Tuning of Electrochromic Properties by Copolymerization of Monoalkoxythiophenes and Dialkoxythiophenes

Shijian Tu,[1] Yuechuan Wang,[2] Jianwu Lan,[3] Qingkang Zheng,[3] Jian Wei,[2] Sheng Chen[3]

[1]Department of Polymer Chemistry and Physics, College of Chemistry, Sichuan University, Chengdu 610065, People's Republic of China
[2]State Key Laboratory of Polymer Materials Engineering, College of Polymer Science and Engineering, Sichuan University, Chengdu 610065, People's Republic of China
[3]Department of Textile Engineering, College of Light Industry, Textile and Food Engineering, Sichuan University, Chengdu 610065, People's Republic of China

ABSTRACT: Monoalkoxysubstituted and dialkoxysubstitued thiophene monomers were synthesized by the nucleophilic substitution and transetherification reactions. Electrochemical homopolymerization of 3-octyloxythiophene (OOT) and 3,4-dioctyloxythiophene (DOOT), copolymerization of OOT with DOOT were performed via potentiodynamic and potentiostatic methods in the supporting electrolyte. Both the copolymer and homopolymers were characterized via cyclic voltammetry, scanning electron microscopy, gel permeation chromatography, and spectroelectrochemical analysis. In the redox process of the polymers, it was linear relationship between the peak current and the scanning rate in their cyclic voltammograms. The copolymer of P(OOT-co-DOOT) showed obvious change of color between red and bright blue in reduced and oxidized states, that has a great difference with the homopolymers. The morphology studies indicated that the electrochemical deposition of P(OOT-co-DOOT) proceeds via a mechanism of nucleation and two-dimensional growth. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2625–2631, 2012

Key words: conjugated polymers; electrochemical polymerization; electrochromic polymers; copolymers

INTRODUCTION

Electrochromic (EC) materials exhibit reversible coloration when applying electrical potential. EC materials have been found great application as "smart material" in advanced displays and smart windows.[1,2] The typical EC materials include inorganic compounds, such as tungsten trioxide (WO_3),[3] and organic materials (viologen[4] and some conducting polymers[5–7]). Polythiophenes (PThs) especially have attracted great attention, owing to their high color contrast and easy fine-tuning of band gap and color through modification of chemical structure.[7] A lot of sophisticated works have been done to design and prepare PThs with desired band gaps (and also spectra properties) and polymer solubility. Introducing substitutes to the thiophene ring and copolymerization of substituted thiophenes and/or with other aromatic compounds are the common and efficient route.[8–12] Thompson et al.[13] prepared soluble polymers with donor–acceptor substitutes and narrow band gap with alkoxythiophenes and cyanovinylenes, and Kumar and Reynolds[14] reported the polymerization of a tetradecyl-substituted 3,4-ethylenedioxythiophene. Most of these synthesis approaches were performed with chemical polymerization, such as using Knoevenagel polycondensation, Suzuki coupling, Stille coupling, and Yamamoto coupling polymerizations. The differences in chemical reactivity arisen from substitute effects and aromatic structures hindered the free combination of monomers for the desired copolymer. From viewpoint of practical application of PThs as EC materials, easy preparation of monomers and polymers are the key issues. Electrochemical polymerization provided an efficient preparation method for direct deposition of EC film on large area surfaces or even curved substrates.

Alkoxy substituted PThs can be readily prepared by electrochemical polymerization of the corresponding thiophene monomers. The donating alkoxy groups decrease the oxidation potential and stabilize the conducting states of the polymers.[7] Their EC properties depend on the structure and amount (mono- or di-substituted) of the alkoxy groups. For example, poly(3-alkoxythiophene) exhibited an optical absorption maximum at 470–530 nm for the reduced state, and at 750–810 nm for the oxide state,[15] whereas the disubstituted poly(3,4-ehtylenedioxythiophene) was blue-black for neutral and almost transparent (with a sky-blue tint) for doped
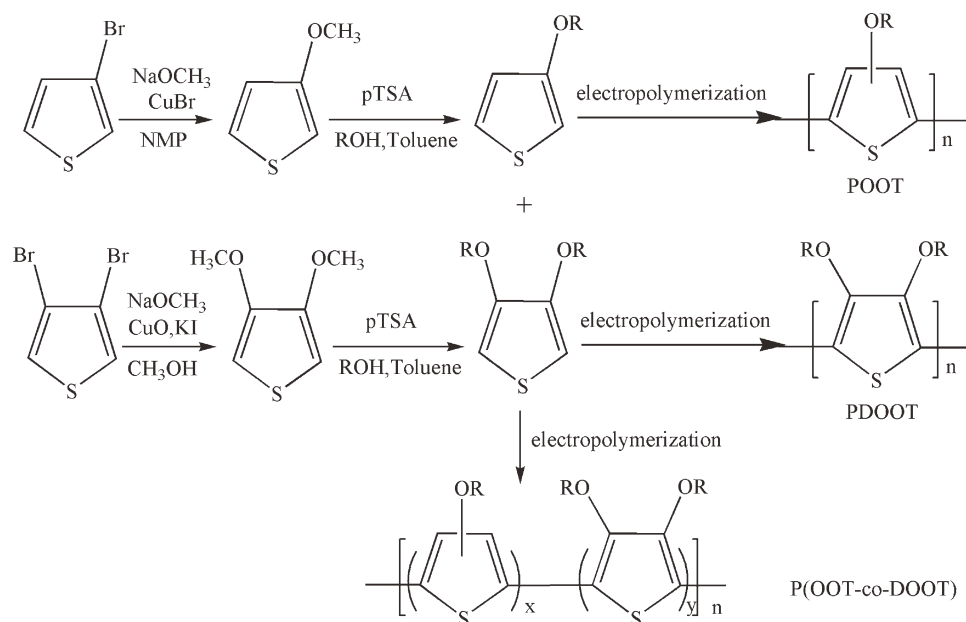
Figure 1 Synthesis of mono- and di-substituted thiophenes and the polymers.

state, respectively.[7] As alkoxy thiophenes can be prepared by transetherification reaction from methoxythiophene (MOT) and alcohols and the former were synthesized by Keegstra's method,[16] both monoalkoxy and dialkoxy substituted thiophenes will be readily available. It is worthy to explore the electrocopolymerization of alkoxythiophenes for practically usable EC materials with tunable properties. In this work, copolymer of monooctyloxyterthiophene and dioctyloxyterthiophene was prepared by electrochemical polymerization. The resulted copolymer was soluble and composed of thiophene monomers with the expected monomer ratio. The electrochemically formed PTh films exhibited interesting morphology and EC properties.

EXPERIMENTAL

Materials

3-Bromothiophene (3-BrT; purity > 98%) and 3,4-dibromothiophene (3,4-DBrT; purity > 98%) were purchased from Zhejiang Shou and Fu Chemical (Jinyun, China). All solvents were purified and dried by standard techniques before use. All other chemicals were of analytical grade and were used without further purification.

Equipment

Electrochemical experiments were performed with a ZF-9 potentiostat/galvanostat by Shanghai Zhengfang Electronic Apparatus (Shanghai, China) Ultraviolet-visible (UV–vis) spectra were recorded on a Purkinje General T6 spectrophotometer (Beijing, China) at a scanning rate of 1 nm s^{-1} from 210 to 1100 nm. ^{1}H-NMR and ^{13}C-NMR analyses were performed with a Bruker Avance AV II 400-MHz NMR spectrometer (Billerica, MA). Molecular weights of the polymers were determined with an Agilent1100 HPLC (Santa Clara, CA, USA) calibrated with linear polystyrene standards and eluted with tetrahydrofuran (THF). Surface morphology of polymer films was examined with Hitachi S-450 scanning electron microscope (SEM), operating at 20 kV.

Synthesis of the monomers

3-Methoxythiophene (MOT) and 3,4-dimethoxythiophene (DMOT) were prepared and purified by nucleophilic substitution reaction following the early methods.[16,17] The substituted thiophene monomers, 3-octyloxythiophene (OOT), and 3,4-dioctyloxythiophene (DOOT) were synthesized by transetherification reaction of MOT/DMOT and *n*-octanol in the presence of a catalytic amount of p-toluene sulfonic acid (p-TSA) in toluene according to Ref. 18 as illustrated Figure 1.

MOT: Yield 79.0%. ^{1}H-NMR (CDCl$_3$): 3.84 (s, 3H), 6.27–6.28 (m, 1H), 6.77–6.79 (m, 1H), 7.19–7.22 (m, 1H) ppm. ^{13}C-NMR (CDCl$_3$): 57.41, 96.65, 119.30, 124.81, 158.82 ppm.

OOT: Yield 94.6%. ^{1}H-NMR (CDCl$_3$): 0.91 (t, J = 6.4 Hz, 3H), 1.31–1.36 (m, 8H), 1.43–1.50 (m, 2H), 1.75–1.82 (m, 2H), 3.96 (t, J = 6.4Hz, 2H), 6.24–6.25 (s, 1H), 6.76–6.78 (d, 1H), 7.17–7.20 (d, 1H) ppm. ^{13}C-NMR (CDCl$_3$): 14.09, 22.67, 26.07, 29.24, 29.29, 29.37, 31.82, 70.29, 96.98, 119.55, 124.48, 158.09 ppm.

DMOT: Yield 78.4%. ^{1}H-NMR (CDCl$_3$): 3.86 (s, 6H), 6.19 (s, 2H) ppm. ^{13}C-NMR (CDCl$_3$): 57.55, 96.26, 147.81 ppm.

DOOT: Yield 92.3%. ^{1}H-NMR (CDCl$_3$): 0.90(t, $J =$ 6.8 Hz, 6H), 1.27–1.36 (m, 16H), 1.39–1.45 (m, 4H), 1.77–2.05 (m, 4H), 3.97 (t, $J = 6.8$ Hz, 4H), 6.16 (s, 2H) ppm. ^{13}C-NMR (CDCl$_3$): 14.11, 22.68, 25.99, 29.03, 29.25, 29.37, 31.83, 70.58, 96.82, 147.55 ppm.

Eletropolymerization and electrochemical characterization

All electrochemical experiments were performed in a conventional, single compartment cell with a platinum (Pt) or a indium-tin oxide (ITO) electrodes as the working electrode (6 × 3 mm^2), a Pt and Ag/AgCl served as the counter electrode and the reference electrode, respectively. Before electrochemical polymerization, the working electrode was washed with 0.5 M·H$_2$SO$_4$ and rinsed with acetone, ethanol, and water successively. All solutions were degassed by flushing with dry N$_2$ for 15 min and experiment was performed under N$_2$. Electropolymerization of POOT, PDOOT, and P(OOT-*co*-DOOT) was performed by potentiostatic electrodeposition on Pt sheets (6 × 3 mm^2) or ITO electrodes from deaerated 0.1 M (0.05 M OOT + 0.05 M DOOT for copolymer) monomer solutions in acetonitrile (ACN) containing 0.1 M LiClO$_4$ as the supporting electrolyte at the potential of 1.25 V in 25–200 s. A potentiodynamic technique (cyclic voltammetry method) was also used in this study to allow a detailed comparison of the electropolymerization processes for three kinds of PThs. After electrochemical polymerization, the thin polymer films on Pt electrode were washed with ACN to remove remaining monomers, then dried in a vacuum oven at 80°C for 24 h to obtain SEM samples or dissolved in THF for molecular weight determination with gel permeation chromatography (GPC).

POOT: ^{1}H-NMR(CDCl$_3$): 0.7–1.0 (m), 1.0–1.7 (m), 1.8–2.0 (m), 4.0–4.3 (m) ppm.

PDOOT: ^{1}H-NMR(CDCl$_3$): 0.7–1.0 (m), 1.0–1.6 (m), 1.7–1.9 (m), 3.9–4.1 (m) ppm.

P(OOT-*co*-DOOT): ^{1}H-NMR(CDCl$_3$): 0.7–0.9 (m), 1.2–1.5 (m), 1.7–2.0 (m), 3.8–4.0 (m), 4.0–4.2 (m) ppm.

Electrochromic and spectroelectrochemistry

For EC and spectroelectrochemistry measurement, the PThs were electrochemically synthesized on ITO glass electrodes by potentiostatic method to control the deposition of polymer. Spectroelectrochemistry measurement was carried out in monomer-free (ACN) solution containing 0.1 M LiClO$_4$. The electrochemical cell was composed of ITO/polymer working electrode and an identical ITO auxiliary electrode in the supporting electrolyte.

RESULTS AND DISCUSSION

Eletrochemical polymerization

Figure 2(a1–a3) show the cyclic voltammograms (CVs) for electropolymerization of POOT, PDOOT, and P(OOT-*co*-DOOT) on Pt electrodes from 0.1 M monomer (0.05 M OOT + 0.05 M DOOT for the copolymerization) solutions in ACN containing 0.1 M LiClO$_4$ as the supporting electrolyte. On sequential cycles, the current intensity was gradually increased, indicating the formation of PTh on the surface of the electrode. The onset oxidation potentials [$E_{onset(ox)}$] of the monomers were determined from the first cycle of CV curves. As shown in Table I, the $E_{onset(ox)}$ of DOOT was lower than that of OOT. When adding OOT into the DOOT solution, the copolymer of the two thiophenes was formed on the electrode surface with $E_{onset(ox)}$ at 960 mV, near to that of DOOT.

The growth CVs showed the increase of current with successive cycles, as the result of successful electroactive film growth. With the increasing of thickness of the deposited film on electrode during polymerization, oxidation, and reduction peaks of the polymers appeared in the curves. The redox potentials of the copolymer and homopolymers, defined as $E_{redox} = (E_{pa} + E_{pc})/2$, were significant different. For example, E_{redox} of P(OOT-*co*-DOOT) was 595 mV, about 180 mV and 12 mV lower than that of POOT and PDOOT, respectively. This could be used as an indication of copolymer formation. Both the copolymer and homopolymers were soluble in 1,2,4-trichlorobenzene, THF, and chloroform, but insoluble in methanol. These PThs were characterized with ^{1}H-NMR. It was found that P(OOT-*co*-DOOT) was composed of OOT segment 54.5 mol % and DOOT segment 44.5 mol %, closing to the feed ratio of 1 : 1. The difference was arisen from the higher activity of OOT cation radical than that of DOOT in the electropolymerization. Actually, the oxidation potential of OOT was 1040 mV, higher than that of DOOT (Table I).

Figure 2(b1–b3) shows the electrochemical response of the resulting polymers in a monomer-free ACN solution at different scanning rates between 5 and 200 mV s^{-1}. The linear relationship between the peak current and the scanning rate [inset of Figure 2(b1–b3)] was indicative of a surface confined redox process that was nondiffusion limited.[19] These results also indicated the formation of redox-active and well-adhered polymers on the electrode.

To determine the molecular weights of the electropolymerization polymers, we dissolved the film
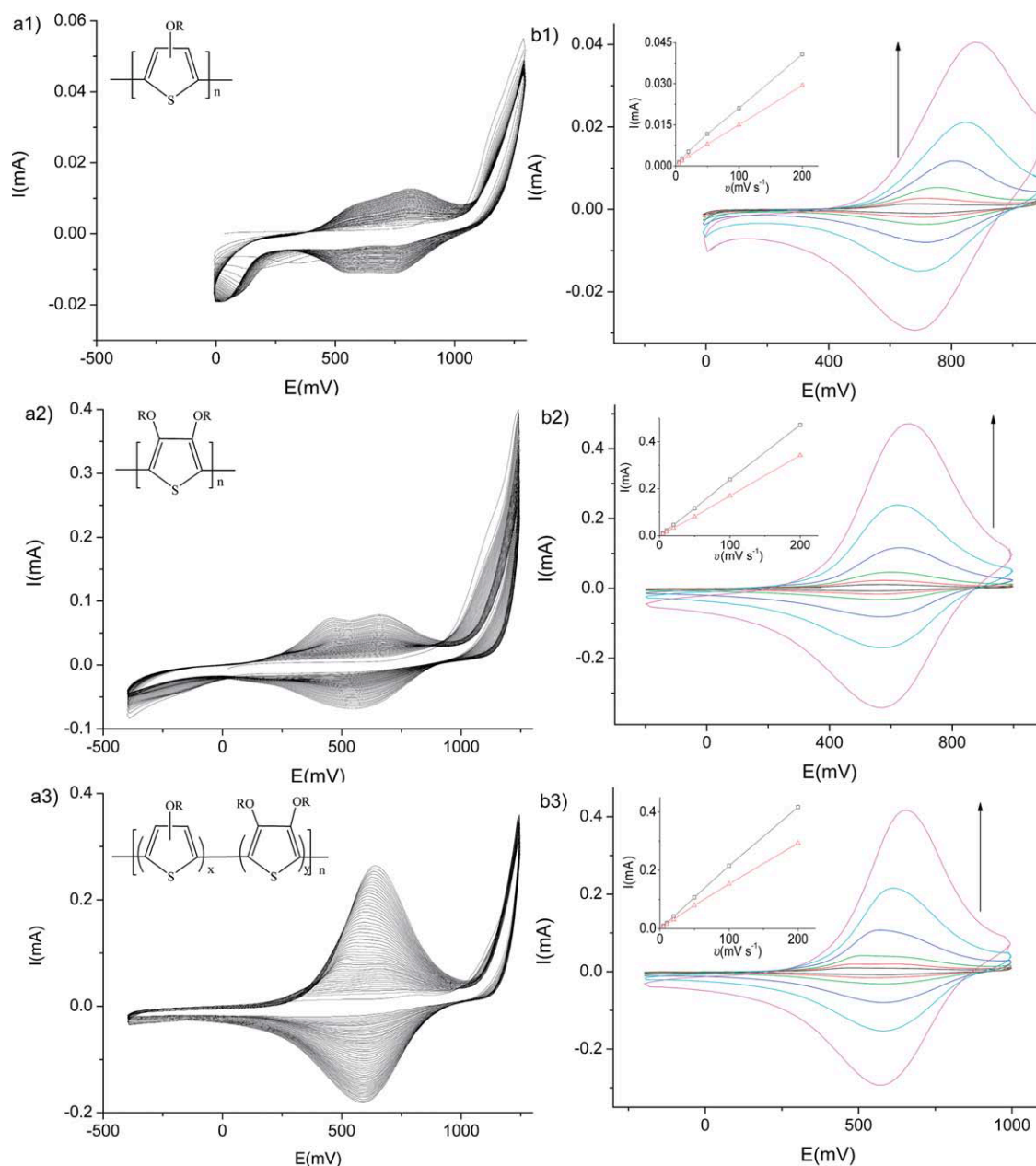
Figure 2 (A) Cyclic voltammograms for electrodeposition of the polymer films on Pt electrode from acetonitrile containing 0.1 M (0.05 M OOT + 0.05 M DOOT for copolymer) monomers and 0.1 M LiClO$_4$: (a1) POOT; (a2) PDOOT; and (a3) P(OOT-*co*-DOOT). The potential scan rate was 100 mV s^{-1}. (B) Cyclic voltammetric response of the deposited polymer films: (b1) POOT; (b2) PDOOT; and (b3) P(OOT-*co*-DOOT). Arrow indicates increasing scan rates: 5, 10, 20, 50, 100, and 200 mV s^{-1}. Inset: the absolute value of the peak currents vs. scan rates (□: anodic peak; △: cathodic peak). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Maximum Absorption (λ_{max}) of the Monomers and the Polymers in the Neutral State, Oxidation Potentials of the Monomers [$E_{\mathrm{onset(ox)}}$], Redox Potentials (E_{redox}) and the Band Gap (E_g) of the Polymers in Acetonitrile, and the Average Molecular Weights (M_n) for the Polymers Studied

Polymer	Monomer		Polymer				
	λ_{max} (nm)	$E_{\mathrm{onset(ox)}}$ (mV)	E_{redox} (mV)	λ_{max} (nm)	E_g (eV)	M_n (10^3 g mol^{-1})	PDI
POOT	219, 253	1040	775	521	2.07	3.1	1.38
PDOOT	211, 254	950	607	508, 549, 595	1.88	7.1	2.04
P(OOT-*co*-DOOT)	–	960	595	502	1.94	3.8	2.09
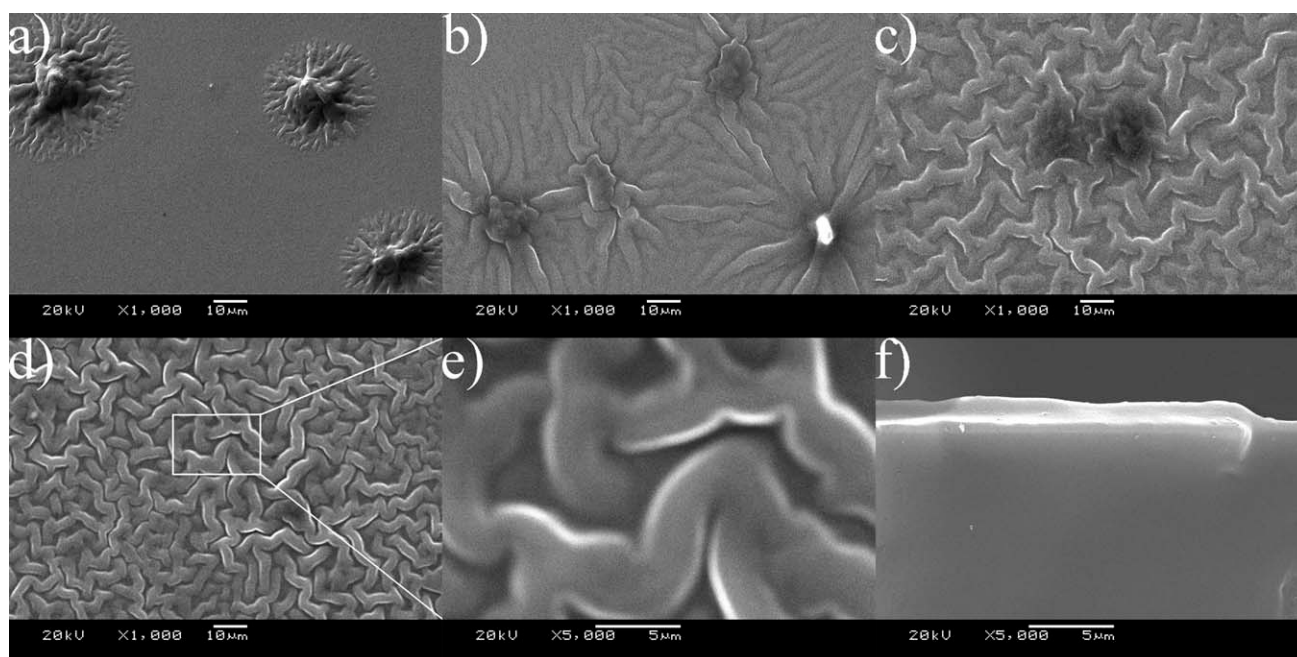
Figure 3 SEM images of P(OOT-*co*-DOOT) on ITO electrode at various growth stages and magnification: 25 s ×1000 (a), 50 s ×1000 (b), 100 s ×1000 (c), 200 s ×1000 (d), 200 s ×5000 (e), 200 s ×5000 of the film's cross section (f).

deposited on the electrode in THF. The number-average molecular weights of the homopolymers POOT and PDOOT were 3100 and 7100, whereas the polydispersities were 1.38 and 2.04, respectively. For the copolymer sample, P(OOT-*co*-DOOT), the number-average molecular weight was 3800, and the polydispersities was 2.09. Therefore, the molecular weight of P(OOT-*co*-DOOT) fall in between that of POOT and PDOOT. This could be due to the poor structural regularity of the copolymer which affected by the monoalkoxysubstituted thiophene units. Research showed that the substitution at the 3- and 4-positions of thiophene prevents the occurrence of α–β and β–β coupling during electropolymerization, yielding more ordered polymers with longer conjugation lengths and higher molecular weight.[2]

Morphologies of deposited films

Morphologies of PThs effects the electronic properties, such as charge carriers mobility through the crystalline PTh films. The morphologies of thiophene copolymer deposited on ITO electrodes by potentiostatic electropolymerization at the potential of 1.25 V were investigated with SEM (Figure 3). As shown in Figure 3(a), PTh grew from the nucleation sites that probably arose at the defects of ITO under layer. With the increasing of polymerization, PTh grew horizontally and the nucleus coalesce. After 200 s of polymerization, the PTh covered the whole surfaces. As shown in Figure 3(d–f), the finally formed PTh film exhibited an interesting worm-woven morphology with thickness of about 1.5 μm. Such a worm-

woven morphology is different from the well-known cauliflower-like morphology[20] of unsubstituted PTh. Although the alkoxy groups on the thiophene rings could hindered the growth or packing of PTh molecules in three-dimensional manner, that would lead to the cauliflower-like morphology, at this moment we do not know the reason for the formation of this different and interesting morphology, and the effects on the properties related to electrochromism and conductivity.

Electrochromism

To gain more insight into the relationship between structure and electrochemical properties, the spectroelectrochemical properties of the three PThs electrochemically deposited on ITO glass plate were examined. Figure 4 shows the spectroelectrochemical spectra of the PTh films with voltages varying from −0.1 V to +1.25 V in 0.1 M LiClO$_4$ solution. At reduced state POOT appeared in dark red color with an absorbance located at λ_{max} of 520 nm. On the stepwise oxidation by applying potential, the absorbance at 520 nm from the π–π* transition gradually vanished, and a new absorption band emerged around λ_{max} of 750 nm because of the increased polaron. At +1.25 V, the POOT at oxidized state turned to blue-green color. The spectroelectrochemistry of all other polymers was performed with the same procedure mentioned for POOT. PDOOT was in purple at reduced state with absorbance λ_{max} at about 510, 550, and 600 nm, and turned to light blue at the oxidized state. The triplet peaks were
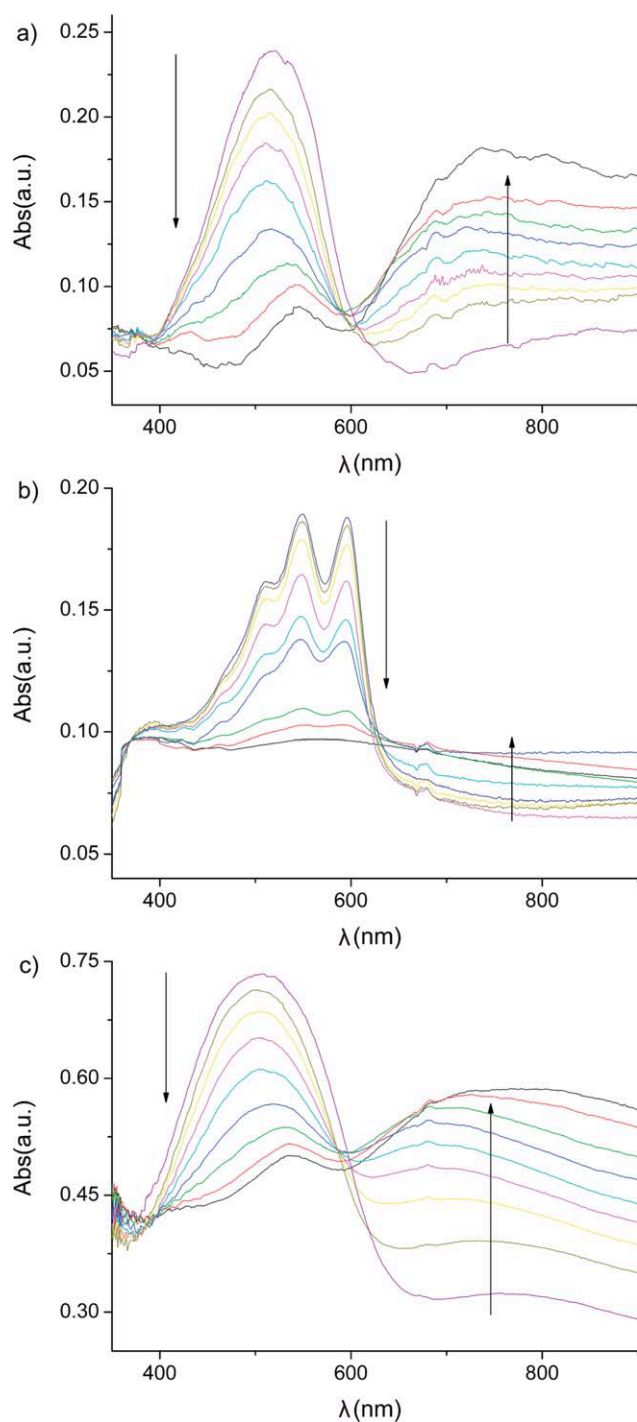
Figure 4 Spectroelectrochemical spectra of the homopolymers and copolymers with applied potentials of −0.1, +0.1, +0.3, +0.5, +0.7, +0.8, +0.9, +1.1, and +1.25 V: (a) POOT; (b) PDOOT; and (c) P(OOT-*co*-DOOT). Arrow indicates increasing potentials. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

contributed by the molecule vibronic coupling of poly(dialkoxythiophene).[21] In addition, PDOOT had low absorbance at its oxidized state. It was different with the PDOOT when we made OOT and DOOT to be copolymerized. The copolymer of these two thio-

phenes was red at the reduced state with single absorption band at $\lambda_{\max}$ 500 nm, and turned to bright blue at the oxidized state. This could be explained that the monosubstituted poly(3-alkoxythiophene) as block decreased the polymer regularity and the intermolecular interaction when it was introduced into the copolymer. From visualization by naked eyes, the color changes of these PThs from reduced to oxidized states by applying potential were: deep red to blue green for POOT, purple to light blue for PDOOT, and for P(OOT-DOOT) red to bright blue. The color of P(OOT-*co*-DOOT) film at reduced or oxidized state was distinctly different from the colors of POOT and PDOOT. In fact, this color change was used to monitor the processes of copolymerization.

The band gaps (E_g) of the three PThs were also listed in Table I. E_g of POOT was higher than that of PDOOT or the copolymer, owing to electron-donating effects of the different number of alkoxy groups. This also produced the difference of the absorption wave length between these two kinds of polymers. The spectroelectrochemical differences were also arisen from this substitute effects and the structurally irregularity by copolymerization.

CONCLUSIONS

In conclusion, we developed two homopolymers and one copolymer which were electropolymerized from monoalkoxythiophene and dialkoxythiophene. The polymerization processes and polymer properties were thoroughly investigated and evaluated. By electrochemical copolymerization, a simple and convenient way to alter the structures of conjugated polymers, the copolymer possessing very different properties with the homopolymers was prepared. The morphology studies indicated that the electrochemical deposition of P(OOT-*co*-DOOT) proceeds via a mechanism of nucleation and two-dimensional growth. Via spectroelectrochemisty studies, it was observed that the copolymer of monoalkoxythiophene with dialkoxythiophene possess distinctly different EC properties when it was compared with the homopolymers.

References

1. Granqvist, C. G.; Evendano, E.; Azens, A. Thin Solid Films 2003, 442, 201.
2. Groenendaal, L. B.; Zotti, G.; Aubert, P. H.; Waybright, S. M.; Reynolds, J. R. Adv Mater 2003, 15, 855.
3. Srivastava, A. K.; Deepa, M.; Singh, S.; Kishore, R.; Agnihotry, S. A. Solid State Ionics 2005, 176, 1161.
4. Ko, H. C.; Kim, S.; Lee, H.; Moon, B. Adv Funct Mater 2005, 15, 905.
5. Gao, J.; Liu, D.; Sansinena, J.; Wang, H. Adv Funct Mater 2004, 14, 537.

6. Ahmad, S.; Singh, S. Electrochem Commun 2008, 10, 895.
7. Rosseinsky, D. R.; Mortimer, R. J. Adv Mater 2001, 13, 783.
8. Koeckelberghs, G.; Vangheluwe, M.; Samyn, C.; Persoons, A.; Verbiest, T. Macromolecules 2005, 38, 5554.
9. Hiromasa, G.; Yong, S. J.; Kazuo, A. Macromol Rapid Commun 2005, 26, 164.
10. Yildirim, A.; Tarkuc, S.; Ak, M.; Toppare, L. Electrochim Acta 2008, 53, 4875.
11. Witker, D.; Reynolds, J. R. Macromolecules 2005, 38, 7636.
12. Szkurlat, A.; Palys, B.; Mieczkowski, J.; Skompska, M. Electrochim Acta 2003, 48, 3665.
13. Thompson, B. C.; Kim, Y. G.; Mccarley, T. D.; Reynolds, J. R. J Am Chem Soc 2006, 128, 12714.
14. Kumar, A.; Reynolds, J. R. Macromolecules 1996, 29, 7629.
15. Chen, S.; Bao, W.; Tu, S.; Wang, Y. J Appl Polym Sci 2008, 109, 120.
16. Keegstra, M. A.; Peters, H. A.; Brandsma, L. Synth Commun 1990, 20, 213.
17. Goldoni, F.; Langeveld-Voss, B. M. W.; Meijer, E. W. Synth Commun 1998, 28, 2237.
18. Brustolin, F.; Goldoni, F.; Meijer, E. W.; Sommerdijk, N. A. J. M. Macromolecules 2002, 35, 1054.
19. Cutler, C. A.; Bouguettaya, M.; Reynolds, J. R. Adv Mater 2002, 14, 684.
20. Yagci,Y.; Yilmaz, F.; Kiralp, S.; Toppare, L. Macromol Chem Phys 2005, 206, 1178.
21. Van D. A.; Perro A.; Meulenkamp E. A.; Brunner K. Org Electron 2003, 4, 131.