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Dendronized electrochromic polymer based on poly(3,4-ethylenedioxythiophene)

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Abstract

In order to improve electrochromic contrast, 3,4-ethylenedioxythiophene (EDOT) substituted with the first generation dendritic wedge based on gallic acid (**M2**) was synthesized by connecting 3,4,5-tribenzyloxy benzyl chloride to hydroxymethyl EDOT (**M1**). Electropolymerization of **M1** and **M2** resulted in the formation of an electroactive and well adhered film on the electrode surface. In the case of PEDOT substituted with the dendritic wedge (**P2**), it was observed that the resistance of the film increases with thickness. Spectroelectrochemical studies indicated that the polymers switch from a highly opaque dark-blue reduced state to highly transmissive oxidized state with a contrast of 67% in **P2** and 46% in **P1**. In situ conductivity studies showed a sharp transition from a dedoped insulating state to doped conducting state at around −0.4 V with maximum in situ conductance of 0.06 S for **P1** and 0.04 S for **P2**. © 2002 Published by Elsevier Science Ltd.

Keywords: Poly(3,4-ethylenedioxythiophene); Dendronized conducting polymer; Electrochromic polymer

1. Introduction

Conducting polymers have been found to be useful materials for sensors, actuators, LEDs and electrochromic devices, etc. [1,2]. Polythiophene is unique among other conducting polymers due to its environmental stability [3,4]. However, the high oxidation potential of the monomer and the possible α, β and β, β linkages in the polymer lead to inferior properties. Therefore, a derivative of thiophene that has low oxidation potential and is free from the possible α, β and β, β linkages would be an ideal material for industrial applications. In this direction, Jonas et al. [5,6] synthesized 3,4-ethylenedioxythiophene (EDOT), that has low oxidation potential and free from the possible α, β and β, β linkages. PEDOT changes its color from opaque blue in its reduced state to transparent light green in the oxidized state [7]. The contrast, which is the difference in %T of the oxidized and reduced states, observed in PEDOT is 44%. This color change is desirable in fabrication of display devices [8,9]. Recently, Reynolds and co-workers have extensively studied the effect of ring size and substitution on the alkylene ring of PEDOT [10]. They found that the contrast increases on increasing the number of carbons in the alkylene ring and on connecting a bulky group on the alkylene bridge of PEDOT. Our group is also interested in increasing the contrast of the polymer by connecting various substituents on the alkylene ring of the EDOT. In this direction, we have connected a rigid mesogen to PEDOT and observed that the contrast increases to 67%, which is 23% higher than that of unsubstituted PEDOT [11]. Recently, we have reported on the synthesis and characterization of dibenzyl substituted poly(3,4-propylenedioxythiophene) which exhibited a contrast of 89% [12]. We have also reported an ionic group (sulfonate) substituted PEDOT that showed almost the same contrast as that of PEDOT [13]. However, the polymer was water soluble. In this direction, we thought that the contrast as well as switching speeds could be improved by substituting a bulky group like a dendron on PEDOT. These kind of dendronized polymers are known in the literature [14]. Schluter and co-workers synthesized a dendronized poly(*para*-phenylene) (PPP) to make polymeric cylinders [15,16]. The dendronized polymer was synthesized by either connecting the dendron to the PPP or by the polymerization of dendronized macromonomer. Diederich

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and co-workers connected a first, second and third generation ‘Frechet Type’ dendrons to poly(triacetylene) and studied their effect on the conjugation of the polymer [17]. Frechet and co-workers have reported oligothiophenes substituted with alkyl ether dendrimers to get soluble oligomers [18]. In this paper, we report on the synthesis and characterization of first generation dendron (based on gallic acid) substituted PEDOT. The polymer was electrochemically synthesized and was characterized by electrochemical and spectroelectrochemical techniques. We found that the contrast of the dendronized PEDOT is 67%. In situ conductivity of the polymers has also been measured and reported.

2. Experimental

2.1. Materials

Hydroxymethyl EDOT **M1** was synthesized as reported earlier [19]. Tetrabutylammonium tetrafluoroborate (TBAFB) was purchased from Fluka and was used without further purification. Acetonitrile was distilled over P_2O_5 and dried over CaH_2. Anhydrous *N*,*N*-dimethylformamide was purchased from Aldrich chemicals. The track etched PET membranes were purchased from Millipore Corporation and were used to make devices for conductance measurement. The membranes used were 25 μm thick with pore diameter of 0.2 μm. In order to measure conductance, gold lines (1000 Å thick) were obtained by vacuum evaporation of gold on both sides by superimposing two masks on the membrane. The polymer was synthesized electrochemically within the pores of these isoporous membranes. Indium doped tin oxide (ITO) coated glass slides were obtained from Delta Technologies.

2.2. Equipments

Electrochemical experiments were carried out in EG and G PAR model 362 potentiostat/galvanostat. UV–vis spectra were recorded in Shimadzu-2100 UV–vis spectrophotometer. Conductance of the polymers was measured in AFRDE4 PINE bipotentiostat. Gold-coated membranes were used as electrodes for conductance measurements [20]. For electrochemical characterization a Pt wire was used as working electrode with Pt foil as counter electrode and Ag/Ag^+ as the reference electrode. ITO coated glasses were used as working electrode for spectroelectrochemical experiments.

2.3. Synthesis of monomer

2.3.1. Synthesis of methyl-3,4,5-trihydroxy benzoate (**2**)

3,4,5-Trihydroxy benzoic acid (20 g, 116 mmol) was dissolved in dry methanol (200 ml) and 5 ml of conc. sulfuric acid was added to it. This mixture was then refluxed for 5 h and the methanol was evaporated. The residue was dissolved in ethyl acetate and washed with sat. aq. $NaHCO_3$ till aqueous layer was neutral. The organic layer was dried over anhydrous Na_2SO_4 and evaporated to get yellowish crystalline solid. The product was recrystallized from ethyl acetate.

Yield: 13 g (60%); mp 202 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.73 (s, 3H), 6.93 (s, 2H), 8.95 (bs, 1H), 9.28 (bs, 2H); IR (cm^{-1}): 3381, 1722, 1689.

2.3.2. Synthesis of methyl-3,4,5-tribenzyloxy benzoate (**3**)

Four grams (21.7 mmol) of methyl gallate (**2**) and 18 g (130 mmol) of anhydrous potassium carbonate were added to 40 ml of dry DMF and were stirred. Then 8 ml (70 mmol) of benzyl chloride was added and the resultant mixture was heated to 70–80 °C with stirring. After 5 h, the reaction mixture was cooled to room temperature and excess of water was added to precipitate the product. The precipitated yellowish brown solid was filtered and dried in oven. It was further recrystallized from petroleum ether.

Yield: 8.8 g (90%); mp 100 °C; ^{1}H NMR (300 MHz, $CdCl_3$) δ 3.88 (s, 3H), 5.11 (s, 2H), 5.13 (s, 4H), 7.25 (m, 2H), 7.33–7.44 (m, 15H); IR (cm^{-1}): 3020, 1713, 1590, 1432, 1216, 1112, 769, 670. Elemental analysis: calcd for $C_{29}H_{26}O_5$ (C, 76.63; H, 5.76). Found: C, 76.71; H, 5.79.

2.3.3. Synthesis of 3,4,5-tribenzyloxy benzyl alcohol (**4**)

A suspension of lithium aluminium hydride (0.786 g, 20 mmol) in dry THF was stirred for 10 min and then methyl-tribenzyl gallate (6.3 g, 13.8 mmol) was added as solid. A vigorous reaction took place with evolution of heat and the gray suspension turned greenish. The reaction mixture was stirred at room temperature for 1 h and then was quenched by pouring in cold dil. HCl and was extracted in ethyl acetate. Organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated. A yellowish white solid was obtained that was purified by column chromatography on silica gel eluting with chloroform.

Yield: 4.6 g (79%); mp 100 °C; ^{1}H NMR (300 MHz $CdCl_3$): δ 1.65 (bs, 1H), 4.6 (s, 2H), 5.04 (s, 2H), 5.1 (s, 4H), 6.6 (s, 2H), 7.4 (m, 15H); IR (cm^{-1}): 3322 (broad), 3029, 2921, 2864, 1595, 1453, 1119, 739, 695. Elemental analysis: calcd for $C_{28}H_{26}O_4$ (C, 78.85; H, 6.14). Found: C, 78.85; H, 6.09.

2.3.4. Synthesis of 3,4,5-tribenzyloxy benzyl-(3,4-ethylenedioxythiophene methyl) ether (***M2***)

Sodium hydride (0.15 g, 6.25 mmol) was suspended in 10 ml of dry DMF was stirred under argon for 15 min. Hydroxymethyl EDOT (0.155 g, 0.9 mmol) was then added to it under argon. The mixture was stirred for 20 min and then 3,4,5-tribenzyloxy benzyl chloride (0.5 g, 1.11 mmol) was added. The stirring was further continued at room temperature for 24 h and was quenched by pouring in water. The product was extracted in ethyl acetate. Organic layer was washed with brine, dried over anhydrous Na_2SO_4 and evaporated. A green viscous liquid was obtained. This was further purified by column chromatography on silica gel eluting at 7–8% ethyl acetate in pet ether to get 0.4 g (80%) of a colorless viscous liquid.

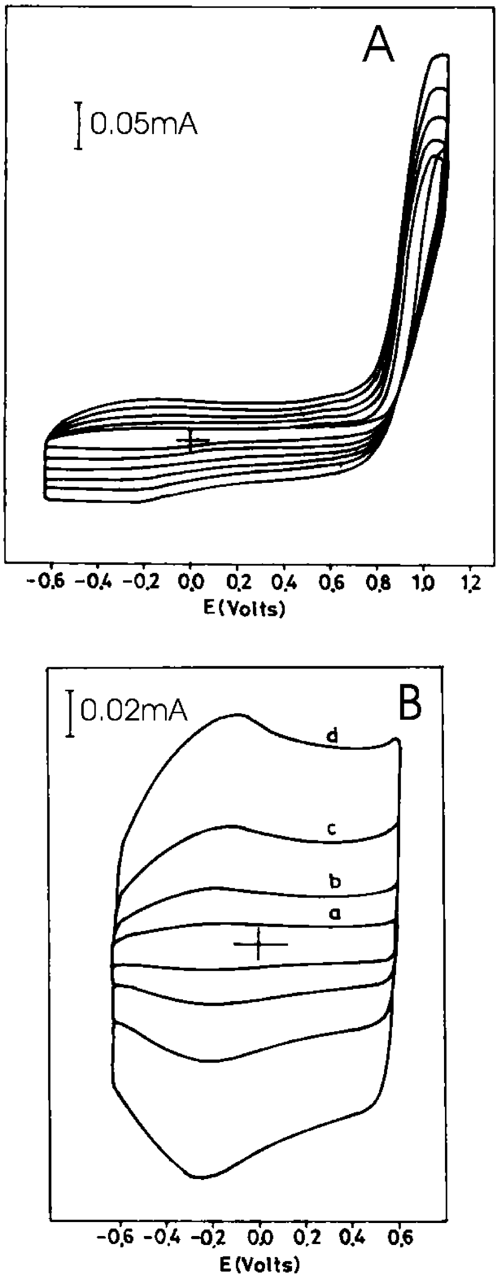


Fig. 1. (A) Repeated potential scan electropolymerization of **M1** at 100 mV/s in 0.1 M TBAFB/ACN. (B) Scan rate dependence of **P1** in 0.1 M TBAFB/ACN: (a) 20 mV/s, (b) 50 mV/s, (c) 100 mV/s, (d) 200 mV/s.

^{1}H NMR (300 MHz, $CdCl_3$): δ 3.6 (m, 2H), 3.96–4.2 (m, 1H), 4.12, 4.18 (dd, 1H), 4.26 (m, 1H), 4.46 (s, 2H), 5.05 (s, 2H), 5.12 (s, 4H), 6.32 (s, 2H), 6.6 (s, 2H) 7.25–7.44 (m, 15H); IR (cm^{-1}): 3111, 3032, 2925, 2866, 1670, 1488, 1374, 1110, 740.

3. Results and discussion

3.1. Synthesis and electropolymerization

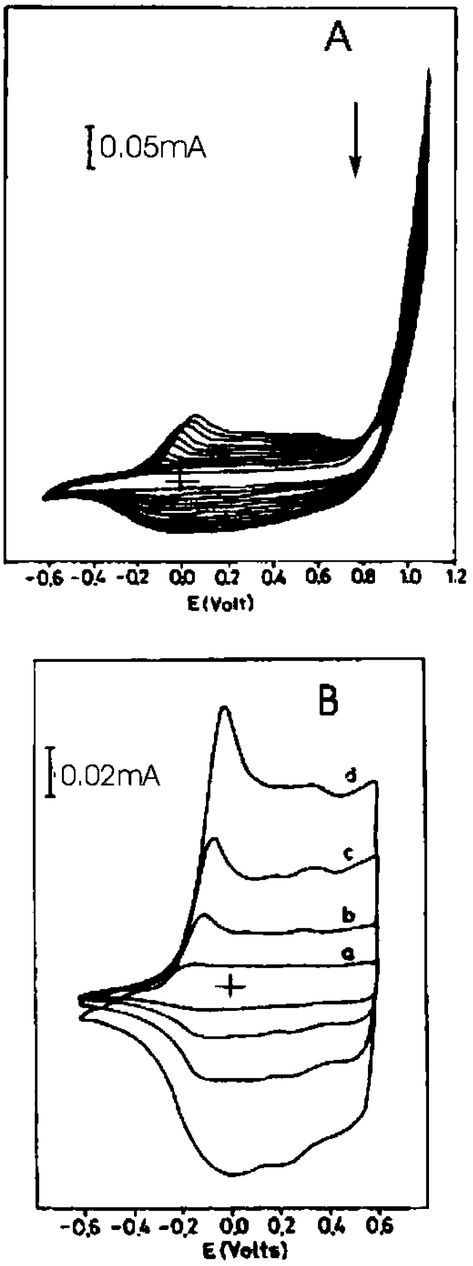
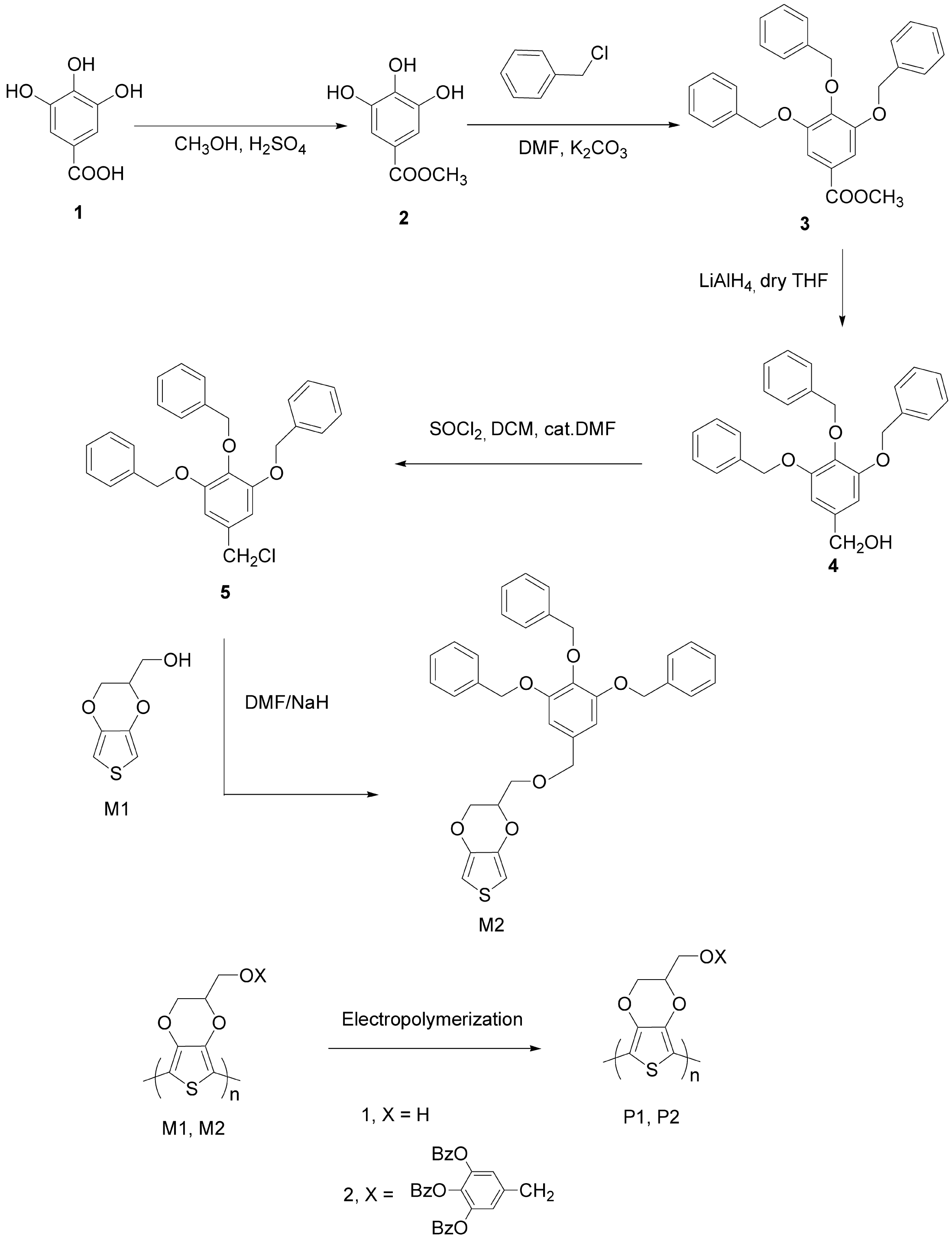


Fig. 2. (A) Repeated potential scan electropolymerization of **M2** at 100 mV/s in 0.1 M TBAFB/ACN. (B) Scan rate dependence of **P2** in 0.1 M TBAFB/ACN: (a) 20 mV/s, (b) 50 mV/s, (c) 100 mV/s, (d) 200 mV/s.

Monomer **M1** was synthesized by the procedure reported earlier [17]. Monomer **M2** was synthesized from hydroxy methyl EDOT by the etherification reaction in presence of NaH in dry DMF and was purified by column chromatography (Scheme 1). ^{1}H NMR and IR spectroscopy corroborated the structure of the monomer. Monomer **M1** was electrochemically polymerized from a solution containing 0.01 M **M1** and 0.1 M TBAFB as supporting electrolyte in ACN. The potential of the working electrode was cycled between -0.6 and $+1.1$ V vs Ag/Ag$^+$, all potentials are reported against Ag/Ag$^+$ unless otherwise stated. The scan rate was 100 mV/s. An irreversible monomer oxidation peak occurred at $+1.1$ V. In the subsequent cycles, the current of



Scheme 1. Synthesis of the monomers and the polymers.

monomer oxidation increases and redox peaks of the polymer starts growing around −0.2 V, that indicates the polymer is redox active (Fig. 1A). The charge for the polymerization is 4.53 mC. The polymer coated electrode was taken out from polymerization solution and washed in monomer free supporting electrolyte to remove adsorbed monomer and oligomers. Cyclicvoltammograms of the polymers were recorded at different scan rates, between −0.6 and +0.6 V in 0.1 M TBAFB in ACN (Fig. 1B). The cyclicvoltammograms of the polymer shows broad redox peaks with a large capacitive component. Charge of anodic and cathodic scans is almost same (charge for anodic scan is 0.54 mC and for cathodic scan 0.51 mC) that indicates that there is no irreversible oxidation of the polymer. The plot of scan rate vs current shows a linear relationship, that further confirms the redox active and well adhered polymer film on the electrode. Polymer **P2** was electrochemically synthesized from a solution of 0.05 M **M2** and 0.1 M TBAFB in ACN, by cycling the potential between −0.6 and +1.1 V (Fig. 2A). Monomer oxidation occurs at +1.1 V and in the subsequent cycles the current of monomer oxidation decreases. The charge for the polymerization is 4.38 mC. The appearance of well-defined redox peaks indicates that the polymer is redox active. The redox peaks are sharper than that for **P1**, and it is a phenomenon observed for bulky group substituted PEDOT [9]. The E_{pa} of the polymer for the third cycle is at −0.1 V and it shifts to the more anodic side in the subsequent cycles. The E_{pa} for the 11th cycle is at 0.1 V. This shift in the redox peaks and the decrease in the monomer oxidation current is due to the increase in resistance of the polymeric film during the thick polymer growth. This behavior has not been observed for PEDOT or its derivatives reported till date [6]. The polymer was removed from the polymerization solution and was washed in monomer free supporting electrolyte. Cyclicvoltammograms of the polymer were recorded at different scan rates (Fig. 2B); the redox peaks are sharp which was observed for other bulky group substituted PEDOT derivatives. Presence of bulky group on the monomer results in a polymer with open morphology, which facilitates the fast movement of counter ions and gives sharp redox peaks. The charge of the anodic scan is 0.42 mC and for cathodic scan is 0.31 mC. The higher charge for anodic scan indicates some irreversible oxidation of the polymer.

3.2. Spectroelectrochemistry

For spectroelectrochemistry, the polymer **P1** was coated on ITO glass plates by electropolymerization of **M1** by applying a static potential of +1.1 V. The polymer film was washed thoroughly with ACN to remove adsorbed monomer. UV–vis spectra of the polymer were recorded at different potentials in 0.1 M TBAFB. At −1 V, the polymer was opaque blue with λ_{max} at 600 nm. This peak is due to π–π^* transition of the polymer. Band gap was calculated from the onset at the higher wavelength side and was found to be 1.5 eV. Upon oxidation of the polymer, the absorbance of the peak at 600 nm decreases and a new peak starts growing in the higher wavelength region. At +1 V the polymer changed to a transparent blue color (Fig. 3).

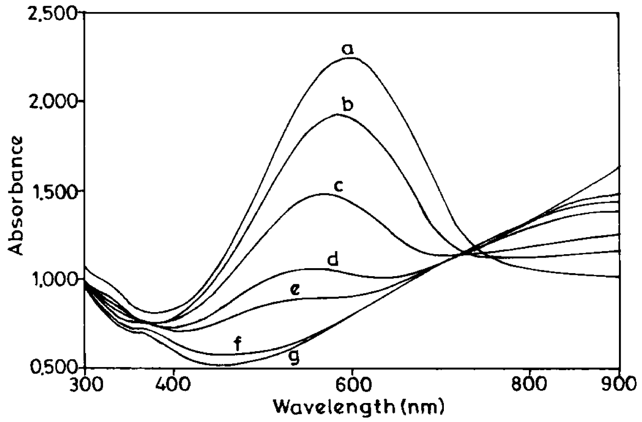


Fig. 3. Optoelectrochemical spectra of **P1** as a function of applied potential in 0.1 M TBAFB/ACN: (a) −1.0 V, (b) −0.2 V, (c) 0.0 V, (d) 0.2 V, (e) 0.3 V, (f) 0.7 V, (g) 1.0 V.

For spectroelectrochemical experiments of **P2**, monomer **M2** was electrochemically polymerized on ITO coated glass by applying a constant potential +1.1 V. Thin film of the polymer formed was washed thoroughly with ACN. UV–vis spectra of the polymer were recorded in 0.1 M TBAFB by applying different potentials. At −1 V, the polymer was opaque blue and two peaks are observed at 600 and 660 nm. This kind of splitting has been observed for other PEDOT derivatives substituted with bulky group and has been attributed to vibronic coupling [10]. The band gap was found to be 1.7 eV from the onset at the higher wavelength region. Upon stepwise oxidation of the polymer, the absorbance of the π–π^* transition decreases and the peak due to polaron increases at the higher wavelength region. The interesting feature in UV–vis spectra of **P2** is that at higher oxidation potentials, the peak due to polaron also starts decreasing (Fig. 4). This decrease results in transmissivity throughout the visible region, because the NIR tail disappears. The contrast calculated from the difference in %T between the fully reduced and the fully oxidized state was calculated to be 46% for **P1** and 67% for **P2**. Thus, it may be concluded that by connecting a bulky dendritic wedge on PEDOT, the contrast increases significantly. Switching studies were also carried out because the response time for color change is also one of key factors for display applications. The measured switching times, at 95% of full contrast, range from 0.6 to 1.0 s.

3.3. In situ conductance measurements

Gold coated 0.2 μm isoporous PET membranes were used for in situ conductance measurements of the polymers.

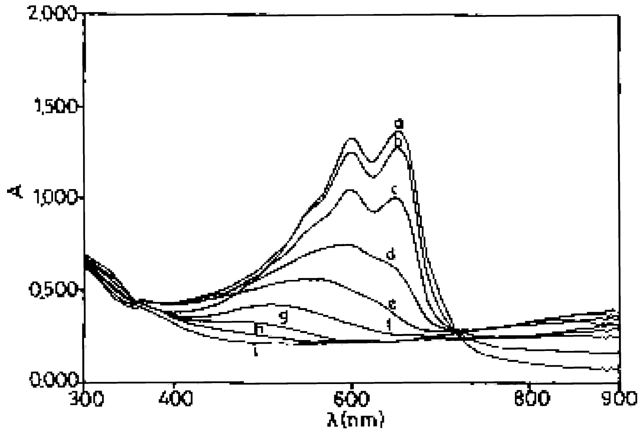


Fig. 4. Optoelectrochemical spectra of **P2** as a function of applied potential in 0.1 M TBAFB/ACN: (a) −1.0 V, (b) −0.3 V, (c) −0.2 V, (d) −0.1 V, (e) 0.0 V, (f) 0.1 V, (g) 0.2 V, (h) 0.3 V, and (i) 1.0 V.

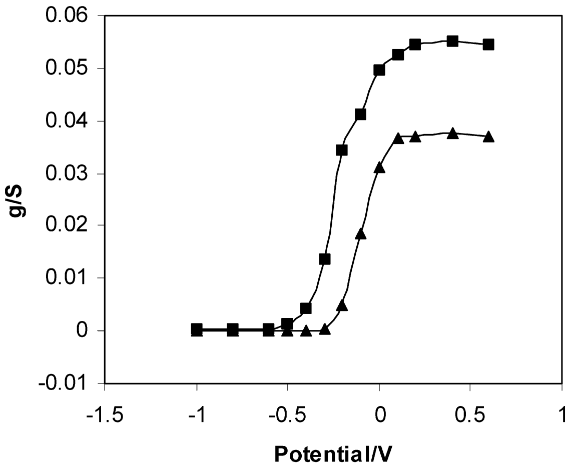


Fig. 5. In situ conductance of **P1** (■) and **P2** (▲) as a function of applied potential.

The polymers were electrosynthesized by cycling the potential between -0.6 and $+1.1$ V at a scan rate of 0.1 V/s. The polymers were grown on gold coated membranes to bridge both sides of the membrane through the pores. After polymerization, the membranes were washed in ACN. Conductance of the polymers was measured in 0.1 M TBAFB by varying the gate voltage V_g from -1 to $+0.6$ V. The resistance of the polymer was measured by holding one gold line (one end of the pore) at fixed potential V_g and the other at $V_g + 20$ mV. The potential difference developed between the electrodes, V_d, resulted in a current flow I_d. The background current I_0 was measured when V_d was 0 mV. The resistance of the polymer $R = V_d/(I_d - I_0)$ and that was converted to conductance. The conductance of **P1** remains almost same till -0.5 V from -1 V and then starts increasing and reaches a plateau at $+0.2$ V. Conductance of **P2** was also measured in 0.1 M TBAFB in the same way as mentioned above. The conductance of **P2** was low at -1 V; increases from -0.2 V and saturates to give a plateau after 0.1 V (Fig. 5). The conductance of **P2** (0.04 S) was found to be lower than that of **P1** (0.06 S).

4. Conclusions

In conclusion, PEDOT with a dendritic substituent was synthesized and characterized. The polymer was found to be electroactive with a contrast of 67%. The contrast is higher than that of unsubstituted PEDOT but is not the best reported till date. The in situ conductance of the polymers was found to be 0.06 S for **P1** and 0.04 S for **P2**.

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References

[1] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. New York: Marcel Dekker; 1998.
[2] Kros A, van Hövell SWFM, Sommerdijk NAJM, Nolte RJM. Adv Mater 2001;13:1555.
[3] Kareiyama K. In: Nalwa HS, editor. Handbook of organic conductive molecules and polymers, vol. 2. New York: Wiley; 1997. p. 271.
[4] Roncali J. Chem Rev 1992;92:711.
[5] Jonas F, Schrader L. Synth Met 1991;41/42:831.
[6] Heywang G, Jonas F. Adv Mater 1992;4:116.
[7] Groenendaal LB, Jonas F, Freitag D, Pielartzik H, Reynolds JR. Adv Mater 2000;12:481.
[8] Rosseinsky DR, Mortimer RJ. Adv Mater 2001;13:783.
[9] Monk PMS, Mortimer RJ, Rosseinsky DR. Electrochromism: fundamentals and applications. Weinheim: VCH; 1995.
[10] Kumar A, Welsh DM, Morvant MC, Piroux F, Abboud KA, Reynolds JR. Chem Mater 1998;10:896.
[11] Krishnamoorthy K, Kanungo M, Contractor AQ, Kumar A. Synth Met 2001;124:471.
[12] Krishnamoorthy K, Ambade AV, Kanungo M, Contractor AQ, Kumar A. J Mater Chem 2001;11:2909.
[13] Krishnamoorthy K, Kanungo M, Ambade AV, Contractor AQ, Kumar A. Synth Met 2002;125:441.
[14] Schluter A-D, Rabe JP. Angew Chem, Int Ed Engl 2000;39:864.
[15] Karakaya B, Claussen W, Gessler K, Saenger W, Schluter AD. J Am Chem Soc 1997;119:3296.
[16] Klopsch R, Franke P, Schluter AD. Chem Eur J 1996;2:1330.
[17] Schenning APHJ, Martin RE, Ito M, Diederich F, Boudon C, Gisselbrecht JP, Gross M. Chem Commun 1998;1013.
[18] Malenfant PRL, Jayaraman M, Frechet JMJ. Chem Mater 1999;11:3420.
[19] Welsh DM, Kumar A, Reynolds JR. Polym Prepr 1998;320.
[20] Sukeerthi S, Contractor AQ. Chem Mater 1998;10:2412.