymer poly_(aniline-*co-o*-anisidine) reveals that there are homogenous compositions of film in which some pores (200.5–402.9 nm), are present (Figure 4). PANI films with micropores doped with perchloric acid seemed to be ideal candidate as electrode material for supercapacitors since they possessed inherent advantage of high surface area, which would have the electrode having more active sites for faradic reaction.
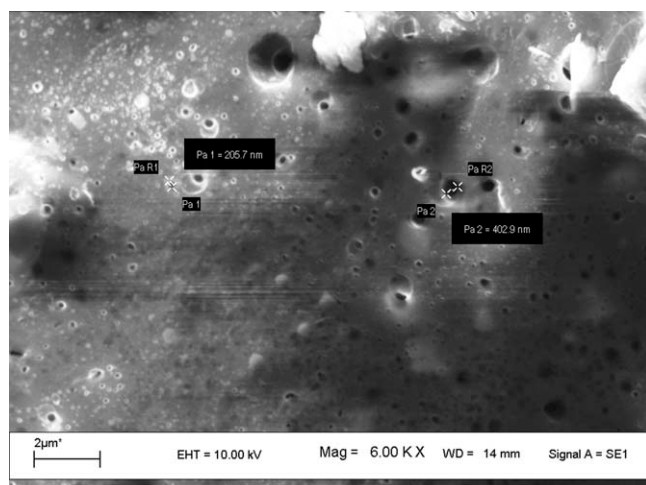
Spectral analysis

(3a) Poly(aniline-*co-o*-anisidine): ^{1}H-NMR (CDCl$_3$, TMS, δ): 3.73 (s, 3H, OCH$_3$), 6.21–7.01 (m, 4H, Ar—H), 5.72–5.77 (m, 3H, Ar—H), 3.96 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C$_1$), 117.9 (C$_2$), 129.4 (C$_3$), 118.0 (C$_4$), 129.4 (C$_5$), 117.9 (C$_6$), 134.7 (C$_7$), 104.0 (C$_8$), 149.4 (C$_9$), 121.8 (C$_{10}$), 117.0 (C$_{11}$), 111.1 (C$_{12}$), 56 (OCH$_3$).

(3b) Poly(aniline-*co-o*-toludine): ^{1}H-NMR (CDCl$_3$, TMS, δ): 2.35 (s, 3H, CH$_3$), 6.21–7.01 (m, 4H, Ar—H), 6.01–6.09 (m, 3H, Ar—H), 3.89 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C$_1$), 117.9 (C$_2$), 129.4 (C$_3$), 118.0 (C$_4$), 129.4 (C$_5$), 117.9 (C$_6$), 140.7 (C$_7$), 116.0 (C$_8$), 127.3 (C$_9$), 118.3 (C$_{10}$), 119.8 (C$_{11}$), 111.1 (C$_{12}$), 12.1.0 (CH$_3$).

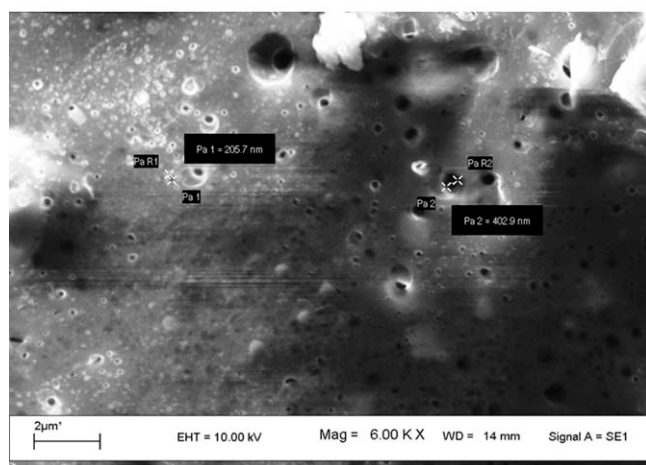**(3c) Poly(aniline-*co-o*-nitroaniline):** ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 6.47–7.14 (m, 3H, Ar—H), 3.98 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C$_1$), 117.9 (C$_2$),

TABLE II
Characteristic Peaks of Aniline-Based Copolymers

Entry	$v_{benzenoid}$ ring stretch (cm^{-1})	$v_{C—N}$ stretching mode (cm^{-1})	$v_{in-plane}$ bending of C—H (cm^{-1})	$v_{out-plane}$ bending of C—H (cm^{-1})	$v_{Aromatic}$ C—H (cm^{-1})	$v_{N—H}$ stretching (cm^{-1})	$v_{Quinoid}$ ring stretch (cm^{-1})
3a	1510.5	1250.0	1115.6	842.7	2932.0	3309.1	1683.4
3b	1499.8	1256.6	1125.6	749.0	2800.0	3400.0	1659.1
3c	1450.2	1282.1	1115.8	810.0	2929.5	3434.1	1659.0
3d	1510.1	1320.1	1118.3	699.0	3045.0	3306.1	1651.2
3e	1479.1	1298.3	1015.9	798.0	3030.0	3400.0	1562.0
3f	1469.0	1250.3	1112.9	796.0	2932.0	3400.0	1682.0
3g	1482.7	1162.0	1111.7	632.0	2951.0	3452.0	1501.1
3h	1482.3	1259.0	1114.6	655.0	2940.2	3450.1	1580.3
3i	1482.0	1250.0	1115.6	676.0	2987.0	3398.0	1590.0

(a)

(b)

Figure 4 (a) SEM image of the copolymer poly_(aniline-*co-o*-anisidine) **3a** at different magnifications: (a) 11.04 K×, Pa1 = 200.5 nm, Pa2 = 322.4 nm. (b) 6.00 K×, Pa1 = 200.7 nm, Pa2 = 402.9 nm.

129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 113.8 (C_8), 135.9 (C_9), 131.2 (C_{10}), 116.2 (C_{11}), 124.8 (C_{12}).

(3d) Poly(anilne-*co-o*-chloroaniline): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 6.09–6.22 (m, 3H, Ar—H), 3.96 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 119.1 (C_8), 121.2 (C_9), 136.2 (C_{10}), 117.4 (C_{11}), 116.8 (C_{12}).

(3e) Poly(aniline-*co-o*-aminophenol): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 5.77–6.04 (m, 3H, Ar—H), 3.88 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—), 4.96 (s, 1H, OH); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 113.8 (C_8), 144.7 (C_9), 123.4 (C_{10}), 117.4 (C_{11}), 111.2 (C_{12}).

(3f) Poly(aniline-*co-o*-Phenylenediamine): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 5.41–5.96 (m, 3H, Ar—H), 4.03 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.0 (C_7), 105.3 (C_8), 134.2 (C_9), 122.4 (C_{10}), 116.8 (C_{11}), 108.7 (C_{12}).

(3g) Poly(aniline-*co*-N-ethyl aniline): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 5.38–5.99 (m, 3H, Ar—H), 3.97 (s, 1H, C$_6$H$_4$—NH—C$_6$H$_4$), 3.0 (m, 2H, CH$_2$), 1.13 (t, 3H, CH$_3$); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 102.5 (C_8), 131.0 (C_9), 120.4 (C_{10}), 116.8 (C_{11}), 107.1 (C_{12}), 44.4 (NH—CH$_2$), 15.5 (CH$_3$).

(3h) Poly(aniline-*co*-N-propyl aniline): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 5.38–5.99 (m, 3H, Ar—H), 3.97 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—), 1.56 (m, 2H, CH$_2$), 3.06 (t, 2H, CH$_2$), 1.13 (t, 3H, CH$_3$); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 102.5 (C_8), 131.0 (C_9), 120.4 (C_{10}), 116.8 (C_{11}), 107.1 (C_{12}), 53.8 (NH—CH$_2$), 24.6 (CH$_2$), 11.4 (CH$_3$).

(3i) Poly(aniline-*co*-N-methyl aniline): ^{1}H-NMR (CDCl$_3$, TMS, δ): 6.21–7.01 (m, 4H, Ar—H), 5.38–5.99 (m, 3H, Ar—H), 3.95 (s, 1H, —C$_6$H$_4$—NH—C$_6$H$_4$—), 2.78 (s, 3H, CH$_3$); ^{13}C-NMR (CDCl$_3$, TMS, δ): 143.0 (C_1), 117.9 (C_2), 129.4 (C_3), 118.0 (C_4), 129.4 (C_5), 117.9 (C_6), 134.7 (C_7), 102.5 (C_8), 131.0 (C_9), 120.4 (C_{10}), 116.8 (C_{11}), 107.1 (C_{12}), 35.3 (NH—CH$_3$).

CONCLUSION

A one-pot electrochemical synthesis of aniline based copolymers was done in excellent yield at room temperature, which is not so easy using the conventional chemical method. We have eliminated the use and production of toxic chemicals. Thus, the method is environmentally benign and a contribution in the field of green chemistry.

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