



Newer dynamic electrochromic nanorods of poly(*o*-anisidine-co-ethyl 4-aminobenzoate) synthesized by electrochemical polymerization

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ABSTRACT

Electrochemical copolymerization of *o*-anisidine with ethyl 4-aminobenzoate was carried out in aqueous 0.1 M HClO₄ by employing cyclic voltammetry. Copolymer films were grown for different molar concentration ratios of ethyl 4-aminobenzoate. Electrochemical homopolymerizations of *o*-anisidine and ethyl 4-aminobenzoate were carried out independently under similar conditions. The copolymers exhibited high solubility in many polar solvents. The scan rate exerted good influence on the polymer effect on this glassy carbon electrode copolymer film, revealing electroactive film's excellent adherent properties. Spectroelectrochemical studies of the copolymer film were carried out on indium tin oxide plates. The copolymer was characterized by FTIR spectral data. The surface morphology was studied using SEM and TEM analysis. The electrical conductivity of copolymer was measured by four-probe conductivity meter.

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1. Introduction

The ability of reversible change in the transmitted or reflected light upon electrochemical oxidation or reduction of materials has aroused the interest of scientists over the past decades [1]. Electrochromic properties have proved promising for automatic anti-glazing mirror, smart windows, electrochromic displays, and chameleon materials [2–7]. There are many chemical systems that are intrinsically electrochromic, such as transition metal oxides, inorganic coordination complexes, organic molecules, and conjugated polymers [8–13]. Among the available electrochromic materials, conjugated polymers represented by polyaniline (PANI) polypyrrole (PPY) and poly(3,4-ethylenedioxythiophene) (PEDOT) and their derivatives have received a great deal of attention because of their attractive electrochromic properties, such as fast response time, high coloration efficiency and contrast ratio, good stability, and wide range of colors [14–21].

PANI is difficult to process due to its poor solubility in most solvents. Efforts have been made to improve the mechanical properties and processability by using functionalized acids as dopants. Among these, *p*-toluenesulfonic acid [22], dodecyl benzenesulfonic acid (DBSA) [23] and camphorsulfonic acid [24] have been commonly used. Another way to increase the solubility is through polymerization of derivatives of aniline, such as 2-methoxyaniline

(*o*-anisidine) [25]. In this case, the substituent group present in the backbone of the polymer chain causes a decrease in the stiffness of the polymer chain and results in more solvation. However, the conductivity of substituted polyanilines is much less than that of simple PANI. Increased torsional angles brought about by the substituent groups result in a decrease in orbital overlap of the *p*-electrons and nitrogen lone pairs, which ultimately leads to a decrease in the extent of conjugation and of conductivity.

Copolymerization was generally performed to improve the processability of PANI. Modifications of the structure of PANI through ring or N-substitution also can be effected to result in different electrochemical characteristics than PANI. Several reports are available on the copolymerization of aniline with substituted anilines [26,27]. Utilization of materials of biological interest for the preparation of newer nano polymeric compounds assumes importance in the present environment [28]. Aligned or ordered, otherwise called poled polyureasulfone thin films having excellent transparency from near UV to visible region were prepared by carrying out additional polymerization of 1,4-phenylene diisocyanate and 4,4'-diaminodiphenyl sulfone simultaneously. Dan and Sengupta synthesized and characterized conducting poly(aniline-co-diaminodiphenylsulfone) and showed that the reactivity of 4,4'-diaminodiphenylsulfone was greater than that of aniline [29]. Electrochemically synthesized copolymer of aniline and 4,4'-diaminodiphenyl sulfone by us exhibited novel electrochromic properties [30].

Electrochemical methods provide special advantages over other methods for preparation of conducting polymers due to the possibility of simultaneous characterization. The present study

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describes the electrochemical copolymerization of *o*-anisidine (OA) with ethyl 4-aminobenzoate (EAB). Cyclic voltammetry was used to synthesize and concomitantly analyze the electrochemical properties of homopolymer/copolymer in the process of obtaining evidence for copolymer deposition when a mixture of *o*-anisidine and ethyl 4-aminobenzoate was used. Additionally, in the present study, the electrochemical growth characteristics of poly *o*-anisidine (POA) films were compared to infer the differences in the growth behavior of the copolymer deposition. Besides that, *in situ* UV–vis spectroelectrochemical studies to identify the electrochromic properties copolymer (OA-co-EAB) formation by following the UV–vis spectral changes at an optically transparent indium-tin oxide (ITO) coated glass electrode electropolymerization of a mixture of *o*-anisidine and ethyl 4-aminobenzoate.

2. Experimental

2.1. Materials

The monomers *o*-anisidine (E-Merck) and ethyl 4-aminobenzoate (Acros Organics) were used without any further purification. All reagents were prepared with double-distilled water. In the present study, 0.1 M perchloric acid solution was used as supporting electrolyte.

2.2. Synthesis of copolymer

All electrochemical studies were performed by using CHI 760C electrochemical workstation (CH Instruments, USA) with Amp Booster (Model 680) having inbuilt software. A three-electrode cell was assembled using glassy carbon electrode (GCE) of area 0.0314 cm² as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. The three electrodes were inserted into the cell and purified nitrogen gas was purged for 20 min to remove the dissolved oxygen under stirred conditions. All electrochemical studies were carried out by thermostating the electrochemical system at 25 ± 1 °C. For the electrochemical copolymerization studies, a mixture of OA and EAB was used in 0.1 M HClO₄. Electropolymerization was carried out through cyclic voltammetry for different concentrations of EAB by sweeping the potential in the range of –0.2 to 0.8 V for 15 cycles while keeping the sweep rate as 0.1 V s^{–1}. Cyclic voltammograms (CVs) were recorded concomitantly with syntheses by keeping different molar feed ratios of EAB in the copolymerization. Polymerization experiments involving OA and EAB alone were also carried out in the same potential range. The deposited films of poly *o*-anisidine (POA)/copolymer (OA-co-EAB) were then placed in a monomer-free background electrolyte 0.1 M HClO₄ and CVs of the film-coated electrode were recorded after stabilization.

2.3. *In situ* UV–visible spectroelectrochemistry

A Shimadzu UV-2401 PC UV–vis spectrophotometer was used to record the *in situ* UV–vis spectra by operating through the time course mode. A quartz cuvette of 1 cm path length with an optically transparent ITO coated glass plate working electrode, platinum wire counter electrode and Ag/AgCl reference electrode was used as an electrochemical cell for UV–vis spectroelectrochemical studies. Before each experiment, the ITO coated glass electrode was cleaned with acetone and then with double distilled water. Constant potential 0.8 V was applied by using a CHI 760C electrochemical workstation (CH Instruments, USA) with Amp Booster (Model 680) on a solution containing the two monomers OA and EAB.

2.4. Characterization

GCE having the electrochemically deposited polymer was dipped into 5 mL high pure DMSO solvent for 10 min. GCE was removed from the solution and the solvent was stripped off under vacuum condition. After drying the solid mass in vacuum desiccator for 6 h, pellet was made with spectral grade KBr (E-Merck) using standard procedure in hydraulic pellet press (Kimaya). Ratio between sample and KBr was fixed at 1:30 after performing pilot studies with different ratios. Constant mass and constant thickness was maintained for all the KBr pellets. These pellets were subjected to FTIR spectroscopic analysis recorded on Perkin-Elmer 783 spectrometer in the range 4000–400 cm^{–1}. The UV–vis spectra of prepared polymer were recorded with Shimadzu UV-2401 PC UV–vis double beam spectrophotometer. The polymer film surface morphology was studied by computer controlled Hitachi S3000 H SEM and Philips CM200 TEM. The electrical conductivity of the polymer film was measured at room temperature with conventional four-probe conductivity meter. The computer controlled XRD system X'pert PRO PANalytical was used to record the X-ray diffraction of polymer coated on ITO plate samples.

3. Results and discussion

3.1. Electrochemical copolymerization/homopolymerization

Cyclic voltammograms (CVs) were recorded continuously for 15 cycles during the polymerization of OA and also for the copolymerization of OA with EAB having different molar feed ratios of EAB (0.02 M, 0.03 M, 0.1 M, 0.2 M, and 0.3 M) (Figs. 1–7). Fig. 1 shows the cyclic voltammogram cycled between –0.2 and 0.8 V at the scan rate 0.1 V s^{–1} for the electrochemical oxidation of 0.1 M EAB in 0.1 M HClO₄ medium on GCE. The first anodic peak was noticed at 0.34 V. The second oxidation peak can be seen as the leading edge of the peak, which would occur beyond 0.42 V. A peak around 0.2 V was observed. The increase in the peak current of the peaks, even though it is small, signifies the continuous buildup of adherent PEAB film on the electrode surface. A brown colored deposition of PEAB was visibly witnessed. The color of the electrolyte medium did not change revealing the absence of oligomeric dissolution. Hence, an ideal condition to deposit PEAB was established.

0.1 M *o*-anisidine was homopolymerized on glassy carbon electrode (GCE) in 0.1 M HClO₄ medium and the CV cycled between

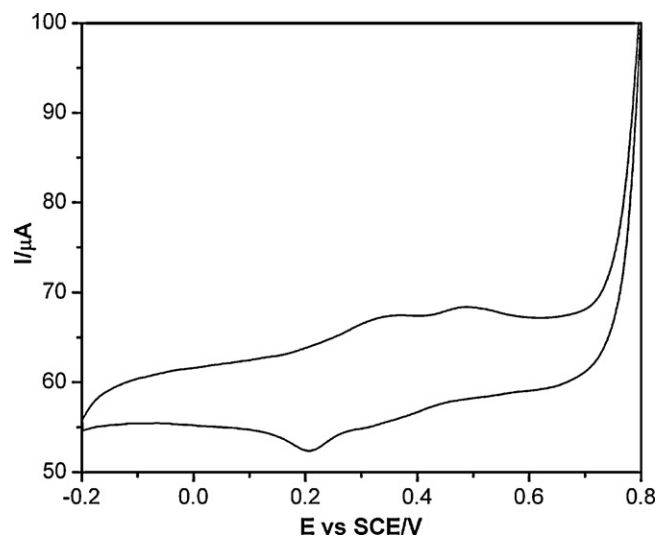


Fig. 1. Cyclic voltammetric behavior of 0.1 M EAB on GCE in 0.1 M HClO₄ medium at scan rate 0.1 V s^{–1}.

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