Electrochemically Polymerized Terthiophene Derivatives Carrying Aromatic Substituents

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Received December 7, 1993; Revised Manuscript Received March 24, 1994[⊗]

ABSTRACT: A series of terthiophene derivatives substitituted with an aryl group R at the 3′-position of the central thiophene [R = H (1), phenyl (2), 4-cyanophenyl (3), 4-methoxyphenyl (4), 4-pyridyl (5), 2-thienyl (6), or 3-methyl-2-thienyl (7)] have been polymerized. Although the substituents force the monomers to a nonplanar conformation, thus preventing the extension of conjugation to the side group, they influence the polymerizability and the properties of the resulting polymers. Solubilities of the oxidation products and inductive effects of the substituents are discussed in order to explain the differences. As-grown films of poly-1, -2, -3, -4, and -6 were soluble in chlorinated organic solvents. Poly-1 consists of monomers and dimers, but the polymerization degree of other soluble polymers was larger, as determined by matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS). The polymers are mixtures of oligomers in all cases, and the highest observed oligomers were heptamers (with poly-2 and -3). With the exception of poly-1, -4, and -5, the films could be both anodically and cathodically doped. A splitting of the cathodic undoping peak in cyclic voltammograms was observed with poly-6 and -7 and polythiophene. This behavior is analogous to the anodic undoping, suggesting a mechanistic symmetry in the doping processes. Spectral changes during undoping are interpreted by reactions of ionic species having different effective conjugation lengths.

Introduction

Studies on electronically conductive polymers have revealed that the behavior of the polymer film is connected to the extent of conjugation along the polymeric chain.[1] The conjugation can be characterized by the effective conjugation length, which determines not only the conductivity but also the electrochemical and spectroscopic properties of the film.[2] A prerequisite for a long effective conjugation length in thiophene-based polymers is a regular 2,5′-linked linear structure with no cross-linking.

One approach to increase the conjugation length in polymers consists of using linear thiophene oligomers as starting materials. Their lower oxidation potentials enable the use of milder polymerization conditions, and the formation of poly(bithiophene) and poly(terthiophene) has been reported by several groups.[3] These "polyoligomers", however, turn out to be generally inferior to polythiophenes in their conductivity and spectral and electrochemical properties. This can be attributed to the enhanced stability of the oligomeric cation radicals and the decreased relative reactivity of their α-positions, which leads to a decrease in the conjugation length.

On the other hand, functionalization of thiophene at the 3-position offers a possibility to control the reactivity of the monomer by the electronic effects of the substituent. Thus, electron-donating substituents are expected to decrease the oxidation potential of the monomer and increase the stability of its cation radical, while electron-withdrawing substituents would exert an opposite effect. In addition, the steric effects of the substituent affect the structure of the polymer chains, *e.g.*, the coplanarity of the aromatic rings, and the morphology of the polymer films. Several substituted thiophenes have been prepared, and poly(3-alkylthiophenes) have been shown to exhibit increased crystallinity and solubility. Aromatic substituents are particularly interesting as they present a possibility for the extension of the conjugation to the substituent. For instance, poly(3-phenylthiophene) and poly[3-(4-methoxyphenyl)thiophene] having good conductivity and facile doping–undoping processes in both the anodic and cathodic regions have been reported by Kaeriyama *et al.*, who also concluded that the phenyl ring is conjugated with the main chain.[4] On the other hand, the same polymers prepared by other groups exhibited much less favorable properties.[5]

It is difficult to distinguish between the electronic and steric effects of the phenyl group. It is, however, expected to exert a strong steric hindrance, thus preventing the adjacent thiophene rings to achieve a coplanar conformation.[5c] A reduction of the steric hindrance, at the same time conserving the electronic effect, may be possible by having the aromatic substituents regularly spaced in the polymer chain instead of occupying the adjacent thiophene rings. This can be effected by using terthiophene derivatives substituted at the 3-position of the central thiophene. In effect, this represents a combination of the strategies presented above, in which the electronic effects of the substituents are hoped to modify the properties of terthiophene, thus overcoming the problems confronted in the polymerization of the parent monomer. The separation of the substituents should also diminish the effect of different possible isomers (head-to-tail, head-to-head, and tail-to-tail coupling) on the properties of the polymers. We present here a study of the polymerization of a series of 3′-aryl-2,2′:5′,2″-terthiophenes (1–7, Chart 1) and the properties of the resulting films. The derivative pair 6 and 7 is especially interesting, as it may allow or prohibit cross-linking of the polymer structure *via* the pendant thienyl group, and the properties of polymers prepared from these monomers have already been discussed.[6] A complete characterization of the monomers 1–7 will be presented elsewhere.[7]

Experimental Section

Synthesis of the substituted terthiophenes 1–7 is published elsewhere.[7] The polymerization was carried out in an one-compartment cell from solutions of the corresponding monomer (0.05 M) and tetrabutylammonium hexafluorophosphate (0.2 M)

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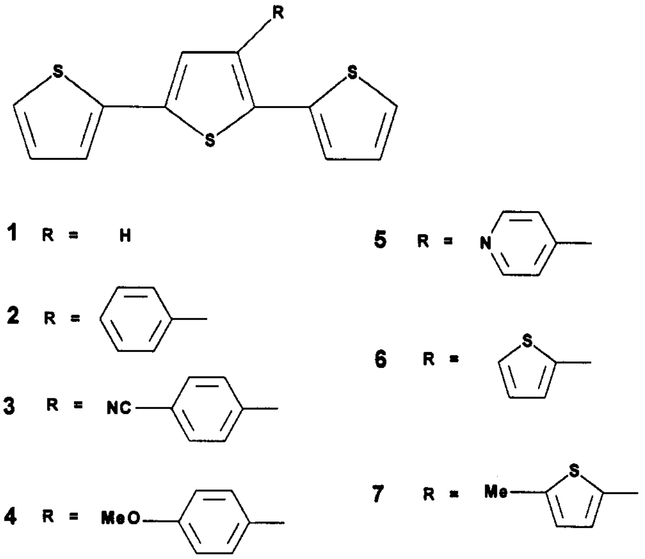
[⊗] Abstract published in *Advance ACS Abstracts*, May 1, 1994.

0024-9297/94/2227-3322$04.50/0

Chart 1



in propylene carbonate or, occasionally, acetonitrile. The working electrode was an indium-tin oxide coated glass (ITO, Planar International, Finland; *ca.* 20 Ω/□), which was cleaned in oxygen plasma immediately before use. Silver and gold electrodes were used as the pseudoreference and the counter electrode, respectively. The supporting electrolyte was dried in vacuum, and the solution was stored over activated Al_2O_3 (Aldrich). The solvents (Merck; anhydrous) were stored over 4-Å molecular sieves, and all the solutions were deoxygenated with dry argon. The water content of the solutions was controlled by coulometric Karl Fischer titration and kept below 30 ppm.

The spectroelectrochemical measuring system has been described earlier.[8] The spectra were recorded with an optical multichannel analyzer (PAR M1461) equipped with a diode array detector. All data acquisition was controlled with an IBM AT-compatible PC computer using an ASYST programming language.

The polymerization was carried out galvanostatically with a current density of 5 mA/cm^2 onto an ITO electrode having a surface area of 0.28 cm^2. The polymerization was stopped after a charge of 50 mC/cm^2 had passed. In the case of compound **5**, the film formation had to be enhanced by applying a short current pulse with higher current density in the beginning of the polymerization.[9] After the polymerization the films were reduced and rinsed several times with the solvent under an argon atmosphere. To study the spectroelectrochemistry of the polymers, the cell was filled with the supporting electrolyte solution.

Some polymeric films were dissolved in chloroform or 1,2-dichloroethane after reduction of the film. The dissolved films were oxidized by adding an acetonitrile solution of copper(II) triflate (trifluoromethanesulfonate), and the spectra of the dissolved films in the neutral and oxidized form were recorded with a Perkin-Elmer Lambda 2 UV-vis spectrophotometer. A Lasermat Mass Analyzer (Finnigan MAT) was used to record the matrix-assisted laser desorption ionization mass spectra (MALDI-MS) of the dissolved polymers. A mixture of 4-nitrophenol and 2-nitrophenyl octyl ether (both Fluka) in 1,2-dichloroethane (*ca.* 0.5% and 1%, respectively) was used as the sample matrix, and the concentration of polymers in the sample solution was on the order of 1 μg/mL. Spectra were recorded with 6-7 laser shots and using relatively high laser power.

Results and Discussion

The electropolymerization of the compounds **1**-**7** was best carried out galvanostatically from propylene carbonate solutions. Examples of the chronopotentiometric curves recorded during the polymerization are shown in Figure 1a. The behavior of the monomers falls into three different classes. Unsubstituted terthiophene (**1**) exhibits a small maximum in the very beginning, whereafter the potential remains almost constant. In galvanostatic electrodeposition, the maxima observed in the potential transients are usually connected to nucleation phenomena.[10] The same kind of initial maxima indicating nucleation and film formation were observed with compound **4** but a steplike increase of potential soon followed, leading to the overoxidation of the film. A similar potential increase was observed with **5** also, and, therefore, with these monomers the polymerization was interrupted earlier in order to obtain an active film. An interesting behavior was observed with compounds **2**, **3**, **6**, and **7**, which showed a peak-type potential-time profile, although the peak was much less pronounced with **6** and **7** than with the other two monomers.

The spectra recorded during the galvanostatic polymerization reflect the spectral evolution observed during chemical oxidation of the monomers.[7] In the case of electropolymerization, it is, however, not possible to distinguish with certainty between the absorption due to solution species and the deposited, oxidized film. Owing to the presence of several dissolved oxidation products and the interference of the film, the spectra exhibit very broad absorption bands. The spectral maxima observed during the early stages of polymerization are listed in Table 1, and some examples of spectra are shown in Figure 1b-d. With unsubstituted terthiophene (**1**), the maximum is at relatively short wavelength with little absorption at longer wavelengths. The position of the maximum is practically independent of the polymerization mode.[3c] On the other hand, compounds **2**, **4**, **6**, **7**, and especially **3** exhibit strong absorption also above 700 nm, indicating the formation of a highly oxidized film. The film formed in the case of pyridyl-substituted monomer **5** was less oxidized, in accordance with the inertness of the compound toward chemical oxidation.[7]

The spectra of the polymerized films, in their neutral state, are shown in Figure 2, and the wavelengths of the spectral maxima are listed in Table 1. It is evident that mainly short oligomers are deposited in the case of unsubstituted terthiophene (**1**), in accordance with previous observations.[3] The absorption maxima of other films were at higher energy than reported for electrochemically synthesized poly(3-phenylthiophene) or poly[3-(4-methoxyphenyl)thiophene] films but lower than reported for the chemically synthesized polymers.[4,5] With poly-**2** the optical band gap edge is close to that of poly(3-methylthiophene).[11] In situ conductivity measurement during the electropolymerization of **2**, using a technique described elsewhere,[12] yielded a value of 10 S/cm for poly-**2**. The measured conductivity is, also, between the values reported for poly(3-phenylthiophene).[4a,5a,c]

The as-grown neutral films of poly-**1**, -**2**, -**3**, -**4**, and -**6** were soluble in chlorinated organic solvents, like chloroform and 1,2-dichloroethane. The dissolution was immediate upon addition of the solvent with only a faint coloration remaining on the ITO electrode, poly-**1** being the least soluble. So far, only a few soluble polythiophenes, mainly 3-alkyl-substituted derivatives, have been reported.[1] The spectra of the dissolved polymers, both in the neutral state and oxidized with copper(II) triflate, are shown in Figure 3, and the corresponding λ_{max} values are listed in Table 1. The spectra of the neutral forms of poly-**2**, -**3**, -**4**, and -**6** were remarkably similar, implying a common unique effective conjugation length for these materials in solution. The length of the chromophore can be estimated to be close to 11-12 thiophene rings, as the absorption maxima of undecathiophenes with widely spaced alkyl chains are located at *ca.* 460 nm.[13] Poly-**1**,

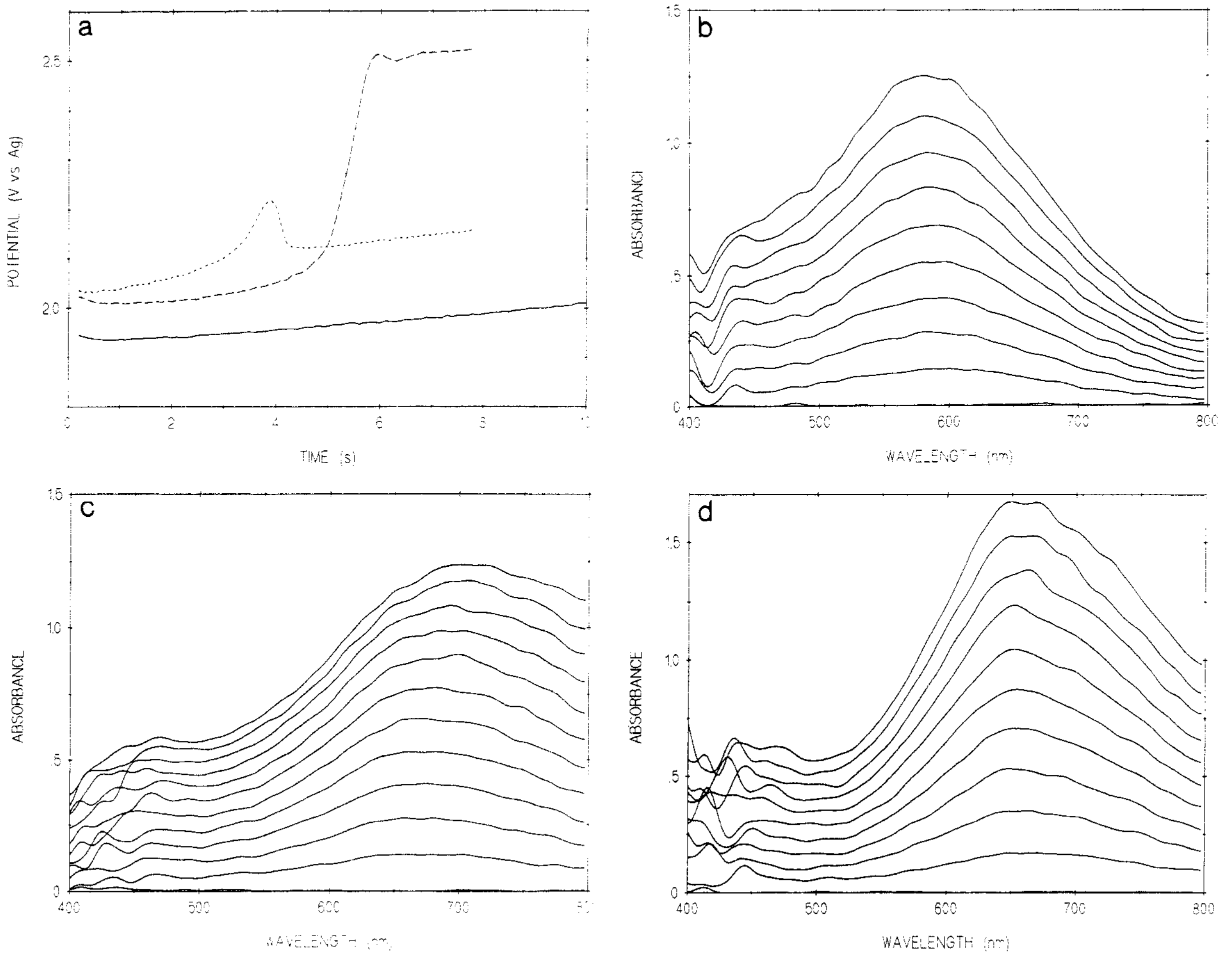


Figure 1. (a) Galvanostatic potential transients during electropolymerization (in propylene carbonate) of **1** (solid line), **3** (dotted line), and **4** (dashed line) and the spectra recorded during the polymerization of (b) monomer **1**, (c) monomer **3**, and (d) monomer **4** at 0.4-s intervals.

Table 1. Absorption Maxima (nm) of the Polymers (in the Solid State and in Solution) and the Maxima Observed during Electropolymerization

	during polym[a]	in solid state[b]	in solution[b,c]
poly-1	585	395	358, 434
poly-2	650	510	469
poly-3	680	500	466
poly-4	655	500	470
poly-5	455	475	*d*
poly-6	645	490	457
poly-7	640	495	*e*

[a] In propylene carbonate. [b] Neutral form. [c] In 1,2-dichloroethane. [d] Insoluble. [e] Not measured.

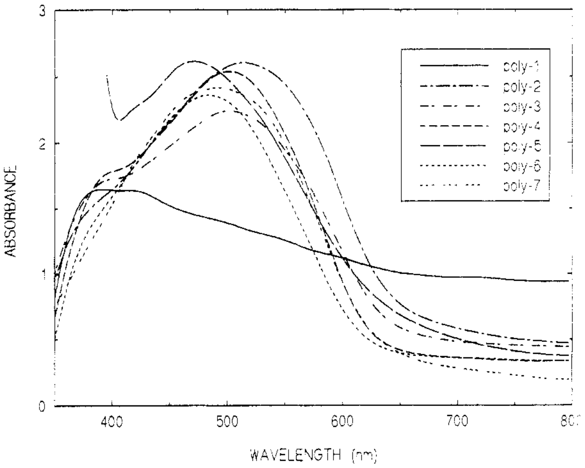


Figure 2. Spectra of the neutral as-grown polymer films on ITO. All films were prepared in propylene carbonate with tetrabutylammonium hexafluorophosphate as electrolyte.

on the other hand, differs clearly from the others. Its spectral maxima agree well with the reported values for terthiophene and sexithiophene in dichloromethane, indicating that an as-grown film of poly-1 is largely composed of monomers and dimers.[14] All polymers exhibit approximately 20–30-nm lower λ_{max} values and markedly lower absorption edges in solution than in the solid state, showing that solid-state structure affects the spectral properties of polymer films.

While the neutral polymers appear to possess an almost constant conjugation length, the situation is different with their oxidized forms (see inset of Figure 3). Although the exact oxidation degree of the polymers could not be determined, several features can be noted. The oxidized poly(terthiophene) exhibits peaks (684, 780, and 1005 nm) characteristic of oxidized sexithiophene.[7,14] With other polymers the wide absorption maxima at around 700 nm consist of several superimposed transitions at different energies, which implies the involvement of several species with different conjugation lengths. The more quinoidal structure of the oxidized polymers may stiffen the chains, thus facilitating the differentiation of different oligomers, while the flexible neutral chains limit the effective conjugation length to a common value. Another limiting factor is the presence of possible 2,4′-couplings in the chains.

In order to find out whether the films really contain several different oligomers, we have carried out molecular weight determinations of the dissolved polymers. In general, the determination of the polymerization degree of conductive polymers is rendered difficult by their

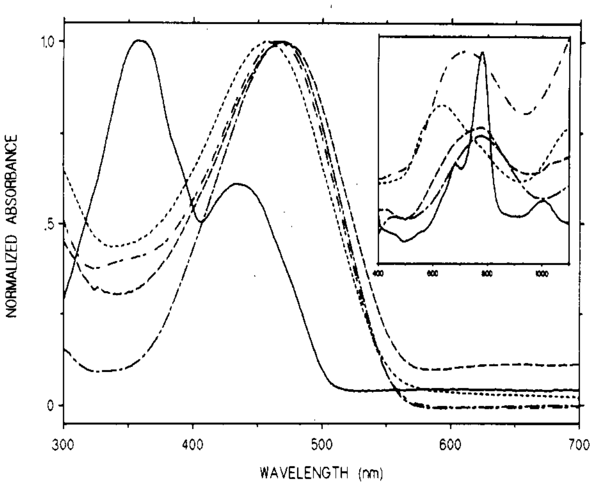


Figure 3. Spectra of the dissolved neutral polymer films in 1,2-dichloroethane. The inset shows the same polymers oxidized with Cu(II). Coding of spectra is as in Figure 2.

insolubility, and the chain lengths of many common polymers, like polythiophene and polypyrrole, have remained unknown. With soluble polythiophenes, the technique often employed is gel permeation chromatography, but the commonly used polystyrene standards have been shown to lead to erroneous results for poly(alkylthiophenes).[1] On the other hand, matrix-assisted laser desorption ionization mass spectrometry (MALDI-MS) has evolved to an increasingly important technique for molecular weight determination of proteins and peptides.[15] Outside biomolecules its applications have, however, remained scarce, and this paper represents, to our knowledge, the first attempt to use MALDI-MS in connection with conductive polymers. The theoretical basis of the method are not yet fully understood, and the choice of the ionization matrix is still largely on a trial-and-error basis. However, protonation of the substrate molecule by excited matrix components has been suggested, and phenols, like 4-nitrophenol, are good candidates owing to the greatly enhanced acidity of their excited state.[16] Homogeneity is another important property of a successful matrix, and, therefore, we have added liquid matrix material, 2-nitrophenyl octyl ether, to improve the miscibility of the components.[17]

An example of the MALDI mass spectra is presented in Figure 4, and Table 2 shows the observed peaks together with the calculated masses of the oligomers. In general, the agreement between the calculated and observed values is very good. The results show that the soluble films consist of a mixture of oligomers, the longest detectable species being heptamers (corresponding to 21 successive thiophene units) in the case of poly-**2** and -**3**. With poly-**6** and -**4** the corresponding species are hexamers and pentamers, respectively. This does not, however, necessarily imply an upper limit to the chain length, as the longer oligomers may escape detection in MALDI. Another problem with MALDI-MS is that the quantification of the results is difficult. However, it is noteworthy that the peaks corresponding to dimers are absent in all other cases except the methoxyphenyl derivative (**4**), whereas tetramers seem to be the prevailing species. Although the MALDI mass spectra show that the films mainly consist of oligomeric species, instead of highly polymerized chains, for simplicity we will be using the term polymer also during the rest of the discussion, as this is a common practice with conductive polymers having unknown polymerization degrees.

Cyclic voltammetry of unsubstituted poly(terthiophene), poly-**1**, shows the existence of two electrochemical steps (Figure 5). Upon reduction, the plateau-type process is followed by a cathodic peak. Considering that the as-grown film of **1** consists mainly of ter- and sexithiophene moieties, as evidenced by the spectra of the dissolved film (Figure 3), the steps observed in the voltammogram of poly-**1** and other thiophene-based polymers may be connected to the reduction of oligomers of different conjugation lengths.[2] The gradual fusing of the steps upon further cycling or long-term anodic polarization, when post polymerization of the film takes place,[3b] supports this interpretation. The cathodic doping of poly-**1** is totally irreversible, but some short-lived anionic intermediates could be detected at high sweep rates. As the reduction of the neutral film is not accompanied by any spectral changes, degradation of the film is assumed to take place.

Films of all other polymers, except the pyridyl derivative (poly-**5**), could also be doped anodically. Cathodic doping could be achieved with poly-**2**, -**3**, -**6**, and -**7** but resulted in the degradation of the poly-**4** film. Figure 5 depicts the electrochemical activity of poly-**3** in acetonitrile and shows clear anodic and cathodic processes separated by *ca.* 2 V, in accordance with the band gap edge estimated from the spectrum of the film (Figure 2). The observation of current is in itself, however, not sufficient proof of a doping process, particularly not at cathodic potentials on ITO electrodes,[18] but the spectra recorded during the voltammogram reveal changes characteristic of doping (Figure 6). When cycled in propylene carbonate solutions, the doping processes were slower, leading to larger separation between the anodic and cathodic branches of the voltammogram. In addition, spectra indicate that much lower doping levels could be achieved in this case.

The latter part of the anodic undoping of poly-**4**, -**5**, and -**6**, when studied using a relatively high sweep rate of 100 mV/s, is accompanied by a marked blue shift of the absorption maximum of the neutral form (Figure 7), due to an asymmetrical change of the interband transition. The polaron–bipolaron band theory predicting gap widening during doping, and not undoping, cannot explain this observation.[19] A similar opposite electrochromism under transient circumstances has already been described for poly(3-methylthiophene).[2] With a thick film of poly-**6**, even an isosbestic point at 520 nm was observed, indicating a late neutralization process accompanied by a small, slow decrease of the midgap absorption.

The extraordinary cyclic voltammetric behavior of the thienyl-substituted poly(terthiophenes) (poly-**6** and -**7**) during their cathodic undoping is unique because of two clearly discernible successive reoxidation steps (Figure 8). This splitting of the undoping peak has been already described.[20] We have also shown that the two steps are accompanied by well-defined spectral changes.[6] Here we present additional results, which show the effect of the polymerization conditions on the film properties. The splitting of the cathodic undoping peaks of poly-**6** could be observed only with films prepared in propylene carbonate. No splitting was observed with films polymerized in acetonitrile, although the measurements were carried out using acetonitrile solutions in both cases (Figure 9). The anodic and cathodic undoping processes are, therefore, symmetrical but strongly dependent on the polymerization conditions. The doping processes of thiophene-based polymers normally exhibit only a single peak in cyclic voltammograms, but we have previously shown by factor analysis of the spectra that, at least in the case of poly(3-methylthiophene), the anodic doping also consists of two closely spaced successive steps.[8]

In general, the order of the electrochemical processes taking place during the doping and undoping of conductive

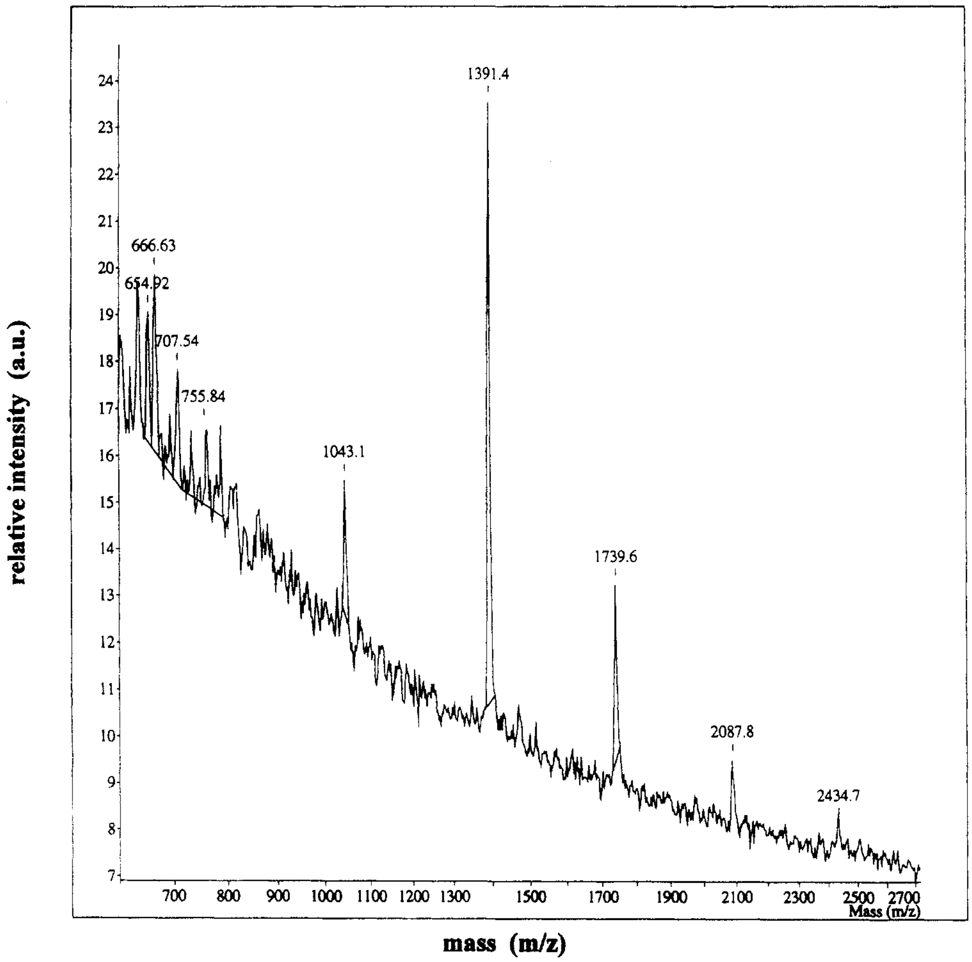


Figure 4. MALDI mass spectrum of poly-3 dissolved in 1,2-dichloroethane.

Table 2. Comparison of the Observed Peaks in MALDI Mass Spectra with the Calculated Masses for the Oligomers

	oligomer	calc mass	obs m/z^a		oligomer	calc mass	obs m/z^a
2	trimer	969.44	968.33	4	dimer	707.02	708.31
	tetramer	1291.9	1291.3		trimer	1059.5	1058.4
	pentamer	1614.4	1614.4		tetramer	1412.0	1412.7
	hexamer	1936.9	1937.5		pentamer	1764.5	1766.2
	heptamer	2259.4	2260.6				
3	trimer	1044.5	1043.1	6	trimer	987.53	988.18
	tetramer	1392.0	1391.4		tetramer	1316.0	1319.7
	pentamer	1739.5	1739.6		pentamer	1644.5	1651.0
	hexamer	2086.9	2087.8		hexamer	1973.0	1975.4
	heptamer	2434.4	2434.7				

[a] Representing $(M_nH)^+$.

polymer films depends on the mode of the perturbation applied.[2] Fast transient electrochemical transformations of thick layers may change the order of the different redox processes because of kinetical coupling to the ingress and expulsion of ionic and nonionic species, leading to an opposite spectral response compared to slower perturbations. Thus, hypsochromic and bathochromic shifts can give information about the order of the processes within the film. It has been shown that under steady-state conditions the doping of thiophene-type polymers—both the anodic and cathodic doping—starts with the transformation of the segments of higher effective conjugation length. On the other hand, the undoping process takes place stepwise and the neutralization of the diions first produces radical monoions together with shorter neutral segments.[2] In order to further clarify the spectral changes during the cathodic undoping of the thiophene-type polymers, a thicker film of polythiophene (polymerization charge 100 mC/cm^2) was prepared. Figure 9 shows (partial) splitting of the reoxidation peak also in this case. Spectral measurements during the doping and undoping (Figure 10) are grouped together to show the two types of changes: during the first period of reoxidation the absorbance increases at both low and high wavelengths. This means that, in addition to the neutral form (n), a species with spectral transition at the midgap energies is also produced. Taking into account that the bipolaron is the most stable charge carrier in polythiophenes[21] and assuming that this holds for n-doping also—supported by the observed symmetry of both processes—the spectral observations during n-undoping may be attributed to a dissociative

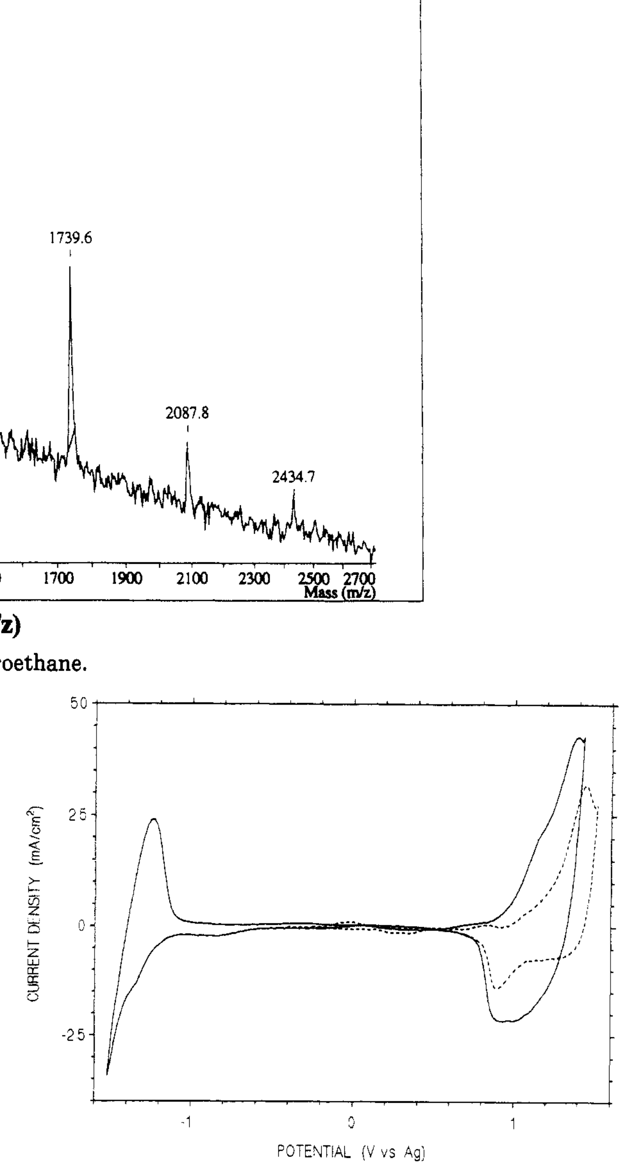


Figure 5. Cyclic voltammograms (100 mV/s) of poly-1 (dotted line) and poly-3 (solid line) on ITO in an acetonitrile solution (0.2 M Bu_4NPF_6).

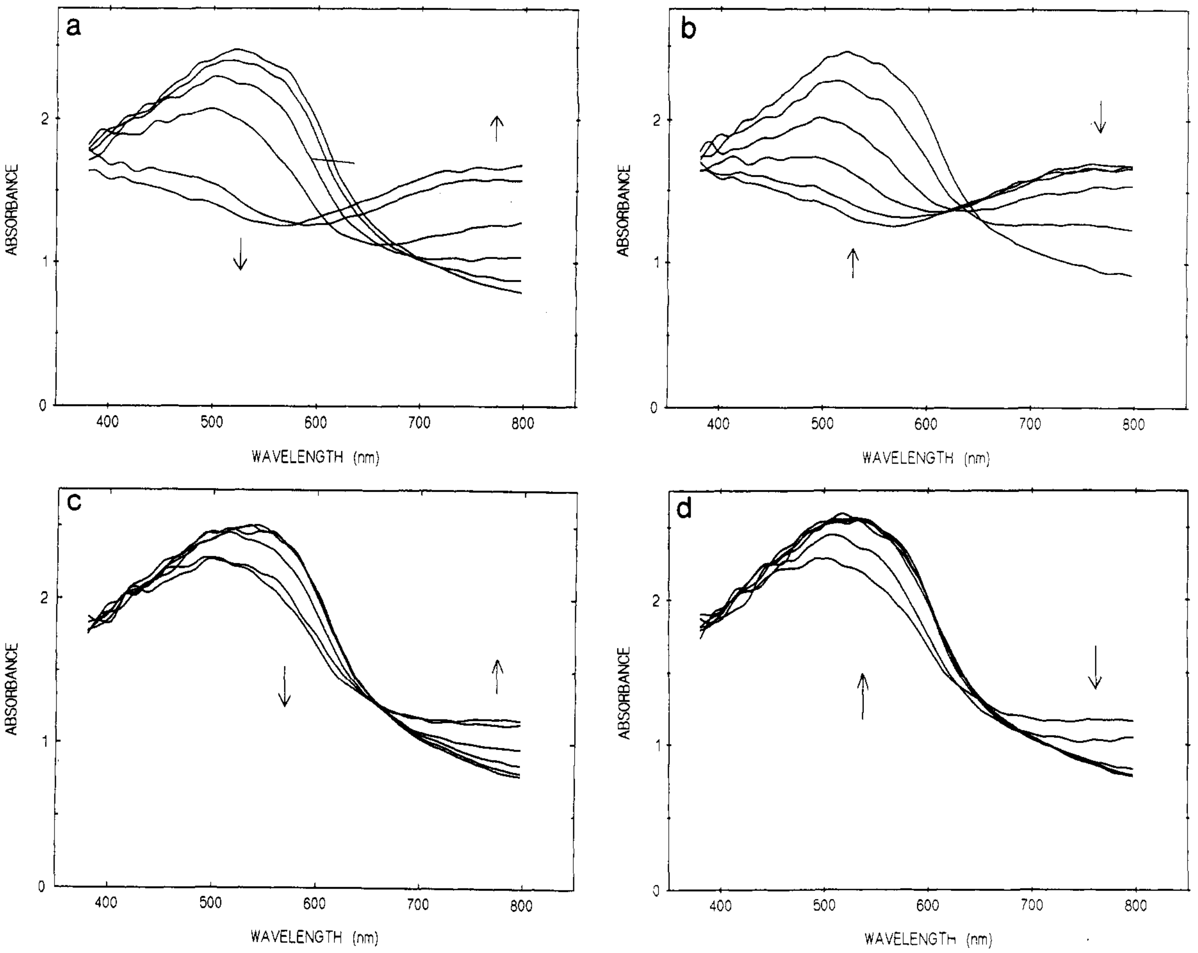


Figure 6. Spectra recorded (ΔE = 100 mV) during (a) anodic doping (1.0 ⇒ anodic turning point ⇒ 1.3 V), (b) anodic undoping (1.3 ⇒ 0.8 V), (c) cathodic doping (−1.15 ⇒ cathodic turning point ⇒ −1.35 V), and (d) cathodic undoping (−1.35 ⇒ −0.85 V) of poly-**3**.

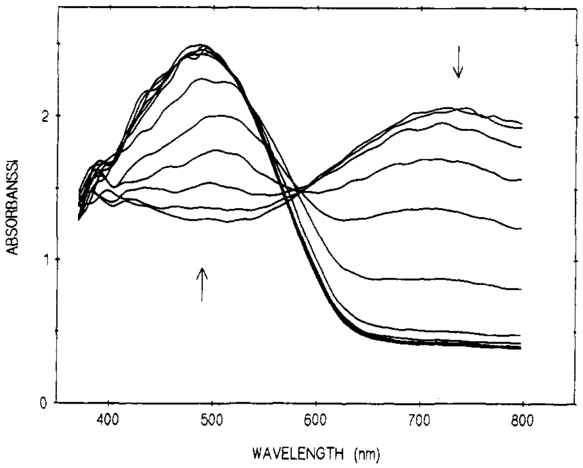


Figure 7. Spectra recorded during anodic undoping of poly-**6** showing a blue shift of the $\pi \rightarrow \pi^*$ transition.

oxidation like

$$A^{2-} - e^- \rightarrow n + A^-$$

where the absorption coefficient of A^- is larger than that of A^{2-} in the midgap wavelength range.

We have shown elsewhere that for sterical reasons the phenyl substituent cannot be in the same plane with the terthiophene ring system.[7] This result is in accordance with the conclusion of Onoda *et al.* that was, however, based on indirect evidence.[5c] Actually, the general structural feature of the substituted monomers is their nonplanarity, the pendant aryl ring forcing the molecule to a very puckered conformation. As a result, the

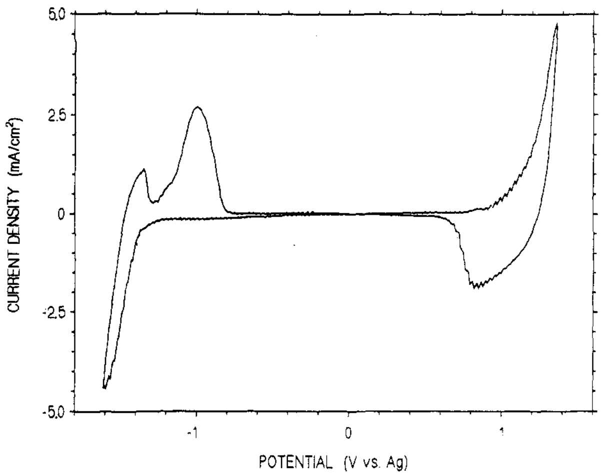


Figure 8. Cyclic voltammogram (100 mV/s) of poly-**6** on ITO (prepared in propylene carbonate) showing splitting of the cathodic undoping process. Measured in an acetonitrile solution (0.2 M Bu_4NPF_6).

conjugation does not extend to the substituent, a fact evidenced by the almost identical maxima in the UV spectra of all the monomers.[7] Therefore, it is really noteworthy that the substituents greatly influence the oxidation behavior and polymerizability of the monomers and the properties of the polymeric films. One might think that the more rigid structure of the oxidized species could facilitate the participation of the aryl substituent to the conjugation. The spectra of the oxidized hexamers show, however, only insignificant shifts in the peak positions with the substituent, which indicates that the pendant aryl group does not interfere with the conjugation in this case either.[7] On the other hand, the solubility of the

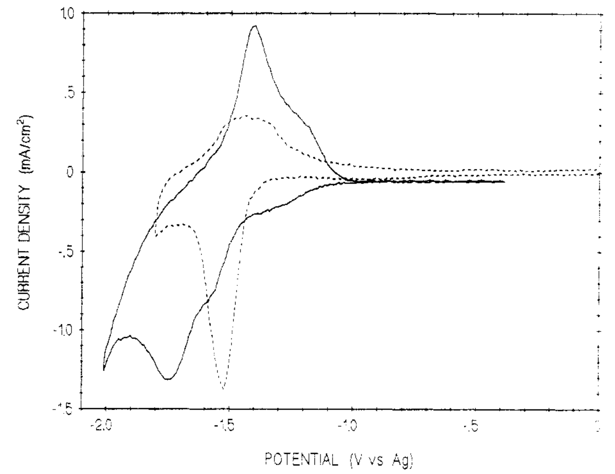


Figure 9. Dotted line: Cathodic doping and undoping of poly-**6** prepared in acetonitrile. Solid line: Cathodic doping and undoping of polythiophene. Both measured with 100 mV/s in acetonitrile solutions (0.2 M Bu_4NPF_6, films on ITO).

oxidation products, *i.e.*, oligomers and their salts with the electrolyte anion, in the polymerization medium may play an important role in determining the attainable chain length in solution. The solubility of unsubstituted thiophene oligomers decreases sharply with increased chain length.[22] For instance, sexithiophene is poorly soluble and octithiophene completely insoluble in acetonitrile. Therefore, alkyl side groups have been used to increase the solubility of longer oligothiophenes.[13] With aryl-substituted terthiophenes in this work, however, the solubility of the parent monomer **1** in propylene carbonate is somewhat higher than that of the phenyl derivative **2** (*ca.* 0.2 and 0.12 M at room temperature, respectively). This does not support different solubilities as the cause for the observed differences in properties, but the interactions between the unsubstituted chains may well increase more rapidly with increasing chain length than in the case of substituted chains, due to the induced nonplanarity in the latter case. The best polymers in this work, in terms of electrochemical and optical properties, were obtained with phenyl- and 4-cyanophenyl-substituted derivatives (**2** and **3**). Poly-**2** and -**3** also contained the longest oligomeric species detected in the MALDI mass spectra. While solubility effects may dominate in the case of derivative **2**, the electron-withdrawing cyano group can exert also an inductive effect, giving rise to a partial positive charge at the carbon atom attached to the thiophene ring. This decreases the stability of the dicationic species with respect to the monoionic ones, an effect clearly observed in the spectra of chemically oxidized monomer,[7] and probably enhances polymerization. In addition, electron-withdrawing groups are supposed to stabilize the negatively charged species, thus facilitating cathodic doping. On the other hand, the addition of the electron-donating methoxy group to the phenyl ring (monomer **4**) resulted in a polymer with inferior properties. The failure of monomer **5** to produce polymer with satisfactory properties can be attributed to the pyridyl substituent, which may act as a built-in nucleophile interfering with the deprotonation of the oxidation intermediates.

Conclusions

A series of terthiophenes substituted with an aryl group at the central thiophene ring have been polymerized in this work. The properties and structures of the neutral monomers are similar, because the aromatic substituent forces the molecule to a nonplanar conformation. However, a clear improvement compared to the unsubstituted poly(terthiophene) was achieved. The best results were obtained with electron-withdrawing substituents, especially with a 4-cyanophenyl substituent that stabilizes the monocation with respect to the dication, while electron-donating ones had an impairing effect. This shows that not only the structure and properties of the neutral monomers but also those of their oxidized forms should be considered in assessing their potential as precursors for conductive polymers.

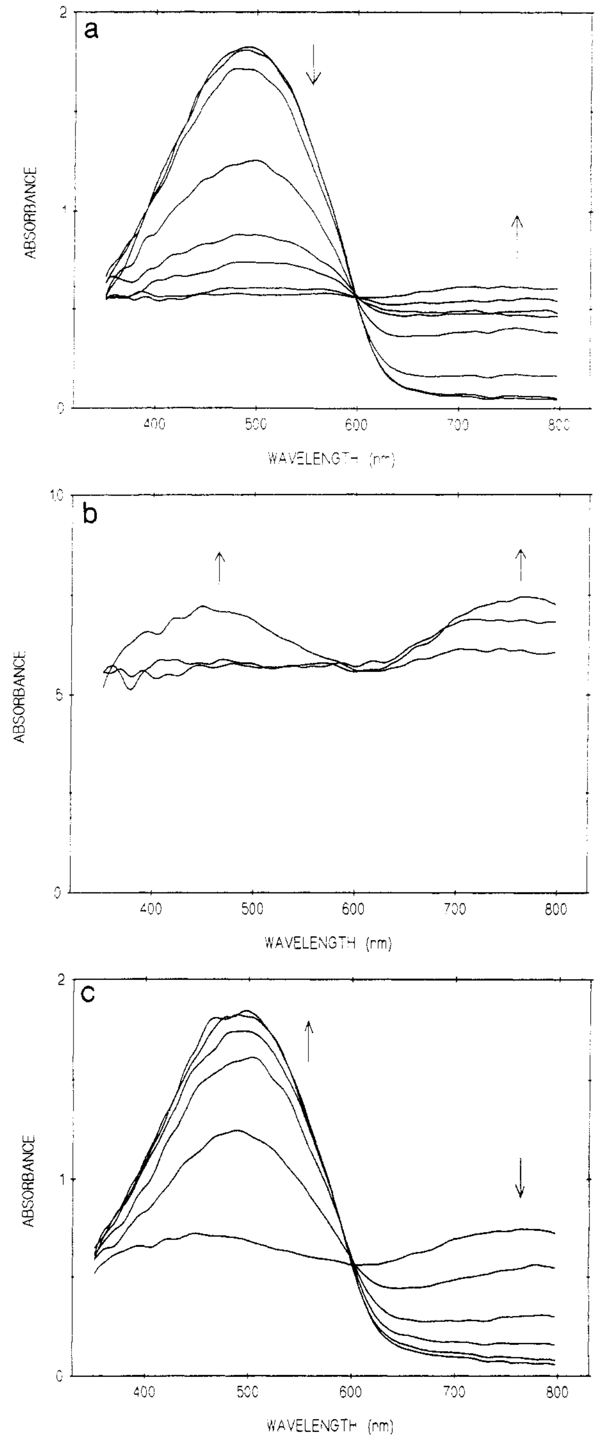


Figure 10. Spectra recorded during cathodic doping and undoping of polythiophene film (ΔE = 80 mV). (a) $-1.5 \Rightarrow$ cathodic turning point $\Rightarrow -1.7$ V; b) $-1.7 \Rightarrow -1.45$ V; (c) $-1.45 \Rightarrow -0.85$ V.

The optical and electrical properties of the films obtained are similar or inferior to the previously reported poly(3-phenylthiophene) and poly[3-(4-methoxyphenyl)-thiophene] films.[4,5] Some of the reported polymers refer to as-grown films, whereas others have been subjected to long annealing treatments, but the posttreatment of the films does not explain the differences. In fact, although poly-1, and -6 have been shown to undergo postpolymerization reactions in the solid state,[3b,6] other polymers studied showed no further polymerization upon oxidation. This emphasizes the complex influence of the polymerization conditions on the properties of the resulting films. We have previously shown that the electrode surface has an important effect on the course of the electropolymerization process.[11] Until the role of all the factors affecting the polymerization is understood, careful attention to the conditions is necessary in order to obtain reproducible results.

The effect of the substituents carries over to the doping behavior of the films. However, general spectral features during the anodic and cathodic doping processes could be observed. Based on the spectroelectrochemical measurements, the first step during the undoping of thiophene-based polymers can be attributed to a dissociative reduction of a diionic segment with long effective conjugation to produce a neutral segment and a shorter monoion,

$$A^{2+} + e^- \rightarrow n + A^+$$

or to a corresponding oxidation

$$A^{2-} - e^- \rightarrow n + A^-$$

in the case of anodic and cathodic undoping, respectively. In addition, the spectra suggest the following relation between the absorption coefficients of the charged species in the midgap range, *i.e.*, above 600 nm.

$$\epsilon_{A-} > \epsilon_{A2-} \quad \text{while } \epsilon_{A+} \cong \epsilon_{A2+}$$

The solubility of most of the as-grown films enabled the determination of their polymerization degree. For this purpose, matrix-assisted laser desorption ionization coupled to mass spectrometry was used for the first time with conductive polymers. The experimental parameters were, however, not optimized, and long oligomers may have remained undetected. The question arises as to what would be the best way of producing ionized thiophene species for MALDI. In this work protonated oligomers were generated, but other possibilities could be oxidation or complex formation with a metal ion. The longest observed oligomers consisted of over 20 thiophene rings. This result has implications to the structure of other polymers also. It shows that reasonably long substituted chains can be produced electrochemically in spite of the greatly reduced reactivity of already medium-sized oligomers. The chain lengths of insoluble polymers, *e.g.*, polythiophene, should be at least of comparable size, unless the insolubility is the result of extensive cross-linking or strong interactions between unsubstituted chains. The latter possibility appears more likely in light of the decreased solubility of thiophene oligomers. The attainable chain length would, therefore, be determined by the solubility of the oxidation products in the polymerization medium used, together with their reduced reactivity, and further polymerization could take place only in the solid state. This would imply, on the other hand, a rather low polymerization degree of polythiophene films.

Acknowledgment. A grant from the Academy of Finland is gratefully acknowledged. We thank Mr. Jorma Hermonen (Turku Centre for Biotechnology) for recording the MALDI mass spectra and Planar International for donation of the ITO electrodes.

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