This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Electrochromic Properties of a Symmetric Polythiophene Derivative: Decanedionic Acid Bis-(2-thiophene-3-yl-ether)ester and its Copolymer with Thiophene

Evren Aslan[a]; Pinar Camurlu[a]; Levent Toppare[a]
[a] Department of Chemistry, Middle East Technical University, Ankara, Turkey

To cite this Article Aslan, Evren , Camurlu, Pinar and Toppare, Levent(2005) 'Synthesis and Electrochromic Properties of a Symmetric Polythiophene Derivative: Decanedionic Acid Bis-(2-thiophene-3-yl-ether)ester and its Copolymer with Thiophene', Journal of Macromolecular Science, Part A, 42: 4, 451 — 462

To link to this Article: DOI: 10.1081/MA-200054346

URL: http://dx.doi.org/10.1081/MA-200054346

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 42:451–462, 2005
Copyright © Taylor & Francis, Inc.
ISSN 1060-1325 print/1520-5738 online
DOI: 10.1081/MA-200054346

Synthesis and Electrochromic Properties of a Symmetric Polythiophene Derivative: Decanedionic Acid Bis-(2-thiophene-3-yl-ether)ester and its Copolymer with Thiophene

EVREN ASLAN, PINAR CAMURLU, AND LEVENT TOPPARE

Middle East Technical University, Department of Chemistry, Ankara, Turkey

Here we describe the electrochemical homopolymerization and copolymerization of decanedionic acid bis-(2-thiophene-3-yl- ether)ester (DATE) in the presence of thiophene. Tetrabutylammonium tetrafluoroborate (TBAFB) was utilized as the supporting electrolyte in acetonitrile (ACN)/borontrifloride ethylether (BFEE) solvent mixture (8:2D, v/v). Electrochemical homopolymerization of DATE and copolymerization with thiophene were studied by cyclic voltammetry (CV). Conducting polymers were characterized by Fourier Transform Infrared (FT-IR) and Thermal Analyses. The morphologies of electrochemically synthesized P(DATE) and P(DATE-co-Th) thin films were analyzed by Scanning Electron Microscopy (SEM). Electrical conductivities were measured by the four-probe technique. Spectroelectrochemical behaviors of P(DATE) and P(DATE-co-Th) films were investigated by UV-Vis Spectrophotometer. Homopolymer revealed color changes between brownish yellow and blue, whereas copolymer revealed changes between orange and blue in reduced and oxidized states respectively. Switching ability of the polymers was investigated via kinetic study upon measuring the % transmittance (%T) at the maximum contrast point. Results implied that copolymerization is a valuable approach to achieve the desired electrochromic properties.

Keywords conducting polymers, electrochromic properties, electrochemical polymerization

Downloaded At: 11:19 24 January 2011

Introduction

At the end of the 1970s, Heeger, McDiarmid and et al. (1) discovered that polyacetylene, $(CH)_x$, synthesized via the method of Shirakawa and colleagues (2), could become highly conducting on exposure to oxidizing or reducing agents. This discovery could be considered as the starting point of the modern area of conducting polymers (3).

The driving force of the extensive studies in this field is a result of their exciting application potential in a wide range of advanced technologies such as optoelectronics,

---

Received August 2004, Accepted October 2004

Address correspondence to Levent Toppare, Middle East Technical University, Department of Chemistry, 06531 Ankara, Turkey. Tel: +903122105148; Fax: +903122101280; E-mail: toppare@metu.edu.tr

Downloaded At: 11:19 24 January 2011

molecular electronics and bioelectronics, but also because these materials provide a demanding challenge to our understanding of charge transport processes (4). For practical applications, conducting polymers should possess good chemical and physical stabilities. Thus, heterocyclic conducting polymers differ from polyacetylene in some ways. Their ground state is nondegenerate as a consequence of the lack of energetic equivalence of their two limiting mesomeric forms, aromatic and quinoid, thus polyheterocyclics are generally more stable. Moreover, their structure may be more readily modified, allowing the modulation of their chemical, electronic, and electrochemical properties (3).

Electrochromism refers to the reversible color change during the electrochemical redox reaction, resulting from energy differences between the π-bonding orbitals and π^*-antibonding orbitals that lies within the visible region. Upon oxidation, the intensity of the π to π^* transition decreases and the two low-energy transitions emerge to produce a second color (5). Recently, polythiophene is of particular interest as electrochromic materials owing to its chemical stability, ease of synthesis, and processability. Polythiophene thin films are blue ($\lambda_{max} = 730\,nm$) in their doped (oxidized) state and red ($\lambda_{max} = 490\,nm$) in their undoped form (6).

Most conductive polythiophene films were prepared by the electrochemical polymerization of thiophene in an organic solvent such as acetonitrile, nitromethane, nitrobenzene, or propylene carbonate. However, electrooxidation of thiophene in these media requires potentials above 1.6 V vs SCE. The high potential (above 1.45–1.55 V) would irreversibly damage the conjugated system due to overoxidation (7). Boron fluoride-ethyl ether (BFEE) is a promising solvent, which has been, used for electrochemical synthesis of some heterocyclics including thiophene, (8, 9) bithiophene (10) and terthiophene (11). The strong electrophilic property of Lewis acid catalyzed the deprotonation of thiophene on the electrode, which resulted in a very low oxidation potential of this monomer (9).

The monomer described here is decanedionic acid bis-(2-thiophene-3-yl-ether) ester, and the acronym used to refer to this monomer is DATE, has several important features like β substitution which is expected to provide an improvement in the long-term stability of the polymer rendering them less susceptible to atmospheric oxidation, whilst reducing defect formation during polymerization. Presence of the carbonyl group also provides ease in the end product characterization. Electrochemical homopolymerization and copolymerization of DATE in the presence of thiophene were studied. Electropolymerizations were achieved by using TBAFB:BFEE/ACN system. The resultant products were characterized by the CV, FTIR, DSC, TGA, SEM, and conductivity measurements. As a second part of the study, we investigated spectroelectrochemical properties, kinetic behavior and L, a, b values of both homopolymer and copolymer.

Experimental

Materials

2-Thiophen-3-yl ethanol (Aldrich), sebacoylchloride (Aldrich), triethylamine (TEA) (Aldrich), acetonitrile (ACN) (Merck), methanol (Merck) and borontrifloride ethylether (BFEE) (Sigma) were obtained from commercial sources. Thiophene (Th) (Aldrich) was distilled before use and stored at 4°C. Reagent quality tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich) and $MgSO_4$ (Aldrich) were used as received.

Downloaded At: 11:19 24 January 2011

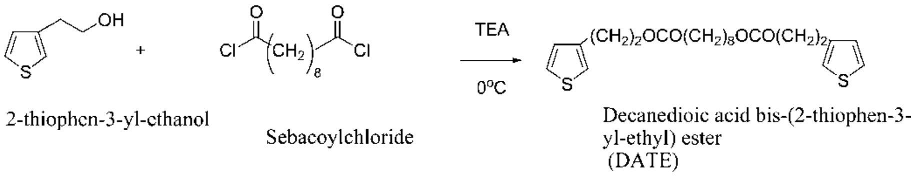
Instrumentation

Wenking POS 73 and Solatron 1285 potentiostats were used to supply a constant potential in electrochemical polymerizations. Electrochemical polymerization was carried out in one compartment cell in a three-electrode system containing working, counter and reference electrodes. Platinum electrodes with an area of 1.5 cm^2 were used as the working and counter electrodes. An Ag/Ag^+ was utilized as the reference electrode. N_2 gas was passed through the solution to provide an inert atmosphere. Oxidation-reduction behavior of the materials was examined by cyclic voltammetry (CV). The CV cell consists of a platinum bead-working electrode 1 cm in length, a platinum spiral counter electrode made from a 3 cm wire, and an Ag/Ag^+ reference electrode. Measurements were carried out at room temperature under nitrogen atmosphere. ^{1}H-NMR and ^{13}C-NMR spectra of monomer were investigated on Bruker-Instrument-NMR Spectrometer (DPX-400) instrument. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS). ^{1}H-NMR data are reported as follows: chemical shift (integration, multiplicity, and peak assignment). A Nicolet 510 FTIR Spectrophotometer was used for FTIR studies. Thermal analysis was carried out by Du Pont 2000 Thermal Gravimetry Analyser and Differential Scanning Calorimetry. Surface morphologies of conducting polymer films were inspected by a JEOL JSM-6400 scanning electron microscope. A Agilent 8453 UV-VIS spectrometer was used to monitor the spectroelectrochemical behavior of polymers and electrochromic properties. Colors were estimated by GretagMacbeth Coloreye XTH. Conductivities were measured by a standard four-probe method at room temperature on films by using osmium contacts.

Synthesis of Decanedionic Acid bis-(2-tiophene-3-yl-ether) Ester (DATE)

2-Thiophene-3-yl-ethanol (1.1 mL, 1 mmol) was dissolved in 10 mL dichloromethane containing (0.07 mL, 0.5 mmol) triethylamine (TEA). To this solution, sebacoylchloride (0.1 mL, 0.5 mmol) was added dropwise in 0.5 h, by cooling in an ice bath and nitrogen atmosphere. The solution was washed with a HCl 1% solution and water. The organic layer was dried over $MgSO_4$ and the solvent was removed via rotaevaporatory. DATE was obtained as a light yellowish solid (0.184 g, 0.436 mmol, 87%) mp 73°C. The representation of synthesis is demonstrated in Scheme 1.

^{1}H-NMR ($CDCl_3$) (δ/ppm) (Figure 1): 7.17 (2H, m, thiophene), 6.94 (2H, m, thiophene), 6.91 ppm (2H, m, thiophene) and 2.88 ppm (4H, t, thiophene–CH_2), 4.23 ppm (4H, t, CH_2–O), 2.23 ppm (4H, m, CO–CH_2), 1.55 ppm (4H, m, –CH_2), 7.2 ppm (s, $CDCl_3$) ^{13}C-NMR ($CDCl_3$) (δ/ppm) (Figure 2): 173.7 ppm from CO, 121.5, 125.6, 128, 138 from (thiophene), 34, 29, 24 ppm from aliphatic group, 64 ppm –OCH_2, 77 ppm (t, $CDCl_3$).



Scheme 1. Synthesis of DATE.

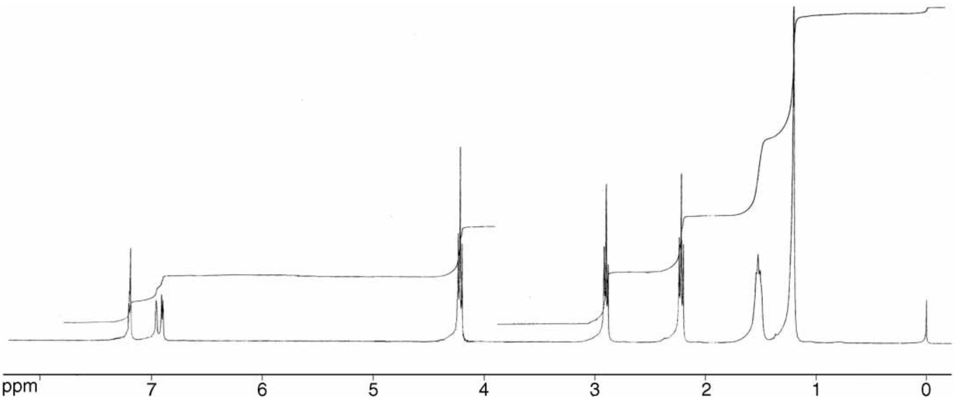


Figure 1. ^{1}H-NMR of DATE.

Synthesis of Conducting Polymers of DATE

Preparative electrochemical homopolymerization was performed under potentiostatic conditions in a one-compartment cell. 40 mg DATE dissolved in ACN/BFEE (8:2, v/v) solvent mixture and 0.2 M TBAFB used as the supporting electrolyte. Electrolyses were carried out at 1.5 V equipped with Pt working and counter electrodes and Ag/Ag^{+} reference electrode at room temperature for 1 h. Copolymerization was achieved under the same conditions in the presence of 15 μL of thiophene. The free standing films were washed with ACN several times to remove unreacted monomer and TBAFB.

Spectroelectrochemistry

Spectroelectrochemical analyses of the homopolymer and copolymer were done to understand the band structure of the new product. For spectroelectrochemical studies,

Downloaded At: 11:19 24 January 2011

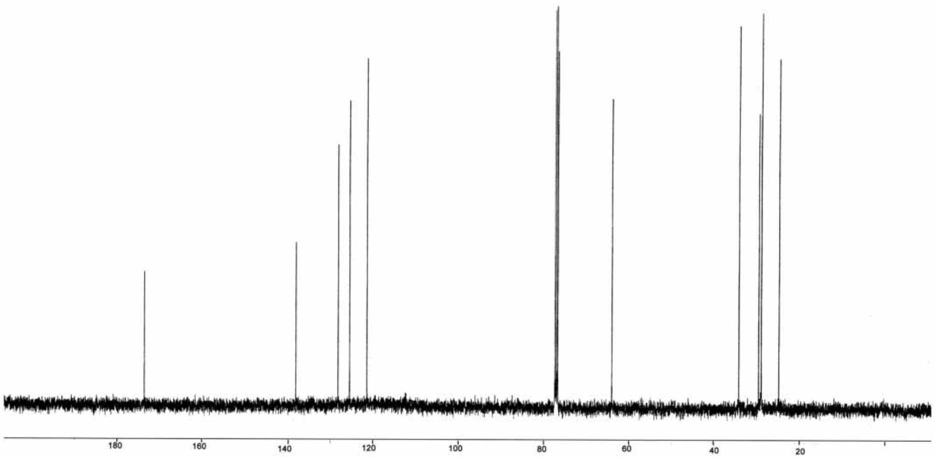


Figure 2. ^{13}C-NMR of DATE.

the homopolymer film was deposited from a solution of 40 mg DATE ACN:BFEE (8:2, v/v)/TBAFB solvent–electrolyte couple on indium tin oxide-coated glass slide (ITO) potentiostatically at 1.5 V vs Ag/Ag^+. UV-VIS spectra of the film were recorded at various potentials in ACN:BFEE/TBAFB. The same procedure was applied for spectroelectrochemistry of the copolymer.

Switching

A square wave potential step method coupled with optical spectroscopy was used to investigate the switching times and contrast in these polymers. In this double potential step experiment, the potential was set at an initial potential (where the conducting polymer was in its one of the extreme states) for 5 seconds and stepped to a second potential for 5 seconds, before switched back to the initial potential again. During the experiment, the percent transmittance (%T) and switching times at λ_{max} of the polymer was measured using a UV-VIS spectrophotometer.

Colorimetry Studies of Polymers

Colorimetry analysis was run in order to visually monitor the sample. In order to assign a quantitative scale to color measurements, the Commission Internationale de l'Eclairage (International Commission of Illumination) color spaces 1976 L∗a∗b system was chosen because of its common use in industry (12). The film prepared for spectroelectrochemical studies was switched in ACN:BFEE/TBAFB (0.2 M) and its colors at fully reduced and oxidized states were read by GretagMacbeth Color-eye XTH.

Downloaded At: 11:19 24 January 2011

Results and Discussion

FT-IR

The identification of DATE was carried out by FT-IR spectroscopy. Figure 3a shows the FT-IR spectrum of the DATE product in the range 4000–400 cm^{-1}. The absorption bands at 1544, 1408, 1053, 855, 789, and 688 cm^{-1} are due to the vibrations of C–H and C=C bonds of thiophene rings. The sharp intense peak at 1731 cm^{-1} is attributed to C=O stretching vibrations and the bands in the region of 1100–1250 cm^{-1} is due to C–O–C symmetric and asymmetric stretching vibrations of spacing methyl chain (13).

After the potentiostatic homopolymerization of DATE, Figure 3(c), a new shoulder appeared at 1637 cm^{-1} indicating the polyconjugation upon polymerization. The band at 796 cm^{-1} indicating *cis* C–H wagging of the thiophene ring and the band at 686 cm^{-1} due to deformations of C–H out of plane of the thiophene ring disappeared completely upon polymerization. Also, evolution of new peak at 824 cm^{-1} indicated the formation of 2,3,5-trisubstituted thiophene structure. The peak appeared at 1083 cm^{-1} revealed the presence of the dopant ion (BF_4^-), which was due to homopolymerization, all of which could be considered as evidence of the polymerization at thiophene ring.

FTIR spectra of electrochemically synthesized copolymer of P(DATE-co-Th), Figure 3(b), showed a band at 1732 cm^{-1} indicating a carbonyl group due to monomer. The peaks indicating the polyconjugation were observed very clearly at 1672 cm^{-1}. FTIR spectra of P(DATE-co-Th) also contain the characteristic monomer peaks. The intense band at 1083 cm^{-1} is related to the dopant anion. All of these peaks are proof of copolymerization.

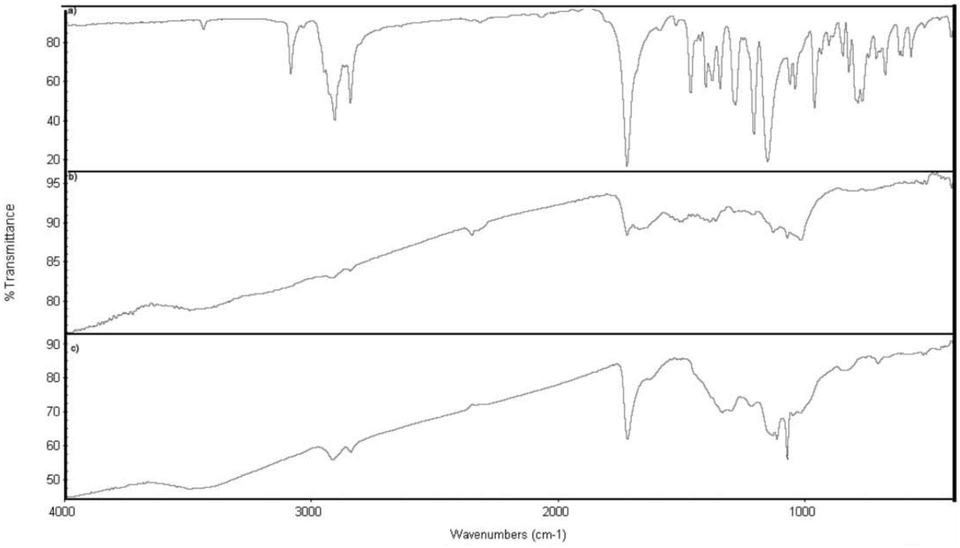


Figure 3. FT-IR spectra of (a) DATE (b) P(DATE-co-Th) (c)P(DATE).

Downloaded At: 11:19 24 January 2011

Cyclic Voltammetry

The oxidation/reduction behavior of the DATE through homopolymerization and copolymerization in the presence of thiophene was investigated via cyclic voltammetry. CV experiments were carried out in a ACN:BFEE/TBAFB solvent-electrolyte couple under nitrogen atmosphere. As seen in Figure 4(a), DATE revealed an oxidation peak at 0.83 V and a reduction at 0.63 V. Upon consecutive cycles, there was a continuous film formation, indicated by the continuous increase of the current intensity. In the presence of thiophene in the same electrolyte system, it was observed that the oxidation and reduction potentials were shifted to 0.91 V and 0.53 V, respectively, Figure 4(b).

When CV of P(DATE-co-Th) is compared with the voltammogram of pristine thiophene and P(DATE), the redox peaks differ. (pure PTh-$E_{p,a}$: +0.98 V, $E_{p,c}$: +0.70). This shift could be considered as an indirect indication for the reaction between thiophene and the thiophene moiety of the monomer, resulting copolymer formation.

Thermal Behavior of Samples

DSC thermogram was obtained under nitrogen atmosphere, in the range of 25°C to 450°C at a heating rate of 10°C/min. DSC thermogram of DATE showed a sharp melting point at 74°C and it was stable up to 269°C. According to TGA studies the onset point of the decomposition was 266°C and it reached its maximum at 376°C. Only 2.286% of the monomer remained after 830°C (Figure 5(a)). Thus, results of DSC and TGA are consistent with each other.

The TGA curve of homopolymer revealed two transitions at 232°C and 433°C (Figure 5(c)). The former weight loss could be attributed to the removal of the solvent, later could be due to decomposition of the polymer matrice. The char residue of P(DATE) was 42.11% after 830°C. TGA thermogram of P(DATE-co-Th) (Figure 5(b))

Downloaded At: 11:19 24 January 2011

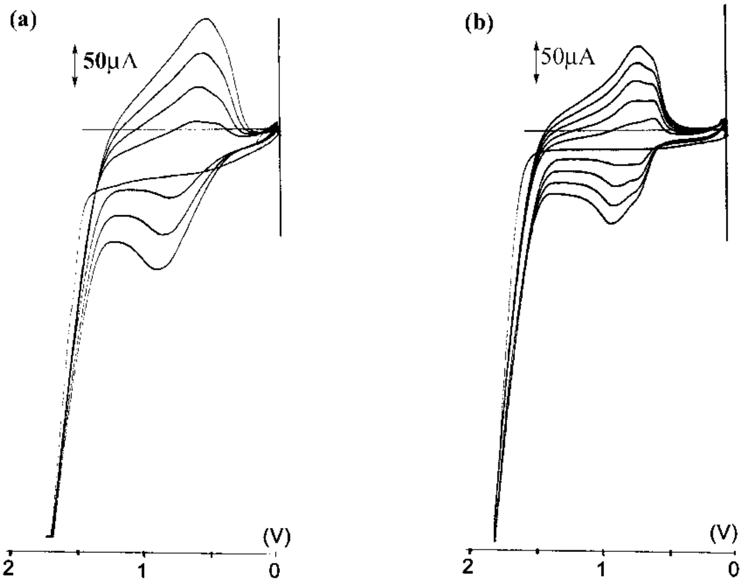


Figure 4. Cyclic voltammogram of (a) P(DATE-co-Th) (b) P(DATE).

revealed different behavior than both homopolymers of DATE and Th. Thus, besides the other techniques used, TGA also reflected the copolymer formation.

Conductivity Measurements

A standard four-probe technique was used to find out the conductivities of homopolymer and copolymer. Conductivities of the films, both solution and electrode sides, were

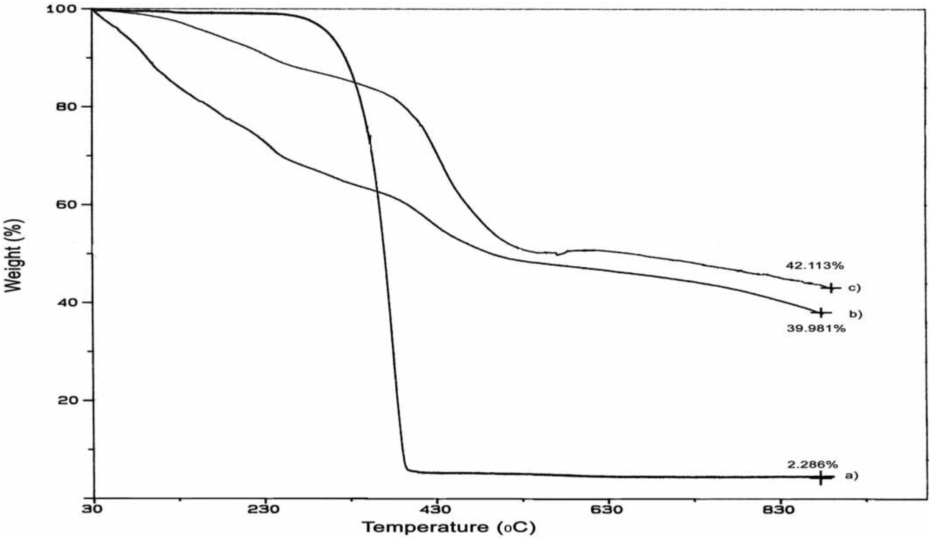


Figure 5. TGA thermogram (a) DATE (b) P(DATE-co-Th) (c) P(DATE).

measured and given in Table 1. Conductivity values of electrode and solution sides were found to be in the same order of magnitude in both homo and copolymer. This observation revealed the homogeneity of the films. In the view of conductivity data reported for PTh, we may conclude that a new product was obtained in a small expense of electrical conductivity.

Morphologies of the Films

Analysis of the surface morphologies of films was done by using JEOL JSM-6400 Scanning Electron Microscope. SEM micrograph of solution side of P(DATE) film showed uniform globular structure (Figure 6(a)). P(DATE-co-Th) revealed a droplet like structure (Figure 6(b)) which was significantly different than both P(DATE) and PTh. The abrupt change in the morphology could be due to incorporation of monomer units in to polythiophene matrices, revealing the existence of an interaction between monomer and polythiophene. This could be considered as another proof of copolymerization.

Downloaded At: 11:19 24 January 2011

Investigation of Electrochromic Properties of Polymers

Spectroelectrochemistry

Spectroelectrochemical analysis of the synthesized conducting polymers showed their electronic structures upon doping and dedoping of the polymers. Furthermore, the band gap (E_g), the difference between the lowest band energy in the conduction band, and the highest band energy in the valence band in an extended system, can be calculated (14).

Spectroelectrochemical analyses of the P(DATE) and P(DATE-co-Th) were studied with UV-VIS Spectrophotometer. Figures 7 and 8 show a series of optoelectrochemical spectra of P(DATE) and P(DATE-co-Th), respectively. The observed band gap was found to be 2.87 eV and 2.06 eV and λ_{max} were 432 nm and 475 nm for P(DATE) and P(DATE-co-Th), respectively, when taken at the onset of the π-to-π^* transition. Stepwise oxidation of P(DATE) showed a reduction in absorbance throughout the visible region as the color changes from brownish yellow (fully reduced state) to blue (highly oxidized state). Upon applied potential, reduction in the intensity of π-to-π^* transitions and formation of charge carrier band was observed. The absorptions observed at 734 nm and 768 nm were attributed to, formation of polarons, absorbtions at 1000 nm and 950 nm were attributed to bipolarons of P(DATE) and P(DATE-co-Th), respectively.

Table 1
Conductivities of the films

Polymer	Conductivity
P(DATE)	1.2×10^{-3}
P(DATE-co-Th)	8×10^{-2}
PTh	5

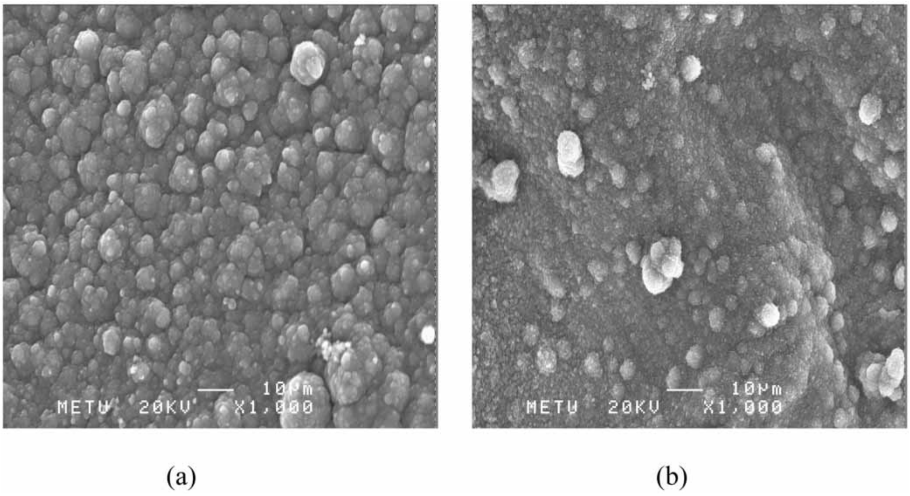


Figure 6. SEM micrographs of (a) P(DATE) (b) P(DATE-co-Th).

Downloaded At: 11:19 24 January 2011

Electrochromic Switching

Spectroelectrochemistry showed the ability of P(DATE) and P(DATE-co-Th) to switch between its neutral and doped states with a change in transmittance. Electrochromic switching behaviors of the films were investigated by recording absorption spectrum while stepping the potential between 0.5 V–1.0 V for P(DATE) and 0.4 V–1.4 V for P(DATE-co-Th) for a switching time of 5 seconds. The optical contrast of P(DATE) was measured as 18% at the 432 nm wavelength. Switching time was measured as 1.3 s. In comparison to the previous studies (15, 16) there appears to be a profound effect on

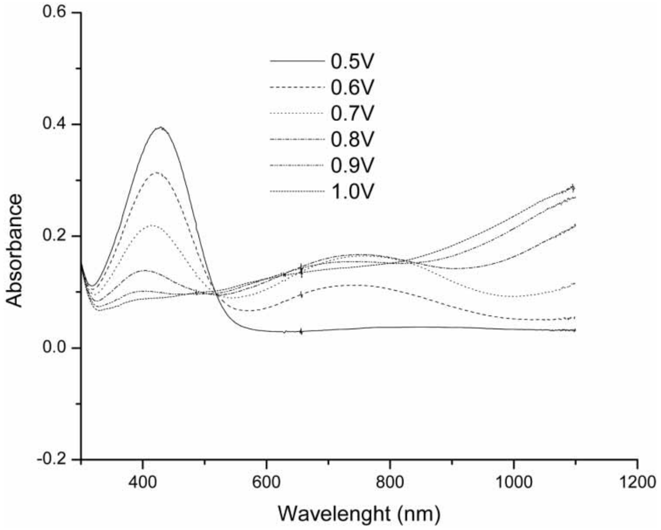


Figure 7. Spectroelectrochemistry of P(DATE).

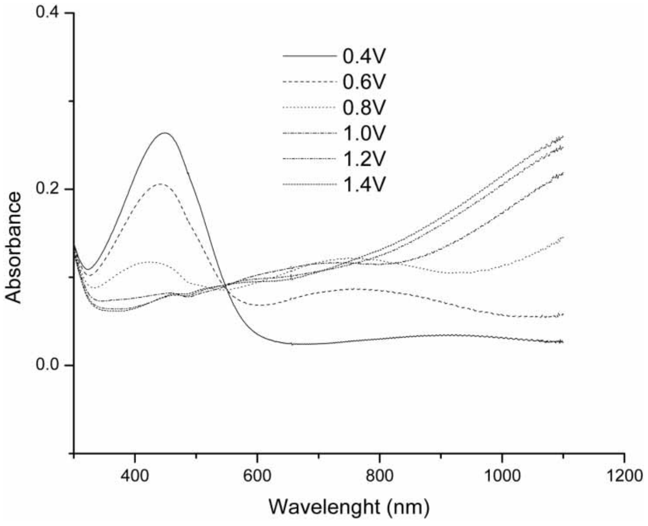


Figure 8. Spectroelectrochemistry of P(DATE-co-Th).

Downloaded At: 11:19 24 January 2011

ΔT, switching time, L,a,b values and color upon variation of size of the aliphatic group between the carbonyl groups of the synthesized monomers.

For P(DATE-co-Th) the contrast measured was 44.3% and the switching time was 0.9 s at 476 nm wavelength (Figure 9). Upon 50 and 100 cycles there was only 2.8 and 3.5% loss in optical contrast respectively. Results implied the superior properties of the

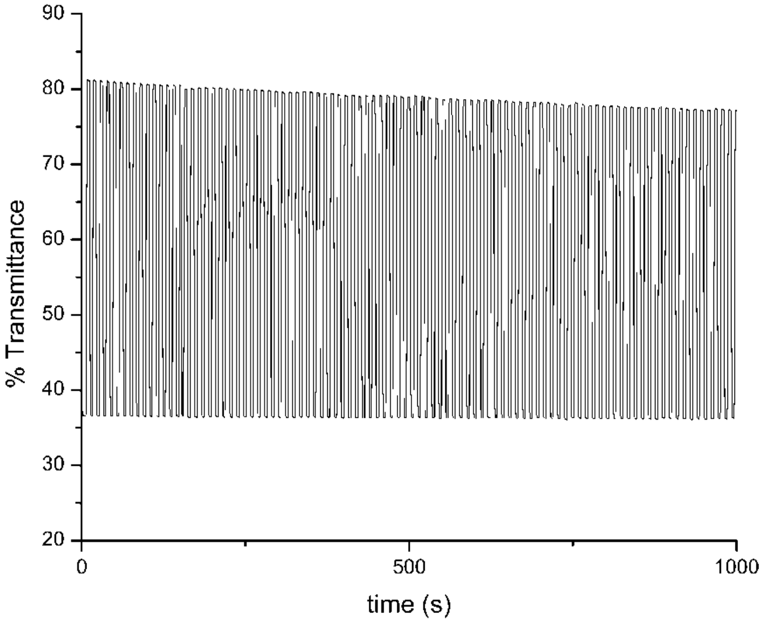


Figure 9. Electrochromic switching of P(DATE-co-Th).

Table 2
Electrochromic properties

Polymers	λ_{max} (nm)	L	a	b	Color	E_g (eV)
P(DATE)	432	ox: 68 red: 61	ox: −7 red: −4	ox: −1 red: 21	ox: blue Red: yellow	2.87
P(DATE-co-Th)	475	ox: 23 red: 48	ox: −5 red: 28	ox: 1 red: 47	Ox: blue Red: orange	2.06
PTh	495	ox: 57 red: 51	ox: −7 red: 52	ox: −2 red: 46	Ox: blue Red: red	1.92

copolymer with respect to homopolymer on the basis of both stability and switching times. Thus, utilization of copolymerization during the synthesis of electrochromic material could be considered as powerful approach to achieve desired properties.

Colorimetry

L∗a∗b values of the films, where L corresponds to luminance, and a, b values to color coordinates, were measured at the fully oxidized and fully reduced states and the data is given in Table 2. P(DATE) was blue in its oxidized state and brownish yellow in its reduced state. However, P(DATE-co-Th) film revealed blue color in its oxidized state and vivid orange in its reduced state. Polythiophene is red in its undoped and blue in doped state. Hence, variation in color as well as band gap values, may point to the formation of a new copolymer.

Downloaded At: 11:19 24 January 2011

Conclusion

Here we describe the synthesis and characterization of conducting polymers of decanedionic acid bis-(2-thiophene-3-yl-ether)ester. The polymerization of monomer was realized via electrochemical methods. Thin films of P(DATE) and P(DATE-co-Th) were electrodeposited on Pt electrode. Results obtained in the characterization of homopolymer and copolymer of DATE supports the idea of achieving the growth of thiophene chains through the thiophene moieties present in the DATE revealing the copolymer formation. Investigation of electrochromic properties of the P(DATE) and P(DATE-co-Th) and evaluation of their switching ability were also achieved. Results implied that both P(DATE) and P(DATE-co-Th) are promising materials for electrochromic applications, both on the basis of their optical contrast and switching times.

Further studies will focus on investigation of the structures of homopolymer and copolymer films via pyrolysis mass spectroscopy and GC-MS. Degradation mechanism and degradation products of the conducting polymers will be investigated.

Acknowledgments

Authors are gratefully thank to DPT2002K120510-IM-4, DPT2003K120920-02, ODTU-BAP-2004-01-03-04 and TUBA grants.

Downloaded At: 11:19 24 January 2011

References

1. Chiang, C.K., Fincher, C.R., Jr., Park, Y.W., Heeger, A.J., Shirakawa, H., Louis, E.J., Gau, S.C., and MacDiarmid, A.G. (1977) Electrical Conductivity in Doped Polyacetylene. *Phys. Rev. Lett.*, 39 (17): 109–101.
2. Ito, T., Shirakawa, H., and Ikeda, S. (1974) Simultaneous Polymerization and Formation of Polyacetylene Film on the Surface of a Concentrated Soluble Ziegler-type Catalyst Solution. *J. Polym. Sci., Part A: Polym. Chem.*, 12 (1): 11–20.
3. Berlin, A. (1998) Heterocycle-Based Electroconductive Polymers. In *Electrical and Optical Polymer Systems*; Wise, D.L., Wnek, G.E., Trantolo, D.J. and Cooper, T.M., and Gresser, J.D., Eds.; Marcel Dekker, Inc.: New York, 47–48.
4. Chen, Y., Imrie, C.T., Cooper, J.M., Glidle, A., Morris, D.G., and Ryder, K.S. (1998) Structure and conductivity in substituted polypyrroles. Part 1. Synthesis and electropolymerization of N-Trimethylsilylethoxymethyl-3-methyl-4-pyrrole Carboxylate Ethyl Ester. *Polym. Int.*, 47 (1): 43–49.
5. Kumar, A. and Reynolds, J.R. (1996) Soluble Alkyl-substituted Poly(ethylenedioxythiophenes) as Electrochromic Materials. *Macromolecules*, 29: 7629–7630.
6. Sotzing, G.A., Reddinger, J.L., Katritzky, A.R., Soloducho, J., Musgrave, R., and Reynold, J.R. (1997) Multiply Colored Electrochromic Carbazole-based Polymers. *Chem. Mater.*, 9: 1578–1587.
7. Cirpan, A., Alkan, S., Toppare, L., David, G., and Yagci, Y. (2001) Synthesis and Electroactivity of Pyrrole End-functionalized Poly(2-methyl-2-oxazoline). *Eur. Polym. J.*, 37: 2225–2229.
8. Shi, G., Jin, S., Xue, G., and Li, C. (1995) A Conducting Polymer Film Stronger than Aluminum. *Science*, 267 (5200): 994–6.
9. Shi, J. and Gi, X. (1997) Interaction Between Thiophene and Solvated Lewis Acids and the Low-potential Electrochemical Deposition of a Highly Anisotropic Conducting Polythiophene Film. *Macromolecules*, 30: 5753–5757.
10. Zhang, D., Jingui, Q., and Xue, G. (1999) Studies of Electrochemically Deposited Films from Bithiophene in Boron Fluoride-ethyl Ether. *Synth. Met.*, 106: 161–164.
11. Donghui, Z., Jingui, Q., and Gi, X. (1999) An Investigation of the Electropolymerization of Terthiophene in Boron Fluoride–ethyl Ether. *Synth. Met.*, 100: 285–289.
12. Thompson, B.C., Schottland, P., Zong, K., and Reynolds, J.R. (2000) In Situ Colorimetric Analysis of Electrochromic Polymers and Devices. *Chem. Mater.*, 12: 1563–1571.
13. Nicho, M.E., Hu, H., Lopez-Mata, C., and Escalante, J. (2004) Synthesis of Derivatives of Polythiophene and Their Application in an Electrochromic Device. *Sol. Energy Mater. Sol. Cells*, 82 (1–2): 105–118.
14. Yang, S., Olishevski, P., and Kertesz, M. (2004) Bandgap Calculations for Conjugated Polymers. *Synthetic Metals*, 141 (1–2): 171–177.
15. Camurlu, P., Cirpan, A., and Toppare, L. (2004) Synthesis, Characterization and Electrochromic Properties of Conducting Poly(hexanedioic acid bis-(2-thiophen-3-yl-ethyl ester) and its Copolymers with Thiophene and Pyrrole. *Synth. Met.*, 146: 91.
16. Coskun, Y., Cirpan, A., and Toppare, L. (2004) Conducting Polymers of Terepthalic Acid bis-(2-thiophen-3-yl-ethyl) Ester and Their Electrochromic Properties. *Polymer*, 45: 4989–4995.