

Spectroelectrochemistry of intrinsically conducting furan-3-chlorothiophene copolymers

Fadi Alakhras · Rudolf Holze

Received: 6 March 2007 / Accepted: 3 May 2007 / Published online: 1 June 2007
© Springer-Verlag 2007

Abstract Electrochemical copolymerization of furan and 3-chlorothiophene was performed at constant electrode potential in a binary solvent system consisting of boron trifluoride diethyl etherate + ethyl ether (BFEE + EE; ratio 1:2) and trifluoroacetic acid (10% by volume). The homopolymers and copolymers obtained were studied with cyclic voltammetry, in situ ultraviolet–visible spectroscopy, in situ resonance Raman spectroscopy, and in situ conductivity measurements. The spectroelectrochemical properties of the copolymers show intermediate features between polyfuran and poly(3-chlorothiophene). The conductivity changes of homo- and copolymer films are almost completely reversible when the potential shift direction is reversed.

Keywords Polyfuran · Poly(3-chlorothiophene) · Electropolymerization · In situ UV–vis spectroscopy · In situ resonance Raman spectroscopy · In situ conductivity

Introduction

Conducting polymers have been studied intensively since the 1970s. Initially, it was the inorganic polysulfonitrile (SN)_x that was discovered to be highly conducting, but interest soon turned to organic polymers, in the hope of exploiting conventional plastics processing technology for the processing of the materials.

Continuous development and research in conductive polymers has revealed numerous areas of application such as materials for battery electrodes [1], gas sensors [2], chemical sensors [3–10], biosensors [11–14], ion sieving [15], corrosion protection [16], and microwave shielding [17].

Among conducting polymers with an extended π -electron system, polyfuran is interesting because of its possible technological applications as a humidity sensor [18]. Polyfuran is very sensitive to humidity, and its electrical resistivity decreases considerably and reversibly upon contact with moisture. In addition, polyfuran can be used as an optoelectronic device, as upon doping, the color changes from yellow-brown to black-brown [19].

Polyfuran is among the most ill defined of conjugated polymers when compared to, e.g., polypyrrole or polythiophene. Polyfuran has been synthesized previously, results pertaining to electrochemical behavior, electrical conductivity, infrared spectroscopy, Raman spectroscopy, and the mechanism of the electrochemical polymerization have been reported [20–26]. Free-standing polyfuran films have been successfully synthesized by electrochemical polymerization of furan at low electrode potential ($E_{\text{Ag}/\text{AgCl}} = 1.2$ V) in a binary solvent system containing boron trifluoride diethyl etherate (BFEE) and additional ethyl ether (EE). The polymer shows good mechanical properties; its electrical conductivity is around 10^{-2} S cm⁻¹ [27].

Polythiophene is an environmentally stable conjugated polymer in both the neutral-insulating and doped-conducting states [28–30]. Much interest has been generated in studies of substituted polythiophenes in view of the fact that introduction of substitutions in the monomers influences significantly the properties of the resulting polymers. A wide range of substituted thiophene-based polymers has gained popularity and importance in conducting polymer

F. Alakhras · R. Holze (✉)
Institut für Chemie, AG Elektrochemie,
Technische Universität Chemnitz,
09107 Chemnitz, Germany
e-mail: rudolf.holze@chemie.tu-chemnitz.de

research [31–33]. However, only few articles have reported poly(3-halide thiophene)s [34–38].

Poly(3-chlorothiophene) films were synthesized electrochemically by direct oxidation of 3-chlorothiophene in mixed electrolytes of BFEE and trifluoroacetic acid (TFA) or sulfuric acid (SA) [39, 40]. The addition of a super acid, such as TFA or simply SA, to BFEE decreases the oxidation potential of the monomer and improves the general quality of the polymer film [41, 42].

Copolymerization is an important method to modify the properties of individual homopolymers. So far, electrochemical copolymerization of furan and 3-methyl thiophene was performed potentiostatically in a binary solvent system consisting of BFEE and additional EE (ratio 2:1) [43]. Recently, in our laboratory, electrochemical copolymerization of furan and thiophene was successfully realized in a binary solution system consisting of BFEE and additional EE at constant electrode potential; the spectroelectrochemical properties of these films were investigated [44–46].

According to our knowledge, there are no reports concerning the electrochemistry of furan-3-chlorothiophene copolymer films. We report here the electrochemical copolymerization of furan and 3-chlorothiophene in the mixed solvent system composed of BFEE + EE (ratio 2:1) with added TFA (10% by volume). The spectroelectrochemical properties of these copolymers were investigated and compared with those of the respective homopolymers.

Experimental

Furan (Aldrich, 99%) and 3-chlorothiophene (Aldrich, 98%) were distilled under nitrogen just before use. EE (Acros) was dried and distilled in the presence of sodium. BFEE (Acros, 48% BF₃) was used as received. Tetrabutylammonium tetrafluoroborate (TBATFB; Aldrich, 99%) was dried under vacuum at 80 °C for 24 h. TFA (Riedel-deHaën, 99%) and acetonitrile (Merck, anhydrous, <10 ppm H₂O) were used without further purification.

Electropolymerization of furan and 3-chlorothiophene was performed potentiostatically in a BFEE + EE (ratio 1:2) and TFA (10% by volume) solution containing, in addition, 0.1 M TBATFB in a one-compartment three-electrode cell at room temperature at constant electrode potential for 2 min. The constant electrode potentials for preparation of copolymer films were chosen according to the threshold polymerization potentials of the homopolymers. Copolymers are labeled according to molar ratio of the monomers in the polymerization solution and to the deposition potential: (a) furan/3-chlorothiophene (mole ratio 1:1), $E_{\text{Ag}/\text{AgCl}}=1.5$ V, (b) furan/3-chlorothiophene (mole ratio 1:1), $E_{\text{Ag}/\text{AgCl}}=1.7$ V, (c) 0.10 M furan and 0.0125 M 3-chlorothiophene (mole ratio 1:8), $E_{\text{Ag}/\text{AgCl}}=1.5$ V, and (d)

0.10 M furan and 0.0125 M 3-chlorothiophene (mole ratio 1:8), $E_{\text{Ag}/\text{AgCl}}=1.7$ V.

A platinum sheet electrode (approximate surface area 1.5 cm²) was used as working electrode, a nonaqueous Ag/AgCl electrode filled with acetonitrile containing 0.1 M TBATFB saturated with AgCl as reference electrode. After polymerization, the film was washed with acetonitrile to remove any traces of mono- and oligomers.

Cyclic voltammetry of the polymers was carried out in a monomer-free acetonitrile solution containing 0.1 M TBATFB as supporting electrolyte. Before every experiment, the solution was deaerated by bubbling with N₂. The reference electrode potential was verified frequently with respect to an aqueous saturated calomel electrode because the employed nonaqueous reference electrode system is prone to potential drift [47]. A custom-built potentiostat interfaced to a standard PC via an ADDA-converter card operating with custom-developed software was used to record cyclic voltammograms (CVs).

Ultraviolet–visible (UV–vis) spectra were recorded for homo- and copolymer films deposited on an optically transparent indium tin oxide (ITO) glass electrode (Merck) in the supporting electrolyte solution in a standard 10-mm cuvette using a Shimadzu UV 2101-PC instrument (resolution 0.1 nm); a cuvette with the same solution and an uncoated ITO glass was placed in the reference beam. The absorption maximum $\lambda_{1\text{max}}$ assigned to the $\pi \rightarrow \pi^*$ transition is observed with the polymer in its neutral state. The absorption maximum $\lambda_{2\text{max}}$ was assigned to an intra-band transition from the valence band into the upper bi-polaron band of the polymer in its oxidized state. The electrode potential where the UV–vis spectrum was measured depended on the type of polymer, it was always positive to the polymer oxidation peak as observed in the respective CVs (see Figs. 2 and 3). Because maxima are weak and shift considerably as a function of electrode potential, all numbers are approximate only.

For the in situ conductivity measurements, the homo- and copolymer films were deposited on a two-band Pt electrode in a one-compartment three-electrode cell. For conductivity measurements, this electrode was connected to a specially designed electrical circuit supplying 10 mV of direct current voltage across the two Pt strips [48, 49]. To ensure good bridges over the gap, CVs of the deposited films on the two-band electrode were recorded before each series of conductivity measurements in the electrolyte solution. Deposition time was 2 min in all experiments; because of the necessary variation of the deposition potential and conceivable different rates of polymerization, the actually deposited amounts of polymer may vary.

A platinum disc electrode (2 × 5 mm) embedded in epoxy resin was used as working electrode for Raman spectroscopy. The platinum disc electrode was polished with

diamond polishing paste down to 0.3 μm and then to 0.05 μm with aqueous alumina slurry. Raman spectra of homo- and copolymer films were recorded using an ISA T64000 spectrometer (Jobin-Yvon) connected to a liquid nitrogen-cooled Spectraview 2D CCD detection system. The spectra were measured using 647.1 nm exciting laser light provided by Coherent Innova 70 series ion laser; the laser power was always maintained at 70 mW to avoid destruction of the samples.

Results and discussion

Electrochemical polymerization and electrochemistry

CVs of a platinum working electrode in the polymerization solution containing the monomers are given in Fig. 1. The background electrolyte solution is electrochemically silent in the whole potential range. The polymerization threshold (the lowest potential needed to sustain growth of a polymer layer) of furan is $E_{\text{Ag}/\text{AgCl}}=1.35$ V (curve a) and of 3-chlorothiophene $E_{\text{Ag}/\text{AgCl}}=1.55$ V (curve c). The addition of TFA (10% by volume) to BFEE + EE (ratio 1:2) decreased the oxidation potential of the monomers; the polymerization rate was also accelerated because TFA increases the ionic conductivity of the electrolyte [40]. The small difference between the oxidation potentials of the two monomers suggests a large probability of copolymerization of the two monomers. Curve b was obtained when a current–potential curve was taken in a solution containing 0.1 M furan and 0.1 M 3-chlorothiophene. The oxidation potential of the mixture of furan and 3-chlorothiophene is around $E_{\text{Ag}/\text{AgCl}}=1.40$ – 1.50 V, which is between the oxidation potentials of the two monomers, implying that

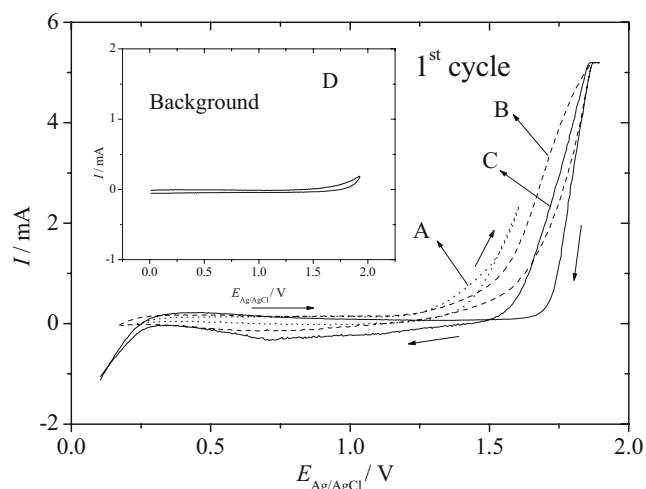


Fig. 1 CVs of (A) 0.1 M furan, (B) 0.1 M furan and 0.1 M 3-chlorothiophene, (C) 0.1 M 3-chlorothiophene, (D) no monomer in 0.1 M TBATFB in BFEE + EE (ratio 1:2) and TFA (10% by volume). $dE/dt=100$ mV/s

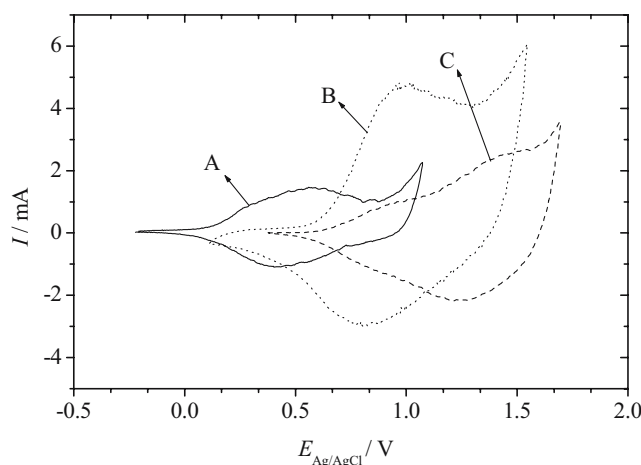


Fig. 2 CVs recorded in a solution of acetonitrile+0.10 M TBATFB: (A) polyfuran deposited at $E_{\text{Ag}/\text{AgCl}}=1.35$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M furan, (B) copolymer deposited at $E_{\text{Ag}/\text{AgCl}}=1.7$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M furan and 0.0125 M 3-chlorothiophene, (C) poly(3-chlorothiophene) deposited at $E_{\text{Ag}/\text{AgCl}}=1.55$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M 3-chlorothiophene. $dE/dt=100$ mV/s

oxidation of both monomers is likely, the copolymer chains may accordingly be composed of both furan and 3-chlorothiophene units [43].

The CVs of polyfuran, the copolymer (D) deposited at $E_{\text{Ag}/\text{AgCl}}=1.70$ V from a solution obtained from a BFEE + EE (ratio 1:2) and TFA (10% by volume) solution containing 0.10 M furan and 0.0125 M 3-chlorothiophene and poly(3-chlorothiophene) in the acetonitrile-based supporting electrolyte solution are shown in Fig. 2. For polyfuran, there is a broad anodic peak at $E_{\text{Ag}/\text{AgCl}}=\sim 0.57$ V caused by polymer oxidation and a corresponding broad cathodic peak around $E_{\text{Ag}/\text{AgCl}}=\sim 0.43$ V due to polymer reduction with a peak potential difference of 0.14 V. For poly(3-chlorothiophene), the respective peaks are at $E_{\text{Ag}/\text{AgCl}}=\sim 1.40$ V and at $E_{\text{Ag}/\text{AgCl}}=\sim 1.24$ V, with a difference of 0.16 V. The difference and the broad, poorly defined current waves are commonly observed in the electrochemistry of intrinsically conducting polymers (ICPs) due to a number of factors including the diffusion of the dopant ions in and out of the film and the change of the conformation of the polymer chain during the redox processes [23, 27]. Substituted polythiophenes prepared from nonsymmetric monomers usually show broad redox waves in their CVs [50]. This phenomenon is ascribable to the presence of coupling defects distributed statistically, this results in a series of energetically nonequivalent chain segments.

The copolymer shows in its typical CV only one anodic/cathodic peak couple at a position quite different from the positions observed with the homopolymers. The appearance of one redox peak implies that if only a single redox

process occurs, the polymer thus behaves uniformly (instead of two redox processes as observed with, e.g., a heterogeneous mixture or a composite material). In addition, it is noteworthy that both the cathodic and the anodic current are higher than those found with the homopolymers. Taking the peak current as an indicator of redox capacity implying that the amount of deposited copolymer is higher after the same time of electropolymerization (2 min).

Electrochemical copolymerization both at different potentials and with different thiophene concentrations was investigated. Fig. 3a shows CVs of the copolymers (A) and (B) obtained by electropolymerization in solutions containing 0.1 M furan and 0.1 M 3-chlorothiophene at $E_{\text{Ag}/\text{AgCl}} = 1.5$ and 1.7 V. The redox peak potential of the copolymers shifts to higher potentials with increasing polymerization potential of the copolymer. This indicates that more 3-

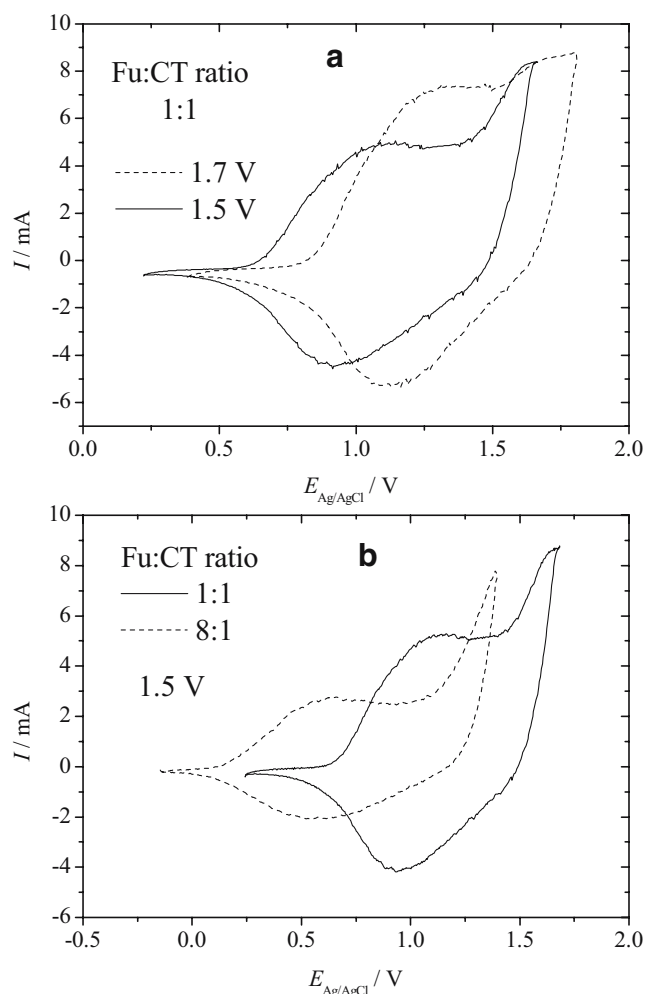


Fig. 3 **a** CVs recorded at $dE/dt = 100$ mV/s in acetonitrile + 0.10 M TBATFB solution of copolymers deposited at $E_{\text{Ag}/\text{AgCl}} = 1.5$ and 1.7 V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 1:1); **b** deposited at $E_{\text{Ag}/\text{AgCl}} = 1.5$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 1:1 and 8:1)

Table 1 Peak potentials of the copolymers prepared at $E_{\text{Ag}/\text{AgCl}} = 1.50$ and 1.70 V from BFEE + EE (ratio 1:2) and TFA (10% by volume) solutions containing different monomer feed ratio

Fu/ClTh (mole ratio)	$E_{\text{pol}} = 1.50$ V		$E_{\text{pol}} = 1.70$ V		PFu ($E_{\text{pol}} = 1.35$ V)		PClTh ($E_{\text{pol}} = 1.55$ V)	
	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V	E_{pa}/V	E_{pc}/V
1:1	1.10	0.92	1.30	1.11	0.57	0.43	1.40	1.24
8:1	0.62	0.60	0.97	0.80				

Peak potentials of homopolymers are added for comparison.

chlorothiophene units are incorporated into the copolymer with increasing preparation potential.

When the furan/3-chlorothiophene feed ratio is changed from 1:1 to 8:1, CVs as shown in Fig. 3b are obtained. Only one redox peak couple appears. When comparing the CVs of the copolymers prepared at the same polymerization potential in these different solutions, it is observed that lower concentration of thiophene leads to a negative shift of the redox peak potentials of the copolymer. This implies that more 3-chlorothiophene units are incorporated into the copolymer film when the concentration of 3-chlorothiophene is increased.

The electrochemical characteristics of the homopolymers and copolymers displayed in Fig. 2 and Fig. 3b indicate that keeping the potential of electrosynthesis of copolymers formed in mixed solutions near the threshold potential for electropolymerization of furan may result in the furan-based copolymers and vice versa.

The peak potential values of the copolymers prepared at different potentials from these three different solutions are listed in Table 1, the peak potentials of the homopolymers are added for comparison.

In situ UV–vis spectroscopy

The in situ UV–vis absorption spectra of polyfuran and poly(3-chlorothiophene) are displayed for reference in Fig. 4. Polyfuran shows a broad absorption band around 407 nm in the neutral state. This broad absorption band with $\lambda_{1\text{max}}$ corresponds to the $\pi \rightarrow \pi^*$ transition, the width indicates the coexistence of segments of both long and short effective conjugation length in the polyfuran films.

In an extended system, the band gap (E_g) can be defined as the difference between the lowest energy in the conduction band and the highest energy in the valence band. According to the zero-order approximation, this is equal to the lowest excitation energy, which can be obtained from the onset value at the lower energy edge of the optical absorption spectra [51, 52]. E_g for polyfuran from a direct inter-band transition can be estimated from the

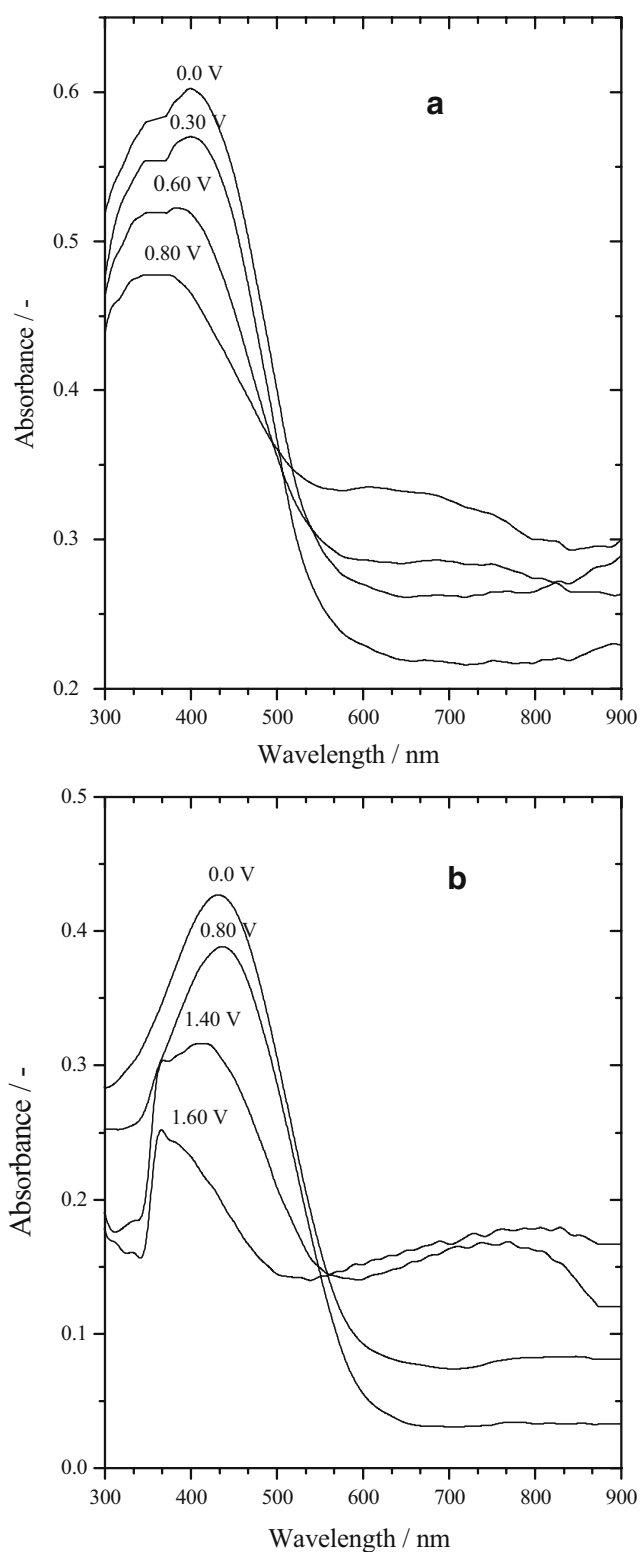


Fig. 4 In situ UV-vis spectra recorded at different applied potentials in a solution of acetonitrile+0.1 M TBATFB of **a** polyfuran deposited at $E_{Ag/AgCl}=1.35$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M furan, **b** poly(3-chlorothiophene) deposited at $E_{Ag/AgCl}=1.55$ V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M 3-chlorothiophene

absorption edge (~ 530 nm) of the spectrum to be about 2.34 eV very close to the value reported in the literature [23] and in our previous work [45].

The passage from the undoped to the doped state is accompanied by weakening as well as a blue shift of the absorption band in the visible and shifting into near infrared (NIR) upon further oxidation. The optical transition with λ_{2max} from the valence band into the higher bi-polaron band (the higher subgap state) is located at 680 nm (1.82 eV), see below and Fig. 5. This assignment has been previously suggested [23, 45].

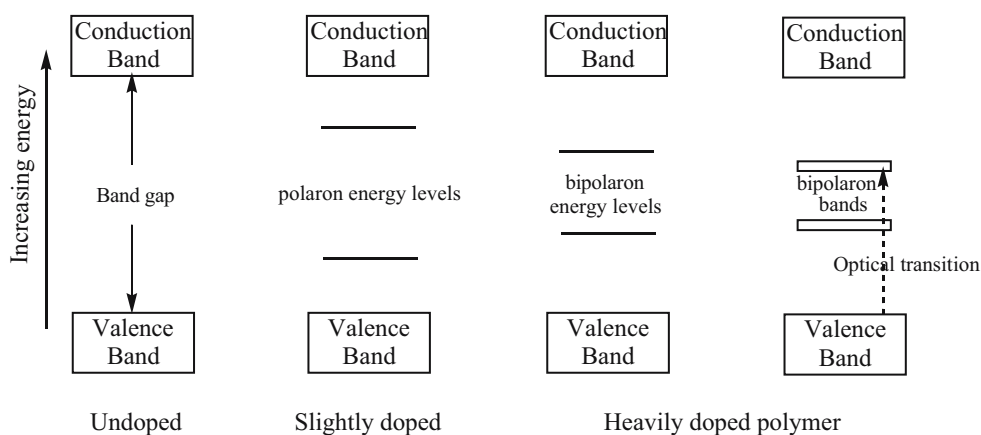
In oxidized polyfuran, furan units have positive charges partially delocalized over several polymer segments and balanced by so-called dopant anions. When a negative potential is applied to the film, anions are expelled from the polymer film (undoping), thus transforming it to the reduced state. As an alternative or competitive process, ingress of cations may occur. Conversely, when a positive potential is applied to oxidize the neutral film (doping), anions are taken up [53, 54], or the cations may be released. Energy levels, conduction and valence bands, as well as optical transitions for polyfuran are shown in Fig. 5 as previously suggested for other ICPs like, e.g., polypyrrole [55].

Poly(3-chlorothiophene) Fig. 4 (b) exhibits an absorption maximum at 440 nm in the neutral state. This broad absorption band corresponds to the $\pi \rightarrow \pi^*$ transition, the width implies again the coexistence of both long and short effective conjugation lengths. Upon oxidation, this absorption almost vanishes; instead, a very broad feature raises around 770 nm (1.61 eV) with its maximum λ_{2max} shifting into the NIR upon further oxidation. E_g for poly(3-chlorothiophene) for the direct inter-band transition between the highest occupied molecular orbital and the lowest unoccupied molecular orbital can be deduced from the energy of the absorption edge (~ 580 nm) of the spectrum at about 2.14 eV. In the band gap, lower and upper polaron/bi-polaron states are formed, the lower ones are located 1.61 eV above the valence band. The absorption bands and band gaps of polyfuran and poly(3-chlorothiophene) are listed in Table 2.

As the steric hindrance of the substituents at the three positions is a major factor interrupting the coplanarity of adjacent thiophene rings, which in turn leads to loss of inter-ring conjugation [56, 57], one would expect the π -conjugation length in the three-substituted polymers to reduce appreciably with bulkier halogen substituents. The slight difference between the band gap in poly(3-chlorothiophene) and that in polythiophene which is around 0.04 eV shows that Cl substituents do not influence the inter-ring π -conjugation significantly, as the inter-ring twist angle is relatively small in the solid state [28].

Figure 6 shows the in situ UV-vis spectra of the copolymers (A...D) obtained from solutions of BFEE +

Fig. 5 Energy levels, conduction, and valence bands in doped polyfuran. For assignment of optical transitions, see text



EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 1:1 and 8:1) at deposition potentials $E_{\text{Ag}/\text{AgCl}}=1.7$ and 1.5 V, respectively. The copolymers have a broad absorption band in the neutral state corresponding to the $\pi \rightarrow \pi^*$ transition indicating the coexistence of both long and short effective conjugation lengths containing furan and 3-chlorothiophene monomer units. A remarkable characteristic of the UV–vis spectra is the shift of the broad absorption band in the neutral state of the copolymers to higher wavelengths with increasing preparation potential of the copolymer. This indicates that more 3-chlorothiophene units are incorporated into the copolymer with increasing preparation potential. Upon oxidation, the absorption assigned to the $\pi \rightarrow \pi^*$ transition almost vanishes, instead a very broad feature rises ($\lambda_{2\text{max}}$) with its maximum shifting into NIR upon higher degree of oxidation which is attributed to polaron/bi-polaron transitions between band gap states. E_g for the copolymers prepared at potentials $E_{\text{Ag}/\text{AgCl}}=1.5$ and 1.7 V from a direct inter-band transition can also be estimated from the absorption edge ($\sim 550, 575$ nm) of the spectrum, being about 2.26, 2.16 eV, respectively, which is less than observed with polyfuran.

When the furan/3-chlorothiophene feed ratio changed from 1:1 to 8:1, these two characteristics, the appearance of a broad absorption band in the neutral state and the blue shift of the absorption band in the visible region observed upon oxidation and the appearance of absorption features in the near IR region, still exist in the UV–vis spectra. When comparing the UV–vis spectra of the copolymers prepared at the same polymerization potential in these different

solutions, it is observed that a lower concentration of 3-chlorothiophene leads to a blue shift of the absorption band of the copolymer obtained. This implies that more 3-chlorothiophene units are incorporated into the copolymer film when the concentration of 3-chlorothiophene is increased. The absorption bands and band gaps of the copolymers prepared at different polymerization potentials from these different solutions are listed in Tables 3 and 4.

In situ resonance Raman spectroscopy

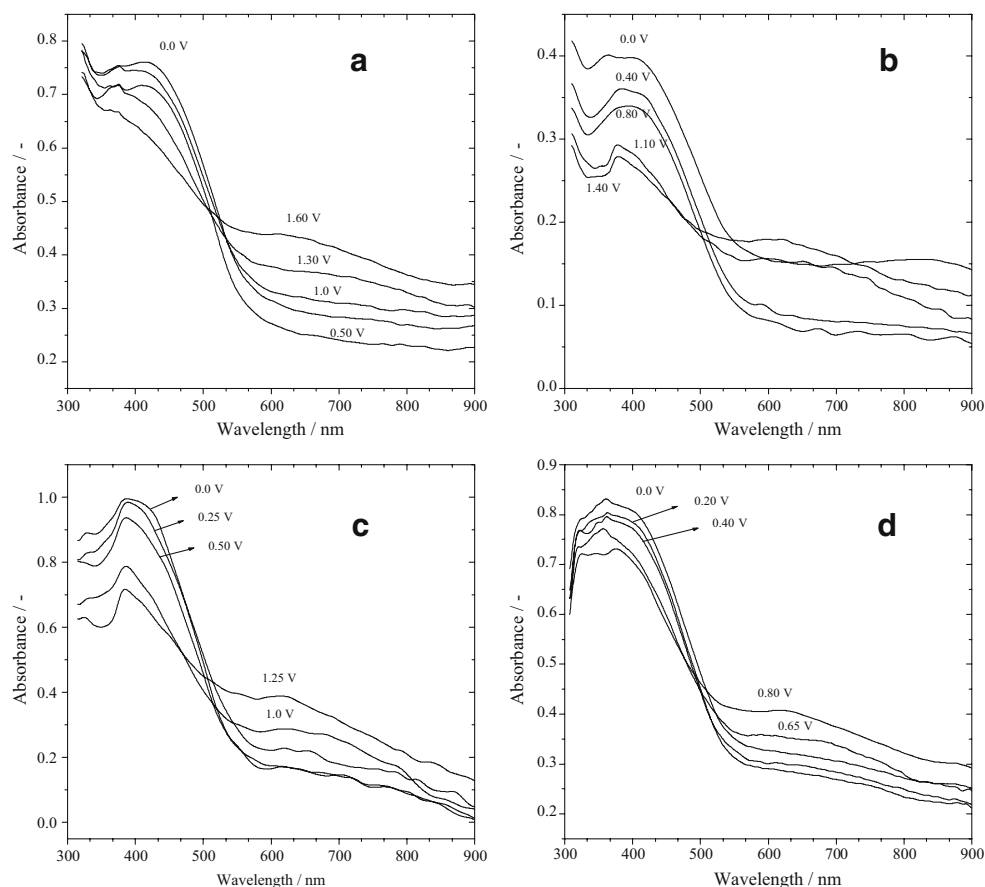
As reported previously [46], laser light at $\lambda_0=647.1$ nm is the best choice in terms of avoiding selective enhancement among the available wavelengths for studying the doping level dependence of the Raman spectra and the bands resulting from the oxidized species of doped polyfuran and polythiophenes. The in situ Raman spectra of polyfuran and polythiophene are displayed for reference in Fig. 7, respectively.

The Raman spectrum of neutral polyfuran shows six major bands at 1,590, 1,532, 1,283, 1,020, 975, and 920 cm^{-1} . These bands are assigned to modes of pristine polyfuran [58]. Polyfuran symmetric C=C intra-ring stretching vibration and C–C intra-ring stretching vibration were observed at 1,532–1,590 cm^{-1} [59, 60]. The band located at 1,283 cm^{-1} is assigned to C–C and C–O ring stretching vibration [61, 62], whereas C–H in-plane deformation modes are located around 1,020 and 975 cm^{-1} [63, 64]. The band located around 920 cm^{-1} is assigned to an in-plane ring deformation and the C–O ring stretching vibration [65, 66]. Furthermore, another noticeable feature in the spectrum is a band around 920 and 850 cm^{-1} , which is characteristic of two-substituted five-membered heterocyclic compounds, suggesting that α -position in the polymer are involved in the polymerization [67, 68]. These results are completely in agreement with our last report [46]. In this spectrum, several weak bands or shoulders are also present at 1,470, 1,370, 1,140, and 1,210 cm^{-1} . The two bands at 1,470 and 1,210 cm^{-1} are assigned to C–H out-of-plane bending, while the bands at 1,370 and

Table 2 Absorption bands and band gaps of polyfuran and poly(3-chlorothiophene)

Homopolymer	$\lambda_{1\text{max}}$		$\lambda_{2\text{max}}$		Band gap	
	nm	eV	nm	eV	nm	eV
Polyfuran	407	3.05	680	1.82	530	2.34
Poly(3-chlorothiophene)	440	2.82	770	1.61	580	2.14

Fig. 6 In situ UV–vis spectra recorded at different applied potentials in a solution of acetonitrile+0.1 M TBATFB of copolymers deposited at $E_{Ag/AgCl}$ (a) 1.7 V, (b) 1.5 V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 1:1), (c) 1.7 V, (d) 1.5 V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 8:1)



1,140 cm^{-1} are related to C–C and C–O stretching vibrations, respectively, [61]. The oxidation potential of polyfuran in acetonitrile-based electrolyte solution is measured to be $E_{Ag/AgCl} \sim 0.57$ V. Thus, at potentials < 0.57 V, the overall features of the Raman spectra are similar to those of neutral polyfuran. With the increase in applied potential, the Raman bands at 1,470, 1,370, 1,140, and 1,210 cm^{-1} are enhanced gradually, whereas the bands associated with the neutral species of polyfuran are still present. Therefore, it is reasonable to conclude that the enhanced bands are caused by the oxidized species of polyfuran. At $E_{Ag/AgCl} = 0.8$ V, the entire spectrum is similar to that of doped polyfuran [26].

The in situ Raman spectra of polyfuran suggest that most of the conjugated structures in polymer chains remain

undestroyed. This may be because overoxidation takes place only at the electrochemically active sites, which may be positively charged sites (polaron) in the chain, and not all the furan rings are defective. Polyfuran shows a strong localization at the site of the electronic perturbation, i.e., the delocalization of the electrons along the polymer backbone is restricted to several furan rings, as a result, the defects of the electrochemically active sites may cause no considerable changes of the effective conjugation length [69].

The in situ Raman spectra of poly(3-chlorothiophene) show a weak fluorescence background and a high signal-to-noise ratio. The band around 1,400–1,500 cm^{-1} is a common feature of Raman spectra of aromatic and heteroaromatic systems; it is always strong and dominates the entire Raman spectrum [70]. As can be seen in Fig. 7b,

Table 3 Absorption bands and band gaps of copolymers obtained from BFEE + EE (ratio 1:2) and TFA (10% by volume) solutions containing 0.10 M furan and 0.10 M 3-chlorothiophene at potentials $E_{Ag/AgCl} = 1.5$ and 1.7 V

Polymerization potential ($E_{Ag/AgCl}$)	$\lambda_{1\text{max}}$		$\lambda_{2\text{max}}$		Band gap	
	nm	eV	nm	eV	nm	eV
1.5	415	2.99	705	1.76	550	2.26
1.7	431	2.88	720	1.72	575	2.16

Table 4 Absorption bands and band gaps of copolymers obtained from BFEE + EE (ratio 1:2) and TFA (10% by volume) solution containing furan/3-chlorothiophene (mole ratio 8:1) at potentials $E_{Ag/AgCl} = 1.5$ and 1.7 V

Polymerization potential ($E_{Ag/AgCl}$)	$\lambda_{1\text{max}}$		$\lambda_{2\text{max}}$		Band gap	
	nm	eV	nm	eV	nm	eV
1.5	410	3.03	690	1.80	540	2.30
1.7	420	2.95	700	1.77	555	2.24

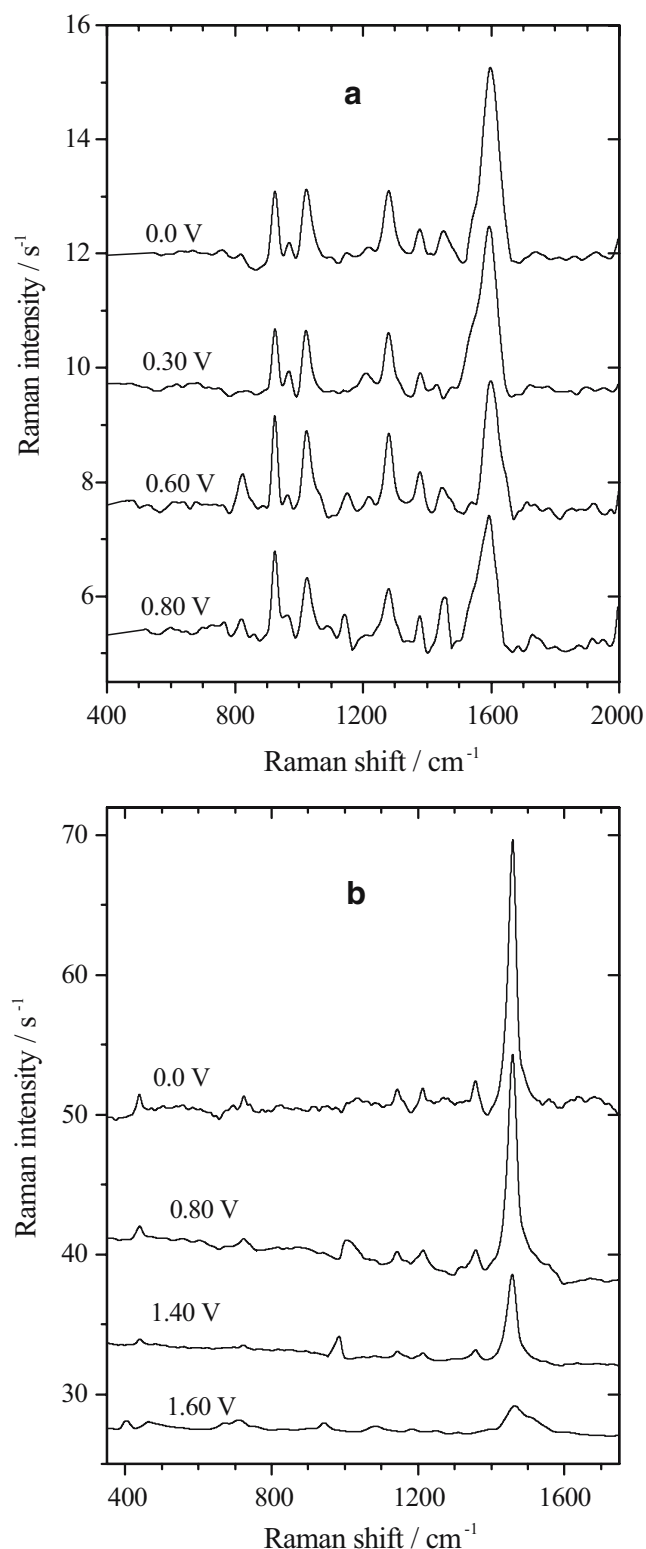


Fig. 7 In situ resonance Raman spectra recorded in a solution of acetonitrile+0.1 M TBATFB of (a) polyfuran deposited at $E_{\text{Ag}/\text{AgCl}} = 1.35$ V from BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M furan, (b) poly(3-chlorothiophene) deposited at $E_{\text{Ag}/\text{AgCl}} = 1.55$ V from BFEE + EE (ratio 1:2) and TFA (10% by volume) containing 0.1 M 3-chlorothiophene, spectra offset for clarity

the most intense band is located at approximately $1,468 \text{ cm}^{-1}$ and is assigned to the totally symmetric in-plane C=C vibration of bulk thiophene rings spread over the whole polymer chain [40, 71, 72]. A decrease in the intensity and a broadening of the band at higher wave numbers (tail) is observed; weaker bands located therein have been assigned to the corresponding asymmetric C=C stretching mode when the polymer film passed from the neutral state to the oxidized form. This is related to changes in the conjugation length distribution in the poly(3-chlorothiophene) skeleton, as the broadness of the tail has been used as an argument for the presence of shorter polymer units and this tail increased with an increase in electrode potential [73, 74]. Bathochromic shift of the C=C skeleton vibration from $1,468$ to $1,450 \text{ cm}^{-1}$ is associated with the increase in applied potential, which is attributed to the symmetric stretching vibration of C=C bond ring of radical cations (quinoid) [39, 75]. The band at $1,357 \text{ cm}^{-1}$ in the spectrum of the neutral state is also found at $1,376 \text{ cm}^{-1}$ in the spectrum of oxidized state and is assigned to the C–C intra-ring symmetric stretching vibration [76, 77]. The well-defined scattering near $1,157 \text{ cm}^{-1}$ is associated with the asymmetric stretching vibration of C–C bonds. Upon doping, this band shifts upwards to $1,162 \text{ cm}^{-1}$ [78].

The bands at 927 and 827 cm^{-1} are assigned to C–H out-of-plane deformations [79], while the bands at 754 and 710 cm^{-1} are related to C–S–C in-plane deformation [80]. Finally, the band ascribable to the C–Cl in-plane deformation observed at 439 cm^{-1} remains basically unchanged when the neutral polymer is oxidized [39, 40].

The observed broadening and blue shift could be attributed to changes in the conjugation length distribution in the polymer chains. This conjugation length associated with π -electron delocalization is favored when the polymer rings are coplanar, owing to the maximum overlap of the C–C inter-ring carbon p_z orbitals. The oxidation produces distorted parts in the polymer, thus reducing the coplanarity of the rings and, therefore, the conjugation length [81]. Comparing the Raman spectra of neutral and oxidized forms of poly(3-chlorothiophene), we can observe that the overall intensity decreased upon increasing the applied potential. This intensity difference is probably caused by a larger resonance enhancement of the reduced film, which is associated with a stronger UV–vis absorption at the laser excitation wavelength. This means that the observed Raman bands are caused by the undoped segments of the polymer which become less and less abundant with increasing doping level [82, 46]. Raman band assignments of polyfuran and poly(3-chlorothiophene) at different electrode potentials are listed in Table 5.

Raman spectra of copolymers obtained both at different polymerization potentials and with different thiophene concentrations were investigated. Fig. 8a shows that the

copolymer has a broad band around $1,552\text{ cm}^{-1}$ in the neutral state. This band corresponding to the symmetric C=C intra-ring stretching vibration suggests the coexistence of both long and short effective conjugated lengths due to furan and 3-chlorothiophene monomeric units. The greater the red shift of this peak, the longer is the effective conjugation length of the conducting polymer [83]. The C–C intra-ring symmetric stretching vibration has been assigned to the band found at $1,315\text{ cm}^{-1}$. The two bands at 930 and $1,055\text{ cm}^{-1}$ are assigned to C–H in-plane deformations, whereas the C–O ring stretching vibration band is located around $1,121\text{ cm}^{-1}$. The bands at 756 and 662 cm^{-1} are related to C–S–C in-plane deformation. The band observed at 843 cm^{-1} ascribed to the C–H out-of-plane deformation mode indicates that α - α' coupling of radical cations has taken place during copolymerization. This is a characteristic of α -substituted five-membered heterocyclic compounds. It is noticed that the features of the Raman spectra of the copolymer are between the features of the Raman spectra of both homopolymers, implying that oxidation of both monomers is possible and the copolymer chains may accordingly be composed of alternate furan and 3-chlorothiophene units.

Comparing Fig. 8a with b, one can notice that the broad band which corresponds to the symmetric C=C intra-ring stretching vibration in the neutral state of the copolymers

shifts to lower wave numbers and the intensity of this band also increases with increasing the preparation potential of the copolymers. When prepared at $E_{\text{Ag}/\text{AgCl}}=1.5\text{ V}$, the copolymer shows a broad band around $1,572\text{ cm}^{-1}$, which is close to the position of the respective band of pure polyfuran. When prepared at $E_{\text{Ag}/\text{AgCl}}=1.7\text{ V}$, the copolymer shows a band around $1,552\text{ cm}^{-1}$. By increasing the preparation potential, the band attributed to C–C ring stretching vibration shifts to lower wave numbers by 20 cm^{-1} and moves closer to that of pure poly(3-chlorothiophene). Furthermore, the band corresponding to the C–Cl in-plane deformation observed at 450 cm^{-1} shifts downwards to 441 cm^{-1} (see Table 6). In addition, the intensity of this band is also enhanced with increasing polymerization potential. This indicates that more 3-chlorothiophene units are incorporated into the copolymer chains with increasing preparation potential.

When the furan/3-chlorothiophene feed ratio is changed from 1:1 to 8:1 (0.1:0.0125 M), Raman spectra as shown in Fig. 8c and d are obtained. The same previously interesting features still exist, i.e., the C=C stretching vibration which is considered as an indicator of effective conjugation length shifts to lower wavenumber, as the concentration of 3-chlorothiophene increases in the polymerization solutions. The band which is attributed to the C–C ring stretching vibration shifts to lower values by 9 cm^{-1} closer to that of

Table 5 Raman band assignments of polyfuran and poly(3-chlorothiophene) at different electrode potentials, all figures in wave numbers per centimeter

Mode	$E_{\text{Ag}/\text{AgCl}}$							
	Polyfuran				Poly(3-chlorothiophene)			
	0.0 V	0.30 V	0.60 V	0.80 V	0.0 V	0.80 V	1.40 V	1.60 V
$\nu(\text{C}=\text{C})_{\text{ring}}$	1,590	1,593	1,597	1,590	1,468	1,458	1,453	1,450
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,532	1,540	1,534	1,532	–	–	–	–
$\omega(\text{C}-\text{H})$	1,470	1,455	1,453	1,450	–	–	–	–
$\nu(\text{C}-\text{C})$	1,370	1,376	1,380	1,383	–	–	–	–
$\nu(\text{C}-\text{C})_{\text{ring}}$	–	–	–	–	1,373	1,370	1,376	1,378
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,283	1,278	1,280	1,280	1,220	1,223	1,224	1,225
$\omega(\text{C}-\text{H})$	1,210	1,208	1,215	1,202	–	–	–	–
$\nu(\text{C}-\text{O})_{\text{ring}}$	1,140	1,152	1,149	1,142	–	–	–	–
$\nu(\text{C}-\text{C})_{\text{antisym}}$	–	–	–	–	1,157	1,150	1,158	1,162
$\delta(\text{C}-\text{H})$	1,020	1,021	1,025	1,030	1,050	1,047	1,051	1,052
$\delta(\text{C}-\text{H})$	975	970	968	973	–	–	–	–
$\gamma(\text{C}-\text{H})$	–	–	–	–	927	925	923	926
$\nu(\text{C}-\text{O})_{\text{ring}}$	920	923	924	922	–	–	–	–
$\delta(\text{Ring})$	918	919	926	923	–	–	–	–
$\gamma(\text{C}-\text{H})$	850	835	830	856	827	823	821	813
$\delta(\text{C}-\text{S}-\text{C})$	–	–	–	–	754	740	736	730
$\delta(\text{C}-\text{S}-\text{C})$	–	–	–	–	710	707	703	700
$\delta(\text{C}-\text{C})_{\text{ring}}$	–	–	–	–	656	650	650	647
$\delta(\text{C}-\text{Cl})$	–	–	–	–	439	437	437	439

δ In-plane deformation; γ out-of-plane deformation; ν stretching; ω out-of-plane bending

Fig. 8 In situ resonance Raman spectra recorded in a solution of acetonitrile+0.1 M TBATFB of copolymers deposited at $E_{\text{Ag}/\text{AgCl}}$ (a) 1.7 V, (b) 1.5 V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 1:1), (c) 1.7 V, (d) 1.5 V in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing furan/3-chlorothiophene (mole ratio 8:1), spectra offset for clarity

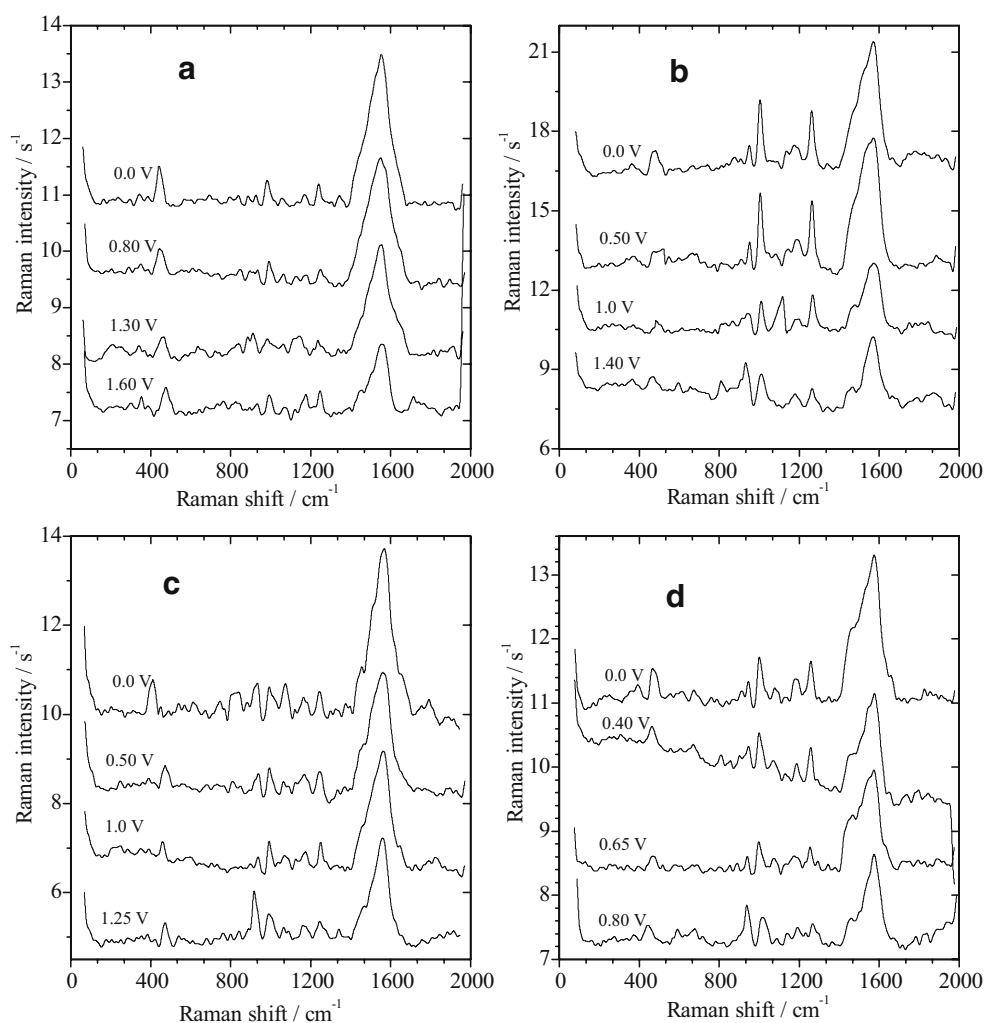


Table 6 Raman band assignments of copolymers deposited at $E_{\text{Ag}/\text{AgCl}}=1.5$ and 1.7 V in a solution containing 0.1 M furan and 0.1 M 3-chlorothiophene, all figures in wave numbers per centimeter

Mode	$E_{\text{Ag}/\text{AgCl}}$							
	1.50 V				1.70 V			
	0.0 V	0.50 V	1.0 V	1.40 V	0.0 V	0.80 V	1.30 V	1.60 V
$\nu(\text{C}=\text{C})_{\text{ring}}$	1,572	1,570	1,568	1,570	1,552	1,554	1,550	1,550
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,514	1,517	1,527	1,525	1,525	1,530	1,531	1,532
$\omega(\text{C}-\text{H})$	1,460	1,455	1,458	1,460	1,442	1,445	1,436	1,438
$\nu(\text{C}-\text{C})$	1,340	1,355	1,335	1,388	1,315	1,330	1,328	1,332
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,261	1,263	1,260	1,264	1,241	1,248	1,239	1,242
$\omega(\text{C}-\text{H})$	1,190	1,193	1,195	1,204	1,176	1,172	1,169	1,158
$\nu(\text{C}-\text{O})_{\text{ring}}$	1,130	1,121	1,110	1,084	1,121	1,133	1,112	1,084
$\delta(\text{C}-\text{H})$	1,032	1,050	1,007	1,012	1,055	1,060	1,056	1,039
$\delta(\text{C}-\text{H})$	932	950	946	937	930	936	960	954
$\gamma(\text{C}-\text{H})$	878	870	863	817	843	847	838	847
$\delta(\text{C}-\text{S}-\text{C})$	750	776	732	735	756	739	733	763
$\delta(\text{C}-\text{S}-\text{C})$	670	693	640	658	662	670	663	666
$\delta(\text{C}-\text{Cl})$	450	449	449	450	441	444	440	445

δ In-plane deformation; γ out-of-plane deformation; ν stretching; ω out-of-plane bending

Table 7 Raman band assignments of copolymer deposited at $E_{\text{Ag}/\text{AgCl}}=1.7$ V with different mole ratios, all figures in wave numbers per centimeter

Mode	$E_{\text{Ag}/\text{AgCl}}$							
	8:1 ^a				1:1 ^a			
	0.0 V	0.50 V	1.0 V	1.40 V	0.0 V	0.45 V	0.90 V	1.20 V
$\nu(\text{C}=\text{C})_{\text{ring}}$	1,564	1,562	1,560	1,560	1,552	1,554	1,550	1,550
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,510	1,501	1,505	1,513	1,525	1,530	1,531	1,532
$\omega(\text{C}-\text{H})$	1,451	1,452	1,447	1,449	1,442	1,445	1,436	1,438
$\nu(\text{C}-\text{C})$	1,330	1,335	1,327	1,343	1,315	1,330	1,328	1,332
$\nu(\text{C}-\text{C})_{\text{ring}}$	1,250	1,251	1,249	1,241	1,241	1,248	1,239	1,242
$\omega(\text{C}-\text{H})$	1,170	1,166	1,172	1,160	1,176	1,172	1,169	1,158
$\nu(\text{C}-\text{O})_{\text{ring}}$	1,070	1,069	1,073	1,061	1,121	1,133	1,112	1,084
$\delta(\text{C}-\text{H})$	1,030	1,025	1,023	1,022	1,055	1,060	1,056	1,039
$\delta(\text{C}-\text{H})$	958	939	955	943	930	936	960	954
$\gamma(\text{C}-\text{H})$	864	834	830	842	843	847	838	847
$\delta(\text{C}-\text{S}-\text{C})$	772	761	758	763	756	739	733	763
$\delta(\text{C}-\text{S}-\text{C})$	710	702	675	703	662	670	663	666
$\delta(\text{C}-\text{Cl})$	451	451	454	449	441	444	440	445

^a Furan/3-chlorothiophene mole ratio

δ In-plane deformation; γ out-of-plane deformation; ν stretching; ω out-of-plane bending

pure poly(3-chlorothiophene); furthermore, the mode associated with the C–Cl bond appears at 441 cm^{-1} when the copolymer is prepared at 1:1 monomer feed ratio (see Table 7). These results show that the number of 3-chlorothiophene units in these copolymer chains increases with an increasing 3-chlorothiophene concentration in the polymerization solutions.

It is obvious that the Raman spectra of the copolymers are more complex than those of pure polyfuran and poly(3-chlorothiophene) making the assignment difficult. This complexity may be due to the change of effective conjugation length and more complex chemical environment of each unit encountered in the copolymer chains. However, the in situ Raman spectra of the copolymers are reminiscent of the in situ Raman spectra of homopolymers; see Fig. 8a–d. We observe a decrease in the intensity and a broadening of the symmetric C=C intra-ring stretching vibration at higher wave numbers with an increase in the applied potential. The overall intensity of the spectra decreases upon increasing the applied potential. The results reveal that the Raman spectra of the copolymers in the doped state are different from those of neutral copolymers. Bands related to the oxidized and, thus, distorted species were identified with in situ Raman spectroscopy.

In situ conductivity measurements

Polyfuran deposited potentiostatically at $E_{\text{Ag}/\text{AgCl}}=1.35$ V shows a single conductivity change by about three orders of magnitude starting around $E_{\text{Ag}/\text{AgCl}}=0.1$ V with a stable conductivity up to $E_{\text{Ag}/\text{AgCl}}=1.2$ V (Fig. 9a). When the potential shift is reversed from 1.2 to -0.2 V, the conductivity is almost completely restored.

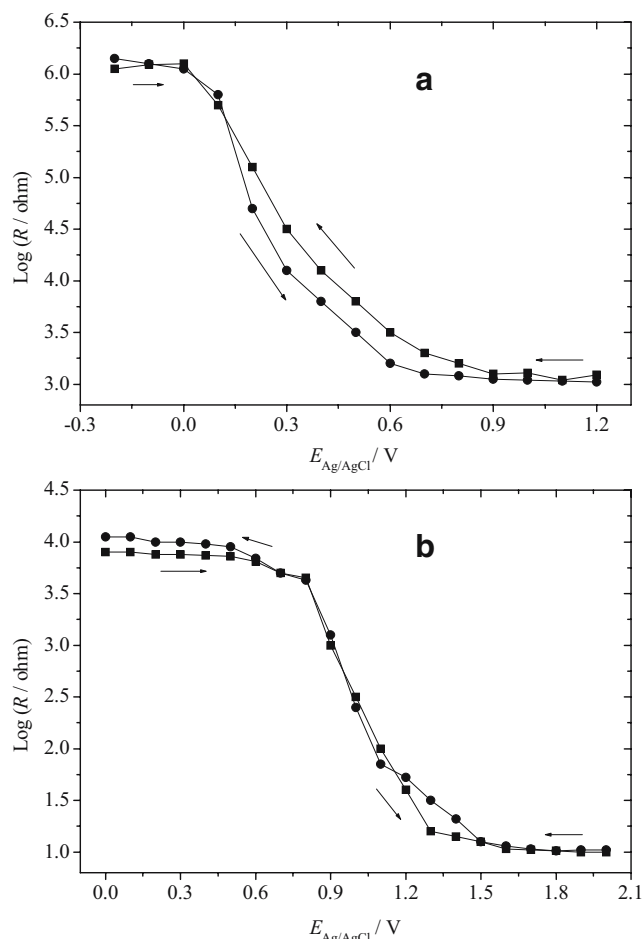
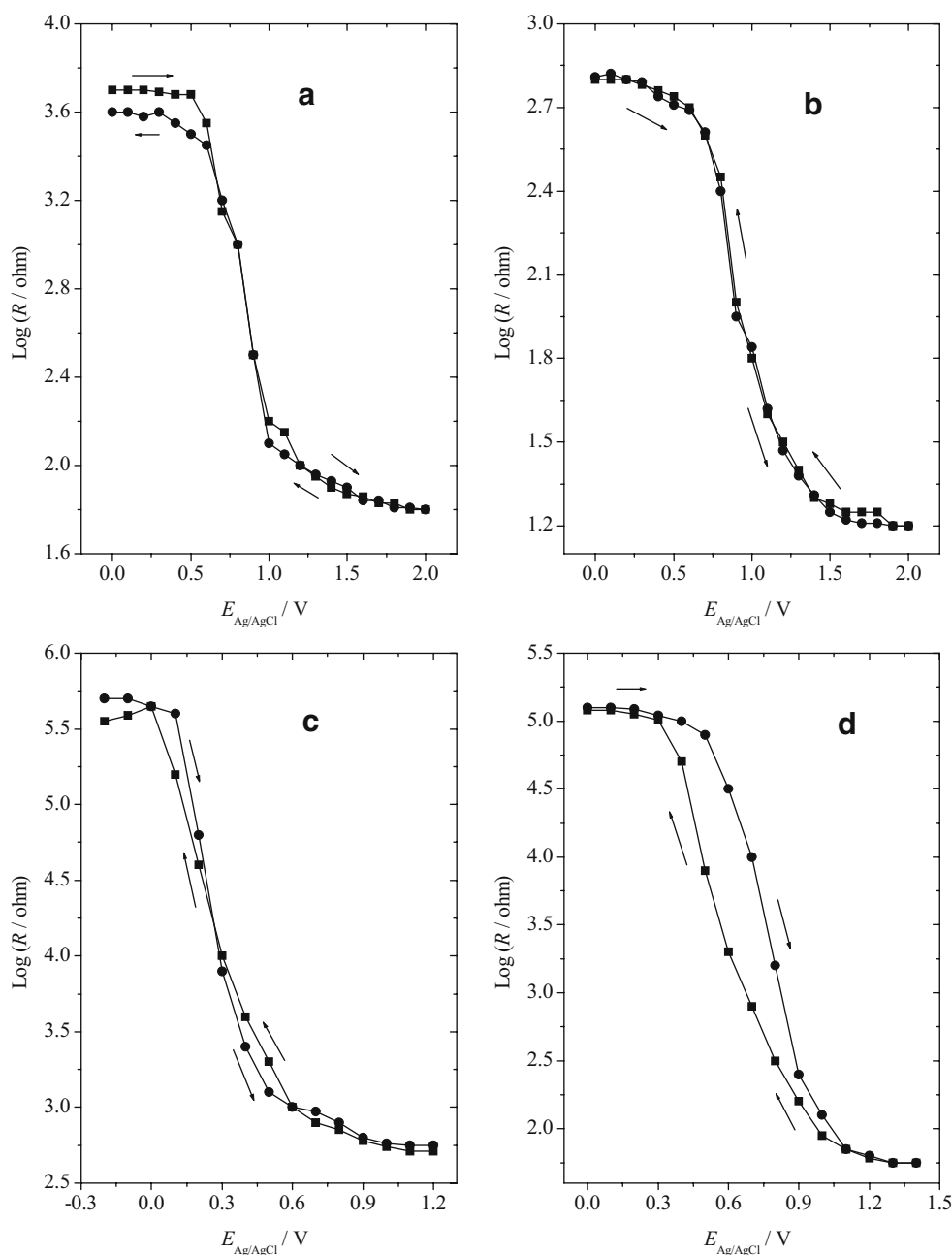


Fig. 9 Resistivity vs electrode potential data in a solution of acetonitrile+0.1 M TBATFB of (a) polyfuran, (b) poly(3-chlorothiophene)

Fig. 10 Resistivity vs electrode potential data in a solution of acetonitrile+0.1 M TBATFB of copolymers deposited at $E_{Ag/AgCl}=1.5$ and 1.7 V, respectively, in a BFEE + EE (ratio 1:2) and TFA (10% by volume) containing (a, b) furan/3-chlorothiophene (mole ratio 1:1), (c, d) furan/3-chlorothiophene (mole ratio 8:1)



The lower electrical conductivity of polyfuran when compared with polythiophene or polypyrrole may be attributed to the shorter conjugation length, which is already evident in the UV–vis spectra [27, 46]. In addition, degradation and ring opening reactions cannot be totally suppressed in the polymerization solution, and nonconjugated regions, although in small amounts, may exist in the polymer chains. As a consequence, the coexistence of high and low electrical conductivity domains in the film restricts the charge carrier migration in the polymer [24, 84].

The resistivity vs the applied potential plot of poly(3-chlorothiophene) deposited potentiostatically at $E_{Ag/AgCl}=1.55$ V is displayed in Fig. 9b. The polymer shows a single

change in resistivity. When the applied potential is increased, the resistivity decreased sharply by three orders of magnitude around $E_{Ag/AgCl}=0.8$ V with a highly stable conductivity up to $E_{Ag/AgCl}=2$ V. In a potential scan back from 2.0 to 0.0 V, the resistivity is almost completely restored.

The conductivity of poly(3-chlorothiophene) is around one order of magnitude lower than that of polythiophene¹.

¹The comparison is only qualitative because the actual amount of polymer is not known and can hardly be determined. Taking the peak currents and peak areas of the respective CVs as qualitative indicators, the comparison seems to be valid nevertheless.

This can be explained qualitatively by invoking the difference between the hydrogen and chlorine radii which is around 0.60 Å. This difference may increase the steric hindrance and distortion along the polymer chain which modifies the structure and thus the properties of the polymer [35]. The lower conductivity can also be ascribed to the physical discontinuity within the polymer matrices, which increases the resistance of the polymer [85].

In situ conductivity measurements both at different electrode potentials and with different 3-chlorothiophene concentrations in the polymerization solution were performed; results obtained with copolymers of different compositions (labeled A...D) are presented in Fig. 10. Copolymer (B) shows a single change in resistivity. When the applied potential is increased, the resistivity decreases sharply at $E_{Ag/AgCl}=0.7$ V with a stable conductivity up to $E_{Ag/AgCl}=2$ V. Furthermore, its conductivity is close to that of poly(3-chlorothiophene) and higher than that of polyfuran by 1.8 orders of magnitude. The resistivity is almost completely restored when the potential is shifted back from $E_{Ag/AgCl}=2.0$ to 0.0 V. The same changes can be observed with copolymer (A). However, its conductivity is higher by 1.2 orders of magnitude as compared to polyfuran. This indicates that more 3-chlorothiophene units are incorporated into the copolymer chains with increasing preparation potential.

When the furan/3-chlorothiophene feed ratio is changed from (1:1) to (8:1), the same interesting features are still existent, i.e., copolymers show a single change in resistivity, when the applied potential is increased, the resistivity decreased, and the resistivity is almost restored when the potential is shifted back to $E_{Ag/AgCl}=-0.2$ V. In the case of copolymer (C), its behavior is close to that of polyfuran with a conductivity higher by 0.3 orders of magnitude, whereas the difference is 1.3 orders of magnitude for copolymer (D).

By comparing copolymers (A, B) with copolymers (C, D), one can conclude that the number of 3-chlorothiophene units in these copolymer chains increases with an increasing 3-chlorothiophene concentration in the polymerization solutions, and the conductivities of the copolymers are between the conductivities of both polyfuran and poly(3-chlorothiophene), implying that oxidation of both monomers is possible and the copolymer chains may accordingly be composed of alternate furan and 3-chlorothiophene units.

Another noticeable feature is the fact that in situ conductivity properties are not the sum of those of the two individual homopolymers. This result may eliminate the possibility that the copolymers can be considered as block copolymers. It may be concluded that copolymers (B) and (C) have structures approaching those of a polythiophene-based random copolymer and a polyfuran-based random copolymer, respectively.

Conclusions

Electrochemical copolymerization of furan and 3-chlorothiophene was successfully realized in a binary system consisting of BFEE + EE (ratio 1:2) and TFA (10% by volume) at constant electrode potential. The spectroelectrochemical properties of the copolymers show intermediate characteristics between polyfuran and poly(3-chlorothiophene), implying that oxidation of both monomers is possible and the copolymer chains may accordingly be composed of alternate furan and 3-chlorothiophene units. At higher polymerization potentials and at higher concentrations of 3-chlorothiophene in the feed, more 3-chlorothiophene units are incorporated into the copolymer. The reversible doping/dedoping behavior of homo- and copolymer films is also reflected in in situ conductivity measurements.

Acknowledgments Financial support from the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg GRK 829/1) is gratefully acknowledged.

References

1. Amanokura J, Suzuki Y, Imabayashi S, Watanabe M (2001) *J Electrochem Soc* 148:D43
2. Sotzing GA, Briglin SM, Grubbs RH, Lewis NS (2000) *Anal Chem* 72:3181
3. Lin CW, Hwang BJ, Lee CR (1999) *J Appl Polym Sci* 73:2079
4. Malinauskas A, Malinauskiene J, Ramanavicius A (2005) *Nanotechnology* 16:R51
5. James D, Scott SM, Ali Z, Ohare WT (2005) *Microchim Acta* 149:1
6. Guernion NJL, Hayes W (2004) *Curr Org Chem* 8:637
7. Vidal JC, Garcia Ruiz E, Castillo JR (2003) *Microchim Acta* 143:93
8. Dai LM, Soundarrajan P, Kim T (2002) *Pure Appl Chem* 74:1753
9. Trojanowicz M, Velkrawczyk TK, Alexander PW (1997) *Chem Anal* 42:199
10. Trojanowicz M (2003) *Microchim Acta* 143:75
11. Cosnier S (2003) *Anal Bioanal Chem* 377:507
12. Bartlett PN, Birkin PR (1993) *Synth Met* 61:15
13. Sadik OA (1999) *Electroanalysis* 11:839
14. Wallace GG, Smyth M, Zhao H (1999) *Trends Anal Chem* 18:245
15. Shinohara H, Aizawa M, Shirakawa H (1986) *J Chem Soc Chem Commun* 1:87
16. Le HNT, Garcia B, Deslouis C, Xuan QL (2002) *J Appl Electrochem* 32:105
17. Buckley LJ, Eashoo M (1996) *Synth Met* 78:1
18. Blanca E, Carrillo I, Gonzalez-Tejera MJ, Hernandez-Fuentes I (2000) *J Polym Sci A Polym Chem* 38:291
19. Ohsawa T, Kaneto K, Yoshino K (1984) *Jpn J Appl Phys* 23:L663
20. Tourillon G, Garnier F (1982) *J Electroanal Chem* 135:173
21. Nessakh B, Kotkowska-Machnik Z, Tedjar F (1990) *J Electroanal Chem* 269:263
22. Zotti G, Schiavon G, Comisso N, Berlin A, Pagani G (1990) *Synth Met* 36:337
23. Glenis S, Benz M, Legoff E, Schindler JL, Kannewurf CR, Kanatzidis MG (1993) *J Am Chem Soc* 115:12519
24. Gonzalez-Tejera MJ, Carrillo I, Hernandez-Fuentes I (1995) *Synth Met* 73:135

25. Demirboga B, Onal AM (1999) *Synth Met* 99:237
26. Liu C, Zhang J, Shi G, Zhao Y (2004) *J Phys Chem B* 108:2195
27. Wan X, Yan F, Jin S, Liu X, Xue G (1999) *Chem Mater* 11:2400
28. Chan H, Ng S, Seow S, Modersheim J (1992) *J Mater Chem* 2:1135
29. Osterholm J, Passiniemi P, Isotalo H, Stubb H (1987) *Synth Met* 18:213
30. Tourillon G, Garnier F (1983) *J Electrochem Soc* 130:2042
31. Hotta S, Soga M, Sonoda N (1988) *Synth Met* 26:267
32. Feldhues M, Kamf G, Litterer H, Mecklenburg T, Wegener P (1989) *Synth Met* 28:C487
33. Heffner G, Pearson D (1991) *Synth Met* 44:341
34. Deffieux D, Bonafoux D, Bordeau M, Biran C, Dunogues J (1996) *Organometallics* 15:2041
35. Kassmi A, Fache F, Lemaire M (1994) *J Electroanal Chem* 373:241
36. Shi L, Roncali J, Garnier F (1989) *J Electroanal Chem* 263:155
37. Zhou L, Xue G (1997) *Synth Met* 87:193
38. Lemaire M, Buchner W, Garreau R, Hoa H, Guy A, Roncali J (1990) *J Electroanal Chem* 281:293
39. Xu J, Shi G, Xu Z, Chen F, Hong X (2001) *J Electroanal Chem* 514:16
40. Xu J, Shi G, Chen F, Wang F, Zhang J, Hong X (2003) *J Appl Polym Sci* 87:502
41. Li C, Shi G, Liang Y (1998) *J Electroanal Chem* 455:1
42. Li C, Shi G, Liang Y (1999) *Synth Met* 104:113
43. Li L, Chen W, Xu N, Xaio ZG, Xue G (2004) *J Mater Sci* 39:2395
44. Alakhras F, Holze R (2007) *J Appl Polym Sci* (in press)
45. Alakhras F, Holze R (2007) *Synth Met* 157:109
46. Alakhras F, Holze R (2007) Redox thermodynamics, conductivity and Raman spectroscopy of electropolymerized furan–thiophene copolymers. *Electrochim Acta* DOI 10.1016/j.electacta.2007.03.024
47. Gritzner G, Kuta J (1984) *Pure Appl Chem* 56:461
48. Holze R, Lippe J (1990) *Synth Met* 38:99
49. Lippe J, Holze R (1991) *Synth Met* 41:2927
50. Chan H, Siu C (1998) *Prog Polym Sci* 23:1167
51. Yang S, Olishevski P, Kertesz M (2004) *Synth Met* 141:171
52. Lyons LE (1980) *Aust J Chem* 33:1717
53. MacDiarmid AG (2001) *Angew Chem Int Ed* 40:2581
54. Negi YS, Adhyapak PV (2002) *J Macromol Sci Polymer Rev* C42:35
55. Brédas JL, Scott JC, Yakushi K, Street GB (1984) *Phys Rev B* 30:1023
56. Bredas J, Silbey R, Bourdreaux D, Chance R (1983) *J Am Chem Soc* 105:6555
57. Salaneck W, Inganas O, Nillson J, Osterholm J, Themans B, Bredas J (1989) *Synth Met* 28:C451
58. Hernandez V, Ramirez FJ, Zotti G, Navarrete JTL (1992) *Chem Phys Lett* 191:419
59. Dollish FR, Fateley WG, Bentley FF (1974) *Characteristic Raman frequencies of organic compounds*. Wiley, New York
60. Guthrie GB, Scott DW, Hubbard WN, Katz C, McCullough JP, Gross ME, Williamson KD, Waddington G (1952) *J Am Chem Soc* 74:4662
61. Hernandez V, Ramirez FJ, Zotti G, Navarrete JTL (1993) *Synth Met* 55:4467
62. Ceppatelli M, Santoro M, Bini R, Schettino V (2003) *J Chem Phys* 118:1499
63. Green JHS, Harrison DJ (1977) *Spectrochim Acta* 33A:843
64. Hernandez V, Navarrete JTL, Zotti G, Veronelli M, Zerbi G (1995) *Synth Met* 69:391
65. Hernandez V, Ramirez FJ, Zotti G, Navarrete JTL (1993) *J Chem Phys* 98:769
66. Hernandez V, Veronelli M, Favaretto L, Navarrete JTL, Jones D, Zerbi G (1996) *Acta Polym* 47:62
67. Matsuno K, Han K (1934) *Bull Chem Soc Jpn* 9:327
68. Han K (1936) *Bull Chem Soc Jpn* 11:701
69. Wan X, Li L, He J, Zhou D, Xue G, Wang T (2002) *J Appl Polym Sci* 86:3160
70. Bongini A, Barbarella G, Zambianchi M, Hernandez V, Navarrete JTL (2000) *Synth Met* 108:27
71. Holze R (1991) *Synth Met* 40:379
72. Sauvajol JL, Poussigues G, Benoit C, Lere-Porte JP, Chorro C (1991) *Synth Met* 41:1237
73. Boukowska J, Jackowska K (1990) *Synth Met* 35:143
74. He JB, Zhou HJ, Wan F, Lu Y, Xue G (2003) *Vib Spectrosc* 31:265
75. Casado J, Hernandez V, Kanemitsu Y, Navarrete JTL (2000) *J Raman Spectrosc* 31:565
76. Dufour B, Rannou P, Travers JP, Pron A, Zagorska M, Korc G, Kulszewicz-Bajer I, Quillard S, Lefrant S (2002) *Macromolecules* 35:6112
77. Fu MX, Zhu YF, Tan RQ, Shi GQ (2001) *Adv Mater* 13:1874
78. Chen F, Shi GQ, Zhang JX, Fu MX (2003) *Thin Solid Films* 424:283
79. Bazzouai EA, Aeiyaeh S, Aubard J, Felidj N, Lancze PC, Sakmeche N, Levi G (1998) *J Raman Spectrosc* 29:177
80. Hernandez V, Casado J, Kanemitsu Y, Navarrete JTL (1999) *J Chem Phys* 110: 6907
81. Furukawa Y, Akimoto M, Harada I (1987) *Synth Met* 18:151
82. Louarn G, Buisson JP, Lefrant S, Fichon D (1995) *J Phys Chem* 99:11399
83. Wan X, Zhang W, Jin S, Xue G, You Q, Che B (1999) *J Electroanal Chem* 470:23
84. Gonzalez-Tejera MJ, Carrillo I, Hernandez-Fuentes I (1998) *Synth Met* 92:187
85. Masuda H, Tanaka S, Kaeriyama K (1989) *Synth Met* 31:29