

# Furan–Thiophene Copolymers: Electrosynthesis and Electrochemical Behavior

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**ABSTRACT:** The electrochemical copolymerization of furan and thiophene was performed at a constant electrode potential in a binary solvent system consisting of boron trifluoride/ethyl ether and an additional amount of ethyl ether (molar ratio = 1 : 2). The obtained homopolymers and copolymers were characterized with cyclic voltammetry and infrared spectroscopy. The influence of the applied electropolymerization potential and the monomer feed ra-

tio of furan and thiophene on the copolymers was investigated. The furan–thiophene copolymers showed good stability of the redox activity in an acetonitrile-based electrolyte solution. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1133–1141, 2008

**Key words:** conducting polymers; copolymerization; electrochemistry

## INTRODUCTION

Electronically conducting polymers, particularly those based on monomers such as pyrrole, thiophene, aniline, and their substituted relatives, have many potential applications, such as materials for battery electrodes,<sup>1</sup> gas sensors,<sup>2</sup> chemical sensors,<sup>3</sup> ion sieving,<sup>4</sup> corrosion protection,<sup>5</sup> and microwave shielding.<sup>6</sup> However, the stability of conducting polymers seems to be a major limiting factor in their practical applications. Thus, their degradation properties under different conditions have been studied extensively.<sup>7</sup> Most studies have been focused on the overoxidation of conventional conducting polymers, such as polypyrrole,<sup>8,9</sup> polythiophene,<sup>10,11</sup> and polyaniline.<sup>12,13</sup>

Among conducting polymers with an extended  $\pi$ -electron system, polyfuran is interesting because of its possible technological applications as a humidity sensor.<sup>14</sup> 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 because, upon doping, the color changes from yellow-brown to black-brown.<sup>15</sup>

Polyfuran is among the most ill defined of conjugated polymers in comparison with polypyrrole and polythiophene. The synthesis of polyfuran films was

first mentioned by Tourillon and Garnier;<sup>16</sup> the reported polymer exhibited low electrical conductivity ranging from  $10^{-5}$  to  $10^{-3}$  S/cm. It was claimed that polyfuran was obtained previously by the electrochemical polymerization of furan, but the high voltage required for the electropolymerization (1.8–2.5 V) resulted in irreversible oxidation of the polymer.<sup>17</sup>

With another method, polyfuran was prepared by the electrochemical reduction of 2,5-dibromofuran in acetonitrile with tris(2,2'-bipyridyl)nickel (II) complex ( $[\text{Ni}(\text{bipy})_3]^{2+}$ ) as a catalyst. The polymer, obtained only in a trace amount on the cathode, was in its neutral insulating form.<sup>18</sup>

Glenis et al.<sup>19</sup> tried to use terfuran as the starting monomer to lower the oxidation potential. The obtained polymer had an electrical conductivity of  $2 \times 10^{-3}$  S/cm when doped with  $\text{CF}_3\text{SO}_3^-$ . Although the oxidation potential was lowered by this method ( $\sim 1.5$  V), the resultant polymer contained a large number of saturated rings, as evidenced by infrared spectrometry.

More recently, furan was electropolymerized in acetonitrile at potentials of electrode potential versus a saturated calomel ( $E_{\text{SCE}} = 2.1\text{--}2.3$  V with  $\text{NaClO}_4$  as an electrolyte.<sup>20</sup> The obtained film showed ill-defined cyclic voltammograms (CVs) in comparison with those obtained by Glenis et al.<sup>19</sup> and by Zotti et al.<sup>18</sup> It was obvious that the polymer underwent irreversible oxidation and contained a large number of saturated rings or ring-opened components at such high potentials.

Polyfuran and poly(2-methylfuran) were prepared by controlled potential electrolysis in acetonitrile at room temperature. The electrical conductivity of polyfuran decreased by a factor of 4 when the methyl

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group was present in the  $\alpha$  position. The temperature effect on the rate of polymerization of furan was studied with a cyclic voltammetry technique; the mechanism of electrochemical polymerization was investigated with *in situ* electron spin resonance spectroscopy.<sup>21</sup>

Freestanding polyfuran films were successfully synthesized by the electrochemical polymerization of furan at a low potential ( $E_{\text{Ag}/\text{AgCl}} = 1.2$  V) in a binary solvent system containing boron trifluoride/ethyl ether (BFEE) and additional ethyl ether (EE). The polymer showed good mechanical properties, and its electrical conductivity was around  $10^{-2}$  S/cm.<sup>22</sup>

Copolymerization is an important method for modifying the properties of individual homopolymers. So far, copolymers of furan and pyrrole were electrochemically prepared in a binary solvent system consisting of BFEE and extra EE. The influence of the applied polymerization potential and the monomer feed ratio of furan and pyrrole on the copolymers was investigated. The obtained film was characterized with cyclic voltammetry, and infrared and Raman spectroscopy.<sup>23</sup> The electrochemical synthesis of the homopolymer and copolymer films of thiophene and furan in acetonitrile-based solutions with different supporting electrolytes was studied by Talu et al.<sup>24</sup> and Kabasakaloglu et al.<sup>25</sup> The electrochemical behavior of the polymers was characterized with cyclic voltammetry, whereas their structures were investigated with scanning electron microscopy and infrared spectroscopy. The conductivity of the prepared polymers was found to be of the bipolaron type because their magnetic susceptibility values were negative; the thermogravimetric analytical data indicated that the polymer bilayers had higher decomposition temperatures than the homopolymers and were thermally more stable than the homopolymers.

In addition, the 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). The obtained copolymer was characterized by cyclic voltammetry, infrared spectroscopy, and electrical conductivity. The copolymerization was carried out at  $E_{\text{Ag}/\text{AgCl},0.1\text{M KCl}} = 1.2$  V, and the polymer had an electrical conductivity of 0.36 S/cm.<sup>26</sup>

In this article, the results of cyclic voltammetry of homopolymers and copolymers of furan and thiophene are reported. The influence of the applied polymerization potential and the monomer feed ratio on the properties of the copolymers is discussed; in addition, a mechanism for the electrochemical formation of furan–thiophene copolymers is proposed. The stability of the redox activity of furan–thiophene copolymers is investigated and compared with that of previously prepared polyfuran films.

The BFEE complex was chosen as a binary system to lower the oxidation potential of furan.<sup>23</sup> The significant decrease in the oxidation potential of furan in a strongly acidic medium can be rationalized in two ways. First, furan forms a complex with the strong acid, thereby reducing the resonance stabilization of the aromatic ring and shifting the oxidation potential to less anodic potentials. Second, the increased acidity of the solvent imparts greater stability to the cation radical, which in turn promotes the electrooxidation and subsequent polymerization. However, the resonance energy of furan is so low that it acts more like a conjugated diene than a heteroaromatic molecule, and this makes it sensitive to acids. Additional polymerization occurs immediately, and a nonconjugated polymer is precipitated when furan is directly added to BFEE, which is a strong Lewis acid. Thus, EE was added to adjust the acidity of BFEE, and the undesirable polymerization was suppressed.<sup>22</sup>

Acetonitrile was used as solvent in the cyclic voltammetry experiments because of its high dielectric constant, low nucleophilicity,<sup>27</sup> low viscosity, and wide potential window ( $-2.8 < E_{\text{SCE}} < 3.3$  V).<sup>28</sup>

The anodic electropolymerization of the monomers presents several advantages, such as the absence of a catalyst, the direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical applications), easy control of the film thickness, and the possibility of performing a first *in situ* characterization of the growing process of the polymer by electrochemical and/or spectroscopic techniques.<sup>29</sup>

## EXPERIMENTAL

Furan (Aldrich, Steinheim, Germany; 99%) and thiophene (Fluka, Buchs, Italy; 98%) were distilled under nitrogen just before use. EE (Acros) was dried and distilled in the presence of sodium. BFEE (Acros; 48%  $\text{BF}_3$ ) was used as received. Tetrabutylammonium tetrafluoroborate (TBATFB; Aldrich, Steinheim, Germany; 99%) was dried *in vacuo* at 80°C for 24 h. Acetonitrile (Merck, Darmstadt, Germany; anhydrous, <10 ppm  $\text{H}_2\text{O}$ ) was used without further purification.

The electropolymerization of furan and thiophene was performed potentiostatically in a 1 : 2 BFEE/EE solution containing in addition 0.1M TBATFB in a one-compartment, three-electrode cell at room temperature at a constant electrode potential for 2 min.

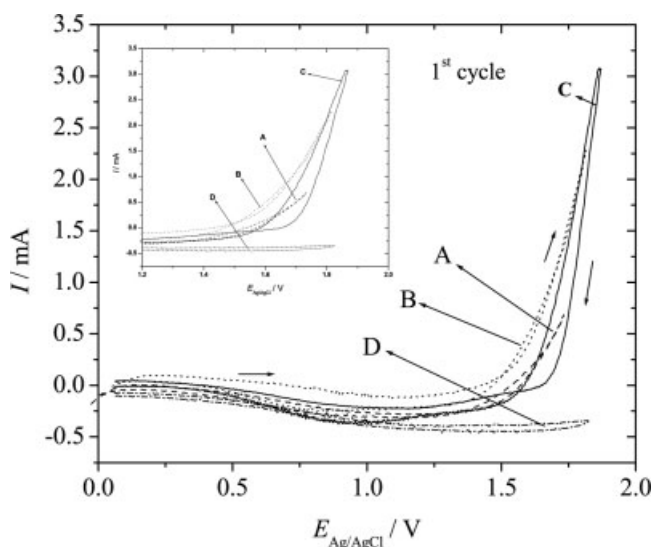
A platinum sheet electrode (approximate surface area = 1.5  $\text{cm}^2$ ) was used as a working electrode; a nonaqueous Ag/AgCl electrode filled with acetonitrile containing 0.1M TBATFB saturated with AgCl was used as a reference electrode. After polymerization, the film was washed with acetonitrile to remove any traces of the monomers and oligomers.

Cyclic voltammetry of the polymers was carried out in a monomer-free acetonitrile solution containing 0.1M TBATFB as a supporting electrolyte. Before every experiment, the solution was deaerated by bubbling with  $N_2$ . The reference electrode potential was verified frequently with respect to an aqueous saturated calomel electrode because the employed nonaqueous reference electrode system was prone to potential drift.<sup>30</sup> A custom-built potentiostat interfaced with a standard personal computer via an ADDA-converter card operating with custom-developed software was used to record CVs.

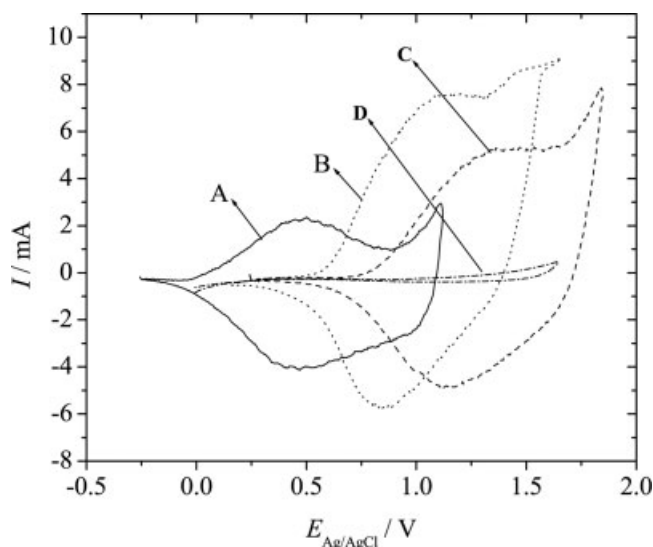
For Fourier transform infrared (FTIR) spectroscopy, the pristine film was scraped off from the electrode and dried. FTIR spectra of the homopolymer and copolymer films were recorded with KBr pellets with a PerkinElmer FTIR 1000 spectrometer at a  $2\text{-cm}^{-1}$  resolution (eight scans).

## RESULTS AND DISCUSSION

CVs of a platinum working electrode in the polymerization solution containing the monomers are given in Figure 1. The background electrolyte is electrochemically silent in the whole potential range. The polymerization threshold (the lowest potential needed to sustain the growth of a polymer layer) of furan is  $E_{\text{Ag}/\text{AgCl}} = 1.45\text{ V}$  (curve a), and that of thiophene is  $E_{\text{Ag}/\text{AgCl}} = 1.65\text{ V}$  (curve c). 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 for a solution containing 0.10M furan and 0.10M thiophene. However, the superposition of curves a and c does



**Figure 1** CVs of (A) 0.1M furan, (B) 0.1M furan and 0.1M thiophene, (C) 0.1M thiophene, and (D) no monomer in 0.1M TBATFB in 1 : 2 BFEE/EE ( $dE/dt = 100\text{ mV/s}$ ).



**Figure 2** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for (A) polyfuran deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.45\text{ V}$  in a 1 : 2 BFEE/EE solution containing 0.1M furan, (B) a copolymer deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.60\text{ V}$  in a 1 : 2 BFEE/EE solution containing 0.1M furan and 0.1M thiophene, (C) polythiophene deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.65\text{ V}$  in a 1 : 2 BFEE/EE solution containing 0.1M thiophene, and (D) polyfuran scanned in an extended scan range from  $E_{\text{Ag}/\text{AgCl}} = 0.0\text{ V}$  to  $E_{\text{Ag}/\text{AgCl}} = 1.65\text{ V}$  ( $dE/dt = 100\text{ mV/s}$ ).

not simply add up to curve b. The current of curve b is smaller than that for thiophene and larger than that for furan. This might be caused by changes in the electrochemical environment, such as electrode roughness, or by the lowered electric conductivity of the formed polymer film accompanying the incorporation of furan rings into the copolymer chain.<sup>23,26</sup> The oxidation potential of the mixture of furan and thiophene is around  $E_{\text{Ag}/\text{AgCl}} = 1.50\text{--}1.60\text{ V}$ , which is between the oxidation potentials of the two monomers, implying that the oxidation of both monomers is likely; the copolymer chains may accordingly be composed of alternating furan and thiophene units.<sup>26</sup>

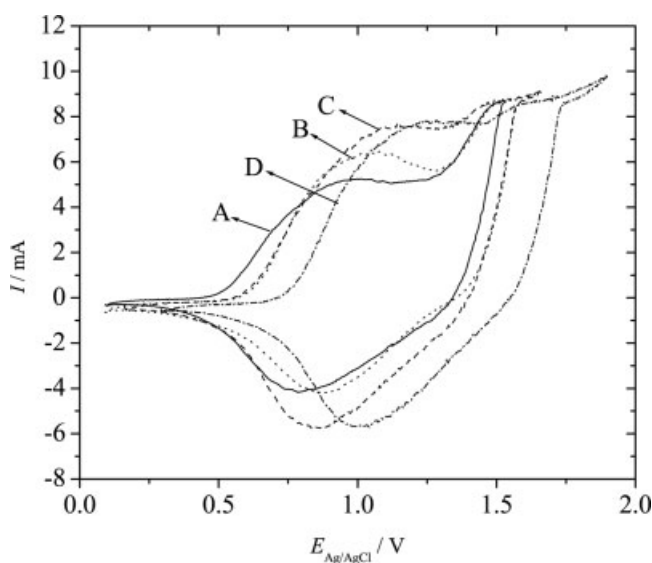
Figure 2(A,C) shows the CVs of polyfuran and polythiophene in the acetonitrile-based electrolyte solution. For polyfuran, there is a broad anodic peak at  $E_{\text{Ag}/\text{AgCl}} \sim 0.50\text{ V}$  caused by polymer oxidation and a corresponding broad cathodic peak around  $E_{\text{Ag}/\text{AgCl}} \sim 0.46\text{ V}$  due to polymer reduction. The difference in the peak potentials of 0.04 V indicates high reversibility of the associated redox processes. For polythiophene, the respective peaks are at  $E_{\text{Ag}/\text{AgCl}} \sim 1.38\text{ V}$  and at  $E_{\text{Ag}/\text{AgCl}} \sim 1.15\text{ V}$ , with a difference of 0.23 V. The redox processes of polythiophene are less close to reversibility, as the peak separation is larger than observed with polyfuran. These differences and the broad, poorly defined current waves are commonly observed in the electrochemistry of intrinsically conducting polymers because of a number of factors,

including the diffusion of the dopant ions in and out of the film and the change in the conformation of the polymer chain during the redox processes.<sup>19,22</sup>

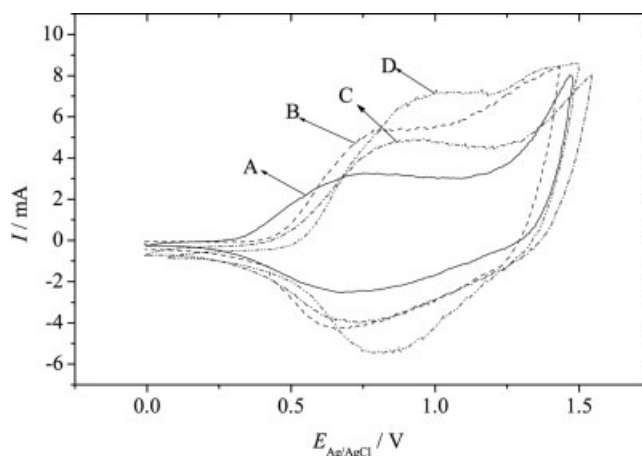
Copolymerization was carried out under potentiostatic conditions. Figure 2(B) shows a typical CV of a copolymer obtained from a 1 : 2 BFEE/EE solution containing 0.10M furan and 0.10M thiophene prepared at  $E_{\text{Ag}/\text{AgCl}} = 1.60$  V. It was impossible to record the CVs of the homopolymers and the copolymer in the same potential range because overoxidation of polyfuran would influence the film response and, as a result, ill-defined CVs, as shown in Figure 2(D) (polyfuran scanned between  $E_{\text{Ag}/\text{AgCl}} = 0.0$  V and  $E_{\text{Ag}/\text{AgCl}} = 1.65$  V), would be obtained. The copolymer is more stable and less affected by overoxidation, presumably because of the existence of thiophene units in the copolymer chains, which may increase the stability of the copolymer.

Only one anodic/cathodic peak couple appears with the copolymer film at a position quite different from the positions observed with polyfuran and polythiophene. The appearance of one redox peak indicates uniform redox properties. In addition, it is noteworthy that both the cathodic and anodic currents are higher than those found with the homopolymers. This implies that the electrochemical activity (redox capacity) of the copolymer is higher after the same time of electropolymerization.

Electrochemical copolymerization both at different potentials and with different thiophene concentrations was investigated. Figure 3 shows CVs of the copolymers obtained with electropolymerization in



**Figure 3** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for copolymers deposited at  $E_{\text{Ag}/\text{AgCl}}$  values of (A) 1.5, (B) 1.55, (C) 1.6, and (D) 1.7 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 1 : 1;  $dE/dt = 100$  mV/s).

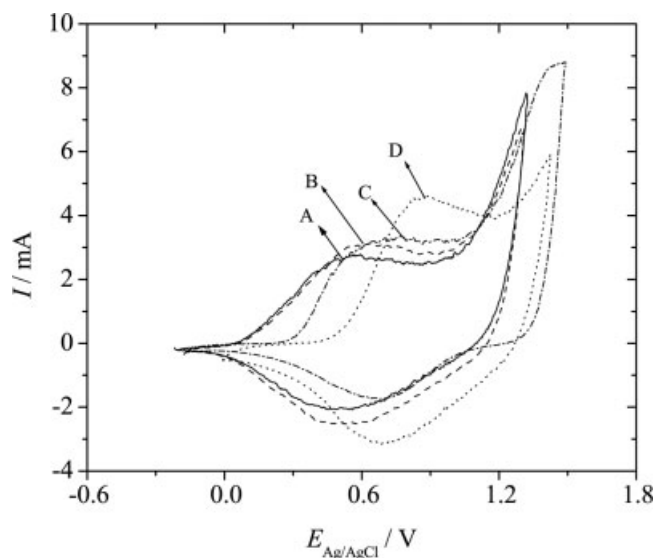


**Figure 4** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for copolymers deposited at  $E_{\text{Ag}/\text{AgCl}}$  values of (A) 1.5, (B) 1.55, (C) 1.6, and (D) 1.7 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 4 : 1;  $dE/dt = 100$  mV/s).

solutions containing 0.1M furan and 0.1M thiophene at potentials ranging from  $E_{\text{Ag}/\text{AgCl}} = 1.5$  V to  $E_{\text{Ag}/\text{AgCl}} = 1.7$  V. The redox peak potential of the copolymers shifts to higher potentials with increasing polymerization potential of the copolymer. When prepared at  $E_{\text{Ag}/\text{AgCl}} = 1.5$  V, the copolymer shows an anodic peak at  $E_{\text{Ag}/\text{AgCl}} = 1.0$  V and a cathodic peak at  $E_{\text{Ag}/\text{AgCl}} = 0.77$  V, whereas the copolymer prepared at  $E_{\text{Ag}/\text{AgCl}} = 1.7$  V shows an anodic peak at  $E_{\text{Ag}/\text{AgCl}} = 1.27$  V and a cathodic peak at  $E_{\text{Ag}/\text{AgCl}} = 1.01$  V. The former peak pair is closer to that of polyfuran, and the latter is closer to that of polythiophene. This indicates that more thiophene units are incorporated into the copolymer with increasing preparation potential.

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

When the furan/thiophene feed ratio is changed from 1 : 1 to 4 : 1 (0.1M/0.025M), CVs as shown in Figure 4 are obtained; at a ratio of 8 : 1 (0.1M/0.0125M), the CVs shown in Figure 5 result. Only one redox peak couple appears, and the positive shift of the redox peak with increasing preparation potentials is again observed. When comparing the CVs of the copolymers prepared at the same polymerization potential in these different solutions, we can observe that a lower concentration of thiophene leads to a negative shift of the redox peak potentials of the copolymer. This implies that more thiophene units are incorporated into the copolymer film when the concentration of thiophene increases (see Fig. 6).



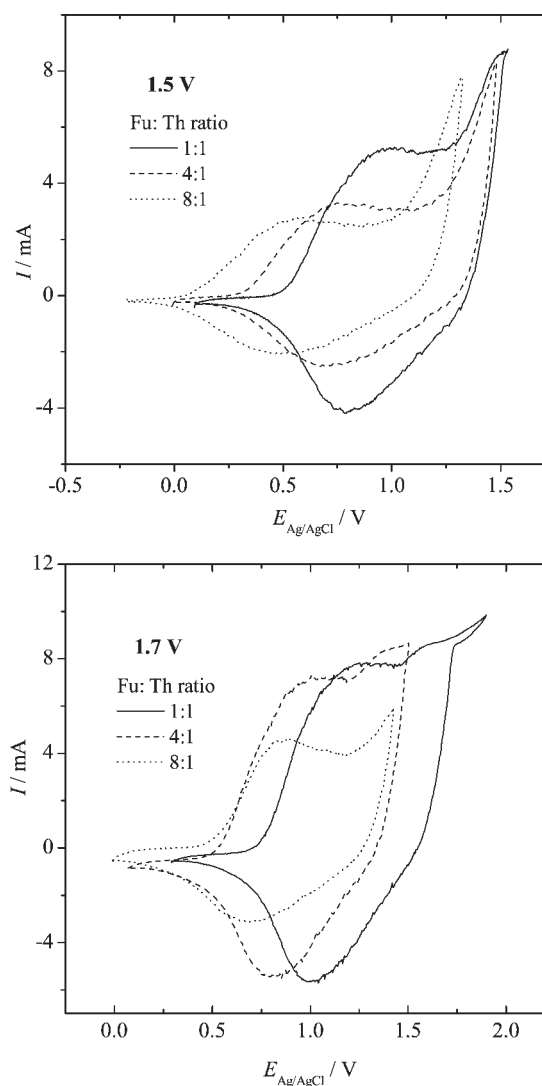
**Figure 5** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for copolymers deposited at  $E_{\text{Ag}/\text{AgCl}}$  values of (A) 1.5, (B) 1.55, (C) 1.6, and (D) 1.7 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 8 : 1;  $dE/dt = 100$  mV/s).

The peak potential values of the copolymers prepared at different potentials from these three different solutions are listed in Table I, and the peak potentials of the homopolymers have been added for comparison. They indicate that the electrochemical properties of the copolymers depend not only on the electrochemical polymerization potential but also on the monomer feed ratio. Presumably, the dependence of the electrochemical properties of the copolymers on the electropolymerization potential and monomer feed ratio reflects the composition and perhaps even the structure of the copolymers. In Figure 7, the relationship between the anodic peak current and the concentration of thiophene in the electropolymerization solutions is linear (linear fit), especially at higher concentrations (0.025–0.1M).

These observations and suggestions are further supported by results obtained with infrared spectroscopy (for a detailed discussion, see ref. 31). Figure 8 shows the FTIR spectra of a copolymer obtained from a 1 : 2 BFEE/EE solution containing 0.10M furan and 0.10M thiophene prepared at  $E_{\text{Ag}/\text{AgCl}} = 1.60$  V; for comparison, FTIR spectra of the respective homopolymers are shown. The most striking feature of the FTIR spectra of the copolymer is the evolution of a strong absorption band located around  $680\text{ cm}^{-1}$ , which is assigned to the overlap between the out-of-plane deformation of the  $=\text{C}-\text{H}$  group and in-plane ring deformation. We can also observe peaks located around  $1070\text{--}1131\text{ cm}^{-1}$  assigned to the combination of the  $\text{C}-\text{O}$  stretching vibration,  $\text{C}-\text{H}$  in-plane bending, and ring deformation. The stretching frequency of the  $\text{C}=\text{C}$  bond in the copolymer appears in the region of

$1470\text{--}1570\text{ cm}^{-1}$ . Furthermore, the presence of bands in the region of  $840\text{--}910\text{ cm}^{-1}$ , characteristic of  $\alpha$ -substituted, five-membered heterocyclic compounds,<sup>23</sup> indicates that  $\alpha$ - $\alpha'$  coupling of radical cations has taken place in the copolymerization. As previously pointed out, coupling in this position is most likely because of the highest unpaired  $\pi$ -electron density at these positions.<sup>32</sup>

FTIR spectra of copolymers obtained both at different potentials and with different thiophene concentrations were recorded. Figure 9(a, b) shows the FTIR spectra of the copolymers obtained with electropolymerization solutions containing 0.1M furan and 0.1M thiophene at potentials of  $E_{\text{Ag}/\text{AgCl}} = 1.5$  V and  $E_{\text{Ag}/\text{AgCl}} = 1.7$  V, respectively. Interestingly, in the FTIR spectra, the out-of-plane deformation mode of



**Figure 6** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for copolymers deposited at  $E_{\text{Ag}/\text{AgCl}}$  values of 1.5 and 1.7 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 1 : 1, 4 : 1, or 8 : 1;  $dE/dt = 100$  mV/s).

**TABLE I**  
**Peak Potentials of the Copolymers Prepared at Various Electropolymerization Potentials from 1 : 2 BFEE/EE Solutions Containing Different Monomer Feed Ratios**

Furan/ thiophene (molar ratio)	Copolymers								Polyfuran ( $E_{\text{pol}} = 1.45$ V)		Polythiophene ( $E_{\text{pol}} = 1.65$ V)	
	$E_{\text{pol}} = 1.50$ V		$E_{\text{pol}} = 1.55$ V		$E_{\text{pol}} = 1.60$ V		$E_{\text{pol}} = 1.70$ V		$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)
	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)				
1 : 1	1.00	0.77	1.06	0.87	1.14	0.84	1.27	1.01	0.50	0.46	1.38	1.15
4 : 1	0.76	0.67	0.82	0.65	0.92	0.72	1.04	0.89				
8 : 1	0.54	0.50	0.65	0.44	0.75	0.67	0.89	0.69				

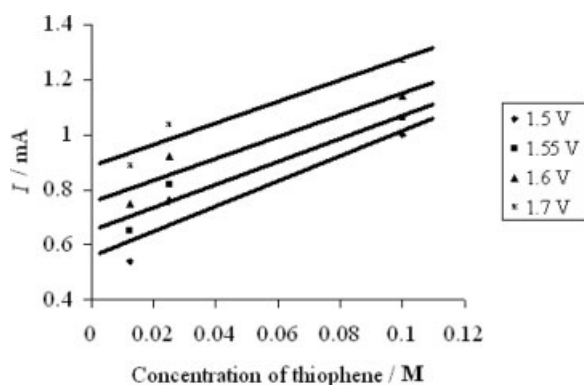
The peak potentials of homopolymers have been added for comparison.  $E_{\text{pol}}$ , electropolymerization potential;  $E_{\text{pa}}$ , anodic peak potential;  $E_{\text{pc}}$ , cathodic peak potential.

the =C—H bond of the copolymers shifts to higher wave numbers, and the intensity of this band also increases with the increasing preparation potential of the copolymer because of overlapping with the in-plane ring deformation band. When the furan/thiophene feed ratio changes from 1 : 1 to 4 : 1 and to 8 : 1, the same interesting features still exist [see Fig. 9(c,d)]. The strong combination band, which corresponds to the out-of-plane =C—H deformation and the in-plane ring deformation band of the copolymers, shifts to higher wave numbers when the thiophene concentration increases, and the intensity of this band also increases with the increasing preparation potential of the copolymers. These peaks differ obviously from those of polythiophene in this region. This may be due to the interaction between furan and thiophene units in the copolymer and may be regarded as evidence of copolymerization; it cannot be explained by the simple addition of the spectra of pure homopolymers.

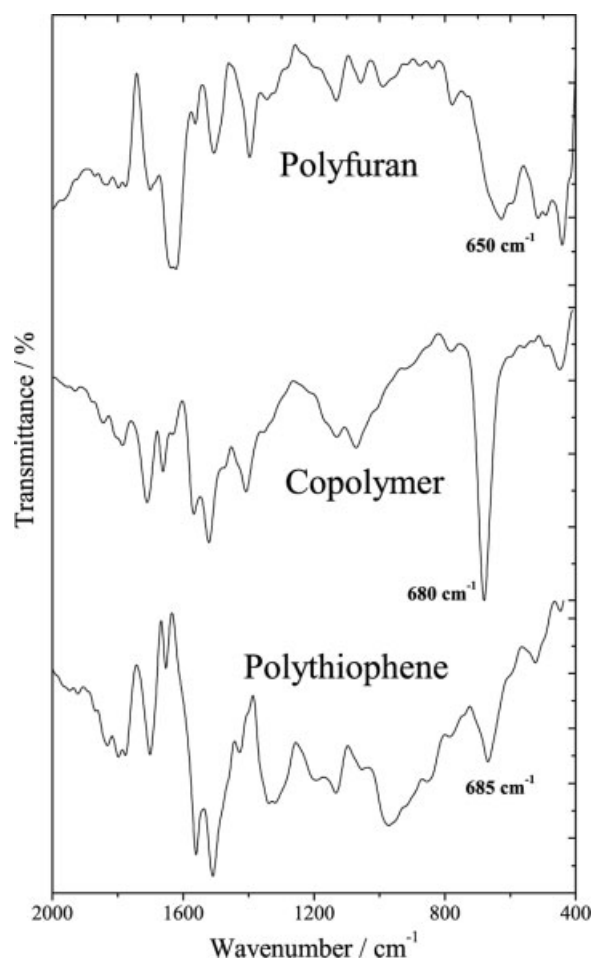
Furan–thiophene copolymers show fairly good long-term stability of the redox activity after cycling in organic solvents such as acetonitrile in comparison with polyfuran films,<sup>22</sup> as shown in Figure 10.

This applies also to the other copolymers studied here and prepared at different feed ratios and/or polymerization potentials. The peak separation of an-

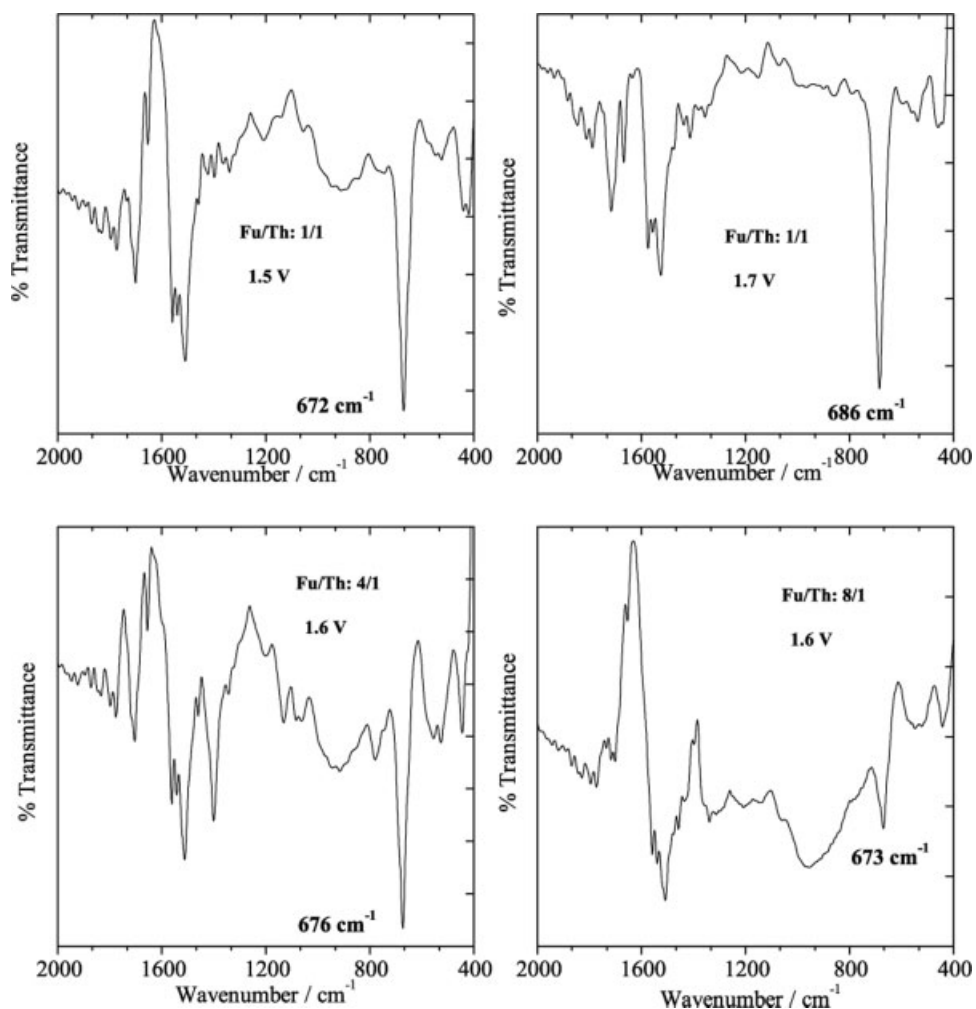
odic and cathodic peak potentials is still small, and this indicates an almost reversible redox reaction. The retention of the redox activity of furan–thiophene copolymers after cycling in dry acetonitrile for 100 times is about 60%. As shown in the inset, the anodic peak current decreases as the number of potential cycles increases, indicating a decrease of the redox activity. However, when a furan–thiophene copolymer is cycled in an aqueous solution, the redox activity is



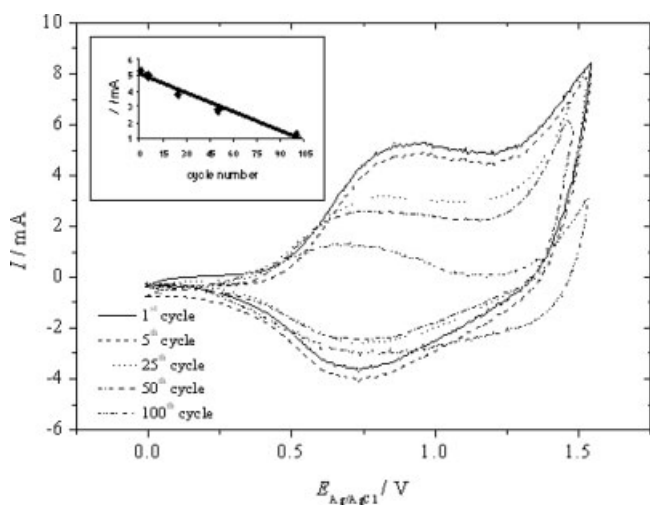
**Figure 7** Dependence of the anodic peak current of copolymers deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.5$ – $1.7$  V on the concentration of thiophene in mixed solutions.



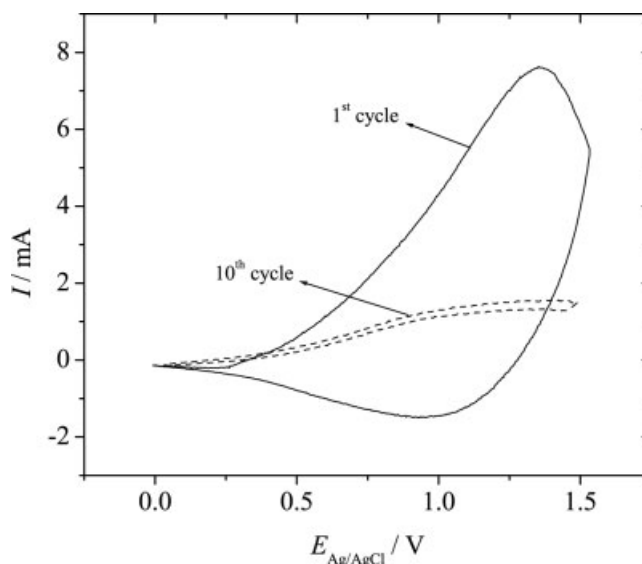
**Figure 8** FTIR spectra of polyfuran, polythiophene, and a copolymer deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.60$  V in a 1 : 2 BFEE/EE solution containing 0.10M furan and 0.10M thiophene.



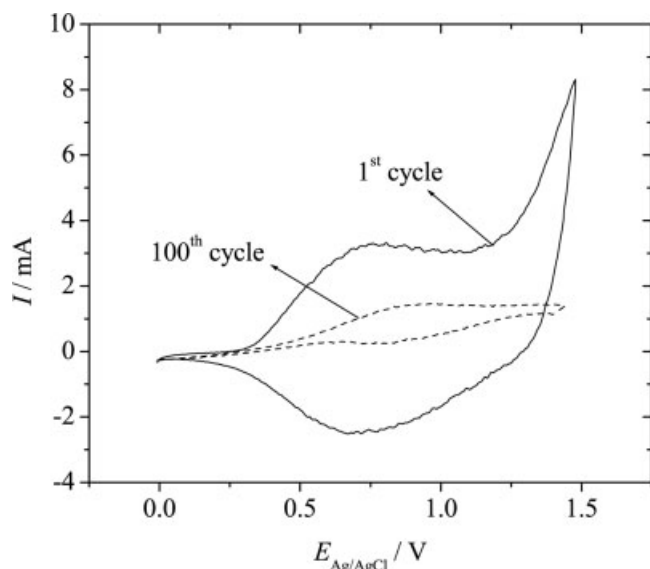
**Figure 9** FTIR spectra of copolymers deposited at  $E_{Ag/AgCl}$  values of 1.5 and 1.7 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 1 : 1) and copolymers deposited at an  $E_{Ag/AgCl}$  value of 1.6 V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 4 : 1 or 8 : 1).



**Figure 10** CVs (1st, 5th, 25th, 50th, and 100th) recorded in a solution of acetonitrile and 0.10M TBATFB for a copolymer deposited at  $E_{Ag/AgCl} = 1.60$  V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 4 : 1;  $dE/dt = 100$  mV/s).



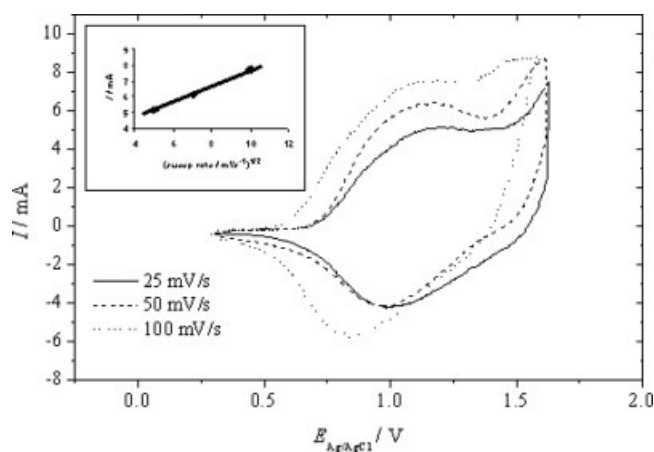
**Figure 11** CVs (1st and 100th) recorded in an aqueous solution containing 0.10M NaTFB for a copolymer deposited at  $E_{Ag/AgCl} = 1.60$  V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 4 : 1;  $dE/dt = 100$  mV/s).



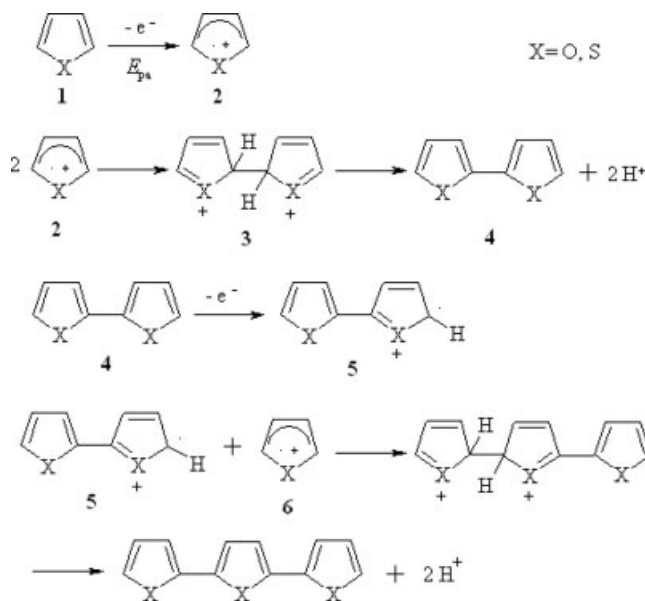
**Figure 12** CVs (1st and 100th) recorded in a solution of acetonitrile/H<sub>2</sub>O (volume ratio = 100 : 1) and 0.10M TBATFB for a copolymer deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.60$  V in a 1 : 2 BFEE/EE solution containing furan/thiophene (molar ratio = 4 : 1;  $dE/dt = 100$  mV/s).

almost totally lost because it shows a very large anodic peak current around 1.36 V but no associated cathodic peak (see Fig. 11). This process is independent of the pH value of the aqueous solution, indicating that water molecules instead of protons or hydroxyl ions are involved in this degradation process.<sup>33</sup>

Figure 12 shows the retention of the redox activity of a furan–thiophene copolymer in a wet acetonitrile solution; the volume ratio of acetonitrile to water is set to 100 : 1. About 20% of the redox activity of the copolymer remains after 100 cycles, and this indicates



**Figure 13** CVs recorded in a solution of acetonitrile and 0.10M TBATFB for copolymer films deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.50$  V in a 1 : 2 BFEE/EE solution containing 0.1M furan and 0.1M thiophene ( $dE/dt = 25, 50,$  or  $100$  mV/s).



**Scheme 1** Proposed mechanism for the electropolymerization of furan–thiophene copolymers.

that the loss rate of redox activity increases with the amount of water in acetonitrile. The associated loss of redox capacity during the oxidation process may be caused by the destruction of conjugated structures.<sup>19</sup>

Figure 13 shows CVs at scan rate ( $dE/dt$ ) values of 25, 50, and 100 mV/s for copolymer films deposited at  $E_{\text{Ag}/\text{AgCl}} = 1.5$  V in a solution containing furan/thiophene (ratio = 1 : 1). The inset depicts the dependence of the anodic peak currents on the square root of the scanning rate. The plot yields a straight line indicating that the electrochemical processes are diffusion-controlled, and the redox couple is attached to the electrode.<sup>19,34</sup> For a diffusion-controlled process, the straight line should pass through the origin, but in the case of conducting polymers, deviations from the ideal behavior may arise from contributions such as double-layer charging, which can disturb the zero intercept.<sup>35</sup>

The electropolymerization mechanism of copolymers is presumably even more complex than that of homopolymers.<sup>29</sup> Scheme 1 shows a proposed mechanism for the electropolymerization of furan and thiophene<sup>21,36</sup> based on already known coupling reactions of aromatic compounds.<sup>29,37</sup> The first electrochemical step is the oxidation of the monomer (1) into its radical cation. The second step involves the coupling of two radicals (2) to produce a dihydrodimer (3) dication that leads to a dimer (4) after the loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step. At the applied electrode potential, the dimer (4), which is more easily oxidized than the monomer, is present in its radical form (5) and undergoes further coupling with a monomeric radical (6). The electropolymeriza-



tion then proceeds through successive electrochemical and chemical steps according to a general E(EC)<sub>n</sub> scheme (where E is the electrochemical step and C is the chemical step) until the oligomer becomes insoluble in the electrolyte solution and precipitates onto the electrode surface; soluble oligomers have been observed to stray away from the electrode at the beginning of the polymerization.

### CONCLUSIONS

The electrochemical copolymerization of furan and thiophene was successfully realized in a binary system consisting of BFEE and additional EE at a constant electrode potential. CVs of the copolymers showed intermediate electrochemical properties between polyfuran and polythiophene. At higher polymerization potentials and at higher concentrations of thiophene in the feed, more thiophene units were incorporated into the copolymer. The furan-thiophene copolymers showed fairly good stability of the redox activity in organic solvents.

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