

Electrosynthesis of Polyfuran in Acetonitrile–Boron Trifluoride–Ethyl Ether Mixture and Its Device Application

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ABSTRACT: Electrochemical polymerization of furan was achieved in acetonitrile/boron trifluoride/ethyl ether (CH₃CN/BF₃/EE) mixture in the presence of tetrabutylammonium tetrafluoroborate via constant potential electrolysis at 1.4 V versus Ag/AgCl. Electrochemical behavior of furan was investigated in the same solvent mixture of varying ratios, utilizing cyclic voltammetry. Free-standing polyfuran (PFu) films were obtained in CH₃CN/BF₃/EE mixture (2/4/4; v/v/v) and characterized using FTIR spectroscopic technique. Spectroelectrochemical behavior of the PFu film was investigated by recording the electronic absorption spectra,

in situ, in monomer-free solution. It is observed that PFu film can be reversibly cycled between –0.1 V (gray) and + 0.6 V versus Ag-wire (gray color); however, this behavior diminishes in the presence of water. Electrochromic device application of PFu film with poly(ethylene dioxythiophene) was also studied. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 871–876, 2007

Key words: polyfuran; electrochemistry; electrochromic properties; device application; spectroelectrochemistry; cyclic voltammetry

INTRODUCTION

Conducting polymers with extensive π -conjugation has attracted great attention because of their wide range of applications in various areas. Among the five-membered heterocyclic monomers, pyrrole, thiophene, and their derivatives have been the subject of detailed studies. Furan, on the other hand, has received little attention due to the difficulties in its synthesis because of its lower aromaticity.

The report of Tournillon and Garnier¹ is the earliest report on the synthesis of polyfuran (PFu) via electrochemical polymerization. Later, Ohsawa et al.² reported the preparation of PFu films via anodic coupling. PFu films found to exhibit lower electrical conductivity in comparison to polythiophene and polypyrrole because of the shorter conjugated chains.

Pons and Hinman³ reported that oxidation of furan on Pt electrode resulted in the formation of an insulating film, which became conducting after pulsing the working electrode potential beyond the oxidation potential of the monomer. Glenis et al.⁴ were able to synthesize PFu films at lower potentials by using terfuran instead of furan. Electrochemical

behavior of furan in acetonitrile was reported by Nessakh et al.⁵ utilizing cyclic voltammetry (CV), however, no polymeric product was mentioned.

Zotti et al.⁶ synthesized polyconjugated PFu via electrochemical reduction of 2,5-dibromofuran, using Ni(bipy)₃²⁺ as catalyst, and they also recorded the electronic absorption spectrum of PFu film on ITO (indium tin oxide) for the first time. Their attempts to polymerize furan via electrochemical oxidation resulted in the low conjugated product because of acid-catalyzed polymerization of the monomer. The effect of polymerization potential in the synthesis of perchlorate-doped PFu films was investigated by Carrillo et al.⁷ It is reported that black, adherent films can be obtained at potentials 2.1 and 2.3 V versus SCE; however, ring rupture was also noted due to acid-catalyzed competitive reaction.

Earlier, we investigated the effect of different supporting electrolytes on the conductivities of PFu films and the effect of temperature on the electrochemical polymerization of furan.⁸ Although, conducting PFu films were obtained when tetrabutylammonium perchlorate or sodium perchlorate were used as supporting electrolyte, we also noted ring opening during anodic oxidation of the monomer.⁹

Wan et al. reported the synthesis of free-standing PFu films at lower potentials by using boron trifluoride (BF₃)–ethyl ether (EE) mixture.¹⁰ The polymer film found to exhibit higher conductivities than previously reported values. 1 : 1 Molar ratio of BF₃ to EE is found

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to be better than the other ratios, since the polymer film obtained contained less aliphatic units. Although polymer film could be obtained during potential cycling, the authors preferred galvanostatic method for the synthesis of polymer films. They also investigated the degradation mechanism of PFu films through successive cycling of the polymer film in acetonitrile and in water.¹¹ The influence of polymerization potential on the electrochemical behavior of perchlorate-doped PFu film was reported by Gonzales-Tejera and Carrillo.¹² Effect of working conditions on the growth mechanism and morphology of PFu was reported by del Valle et al.^{13,14} It is emphasized that anhydrous conditions are necessary for the PFu film formation. They also reported variation of oxidation potential of furan depending on the type of the anion in electrolyte.

As it is seen from the above cited limited number of references, synthesis of PFu via electrochemical polymerization is still controversial. Here in, we report the result of our investigations on the electrochemical synthesis of PFu films via constant potential electrolysis (CPE) in CH₃CN/BF₃/EE mixture. Spectroelectrochemical behavior of the PFu film, obtained via CPE, on ITO-coated quartz glass electrode and its device application was also investigated.

EXPERIMENTAL

Materials

The monomer furan (Aldrich Chemical, 98%, Germany) was distilled under N₂ atmosphere prior to its use. CH₃CN was dried over CaH₂ for 48 h and distilled over CaH₂. Tetrabutylammonium tetrafluoroborate (TBABF, Fluka, Switzerland) was used as supporting electrolyte both for CV measurements and for CPE without any further recrystallization. Ethyl ether (EE) was dried and distilled in the presence of sodium. BF₃ (Aldrich Chemical, Germany) was used as received.

Electrochemical experiments

The oxidation–reduction behavior of the monomer was determined by CV using a Gamry potentiostat (equipped with PHE 200 Physical Electrochemistry software). A Pt-disc ($d = 1$ mm) working electrode, a Pt coil counter electrode, and a Ag/AgCl reference electrode were used for CV studies. Measurements were made in TBABF dissolved in CH₃CN and a mixture of CH₃CN/BF₃/EE with different ratios at room temperature under N₂ atmosphere.

Polymer synthesis and characterization

Electrochemical polymerization of furan was carried out by CPE in a three-electrode H-type cell utilizing a solvent mixture consisting of CH₃CN-BF₃-EE together

with TBABF as supporting electrolyte, at room temperature. For preparative electrolysis, the working and counter electrodes were made of a rectangular platinum sheet (total area of about 1.5 cm²). At the end of the electrolysis, the polymer film was peeled off from the electrode surface and washed with CH₃CN to remove the electrolyte, unreacted monomer, and oligomeric species, and dried under vacuum.

FTIR spectra of polyfuran (PFu) films were recorded on a Varian Vertex 70 spectrometer. The electrical conductivity of the films was measured using four-probe in-line method. SEM studies were achieved by using JEOL JSM-6400 scanning electron microscope.

The spectroelectrochemical behavior of the film was investigated in monomer free solutions using UV–vis (Hewlett–Packard 8453A diode array UV–vis spectrophotometer) spectroscopic technique. An indium tin oxide-coated quartz glass, ITO (Delta Tech. 2–4 Ω/cm²) working electrode, a Pt wire counter electrode, and a Ag wire reference electrode were used for spectroelectrochemical studies. The pseudo reference electrode, Ag wire, was used after checking the correction between Ag and Ag/AgCl reference electrode.

Preparation of gel electrolyte

The preparation of gel electrolyte was achieved by using solution of acetonitrile, poly(methyl methacrylate) (PMMA), and TBABF. Slow evaporation of acetonitrile was followed by addition of few drops of propylene carbonate, which reduced the vapor pressure of gel electrolyte. The percentage composition of gel was 70/20/7/3 of CH₃CN/PC/PMMA/TBABF by weight, respectively.

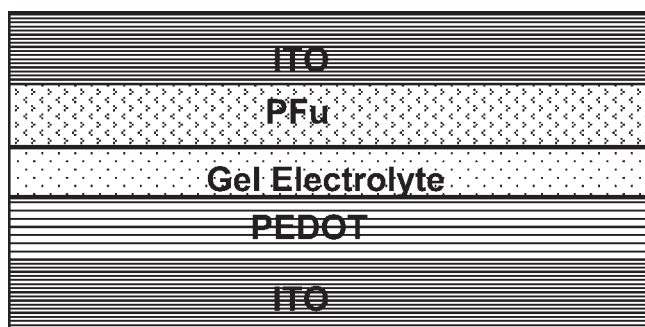
Construction of electrochromic device

For the device application, PFu film was deposited onto ITO-coated glass in a mixture of CH₃CN/BF₃/EE (2/4/4; v/v/v), and 0.05M TBABF at 1.4 V. PEDOT was synthesized in CH₃CN containing 0.05M 3,4-ethylenedioxythiophene (EDOT) and 0.1M TBABF at 1.5 V. Device was prepared by in sandwich configuration with PFu- and PEDOT-coated ITO layers (neutral and oxidized state), which were separated by gel electrolyte as depicted in Scheme 1 (not scaled). The device was derived via potentiostat where the working electrode was biased to PFu layer as well as the reference electrode and the counter electrodes were short cut.

RESULTS AND DISCUSSION

Cyclic voltammetry of furan

Electrochemical behavior of furan was investigated in 1 : 1 mixture of BF₃/EE mixed with CH₃CN in different ratios containing TBABF as supporting electrolyte.



Scheme 1 Construction of device.

CV results are given in Figure 1. CV of furan in pure CH₃CN-TBABF solvent–electrolyte couple exhibits an irreversible oxidation peak at 2.0 V versus Ag/AgCl. However, when BF₃/EE mixture was added, a shift in the oxidation peak to less anodic potentials was observed with increasing amount of BF₃/EE mixture in the solution. Furthermore, a new reversible peak at about 0.7 V versus Ag/AgCl was also observed during repetitive cycling. The consecutive cycles show a newly intensifying reversible peak during the polymerization of furan in the given solvent composition (Fig. 2). The CV studies clearly showed that oxidation potential of furan is lowered in the presence of BF₃. Such a potential lowering effect was also observed for thiophene and explained to be due to interaction of BF₃ with thiophene ring, which lowers its aromatic resonance energy.¹⁵ This kind of interaction is also possible in the case of furan. Lewis acid might form a π -complex with furan and destabilizes it and lowers its oxidation potential. To investigate the lowering of the peak potential, we have recorded the electronic absorption spectrum of furan both in pure CH₃CN

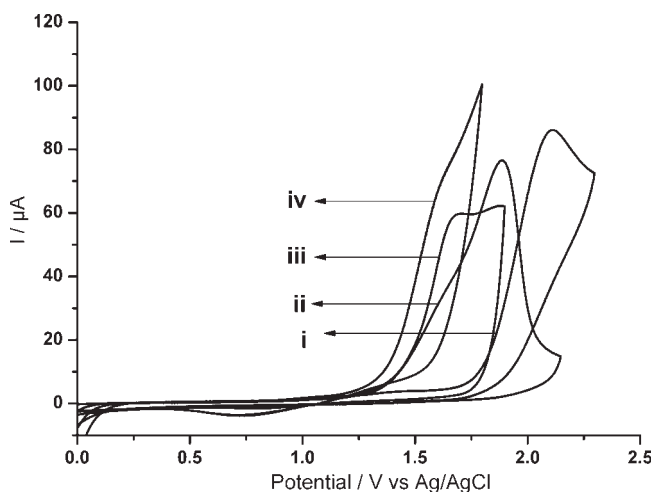


Figure 1 CV of furan recorded in (i) acetonitrile, (ii) CH₃CN/BF₃/EE mixture (9/0.5/0.5; v/v/v), (iii) CH₃CN/BF₃/EE mixture (6/2/2; v/v/v), and (iv) CH₃CN/BF₃/EE mixture (2/4/4; v/v/v) versus Ag/AgCl, in the presence of 0.05M TBABF.

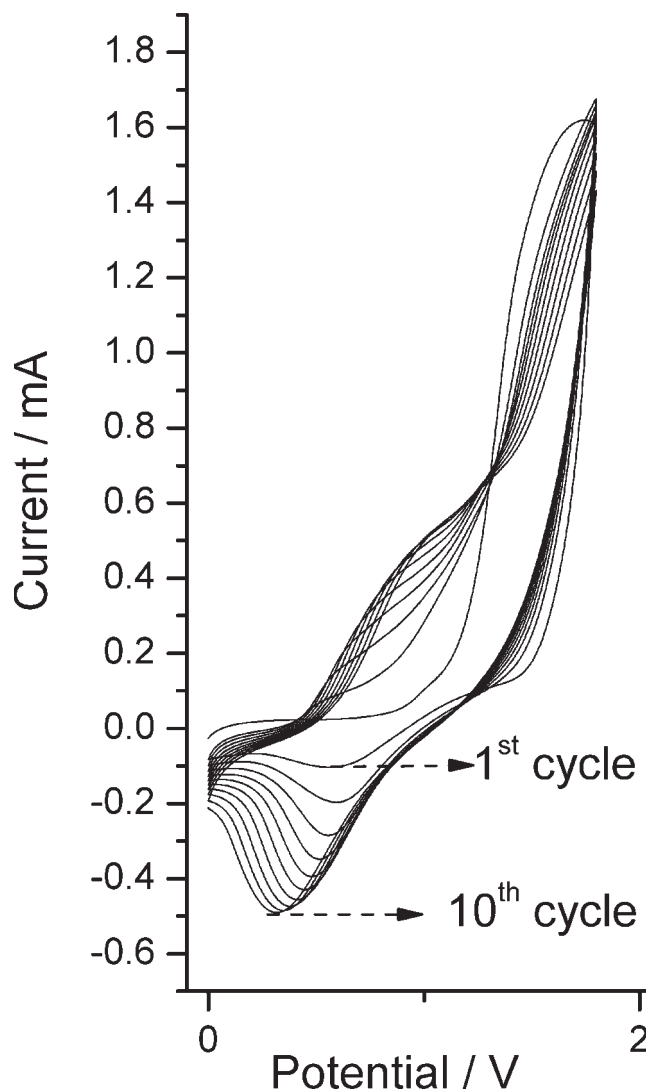


Figure 2 CV of furan recorded during repetitive cycling in CH₃CN/BF₃/EE mixture (2/4/4; v/v/v).

and in the solvent mixture that is used in electrochemical studies. Although the electronic absorption spectrum of monomer in acetonitrile exhibits one absorption band at 225 nm due to π - π^* transition, a new band appeared at 275 nm when the spectrum was recorded in presence of BF₃-EE mixture (Fig. 3). This new band can be ascribed to π - π^* transition of oligomeric species. Thus, although the acidity of BF₃ was lowered by mixing it with EE to avoid chemical polymerization of the monomer, it is still active to some extent to form oligomeric species, which have lower oxidation potential than the monomer.

Electrochemical polymerization

Electrochemical polymerization was performed by means of the anodic oxidation of a 0.05M solution of furan, in CH₃CN/BF₃/EE mixture (2/4/4; v/v/v) at +1.4 V versus Ag/AgCl and in pure CH₃CN at +2.0

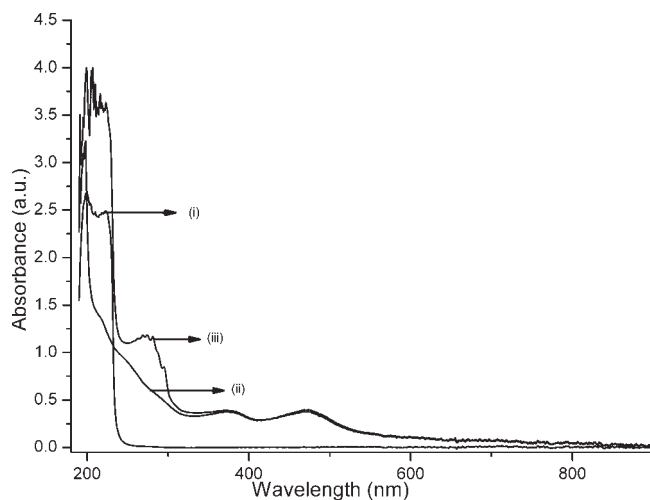


Figure 3 Electronic absorption spectrum of (i) 30 μL furan in pure CH_3CN ; (ii) $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture (2/4/4; v/v/v); (iii) 30 μL furan in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture (2/4/4; v/v/v).

V versus Ag/AgCl, utilizing TBABF as supporting electrolyte. Free-standing polymer film of thickness, 60 μm , was obtained in 10 min. At the end of the electrolysis, polymer films were peeled off from the electrode surface and washed with CH_3CN and dried under vacuum at 70°C for 24 h. Its conductivity was measured by four-probe technique and found to be 0.35 S/cm. The peeling of PFu, synthesized in pure CH_3CN , is quite hard without rupturing because it is more brittle than the one synthesized in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture.

Polymer characterization

Spectroscopic analysis of the polymer film obtained via CPE at 1.4 V in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture was carried out using FTIR spectroscopy. The peak that appears around 3150 cm^{-1} , attributed to aromatic C–H stretching, together with the peaks at 1510 and 1466 cm^{-1} , indicates that the furan rings along the polymer chains are not affected during electrochemical polymerization. Furthermore, the 788 cm^{-1} peak indicates α – α coupling of the furan rings.

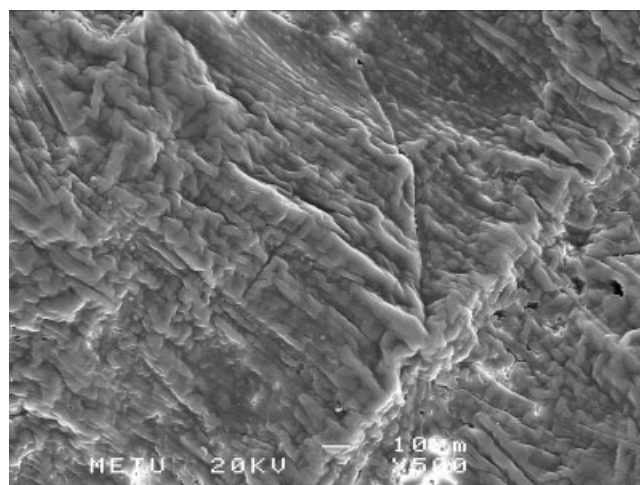
Scanning electron micrographs of solution sides of two polymer films prepared using pure CH_3CN and $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ solvent mixture are depicted in Figure 4(a, b), respectively. As seen from Figure 4(a), the PFu film prepared in CH_3CN is more dense than the one that is prepared in the solvent mixture. The different surface morphologies of two PFu films may be the evidence of effect of BF_3 during polymerization.

Spectroelectrochemistry of PFu

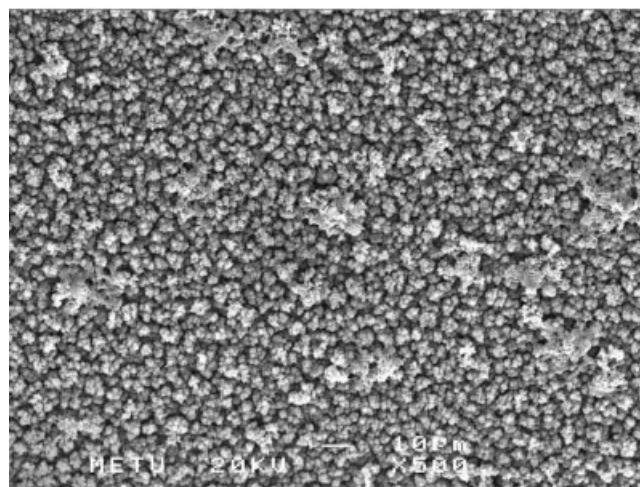
To investigate the spectroelectrochemical behavior of PFu, the polymer film was deposited on ITO work-

ing electrode at 1.4 V in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture (2/4/4; v/v/v). The changes in the electronic absorption spectrum were monitored during incremental increase in applied potential in the monomer-free CH_3CN containing 0.05M TBABF and the results are depicted in Figure 5.

In the neutral form (yellowish-green colored film), PFu exhibits one broad absorption band at about 415 nm, which can be ascribed to π – π^* transition. The electronic band gap, defined as the onset energy for the π – π^* transition, was found to be 2.1 eV, which was calculated from the energy absorption edge of the spectrum, which is in accordance with the previously reported value.⁶ Upon incremental increase in the applied potential, a new band at about 640 nm intensifies due to formation of polarons during oxidation (doping) of the film.



(a)



(b)

Figure 4 SEM images of PFu films (solution side): (a) synthesized in CH_3CN ; (b) synthesized in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$.

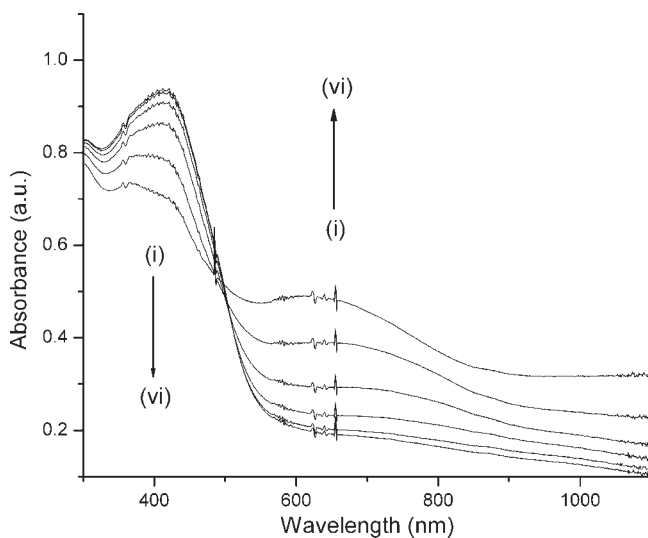


Figure 5 Spectroelectrochemistry of PFu as a function of applied potential: (i) -0.1 V, (ii) 0.0 V, (iii) $+0.2$ V, (iv) $+0.4$ V, (v) $+0.5$ V, to (vi) $+0.6$ V.

Since it is reported that PFu loses its electroactivity due to its degradation via nucleophilic attack,^{8,9} we have reinvestigated the reversible cycling of PFu films coated on ITO in monomer-free CH₃CN containing various amounts of water. For this purpose, we have monitored the changes in the absorbance value of 640 nm band during cycling of the potential of PFu-coated ITO electrode between -0.1 V and 0.6 V (100 cycles) and the results are depicted in Figure 6. As seen from Figure 6, the transmittance of 640 nm band remains almost constant up to 100 scans. However, in presence of water, the transmittance becomes smaller and smaller with successive scans indicating the loss of electroactivity of the film, which might be due to attack of water to PFu film destroying conjugation.

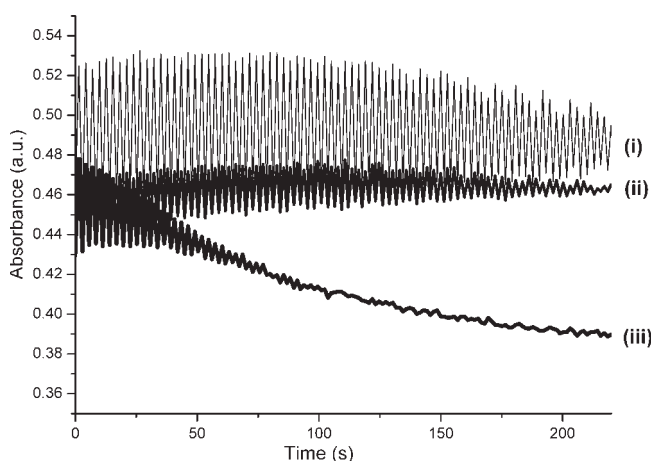


Figure 6 *In situ* UV-vis spectrum of PFu on ITO recorded during CV between -0.1 V and 0.6 V at a scan rate of 500 mV/s: (i) $<3 \times 10^{-4}\%$ (v/v) H₂O in CH₃CN; (ii) 1% (v/v) H₂O in CH₃CN; (iii) 10% (v/v) H₂O in CH₃CN.

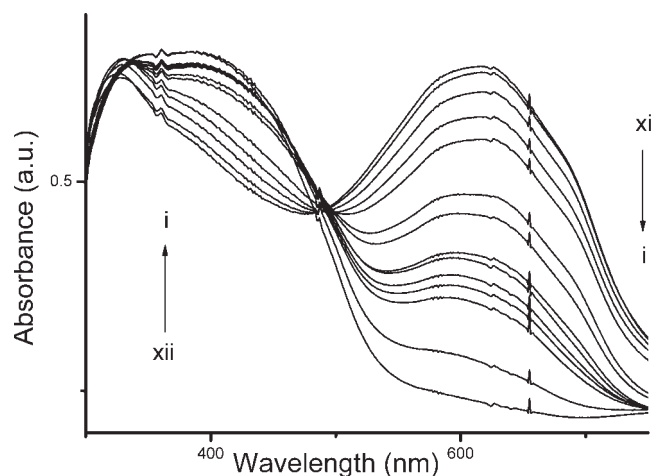


Figure 7 Spectroelectrochemistry of PFu/PEDOT device as a function of applied potential: (i) -0.8 V, (ii) 0.0 V, (iii) $+0.4$ V, (iv) $+0.6$ V, (v) $+0.7$ V, (vi) $+0.8$ V, (vii) $+0.9$ V, (viii) $+1.1$ V, (ix) $+1.2$ V, (x) $+1.4$ V, (xi) $+1.5$ V, to (xii) $+1.6$ V.

Characterization of PFu/PEDOT device

Spectroelectrochemistry of device

In this study, we constructed the dual type electrochromic device of PFu and PEDOT, using transparent ITO electrodes. In this device, PFu and PEDOT functioned as anodically and cathodically coloring electrochromic materials, respectively. To evaluate the spectral variations during the operation of the device, we monitored *in situ* UV-vis spectra of the device during the incremental increase in applied potential in the range of -0.8 V to $+1.6$ V (Fig. 7). Results implied that, as lower potential bias to PFu layer was applied, the spectral features of the device were dominated by the anodically coloring electrochromic material. Thus, device revealed the yellowish-green color with a maxi-

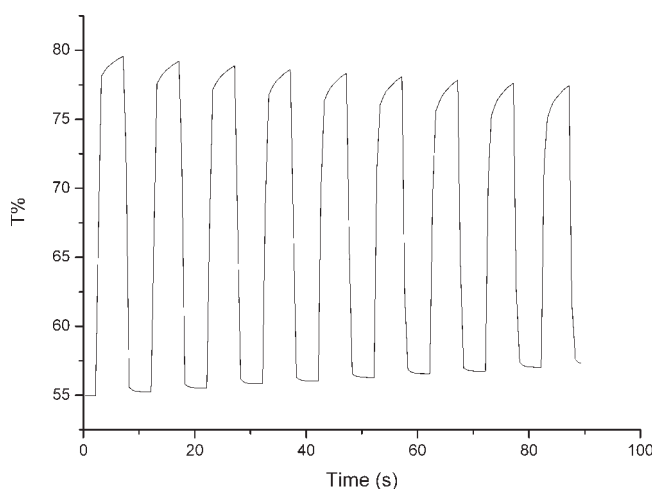


Figure 8 Electrochromic switching, optical transmittance change monitored at 415 nm for PFu/PEDOT device.

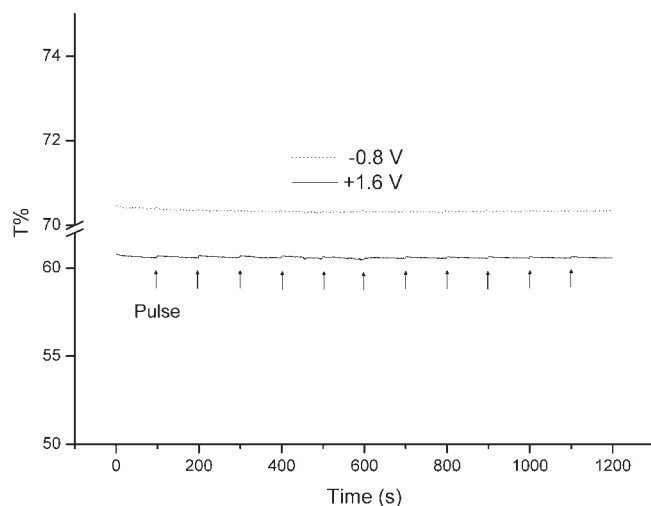


Figure 9 Open circuit memory of PFu/PEDOT device at 615 nm.

imum absorption at around 415 nm due to PFu's π - π^* transition. As the applied potential was increased, especially beginning from 0.7 V, spectral signature of PEDOT layer became dominant, due to its neutralization, where new λ_{max} was at 615 nm and the color of device was blue.

Electrochromic switching and open circuit stability of device

For electrochromic applications, the ability of a polymer to switch rapidly and to exhibit a striking color change is important.¹⁶ Switching time of PFu between its redox states was studied at fixed wavelength (415 nm) and the time to reach ultimate transmittance was found as 1.1 s. The switching between two colored states of both PFu and PFu/PEDOT electrochromic devices was also studied with chronoabsorptometry. UV-vis spectrophotometry was used to measure % transmittance (% T) of polymer film and its device at the wavelength of maximum contrast. The maximum contrast of the electrochromic device was found to be 23% with a switching time of 1.2 s (Fig. 8).

The color persistence in electrochromic devices is an important property because of energy consumption during their utilization.¹⁷ Polarization of PFu/PEDOT device was achieved by applying -0.8 V and $+1.6$ V pulses for 1 s and then keeping it at open circuit conditions for 100 s. At the same time, transmittance of device was monitored at 415 nm (Fig. 9). It is observed that, the device does not reach equilibrium under open circuit conditions and it is not stable in blue colored state. However, PFu film

was found to be stable in its neutral (yellowish-green) form, exhibiting fine optical memory.

CONCLUSIONS

In this article, we have reported the synthesis of free standing PFu film in $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture at low potentials. PFu films can be reversibly cycled in the potential range of -0.1 to $+0.6$ V, which is accompanied with color change from yellowish-green to gray color. In accordance with previous reports,¹¹ PFu film was found to lose its electroactivity in the presence of water. The reversible oxidation and reduction of the polymer film and its reversible electrochromic behavior indicates that the PFu film, prepared in the $\text{CH}_3\text{CN}/\text{BF}_3/\text{EE}$ mixture, is a conjugated polymer. In this study, we also investigated the utilization of dual type electrochromic devices made up of PFu and PEDOT in sandwich configuration. These devices exhibited color changes between yellowish-green and blue with switching time of 1.2 s.

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