

Electrochemical Behavior of Electropolymerized and Chemically Synthesized Hyperbranched Polythiophenes

Steffen Link,^{†,‡} Thomas Richter,^{†,‡} Olena Yurchenko,^{†,‡} Jürgen Heinze,^{*,†,||} and Sabine Ludwigs^{*,†,‡,§}

Institut für Makromolekulare Chemie, Universität Freiburg, Stefan-Meier-Strasse 31, 79104 Freiburg, Germany, Freiburger Materialforschungszentrum, Universität Freiburg, Stefan-Meier-Strasse 21, 79104 Freiburg, Germany, Freiburg Institute for Advanced Studies (FRIAS), School of Soft Matter Research, Universität Freiburg, Albertstrasse 19, 79104 Freiburg, Germany, and Institut für Physikalische Chemie I, Universität Freiburg, Albertstrasse 21, 79104 Freiburg, Germany

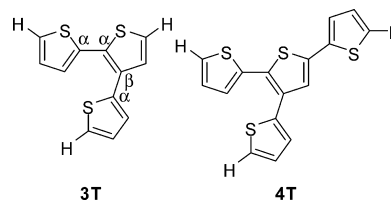
Received: April 20, 2010

Hyperbranched polythiophenes were synthesized by potentiodynamic electropolymerization of 2,2';3',2''-terthiophene and 5'-(2-thienyl)-2,2';3',2''-terthiophene. The molecular architecture, i.e., the extent of branching of the resulting polymers, could be adjusted by varying the switching potentials. We compare these systems to hyperbranched polythiophenes which we obtained via a simple one-pot synthesis route based on FeCl₃ oxidative polymerization of the monomers. Interestingly, we find that the properties of the electropolymerized materials obtained with high switching potentials are comparable to those of the chemically synthesized polythiophenes. A detailed optical and electrochemical characterization of these systems is performed showing the high potential of this material class for optoelectronic applications. Cyclic voltammetry coupled with in situ conductance measurements further reveal reversible doping upon oxidation (p-doping) and reduction (n-doping) and comparable values for the conductance for the chemically and electrochemically synthesized materials.

Introduction

Conjugated polythiophenes have turned out to be one of the most promising candidates for the development of effective, versatile, and durable polymer electronics. In particular poly(3-hexylthiophene) has been successfully employed in organic solar cells^{1,2} and organic field effect transistors.³ Due to the linear conjugated backbone poly(3-hexylthiophene) is semicrystalline and can show anisotropic charge carrier mobilities which are typically highest in the π -stacking direction.^{4,5} Processing and assembly of efficient optoelectronic devices with these polymers requires strict control over the crystallization of the polymer. The development of new polymer architectures allowing isotropic charge carrier mobilities and at the same time good solubility and processability is a challenge of current research. Examples of recent developments include star-⁶ and X-shaped oligothiophenes,^{7,8} swivel-cruciform oligothiophene dimers,⁹ and spider-like oligothiophenes.¹⁰ Polythiophene dendrimers were first synthesized by Advincula and co-workers.¹¹ Bäuerle et al. presented thiophene dendrimers containing up to 90 thiophene units.^{12,13} The main advantage of dendrimers is their well-defined structure and the high branching density. A drawback, however, is the high synthetic effort requiring multiple-step syntheses and elaborate purification methods. Hyperbranched polymer systems are expected to show similar characteristics with respect to their dendrimer analogues. Xu and Pu showed the first synthesis of

CHART 1: Structures of the Monomers Used in This Work



hyperbranched polythiophenes utilizing a synthetic procedure developed by McCullough.¹⁴

In a previous paper we reported a one-pot synthesis yielding hyperbranched polythiophenes that are soluble in common organic solvents without alkyl substituents using oxidative coupling of the branched monomers 2,2';3',2''-terthiophene (**3T**) and 5'-(2-thienyl)-2,2';3',2''-terthiophene (**4T**) (see Chart 1) with FeCl₃.¹⁵ These branched monomers feature thiophene rings that are either connected by α - α - or α - β -couplings. Their chemical polymerizations using FeCl₃ as oxidant in dry chloroform at room temperature resulted in the formation of polymers (**CH-p3T** and **CH-p4T**) that could be fractionated by solubility in chloroform **TCM** and chlorobenzene **CB**, applying Soxhlet extraction. The molecular weights of the different fractions were determined by SEC analysis and MALDI-TOF mass spectra. As shown in Table 1 the molecular weights determined by MALDI-TOF are higher than those determined by SEC, which indicates a branched structure of the polymers.

The density of branching is inherently higher for the **CH-p3T** compared to **CH-p4T** systems, which means that the tetrathiophene containing polymers have longer linear, i.e., α -conjugated segments in the structure.

* To whom correspondence should be addressed. E-mail: sabine.ludwigs@makro.uni-freiburg.de; juergen.heinze@physchem.uni-freiburg.de. Phone: (+49)761-203-4735. Fax: (+49)761-203-4709.

[†] Institut für Makromolekulare Chemie.

[‡] Freiburger Materialforschungszentrum.

^{||} Institut für Physikalische Chemie I.

[§] Freiburg Institute for Advanced Studies.

TABLE 1: MALDI-TOF and SEC Data of the Chemically Synthesized Polymers

polymer	MALDI-TOF ^a		SEC ^b	
	M_w [g mol ⁻¹]	PDI	M_w [g mol ⁻¹]	PDI
CH-p3T-TCM	2560	1.27	1650	1.74
CH-p3T-CB	3640	1.26	3200	1.23
CH-p4T-TCM	1500	1.16	1300	1.40
CH-p4T-CB	2470	1.10	n.d. ^c	n.d. ^c

^a Matrix: dihydroxybenzoic acid. ^b Against polystyrene as standard; chloroform as solvent allowed in some cases only highly diluted solutions to be measured; ^c Solubility of chlorobenzene soluble fraction was too low to allow SEC analysis in chloroform. n.d. = not determined.

Considering an oxidation potential of dissolved FeCl₃ in chloroform of approximately +0.9 V vs Fc/Fc⁺,¹⁶ an alternative approach to hyperbranched polythiophenes should be possible by electropolymerization. **4T** has already been electropolymerized galvanostatically by Visy et al., who obtained a soluble polymer.^{17,18} The potentiodynamic polymerization of alkoxy substituted **4T** leading to insoluble polymer films was shown by Zotti.¹⁹ Few other electropolymerizations of branched thiophene monomers have been reported so far.^{20–22}

In this contribution we show that **4T** and **3T** can be polymerized electrochemically to yield polymers (**EC-p3T** and **EC-p4T**) that feature similar optoelectronic properties as those that are chemically polymerized utilizing FeCl₃. Comparing the absorption spectra both in films and in solution allows us to draw conclusions about their branched architecture. The choice of the monomer as well as the switching potentials during potentiodynamic polymerization allow control over the effective conjugation lengths and thus to tailor make the optoelectronic properties.

Experimental Methods

The synthesis of the monomers and the polymerization involving FeCl₃ have already been published elsewhere.¹⁵ Acetonitrile (hypergrade) was purchased from Merck and used as received. Tetrabutylammonium hexafluorophosphate (puriss.) was purchased from Fluka and used as received. Electrochemical experiments were carried out under argon atmosphere in cells similar to those designed by Kieseles.²³ The cells are equipped with an internal drying column that can be filled with highly activated alumina as drying agent. The solvent containing the supporting electrolyte was dried by passing it several times through the filled column at 253 K before each measurement. As working electrodes interdigitated platinum structures as well as indium–tin oxide covered glass electrodes were used. The interdigitated platinum structures consisted of two comb-shaped platinum bands with a gap of 10 μm. By applying a voltage of 10 mV between these combs and simultaneous detection of the resulting current the resistance of the sample over the gap could be obtained employing Ohm's law. The electropolymerizations were generally carried out potentiodynamically with 10⁻³ M solutions of the monomers in acetonitrile/TBAPF₆ (0.1 M) at room temperature with scan rates of 50 mV/s. The optical absorption spectra were taken on a Perkin-Elmer Lambda 9 spectrometer. Spectra of the electrodeposited films were recorded either on ITO coated glass or in solution after dissolution of the electropolymerized materials in chloroform or chlorobenzene. Absorption spectra of the chemically synthesized polymers were recorded either of polymer films that were spin-coated (from 20 mg/mL solutions) on glass or of solutions in

chloroform or chlorobenzene. Optical band-gaps were obtained from the absorption onset values.

Results and Discussion

Optical Investigation. Cyclic voltammograms (CVs) of the electropolymerizations of **4T** and **3T** yielding the corresponding polymers, **EC-p4T** and **EC-p3T**, are shown in Figure 1A,B. Both monomers show trace-crossing in the first oxidation cycle, i.e., a higher current on the reverse sweep than on the forward scan. This phenomenon, often observed when the switching potential (E_s) of the electropolymerization is set higher than the peak maximum of the oxidation of the monomer, can be related to homogeneous comproportionation reactions between highly charged oligomers and monomers.^{24,25} If charged oligomeric species formed in the first oxidation process subsequently react with monomers by a comproportionation reaction, the oxidation of the monomers is facilitated. The shift of the monomer oxidation potential to lower values in the following cycles gives further evidence for an autocatalytic mechanism. The initial oxidation of the **3T** and **4T** monomers begins at approximately +0.73 and +0.57 V vs Fc/Fc⁺, respectively. The peak oxidation potentials are +0.91 (**3T**) and +0.73 V (**4T**). The values are only slightly lower than those of linear bithiophene (+0.970 V vs Fc/Fc⁺) and terthiophene (+0.757 V vs Fc/Fc⁺) as reported by Ryder et al.²⁶

The monomer **4T** has an absorption maximum at 350 nm. This matches the value reported for linear terthiophene¹⁸ and strongly suggests that in the **4T** molecule the conjugation of one of the thienyl groups is only weak. Therefore it can be expected that an electropolymerization close to the onset oxidation potential of the monomers should yield mostly linear polymers with one thienyl group as the side group.¹⁹ To ensure a high participation of the thienyl side group during the polymerization, the anodic switching potentials were set higher than the peak maxima of the oxidation of the monomers. In panels A and B of Figure 1 the switching potentials are +0.80 V for **4T** and +1.15 V for **3T** (vs Fc/Fc⁺ respectively). To investigate how the choice of the switching potential influences the molecular architecture of the resulting polymer, the electropolymerization of **4T** was conducted on ITO electrodes at switching potentials of +0.57 (i.e., at the oxidation onset), +0.8 (i.e., close to the oxidation peak potential), and +1.0 V (i.e., higher than the oxidation peak potential). The obtained films were carefully washed with acetonitrile to remove unreacted monomers and then characterized with UV–vis spectroscopy. Figure 1C shows that the polymer films obtained by switching the potential at +0.57 V have an absorption maximum at 390 nm and a shoulder at 530 nm. The rather sharp maximum at 390 nm is likely to originate from the dimer of **4T**, i.e., six α-conjugated thiophene rings with two thienyl side groups. For comparison, another double substituted sexithiophene (3'''-4'-didodecyl-2,2': 5',2'': 5'',2''': 5''',2''''': 5''''',2''''''-sexithiophene) has its absorption maximum at 416 nm.²⁷ Polymer films synthesized with switching potentials at +0.8 V reveal a broad maximum at 452 nm and also a shoulder at 530 nm. Switching the potential at +1.0 V exhibits polymers with a much broader absorption and a maximum at 502 nm.

Comparing the absorption spectra in Figure 1C reveals a lower absorption around 350 nm for the polymers electropolymerized at E_s = +0.57 and +0.80 V compared to the polymer obtained at E_s = +1.0 V. The increased absorption below 390 nm can be attributed to short conjugation lengths and is an indication for a branched structure¹² that is only obtained at E_s = +1.0 V. In this case an enhanced participation of the weakly

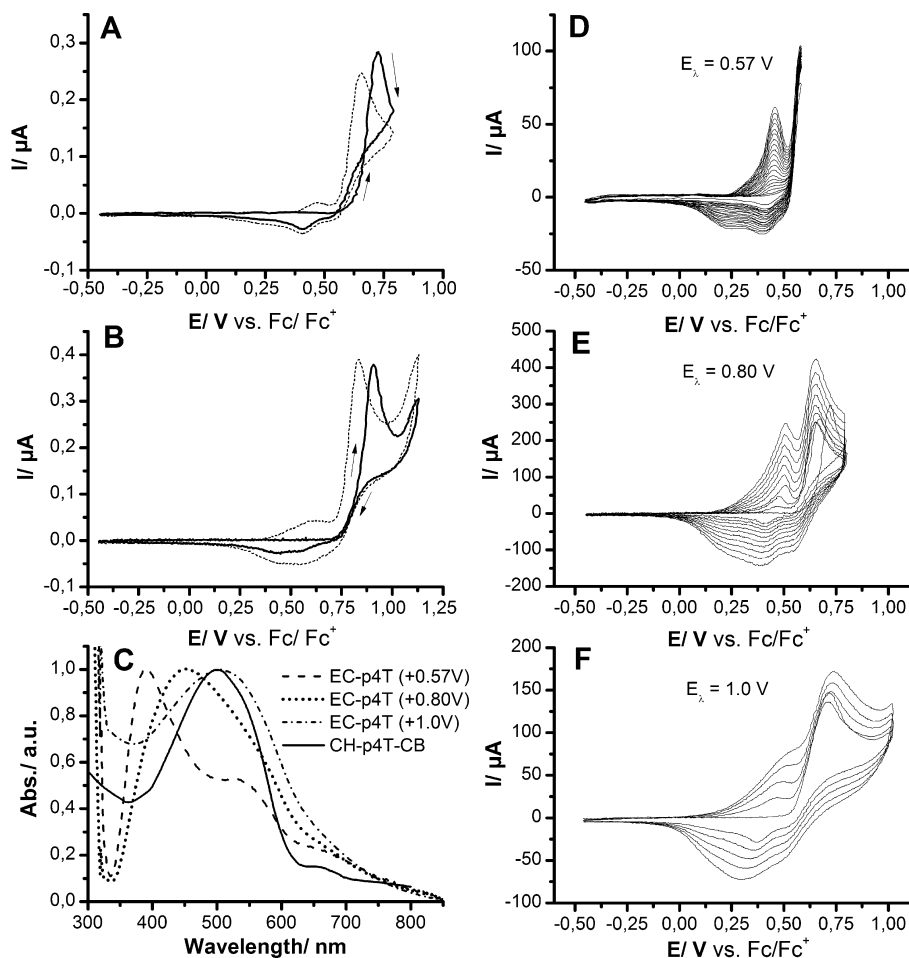


Figure 1. First (solid line) and second cycle (dotted line) of the electropolymerization of tetrathiophene (A) and trithiophene (B), both at 20 mV/s. (C) Absorption spectra of **p4T** as film on ITO-coated glass, electropolymerized at 20 mV/s with switching potentials of +0.57, +0.80, and +1.0 V and chlorobenzene fraction of **CH-p4T** polymerized with FeCl_3 as oxidant. (D–F) Cyclic voltammograms of the electropolymerizations (10^{-3} M, 50 mV/s, room temperature) of **4T** with switching potentials at +0.57 (D), +0.80 (E), and +1.0 V (F).

conjugated thienyl side group is anticipated, which by coupling with the three α -conjugated thiophene units should result in the formation of short effective conjugation lengths. This includes also augmented interruptions of the conjugation paths due to increased steric intramolecular interactions. Although the **4T** monomer itself shows an absorption maximum at 359 nm (Figure S1, Supporting Information), the absorption below 390 nm is not likely to be caused by monomer embedded in the polymer as repeated washing with acetonitrile did not lower the absorption in that region. The matching of the minima in the spectra of the **EC-p4T** polymerized at switching potentials of +0.57 and +0.8 V shows that the thienyl side group is not yet involved in the electropolymerization in both polymerizations. These findings are in excellent agreement with the cyclic voltammograms of the respective electropolymerizations in panels D, E, and F of Figure 1. Figure 1D shows the development of a sharp oxidation peak below +0.5 V corresponding to the deposition of a well-defined species, probably the dimer. This oxidation peak is clearly broadened in Figure 1E and appears as a broad wave in Figure 1F corresponding to a material with different conjugation lengths.

Interestingly, the absorption spectrum of **EC-p4T** electropolymerized at an E_{λ} of +1.0 V matches to a large extent that of **CH-p4T-CB** (see Figure 1C); in particular the absorption maximum is at almost the same wavelength. This indicates that the electropolymerization of **4T** with use of high switching potentials results in similar architectures as the polymerization

of **4T** with FeCl_3 as oxidant. The absorption spectra can be explained by a superimposition of independently absorbing chromophores with different effective conjugation lengths, which can be related to a branched structure of the polymer as has been shown for thiophene dendrimers.¹² The discrepancies at wavelengths higher and lower than the absorption maximum can be explained by the fact that an insoluble residue of the chemical synthesized polymer was left on the Soxhlet extraction thimble and could not be investigated by optical characterization. On the other hand, the spectra of the electropolymerized films can also comprise insoluble fractions. Considering that these insoluble fractions result from network formation or long linear chains, they should enhance the absorption at shorter and longer wavelengths.

For all further characterizations, the polymerizations where conducted at switching potentials of +1.0 V in the case of **4T** and +1.2 V in the case of **3T** to ensure a high participation of the thienyl side groups and a preferably wide absorption spectrum of the resulting branched polymer. Higher switching potentials did not lead to a further red-shift of the absorption spectrum.

Motivated by the possibility of obtaining fractions of different molecular weights by Soxhlet extraction in the case of the chemically synthesized hyperbranched polythiophenes and by the report of Visy about the good solubility of his electropolymerized systems,¹⁸ we first washed the electropolymerized films on the ITO with chloroform, leading to solutions of **EC-**

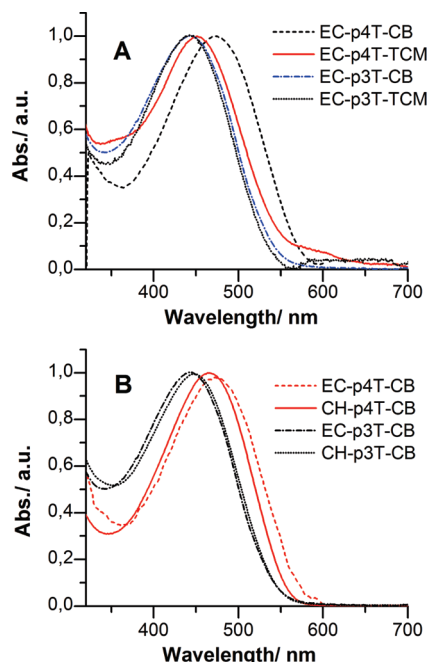


Figure 2. (A) Absorption spectra of soluble fractions of the electropolymerized polymers in solution (chloroform and chlorobenzene). (B) Comparison of the absorption spectra of the chlorobenzene fractions of both electrochemically and chemically synthesized polymers in chlorobenzene.

p4T-TCM and **EC-p3T-TCM**, and then with chlorobenzene, leading to **EC-p4T-CB** and **EC-p3T-CB** solutions. In Figure 2A the absorption spectra of the solutions of these materials are shown. In case of **EC-p3T**, nearly the whole polymer film was washed down from the electrode by chloroform leaving only a small chlorobenzene fraction, whose absorption spectrum, however, hardly differs from the corresponding spectrum of the chloroform fraction. On the other hand, after washing **EC-p4T** with chloroform there was still a dark red film left on the electrode that was only partly soluble in chlorobenzene. Even after washing the ITO electrodes with chlorobenzene a thin film of insoluble **EC-p4T** remained. The absorption of the **EC-p4T-CB** is shifted to higher wavelengths than the absorption of **EC-p4T-TCM**, indicating longer effective conjugation lengths in the case of the chlorobenzene fraction. Additionally, it can be seen that **EC-p4T** exhibits longer effective conjugation lengths than **EC-p3T**.

The good solubility of electropolymerized terthiophenes with aromatic substituents in chlorinated organic solvents has already been reported by Visy et al.¹⁸ However, polymerization of a triple substituted **4T** analogue (2,3,5-Tris(4-pentoxy-2-thienyl)thiophene) resulted in a polymer that was completely insoluble in chloroform what was ascribed by Zotti to a high degree of polymerization.¹⁹ Regarding the fact that **EC-p3T** is nearly completely soluble in chloroform, the improved solubility of **EC-p3T** compared to **EC-p4T** can be related to a higher branching density in **EC-p3T**. The good solubilities of **EC-p3T** and **EC-p4T** are consistent with those of **CH-p3T** and **CH-p4T** prepared by oxidative polymerization with FeCl_3 .¹⁵

A direct comparison of the solution absorption spectra of the chlorobenzene fractions of the polymers obtained by electrochemical and chemical polymerizations is given in Figure 2B. The corresponding values of the absorption maxima and absorption onsets are shown in Table 2. It is evident that both polymerization methods yield polymers with comparable absorption properties, especially regarding **p3T**. In the case of

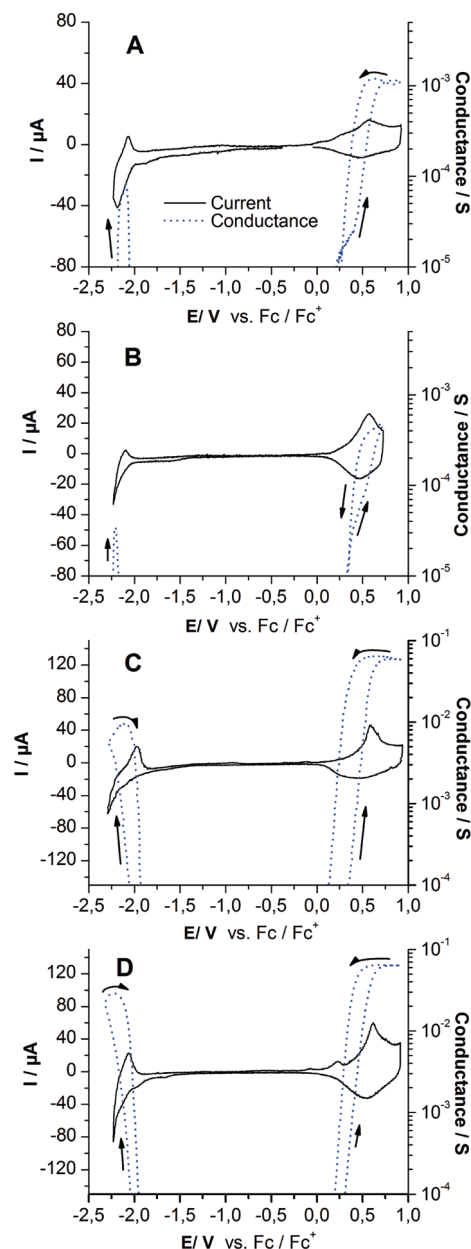


Figure 3. Cyclic voltammograms and in situ conductance of films of (A) **CH-p4T-CB**, (B) **CH-p3T-CB**, (C) **EC-p4T**, and (D) **EC-p3T**. The CV data were taken at a scan rate of 20 mV/s at room temperature in acetonitrile/TBAPF₆ (0.1 M).

p4T the absorption onset is red-shifted and the absorption minimum is more pronounced when compared to **p3T**. This again is a reference to higher branching densities in **p3T** and a more linear structure in **p4T**, which correlates with the above-mentioned solubilities. Interestingly the absorption spectrum of **EC-p4T-CB** is slightly red-shifted compared to the spectrum of **CH-p4T-CB**.

Electrochemical Investigation. To investigate the stability and the conductance of **p3T** and **p4T** in their doped state solid-state cyclic voltammograms with in situ conductance measurements were performed (see Figure 3). For this purpose **EC-p3T** and **EC-p4T** were directly electrodeposited on interdigitated platinum structures. Chemically synthesized **CH-p3T-CB** and **CH-p4T-CB** were spin-coated onto these substrates. For all polymers the oxidation as well as the reduction processes were reversible. The conductance in the n-doped state was not much lower than that observed in the p-doped state, particularly

TABLE 2: Data Obtained from Cyclic Voltammetry in Films and UV/Vis–Absorption Spectroscopy in Chlorobenzene Solution

	$E_{\text{onset}}^{\text{ox}}$ [V vs Fc/Fc ⁺]	$E_{\text{onset}}^{\text{red}}$ [V vs Fc/Fc ⁺]	λ_{max} [nm (eV)]	λ_{onset} [nm (eV)]
CH-p3T-CB	0.28	−2.02	449 (2.76)	544 (2.28)
EC-p3T-CB	0.31	−2.04	442 (2.81)	537 (2.31)
CH-p4T-CB	0.26	−1.99	464 (2.67)	563 (2.20)
EC-p4T-CB	0.25	−1.95	472 (2.63)	572 (2.17)

obvious for the electrodeposited polymers (see Figure 3C,D). This is remarkable as the n-conductivity of other polythiophenes has been reported to be only 1% of the p-conductivity.^{28–30} In branched systems, however, n-doping might be facilitated as the more-open structure enhances the influx of cations into the polymer film compared to linear systems.³¹ The lower conductivities of the chemically synthesized polymers (Figure 3A,B) may be caused by the lower quality of the films spin-coated on the uneven platinum structures.

From the CVs the onset potentials of the p- and n-doping processes could be estimated. The onset potentials were estimated from CVs which were measured separately in the oxidation (p-doping) or reduction (n-doping) region to avoid confusion with charge-trapping phenomena that are typically observed in cycles comprising both regions (see discussion below). The resulting values of $E_{\text{onset}}^{\text{ox}}$ and $E_{\text{onset}}^{\text{red}}$ are listed in Table 2. Generally it can be stated that the electrochemical properties of polymers synthesized by chemical and electrochemical oxidative polymerization are comparable. The onset of oxidation of **p3T** is shifted to slightly more positive potentials compared to **p4T**, whereas the onset of reduction always occurs at similar potentials.

Figure 4A shows a cyclic voltammogram together with in situ conductance data from −0.5 to +1.5 V vs Fc/Fc⁺. The conductivity profile shows a broad plateau of high conductivity, extending over a range of about 0.7 V. Only around +1.5 V does the conductance drop to lower values, and on the reverse scan much lower conductances are measured. As the conductivity drops, the current in the CV rises steeply. This strongly indicates the degradation of the polymer, e.g. by a nucleophilic attack of acetonitrile or traces of water. The polymer shown in Figure 4A was electropolymerized at switching potentials of +1.0 V; however, the CV was measured up to +1.5 V. The current increase might also be partially explained by further branching of the polymer, which may take place when the potentials are scanned to values higher than the switching potentials of its electrodeposition. However, the large conductivity plateau together with the decrease in conductivity is a characteristic of many conjugated polymers and might be explained by mixed-valence conductivity.^{29,32} According to this conductivity model, charge transport in conjugated polymers is ascribed to a hopping process between redox pairs.³³ Conductivity drops when all redox states are occupied.

Our hyperbranched system contains a large number of different conjugation lengths that was deduced from the absorption spectra and therefore a large number of different redox states which are overlapping. Only at very high oxidation potentials, segments with short effective conjugation lengths should be charged. One could anticipate that the nonconductive state of this system is only accessible at potentials where degradation of the polymer occurs.

Memory Effect. Figure 4B shows an interesting feature that we normally observed for solid-state CV measurements of **p4T** and **p3T** for the example of **EC-p4T**. The first cycle of each

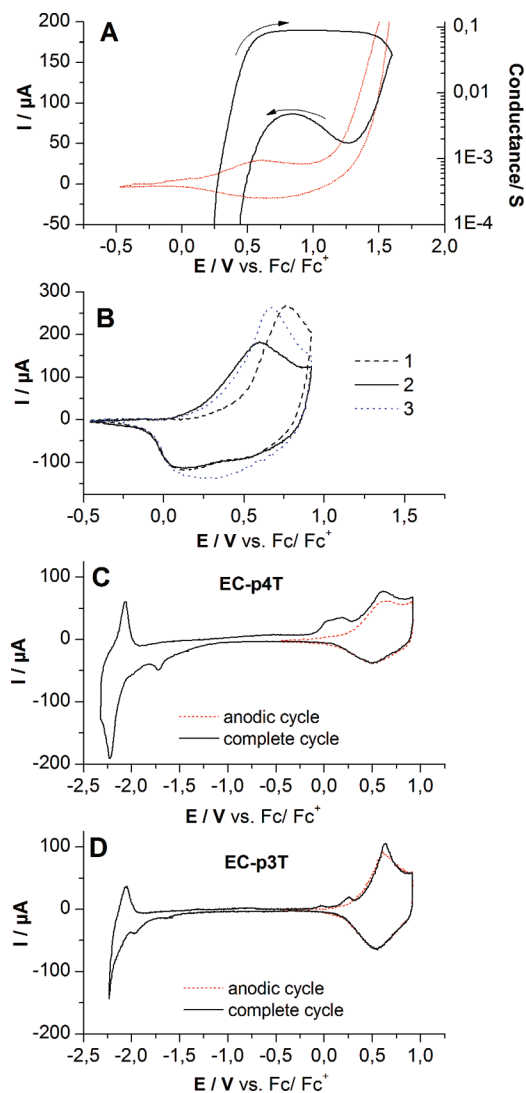


Figure 4. Cyclic voltammograms on interdigitated platinum electrodes (A) and on ITO (B, C, D). (A) Conductance at high p-doping levels (20 mV/s). (B) Memory effect of **EC-p4T** on ITO (20 mV/s): (1) very first cycle after electropolymerization, (2) second cycle, and (3) first cycle after holding at −0.78 V for 1 h. (C) Charge trapping (50 mV/s) in **p4T** at 298 K. (D) Charge trapping (20 mV/s) in **p3T** at 298 K.

measurement always showed a delayed oxidation onset and an increased maximum peak current (dashed line in Figure 4B) in comparison to the following cycles (solid line in Figure 4B). This behavior was observed for both chemically and electrochemically polymerized polymer films but it always was more pronounced for the **p4T** than for the **p3T** polymers. The first-cycle delay of the oxidation onset and the increase of the maximum peak current could be to some extent restored afterward by keeping the polymer film at negative potentials for at least 1 h (dotted line in Figure 4B). This so-called first-cycle or memory effect can be related to conformational changes occurring when a polymer film is oxidized for the first time or after holding a polymer film at negative potentials.^{34,35} A possible explanation of the memory effect is given by the ESCR (“electronically stimulated conformational relaxation”) model developed by Otero et al.³⁶ According to this model the first oxidation cycle is controlled by structural relaxation involving conformational changes of the chain segments. In the subsequent cycles the conformational changes formed in the first cycle are still largely present and the oxidation is only controlled by diffusion of the counterions into the polymer film. However,

the fact that the memory effect is absent in ionic liquids³⁷ but observable for dilute species in acetonitrile³⁸ leads to a different explanation suggesting a thin film of polymeric acetonitrile formed at negative potentials to be responsible for the memory effect.³⁸ This film of polymeric acetonitrile would act as a passivating layer that is rapidly destroyed upon oxidation. In Figure 4B the first cycle after holding the film at -0.78 V for 1 h shows a slight shift of the oxidation onset to higher potentials and an increased maximum peak current.

Charge Trapping. Another distinctive feature of the electrochemical behavior of **p3T** and **p4T** is the appearance of additional prepeaks when full cycles are recorded containing both the p-type and the n-type region. In Figure 4C,D the complete cyclic voltammograms of **EC-p3T** and **EC-p4T** and cycles involving only the p-doping region are shown. Both polymers show CVs where the oxidation peak is accompanied by a prepeak that is absent if the oxidation is conducted without a previous reduction. Likewise the reduction peak is accompanied by one or more prepeaks. This phenomenon is known as charge trapping and is still controversially discussed in the literature.^{39–43}

One possible explanation is that doped material is trapped during an undoping process in a matrix of already insulating material. The undoping of the trapped material cannot occur until the ambient material becomes conducting again.^{39,43} That means, after a p-doping cycle, the trapped charges are dedoped at the beginning of the n-doping range, resulting in the prepeak. Furthermore, the involvement of structural reconfiguration processes has been proposed.^{42,43}

Conclusion

In this contribution branched thiophene monomers are electropolymerized to yield products that exhibit well-defined optical and electrochemical properties. The absorption data show that the molecular architecture resulting from electropolymerization of **4T** can be strongly tuned by the switching potentials of the potentiodynamic electropolymerization. Lower switching potentials lead to defined oligomers, whereas higher switching potentials yield branched polymers. The absorption and electrochemical data of the polymers **p4T** and **p3T** electropolymerized at higher potentials resemble those of the corresponding polymers synthesized chemically by oxidative FeCl_3 mediated coupling.

CV coupled with in situ conductance measurements reveal comparable conductance values upon n- and p-type doping. The optoelectronic properties of the presented class of branched conjugated polymers suggest possible applications in optoelectronic devices. The first tests in organic solar cells are currently underway.

Acknowledgment. Financial support is acknowledged by the DFG for an Emmy Noether grant, a grant within SPP-1355, a Junior Fellowship in FRIAS and by the “Fonds der Deutschen Chemischen Industrie”. We thank N. Codogni, H. Mangold, and M. Semmelbeck for lab assistance in synthesis and characterization.

Supporting Information Available: UV/vis-absorption spectra of the monomers **3T** and **4T**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

(1) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.

- (2) Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617.
- (3) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741.
- (4) Sirringhaus, H.; Brown, P. J.; Friend, R. H.; Nielsen, M. M.; Bechgaard, K.; Langeveld-Voss, B. M. W.; Spiering, A. J. H.; Janssen, R. A. J.; Meijer, E. W.; Herwig, P.; de Leeuw, D. M. *Nature* **1999**, *401*, 685.
- (5) Brown, P. J.; Sirringhaus, H.; Harrison, M.; Shkunov, M.; Friend, R. H. *Phys. Rev. B* **2001**, *63*, 125204.
- (6) Nicolas, Y.; Blanchard, P.; Levillain, E.; Allain, M.; Mercier, N.; Roncali, J. *Org. Lett.* **2004**, *6*, 273.
- (7) Sun, X. B.; Liu, Y. Q.; Chen, S. Y.; Qiu, W. F.; Yu, G.; Ma, Y. Q.; Qi, T.; Zhang, H. J.; Xu, X. J.; Zhu, D. B. *Adv. Funct. Mater.* **2006**, *16*, 917.
- (8) Wang, Y.-N.; Zhou, Y.-H.; Xu, Y.; Sun, X.-B.; Wu, W.-C.; Tian, W.-J.; Liu, Y.-Q. *Chin. Phys. B* **2008**, *1448*.
- (9) Bilge, A.; Zen, A.; Forster, M.; Li, H.; Galbrecht, F.; Nehls, B. S.; Farrell, T.; Neher, D.; Scherf, U. *J. Mater. Chem.* **2006**, *16*, 3177.
- (10) Benincori, T.; Capaccio, M.; De Angelis, F.; Falcicola, L.; Muccini, M.; Mussini, P.; Ponti, A.; Toffanin, S.; Traldi, P.; Sannicolò, F. *Chem.-Eur. J.* **2008**, *14*, 459.
- (11) Xia, C.; Fan, X.; Locklin, J.; Advincula, R. C. *Org. Lett.* **2002**, *4*, 2067.
- (12) Ma, C.-Q.; Mena-Osteritz, E.; Debaerdemaeker, T.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2007**, *46*, 1679.
- (13) Ma, C.-Q.; Fonrodona, M.; Schikora, M. C.; Wienk, M. M.; Janssen, R. A. J.; Bäuerle, P. *Adv. Funct. Mater.* **2008**, *18*, 3323.
- (14) Xu, M.-H.; Pu, L. *Tetrahedron Lett.* **2002**, *43*, 6347.
- (15) Richter, T. V.; Link, S.; Hanselmann, R.; Ludwigs, S. *Macromol. Rapid Commun.* **2009**, *30*, 1323.
- (16) Machida, S.; Miyata, S.; Techagumpuch, A. *Synth. Met.* **1989**, *31*, 311.
- (17) Visy, C.; Lukkari, J.; Kankare, J. *Macromolecules* **1993**, *26*, 3295.
- (18) Visy, C.; Lukkari, J.; Kankare, J. *Macromolecules* **1994**, *27*, 3322.
- (19) Zotti, G.; Salmaso, R.; Gallazzi, M. C.; Marin, R. A. *Chem. Mater.* **1997**, *9*, 791.
- (20) Sankaran, B.; Vaia, R. A.; Tan, L.-S. *Polym. Prepr.* **2001**, *42*, 602.
- (21) Heuer, H.-W.; Wehrmann, R. EP1541577, 2005.
- (22) Velez, J. H.; Diaz, F. R.; del Valle, M. A.; Bernede, J. C.; Soto, J. P. *J. Appl. Polym. Sci.* **2008**, *109*, 1722.
- (23) Kiese, H. *Anal. Chem.* **1981**, *53*, 1952.
- (24) Heinze, J.; Rasche, A.; Pagels, M.; Geschke, B. *J. Phys. Chem. B* **2007**, *111*, 989.
- (25) Heinze, J.; Frontana-Urbe, B. A.; Ludwigs, S., *Chem. Rev.*, published online June 17, <http://dx.doi.org/10.1021/cr900226k>.
- (26) Ryder, K. S.; Schweiger, L. F.; Glidle, A.; Cooper, J. M. *J. Mater. Chem.* **2000**, *10*, 1785.
- (27) Bäuerle, P.; Segelbacher, U.; Gaudl, K.-U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed.* **1993**, *32*, 76.
- (28) Crooks, R. M.; Chyan, O. M. R.; Wrighton, M. S. *Chem. Mater.* **1989**, *1*, 2.
- (29) Ahonen, H. J.; Lukkari, J.; Kankare, J. *Macromolecules* **2000**, *33*, 6787.
- (30) Zotti, G.; Schiavon, G. *Synth. Met.* **1994**, *63*, 53.
- (31) Huang, J.-H.; Hsu, C.-Y.; Hu, C.-W.; Chu, C.-W.; Ho, K.-C. *ACS Appl. Mater. Interfaces* **2010**, *2*, 351.
- (32) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.
- (33) Skompska, M.; Mieczkowski, J.; Holze, R.; Heinze, J. *J. Electroanal. Chem.* **2005**, *577*, 9.
- (34) Kalaji, M.; Nyholm, L.; Peter, L. M. *J. Electroanal. Chem.* **1992**, *325*, 269.
- (35) Odin, C.; Nechtschein, M. *Synth. Met.* **1991**, *43*, 2943.
- (36) Otero, T. F.; Boyano, I. J. *Phys. Chem. B* **2003**, *107*, 6730.
- (37) Randriamahazaka, H.; Plesse, C.; Teyssié, D.; Chevrot, C. *Electrochem. Commun.* **2003**, *5*, 613.
- (38) Heinze, J.; Rasche, A. *J. Solid State Electrochem.* **2006**, *10*, 148.
- (39) Borjas, R.; Buttry, D. A. *Chem. Mater.* **1991**, *3*, 872.
- (40) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275.
- (41) Semnikhin, O. A.; Ovsyannikova, E. V.; Ehrenburg, M. R.; Alpatova, N. M.; Kazarinov, V. E. *J. Electroanal. Chem.* **2000**, *494*, 1.
- (42) Casalbore-Miceli, G.; Camaioni, N.; Geri, A.; Ridolfi, G.; Zanelli, A.; Gallazzi, M. C.; Maggini, M.; Benincori, T. *J. Electroanal. Chem.* **2007**, *603*, 227.
- (43) Hillman, A. R.; Daisley, S. J.; Bruckenstein, S. *Electrochim. Acta* **2008**, *53*, 3763.