ELSEVIER

Electrochemical and electrochromic properties of poly(ether naphthalimide)s and related model compounds

H.B. Zheng, W. Lu, Z.Y. Wang[*]

Department of Chemistry, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, Canada K1S 5B6

Abstract

The electrochemical and electrochromic properties of poly(ether naphthalimide)s were studied and compared with related model compounds. The electroactive sites within the poly(ether naphthalimide)s were identified to be ketone and imide groups. The stepwise coloration process, colorless–red–dark blue corresponding to the neutral, radical anion and dianion species, was found to be related to the first reduction of the imide group and the second reduction of the ketone group. Based on this new polyimide a high-contrast switch between colorless and red or colorless and dark blue can be achieved and controlled electrically. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimides; Electrochromism; Electrochemistry

1. Introduction

Polymeric materials capable of undergoing a reversible electrochemical reduction/oxidation process are currently of interest in connection with electrochromic displays [1,2], light-emitting electrochemical cells [3] and solid-state batteries [4]. Electrically conducting polymers such as polythiophene, polypyrrole, polyaniline and their derivatives are under extensive investigation as electrochromic materials because of the advantages they offer in tailorability of color and processability. Most of these polymers are anodically coloring materials and undergo a reversible p-doping–undoping process, which involves anion transport in and out of the polymer matrix to balance the electronic charge. Some conjugated polymers also undergo an n-doping process with cation insertion to balance the injected charge and are potentially cathodically coloring materials. However, the study on n-doping polymers is rather limited. The polythiophene derived from 3,4-ethylenedioxythiophene (Baytron P from Bayer Inc.) [5,6] is one of the few cathodically coloring polymers.

Polyimides are widely used in the electronics industry owing to their excellent chemical, thermal and dielectric properties [7]. Following the early studies by Haushalter and Krause [8], the redox properties of various imides and polyimides have been described [9–11]. But their electro-chromic properties are scarcely investigated. Most imide compounds and polyimides studied so far contain a diimide unit, in which the two identical imide groups are attached symmetrically to an aromatic core. These diimides undergo a typical redox process involving the formation of a radical anion upon the first reduction and a dianion upon the second reduction [9–11]. Regarding the electrochromic behavior, it has been confirmed that the formation of a radical anion results in a bathochromic shift in the visible region. But the formation of the dianion causes a hypsochromic shift due to the fact that the additional energy generated from the electron spin pairing for the dianion HOMO excites an electron to the next highest level [11]. This hypsochromic shift also reflects the loss of aromaticity in the benzene ring as the quinoid character increases. Since the difference between the first and second reduction potentials for these known diimides is usually rather small, the electrochemical control of a reversible high-contrast coloration at two distinct wavelengths or between the neutral state and the radical anion would be extremely difficult.

Viehbeck and coworkers investigated the structural effect of aromatic imides on the reduction potentials and UV–Vis absorption [11]. Their study showed that the electrochemical reduction was facilitated with an increase in electron deficiency of an aromatic imide. For example, a naphthalene-1,4,5,8-tetracarboxylic diimide has a lower reduction potential than that of a naphthalimide and the latter is less colored than the former in the neutral state. Therefore, to have a colorless imide or polyimide with a low reduction
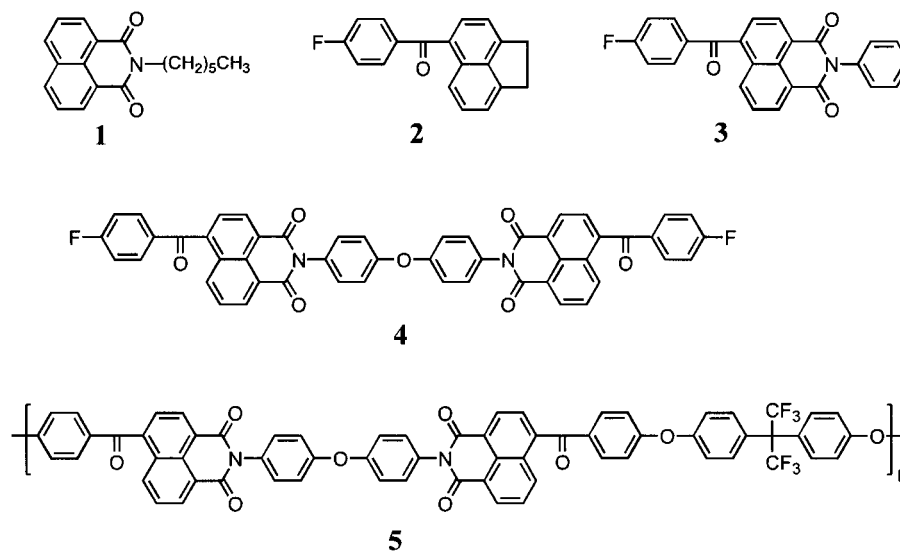

Fig. 1. Structures of model compounds **1**–**4** and polyimide **5**.

potential, one would need to incorporate a strong electron-withdrawing group that does not cause an increase in absorption in the visible spectral region. Recently, we synthesized a new class of colorless poly(ether naphthalimide)s with good thermal stability and solubility (e.g. polyimide **5**, Fig. 1) [12]. The electron-withdrawing carbonyl group on the naphthalimide ring should be able to enhance the imide reactivity towards electrochemical reduction. Thus, such a substituted naphthalimide may serve as an electrochromic material with desired properties such as low redox potential and high-contrast coloration. In the present work, the electrochemical and electrochromic properties of polyimide **5** as well as the related compounds are studied.

2. Experimental

2.1. Reagents and materials

1,8-Naphthalic anhydride, *n*-hexylamine, acetonitrile (AN), *N,N'*-dimethylforamide (DMF), propylene carbonate (PC) and 1,1,2,2-tetrachloroethane (TCE) were purchased from Aldrich Chemical Co. and used as received. Supporting electrolytes, tetra-*n*-butylammonium perchlorate (*n*-Bu₄NClO₄), tetraethylammonium perchlorate (Et₄NClO₄),

lithium perchlorate (LiClO₄), sodium perchlorate (NaClO₄) and potassium perchlorate (KClO₄) were purchased from Fluka, Aldrich and Sigma and used without further purification. All other chemicals were reagent grade unless otherwise stated. Indium tin oxide (ITO)-coated glass were purchased from Delta Technologies Ltd.

2.2. Model compounds and polymer

Model compounds **2**–**4** and polyimide **5** (Fig. 1) were synthesized according to the method reported previously [12].

Compound 1. 1,8-Naphthalic anhydride (1.50 g, 7.57 mmol) and *n*-hexylamine (3.0 ml) were placed in a 10 ml round bottom flask. The mixture was heated to reflux for 5 h. The reaction was cooled and poured into an aqueous HCl solution (20 ml of water and 4 ml of concentrated HCl). The resulting solid was filtered and washed with water until free from acid. After recrystallization from methanol and drying in a vacuum oven at 50°C, compound **1** was obtained: 2.02 g (95%); m.p. 75–77°C; IR (KBr) 1702, 1664 cm^{-1} (imide); HRMS for $C_{18}H_{19}NO_2$, calcd. 281.1416, found 281.1400 (Int, 74.1%); ^{1}H NMR (200 MHz, CDCl₃) 8.47–8.43 (d, 2 H, $J = 7.18$ Hz), 8.09–8.05 (d, 2 H, $J = 8.28$ Hz), 7.66–7.58 (m, 2 H), 4.12–4.03 (t, 2 H, $J = 7.55$ Hz), 1.66 (m, 2 H), 1.29

Table 1
Cyclic voltammetric data for model compounds **1**–**4** and polyimide **5** (electrolyte solution: 0.1 M *n*-Bu₄NClO₄ in DMF; scan rate: 100 mV/s)

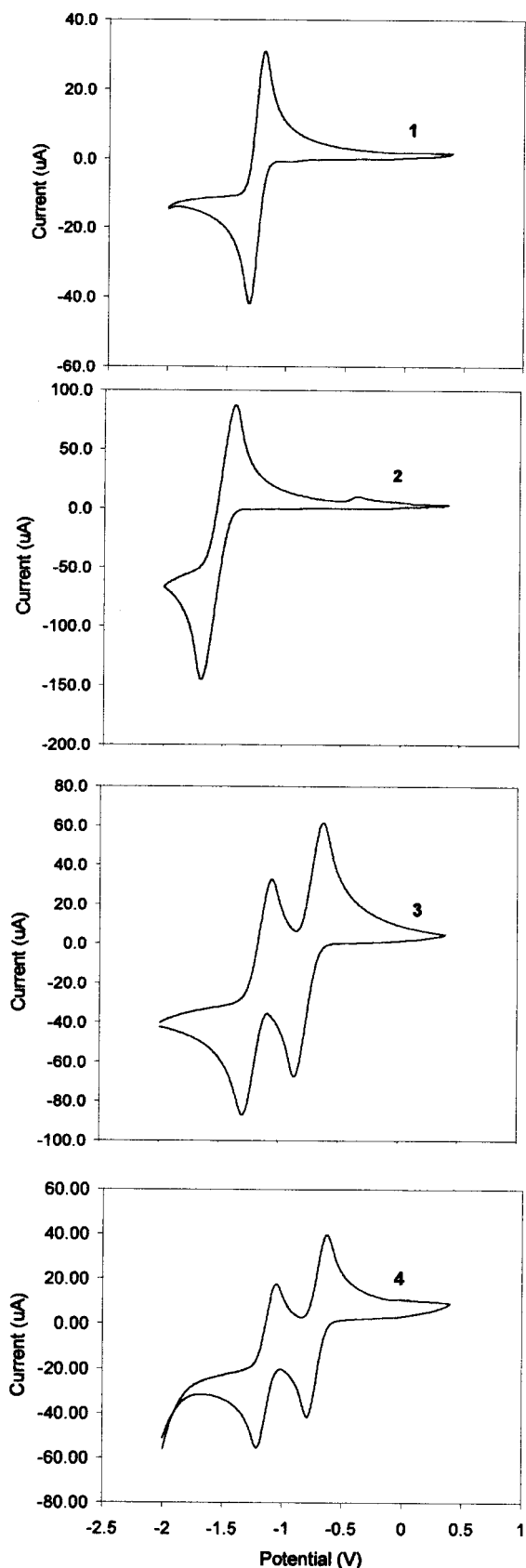| Model/polymer	E_{pc_1}/E_{pa_1} (V)	ΔE_{p_1} (V)	E_{pc_2}/E_{pa_2} (V)	ΔE_{p_2} (V)	$E_{pc_1} - E_{pc_2}$ (V)
1	−1.31/−1.19	0.12	–	–	–
2	–	–	−1.68/−1.41	0.27	–
3	−0.88/−0.64	0.24	−1.30/−1.06	0.24	0.42
4	−0.79/−0.63	0.15	−1.21/−1.16	0.15	0.42
5	−0.82/−0.66	0.16	−1.21/−1.08	0.13	0.39

Fig. 2. Cyclic voltammograms of model compounds **1–4** obtained at platinum electrode in DMF. Electrolyte: 0.1 M *n*-Bu$_4$NClO$_4$. Scan rate: 100 mV/s.

(m, 6 H), 0.82 (m, 3 H); ^{13}C NMR (50 MHz, CDCl$_3$) 164.17, 134.13, 131.45, 127.26, 123.09, 40.89, 32.01, 28.51, 27.27, 23.03, 14.53.

2.3. Preparation of polymer-coated electrodes

A solution of polymer **5** in TCE (25.0 mg/ml) was drop cast or spin coated onto a platinum disc electrode or ITO glass electrode and then dried in an oven at 80°C for 10 min.

2.4. Measurements

The ^{1}H and ^{13}C NMR spectra were recorded on either a Varian Gemini-200 or a Bruker-400 instrument using tetramethylsilane as internal reference. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrometer. Melting points were taken from a Fisher–Johns melting apparatus or from a Seiko 220C differential scanning calorimeter (DSC) at a heating rate of 10°C/min in nitrogen (200 ml/min).

Electrochemical measurements were performed using a BAS 100B/W electrochemical workstation interfaced and monitored with a personal computer. The three-electrode system was employed throughout this work, which consists of a working electrode, a silver wire reference electrode and a platinum wire auxiliary electrode. The platinum disc electrode ($s = 0.018$ cm^2) for cyclic voltammetry and ITO-coated glass electrode (0.5×2.5 cm^2) for UV–Vis spectrophotometry were used, respectively. In all cases, the electrolyte solutions were deoxygenated with nitrogen for 10 min prior to use.

Spectroelectrochemical measurements were carried out by combining electrochemical workstation with a Perkin–Elmer Lambda 900 Spectrophotometer and using a quartz cuvette cell containing an ITO working electrode, a platinum wire auxiliary electrode and a silver wire reference electrode. A blank ITO glass electrode with the electrolyte solution was used as reference.

3. Results and discussion

3.1. Electrochemistry of model compounds

In order to correlate the functional groups in the polyimide with its electrochemical behavior, cyclic voltammetry of model compounds **1–4** (Fig. 1) was first investigated. The reversible and stable cyclic voltammograms were obtained for all compounds in DMF containing 0.1 M *n*-Bu$_4$NClO$_4$. The voltammetric data are listed in Table 1. For comparison, cyclic voltammograms of model compounds **1–4** are shown in Fig. 2. Naphthalimide **1** displayed a pair of reversible peaks at -1.31 V (E_{pc_1}) and -1.19 V (E_{pa_1}). The observed electrochemical reduction of the imide compound is the same as reported previously [9–11], confirming the imide's carbonyl group as the electroactive site. One pair of reversible peaks was also observed for ketone **2**, showing that the
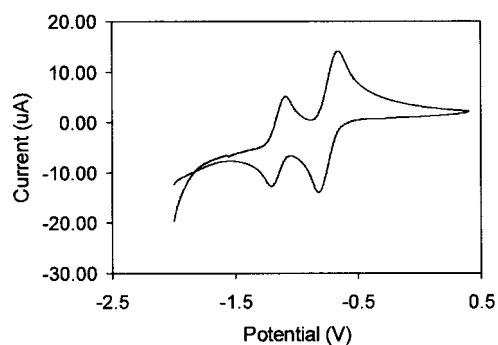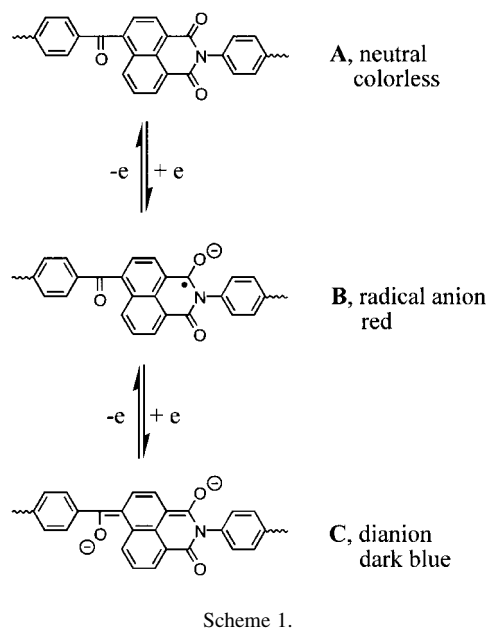
Scheme 1.

Fig. 3. Cyclic voltammograms of polyimide **5** obtained at platinum electrode in DMF. Electrolyte: 0.1 M n-Bu$_4$NClO$_4$. Scan rate: 100 mV/s.
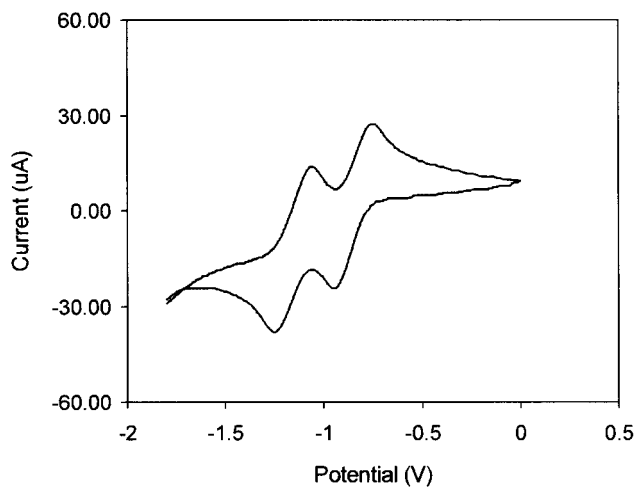

Fig. 4. Cyclic voltammogram of polyimide **5**-coated platinum electrode in propylene carbonate. Electrolyte: 0.1 M n-Bu$_4$NClO$_4$. Scan rate: 100 mV/s.

carbonyl group also undergoes a reversible electrochemical redox reaction. The reduction of ketone **2** occurred at a more negative potential than imide **1** (Table 1 and Fig. 2), which clearly indicates that the reduction potential relates to the electron affinity of the carbonyl group. Accordingly, two pairs of reversible peaks appeared for the keto imide **3** (Fig. 2), which can be assigned to reductions of the imide ($E_{pc_1} = -0.88$ V) and ketone ($E_{pc_2} = -1.30$ V) groups. A shift of the two reduction peaks for compound **3** to the less negative potential region can be attributed to the electron-withdrawing effect of the ketone and imide groups on each other. Compound **4**, a representative dimer of compound **3**, displayed the same two pairs of redox peaks as compound **3**. It is interesting to note that the peak separations of both imide (ΔE_{p_1}) and ketone (ΔE_{p_2}) groups of compound **4** are nearly half of those of the corresponding groups in compound **3**. According to the inversely proportional relationship between peak separation (ΔE) and the number of electron (n) transferred during redox process [13], it clearly shows that the numbers of electron gained during the reduction of compound **4** are, respectively, twice those of the corresponding functional groups of compound **3**. This strongly indicates that the two imide groups or the two ketone groups in compound **4** are concurrently reduced, as the result of breaking the π-conjugation between two naphthalimide units by the oxydiphenylene group. Thus, the redox behavior of compound **4** is unique and different from that reported previously for conjugated aromatic diimides and related polyimides such as pyromellitimides and naphthalene-1,4,5,8-tetracarboxylic diimides [9–11], where the two pairs of typical redox peaks are due to the successive reduction of two conjugated imide groups. According to above electrochemical studies, a different redox process is proposed for this type of polyimide (Scheme 1: proposed two-step redox reaction for model compound **3**). The first electron reduces the neutral naphthalimide **A** to the corresponding radical anion **B**, which upon receiving another electron by the carbonyl group yields the dianion **C**.

3.2. Electrochemistry of polyimide

Since polyimide **5** was made from compound **4**, its electrochemical behavior should be similar to that of its monomer. Indeed, by comparing the redox potentials, peak separations (ΔE) of both imide and ketone groups as well as the difference between the reduction of imide and ketone groups ($\Delta E_{p_1} - \Delta E_{p_2}$), compound **4** and polyimide **5** showed similar electrochemical behaviors in solution. The cyclic voltammograms of polyimide **5** is shown in Fig. 3. The electrochemical study on polyimide **5** in the solid state was then performed. The cyclic voltammetry of the polymer-coated electrode was carried out in PC containing 0.1 M n-Bu$_4$NClO$_4$. Two pairs of reversible peaks ($E_{pc_1} = -0.97$ V, $E_{pc_2} = -1.27$ V) were observed (Fig. 4). In order to compare to the results obtained in solution (Fig. 3), the
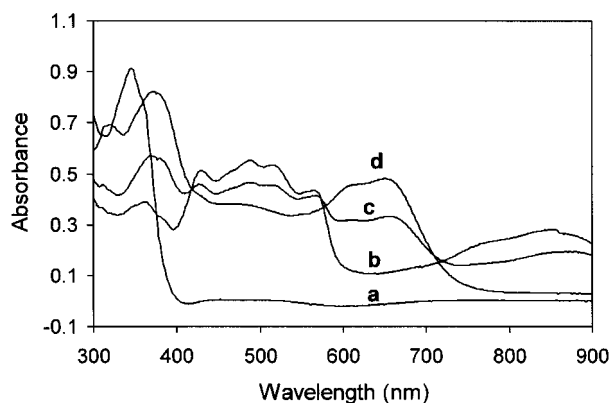
Fig. 5. In situ UV–Vis spectra of polyimide **5**-coated ITO glass electrode in propylene carbonate containing 0.1 M n-Bu$_4$NClO$_4$: (a) 0.0 V; (b) −1.1 V; (c) −1.3 V; and (d) −1.8 V.

silver reference electrode was calibrated using ferrocene in PC and DMF solution containing 0.1 M n-Bu$_4$NClO$_4$. The E_{pc} values of ferrocene are 0.28 V in PC and 0.31 V in DMF. By calculation, a slightly negative shift of potentials was expected for reduction of both imide and ketone groups of polyimide **5** in the solid state due to slower transport of compensating ions within the polymer network.

The effects of electrolyte concentration and composition on the electrochemical behavior of polyimide **5** were also investigated. It was found that, when the concentration of n-Bu$_4$NClO$_4$ increased from 0.001 to 1.0 M, the redox potentials shifted anodically, indicating that cation insertion/deinsertion is responsible for the electro-neutrality during the redox process. The composition of the electrolyte solution was also found to be another important factor governing the electrochemical response. In the solution containing n-Bu$_4$NClO$_4$ or Et$_4$NClO$_4$ as a supporting electrolyte, no difference in electrochemistry was found. But poor electrochemical responses were observed in solutions containing an inorganic electrolyte such as LiClO$_4$, NaClO$_4$ or KClO$_4$. Once again, it was confirmed that larger cations facilitate the imide reduction due to the enhanced solvophobic interactions [14].

Moreover, the redox potentials were found to be independent of potential scan rate (v), while the redox currents increased as the scan rate increased. This phenomenon may be due to very fast electron transfer rate (reversible rate). The plot of the current according to the maximum of reduction peak against the square root of scan rate (v) is linear in the range of 10–100 mV/s, indicating that the redox process is kinetically controlled by the diffusion process and the insertion of cations [15,16].

3.3. In situ UV–Vis–NIR spectroscopic studies

The electrochromic property of polyimide **5** was then studied by applying a range of negative potentials on the polymer-coated ITO glass electrode. It was found that the color of polymer film was greatly affected by the degree of reduction. Fig. 5 shows the in situ UV–Vis spectra for polyimide **5** at different redox states. At 0.0 V, the polymer film is nearly colorless with a maximum absorption at 342 nm. When the applied potential decreased to −1.1 V, the intensity of this band decreased and the polymer film turned to red with the appearance of new peaks at 483 and 850 nm and two shoulder peaks at 426 and 512 nm. The intensity of these new absorption bands decreased with further decrease of the applied potential to −1.8 V. The polymer film became dark blue with the occurrence of two major absorption bands at 368 and 648 nm and a shoulder peak at 605 nm. The intensity of these new bands increased concurrently with the decrease of the 483 and 850 nm bands. A tight isosbestic point was found at 417 nm for gradual conversion from a radical anion to a dianion (Fig. 5, spectra b–d). It is clear that the band at 342 nm corresponds to the π–π^* electronic transition and the bands at 483 and 850 nm belong to the electronic transition of the radical anion. As shown in Fig. 5, polyimide **5** does not have any absorption in the near infrared (NIR) region at the neutral state. When applying a potential of −1.1 V, the polymer shows a broad absorption with a maximum at 850 nm due to the π-stacking (e.g. a dimer) of the radical anion within the polymer film [17,18]. With further decrease of a potential to −1.8 V, this NIR band disappeared, indicating the complete formation of a dianion species.

It should be noted that for model compound **4** and polyimide **5** studied in this work, the fully reduced dianion species consist of the imide and ketone groups, rather than a dianion of the two imides as in the case for the conjugated diimides. As being reduced gradually, polyimide **5** becomes darker without a reversed shift of the visible chromophore as seen for naphthalene-1,4,5,8-tetracarboxylic diimides and related polyimides [11].

4. Conclusions

The electrochromic responses associated with the redox of the imide and ketone groups in poly(ether naphthalimide)s have been demonstrated. An electrically controlled and high-contrast switch between the colorless bleached state and the red or dark blue colored state has been realized with this new type of non-conjugated polynaphthalimides (e.g. polyimide **5**).

References

[1] Gustafsson JC, Inganas O, Andersson AM. Synth Met 1994;62:17.

[2] Sankaran B, Reynolds JR. Macromolecules 1997;30:2582.

[3] Pei Q, Yang Y, Yu G, Zhang C, Heeger AJ. J Am Chem Soc 1996;118:3922.

[4] Arbizzani C, Mastragostino M, Meneghello L, Paraventi R. Adv Mater 1996;8:331.

[5] Dietrich M, Heinze J, Heywang G, Jonas F. J Electroanal Chem 1994;369:87.

[6] Gustafsson JC, Liedberg B, Inganas O. Solid State Ionics 1994;69:145.

[7] Sroog CE. J Polym Sci Macromol Rev 1977;11:161.

[8] Haushalter RC, Kraus LJ. Thin Solid Films 1983;102:161.

[9] Mazur S, Lugg PS, Yarnitzky C. J Electrochem Soc 1987;134:346.

[10] Krause LJ, Lugg PS, Speckhard TA. J Electrochem Soc 1989;136:1379.

[11] Viehbeck A, Goldberg MJ, Kovac CA. J Electrochem Soc 1990;137:1460.

[12] Zheng HB, Wang ZY. J Polym Sci, Part A: Polym Chem 1999;37:3227.

[13] Sawyer DT, Sobkowiak A, Roberts JL. Electrochemistry for chemists, 2nd ed. New York: Wiley, 1995. p. 72–3.

[14] Lu W, Gao JP, Wang ZY, Qi Y, Sacripante GG, Duff JD, Sundararajan PR. Macromolecules 1999;32:8880.

[15] Bard AJ, Faulkner LR. Electrochemical methods: fundamentals and applications. New York: Wiley, 1980 (chaps. 3, 6 and 10).

[16] Ko JM, Rhee HW, Park SM, Kim CY. J Electrochem Soc 1990;137:905.

[17] Miller LL, Zhong CJ, Kasai P. J Am Chem Soc 1993;115:5982.

[18] Penneau JF, Stallman BJ, Kasai P, Miller LL. Chem Mater 1991;3:791.