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Electrochemical Synthesis of a Water-Soluble and Self-Doped Polythiophene Derivative

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Abstract
A new monomer, 4-(thiophen-3-yl methyleneamino)benzene sulfonate) (ThSA), was synthesized and characterized. Electrochemical polymerization of ThSA yields a water-soluble and self-doped polymer (PThSA). This polymer was characterized by FT-IR, NMR, DSC, XRD and conductivity measurements.
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Keywords
Water-soluble polymer, conducting polymer, self doping, electrochemistry

1. Introduction

Extended conjugated polymers can, in general, be transformed into conducting materials by doping [1, 2]. In the doping procedure, reduction (*n*-type doping) or oxidation (*p*-type doping) yield highly charged polymer backbones. The charges are neutralized by counterions. The doping process is often reversible, and the counterions or other neutralizing ions can move in and out. In self-doped conducting polymers, however, the counterions are covalently attached to the polymer backbone. The concept of self-doping has been introduced by Patil *et al.* [3]. In contradiction with other doped polymers, dedoping of these self-doped polymers cannot be obtained by the loss of counterions, and should be performed by the diffusion of foreign cations into the polymer. Moreover, the polymers in the self-doped state proved to be slightly soluble in water. The first-reported self-doped polymers were poly(3-alkylsulfonate thiophenes), obtained by hydrolysis of the poly(3-alkylsulfonate thiophene) methyl esters [4]. These were prepared by elec-

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trochemical polymerization of the corresponding monomeric thiophenes. Since the synthesis of the doped polymers was performed in the presence of 'foreign' conducting salts, various experiments and arguments were put forward to prove self-doping, including cyclic voltammetry experiments combined with pH measurements in organic solvents [5].

Self-doped polyconjugated polymers with low solubility (e.g., 0.5 g/l) [6] and conductivity (10^{-7}–10^{-2} S/cm) have been reported in the past [4]. Zotti *et al.* reported that anodic coupling of tetrabutylammonium 4-(4H-cyclopentadithien-4-yl)butane sulfonate in acetonitrile produces self-doped polythiophene films with fairly high conjugation length, conductivity (0.6 S/cm) and good water solubility (*ca*. 10 g/l) [7]. The structure and effect of the side-chain length on the doping level of poly(*n*-(3-thienyl)-propanesulfonic acid) with alkanes with carbon number 2, 6 and 10 have been reported. It was found that the doping level depends on the side-chain length where the doping also causes oxidation of the polymer [8]. In an another study, water-soluble poly(*n*-(3-thienyl)-alkanesulfonate) was prepared by oxidative coupling using ferric chloride. The acid form of the self-doped polymers exhibits electronic conductivities between 5×10^{-2} and 5×10^{-1} S/cm [9].

There is no single method for synthesizing polymers that can be transformed into conductive ones. Conductive polymers may be synthesized using conventional polymerization methods, as well as specific routes. Electrochemical polymerization is normally carried out in a single- or dual-compartment cell by adopting a standard three-electrode configuration in a supporting electrolyte, both dissolved in an appropriate solvent. The focus of electrochemical studies of polymers has often been on electrochemically synthesized polymers, presumably because of the easy combination of synthesis and characterization methods. However, the nature of polymers produced by electrochemical polymerization is seldom well-defined, and almost difficult to measure, as most of these polymers are not soluble [10].

Here we report the synthesis and characterization of a new sulfonic acid containing thiophene monomer. After the electrolysis in water, we obtained a water-soluble and self-doped polythiophene derivative. FT-IR, NMR, DSC and cyclic voltammetry (CV) were used to characterize the monomer. The polymer was also synthesized *via* potentiostatic electrochemical polymerization in distilled water. Characterizations of the resulting water-soluble polymer were performed by FT-IR, NMR, DSC and XRD. A four-probe technique was used to measure the conductivities of the self-doped polymer.

2. Experimental

2.1. Materials

Sulfanilic acid and thiophene-3-carboxaldehyde were purchased from Aldrich. Methanol, Dichloromethane (DCM), nitromethane and silica gel were supplied by

Merck. Sodium hydroxyde was purchased from Carlo Erba. All chemicals were used as received.

2.2. Equipment

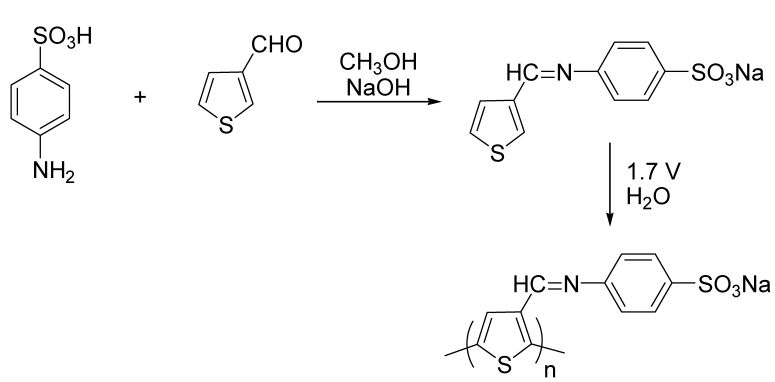
The ^{1}H-NMR spectra of the monomer and polymer were recorded on a Bruker Instrument NMR spectrometer (DPX-400) using D_2O as the solvent. The FT-IR spectrum was recorded on a Nicolet 510 FT-IR spectrometer. CHI 600 potentiostat was used to supply a constant potential during electrochemical synthesis. Thermal behavior of samples were investigated using DuPont 2000 differential scanning calorimetry. X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K_α (30 kV, 15 mA, $\lambda = 1.54051$ Å) radiation.

2.3. Synthesis of 4-(Thiophen-3-yl Methyleneamino)benzene Sulfonate) (ThSA)

A round-bottomed flask equipped with a magnetic stirrer was charged with sulfanilic acid (2.5 mmol, 435 mg), thiophene-3-carboxaldehyde (4.34 mmol, 486.4 mg), NaOH (4.73 mmol, 189 mg) and methanol (20 ml). The resultant mixture was stirred and refluxed for 24 h at 60°C. Evaporation of the methanol, followed by flash column chromatography (SiO_2 column, elution with dichloromethane) afforded the desired compound (Scheme 1).

2.4. Electrochemical Synthesis of Poly(4-(Thiophen-3-yl Methyleneamino)benzene Sodium Sulfonate)) (PThSA)

Polymerization of ThSA was performed in the presence of 50 mg ThSA in water in a one-compartment cell (20 ml) equipped with Pt working and counter electrodes and a Ag/Ag^+ reference electrode. Constant potential electrolysis was run at 1.7 V for 8 h at room temperature under inert atmosphere (Scheme 1).



Scheme 1. Synthesis of poly(4-(thiophen-3-yl methyleneamino)benzene sodium sulfonate)) (PThSA).

3. Results and Discussion

The sulfonate side-groups supply a polyelectrolytic character to the polymer. Therefore, they are soluble in water, although only to a very limited extent (order of magnitude 0.1–0.5 g/l) [6].

3.1. NMR Spectra of ThSA and PThSA

^{1}H-NMR spectrum of ThSA, δH (DMSO): 8.61 (s, 1H, a), 8.21 (s, 1H, b), 7.67–7.64 (2H, c and 2H, d), 7.16 (d, 2H, e) and 2.51 (DMSO) (Fig. 1).

^{1}H-NMR spectrum of PThSA δH (DMSO): 8.44 (s, 1H, a), 7.66 (s, 1H, b), 7.40 (s, 2H, c), 6.86 (s, 2H, d) and 2.21 (DMSO) (Fig. 2).

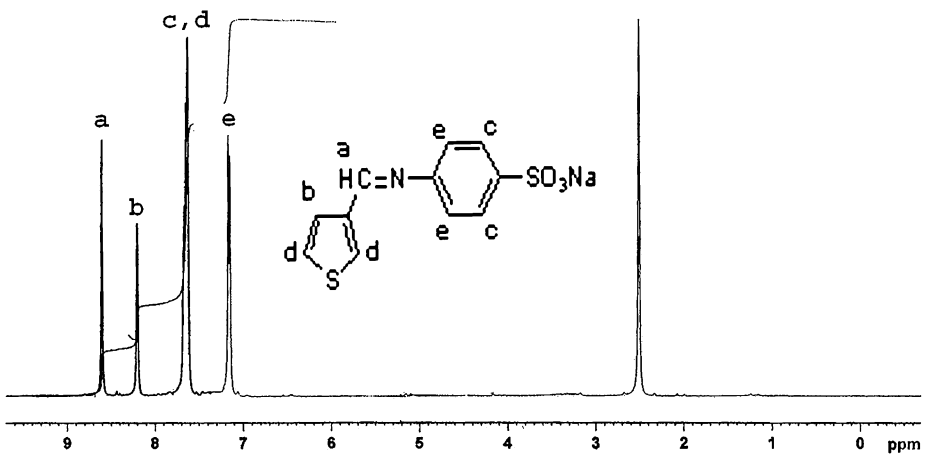


Figure 1. ^{1}H-NMR spectrum of ThSA.

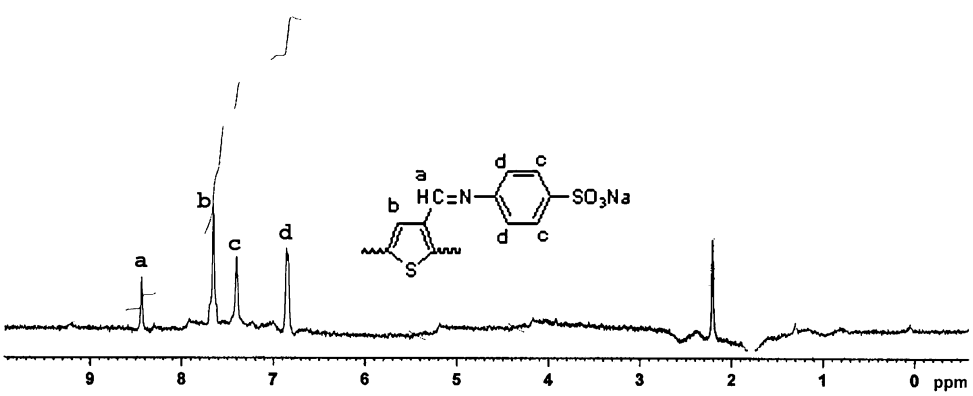


Figure 2. ^{1}H-NMR spectrum of PThSA.

3.2. FT-IR Spectra

FT-IR spectral data of ThSA (Fig. 3a): 3429 cm^{-1} (–OH), 3088 cm^{-1} (C–H of thiophene), 2929 cm^{-1} (aromatic C–H), 2876 cm^{-1} (aliphatic C–H), 1621 cm^{-1} (–CH=N), 1566–1446 cm^{-1} (–C=C–), 1187 cm^{-1} (C–S of thiophene), 1132 cm^{-1} (SO_3, S=O stretching), 1049 cm^{-1} (C–H in-plane bending), 879 cm^{-1} (C–H out-of-plane bending), 689 cm^{-1} (SO_3, S–O stretching) and 624 cm^{-1} (SO_3, C–S stretching).

FT-IR spectra of electrochemically synthesized PThSA (Fig. 3b): 3372 cm^{-1} (–OH), 2971cm^{-1} (aromatic C–H), 2931 cm^{-1} (aliphatic C–H), 1626 cm^{-1} (–CH=N), 1598, 1552, 1513, 1456 cm^{-1} (–C=C–), 1176 cm^{-1} (C–S of thiophene), 1123 cm^{-1} (SO_3, S=O stretching), 1032 cm^{-1} (C–H in-plane bending) and 687 cm^{-1} (SO_3, S–O stretching). The band at 879 cm^{-1} indicating C–Hα stretching of the monomer disappeared completely. The new broad band at around 1640 cm^{-1} was due to polyconjugation (Fig. 3).

3.3. Cyclic Voltammetry

The oxidation/reduction behavior of the monomer was investigated by CV. The system consists of a potentiostat and a CV cell containing platinum foil working and counter electrodes and a Ag/Ag^+ reference electrode.

Cyclic voltammogram of ThSA in nitromethane indicated oxidation peaks at 1.7 V and 1.25 V, and an reduction peak at 0.4 V. When the range between 0.0 V

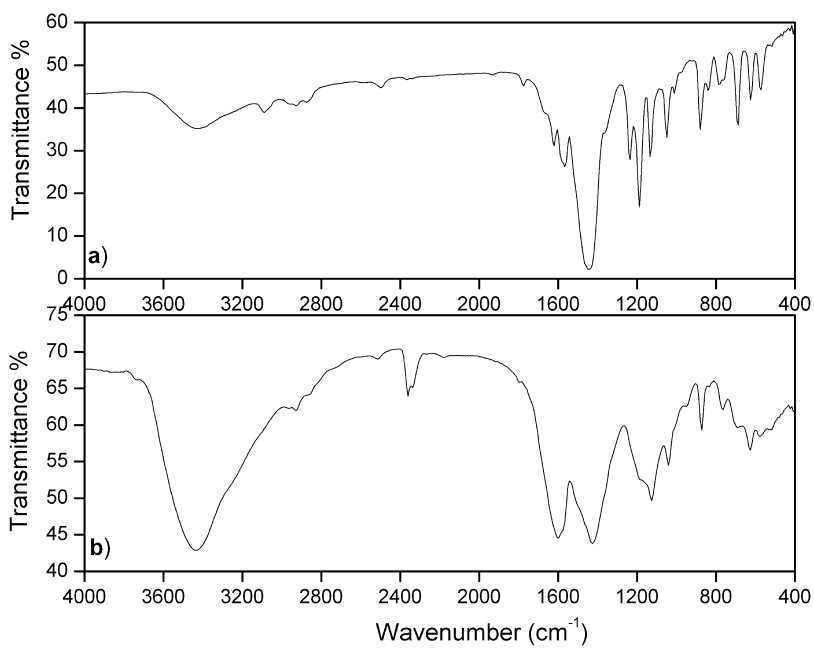


Figure 3. FT-IR spectrum of (a) ThSA and (b) PThSA.

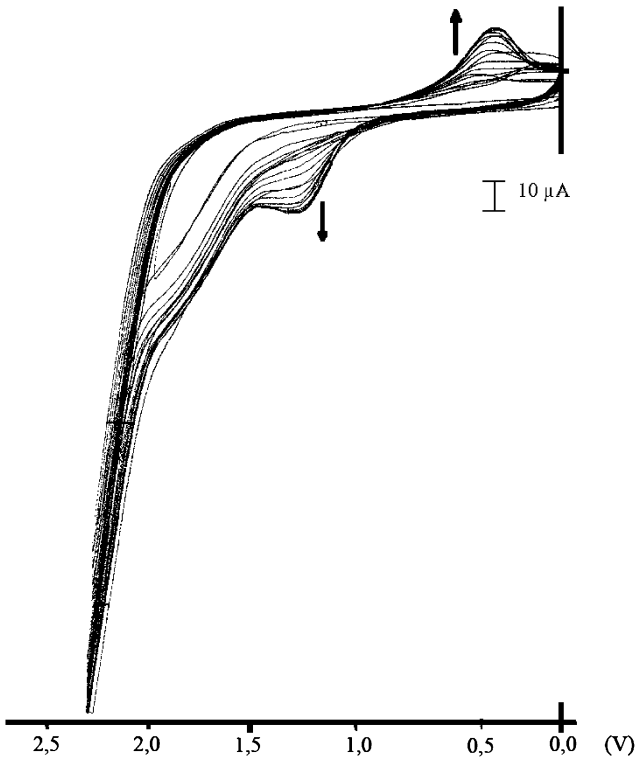


Figure 4. Cyclic voltammogram of PThSA.

and +2.5 V was scanned, electroactivity increased with increasing scan number (Fig. 4).

3.4. Conductivity of the Film

Electrical conductivity of the polymer materials was measured at room temperature by using four-probe technique with a home made instrument. Pellets of the polymer for conductivity measurement were prepared by hydraulic press. The conductivities of electrochemically prepared PThSA was measured as 2×10^{-5} S/cm.

3.5. Thermal Analysis

DSC thermograms were examined in the range between 25 and 450°C at a heating rate of 10°C/min. DSC thermograms of ThSA and PThSA show differences in thermal behavior. The DSC thermogram of ThSA exhibits two thermal events; decomposition at 382.64°C and 407.31°C (Fig. 5). The DSC thermogram of PThSA exhibits no thermal events, as expected for the entrapped solvent (Fig. 6). There is no peak referring to doping anions, which proves that the conductive polymer is self-doped.

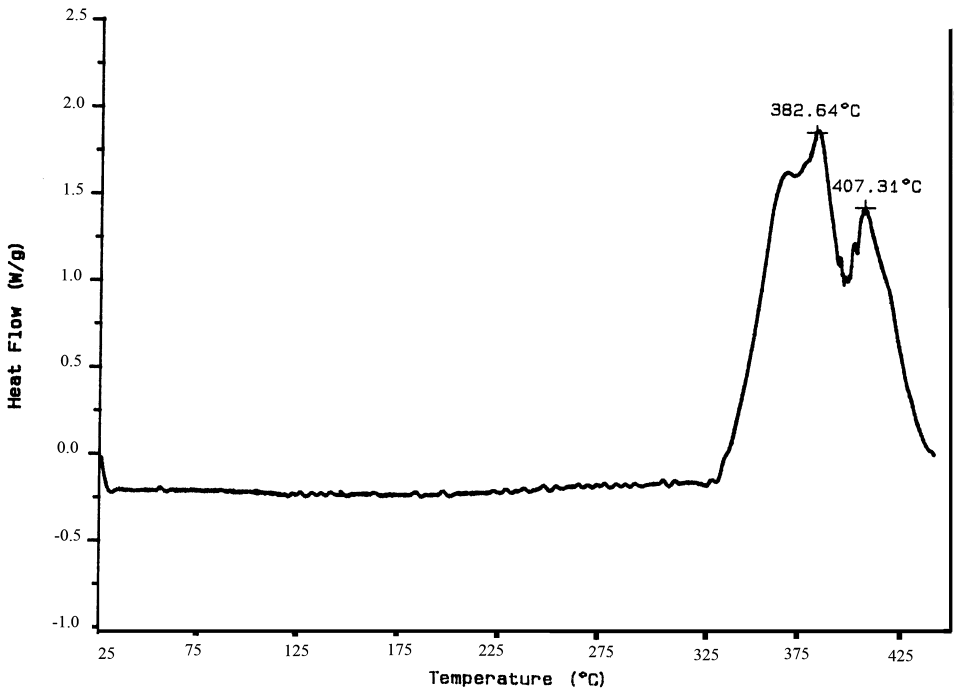


Figure 5. DSC thermogram of ThSA.

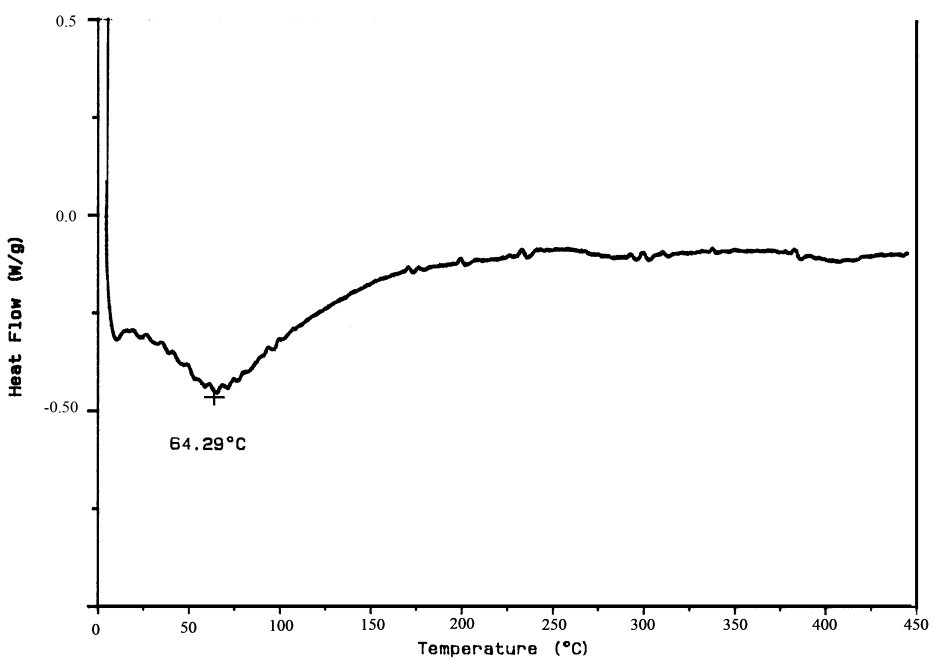


Figure 6. DSC thermogram of PThSA.

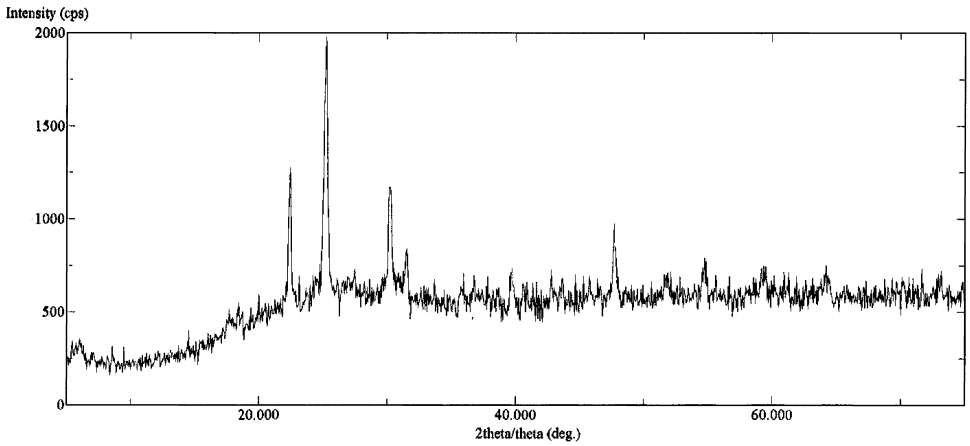


Figure 7. X-ray diffraction pattern of PThSA.

3.6. X-Ray Diffraction Studies

X-ray diffraction data for PThSA indicated that polythiophene was polycrystalline (Fig. 7). The crystallinity in the compensated sulfonated polythiophene may be due to the sodium sulfonate moieties in the polythiophene lattice. Amorphous structures are common in polypyrroles, the main exception being polypyrroles doped by sulfonic acids with rather long alkyl chains. An X-ray diffraction peak at low angle was taken as an evidence of ordered stacking of parallel main chains separated by the dopant molecules [11].

4. Conclusion

In this study, a thiophene-functionalized monomer 4-(thiophen-3-yl methyleneamino)benzenesulfonate) was successfully synthesized. A tedious purification of the sodium salts of these monomers for self-doped polythiophene has been adopted. The polymerization of the monomer was achieved *via* electrochemical methods. As a result of the electrochemical polymerization, a water-soluble polymer was produced. X-ray analysis shows that the polymer is polycrystalline. The structures of both the monomer and the water-soluble polymer were investigated by ^{1}H-NMR and FT-IR.

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References

1. T. A. Skotheim, *Handbook of Conducting Polymers*, Vol. 1. Marcel Dekker, New York, NY (1986).

2. T. A. Skotheim, *Handbook of Conducting Polymers*, Vol. 2. Marcel Dekker, New York, NY (1986).
3. A. O. Patil, Y. Ikenoue, N. Basescu, N. Colneri, J. Chen, F. Wudl and A. J. Heeger, *Synth. Met.* **20**, 151 (1987).
4. A. O. Patil, Y. Ikenoue, F. Wudl and A. J. Heeger, *J. Am. Chem. Soc*. **109**, 1858 (1987).
5. Y. Ikenoue, J. Chiang, A. O. Patil, F. Wudl and A. J. Heeger, *J. Am. Chem. Soc.* **110**, 2983 (1988).
6. E. E. Havinga, W. Ten Hoeve, E. W. Meijer and H. Wynberg, *Chem. Mater.* **1**, 650 (1989).
7. G. Zotti, S. Zecchin, G. Schiavon, A. Berlin, G. Pagani and A. Canavesi, *Chem. Mater.* **9**, 2940 (1997).
8. S. A. Chen and M. Y. Hua, *Macromolecules* **26**, 7108 (1993).
9. M. I. Arroyo-Villan, G. A. Diaz-Quijada, M. S. A. Abdou and S. Holcroft, *Macromolecules* **28**, 975 (1995).
10. S. Tarkuc, E. Sahmetlioglu, C. Tanyeli, I. M. Akhmedov and L. Toppare, *Electrochim. Acta* **51**, 5412 (2006).
11. W. Wernet, M. Monkenbusch and G. Wegner, *Makromol. Chem. Rapid Commun.* **5**, 157 (1984).