Effect of molecular weight on electronic, electrochemical and spectroelectrochemical properties of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene)†

Rafal Pokrop,[a] Jean-Marie Verilhac,[b] Anna Gasior,[a] Ireneusz Wielgus,[a] Malgorzata Zagorska,*[a] Jean-Pierre Travers[c] and Adam Pron[c]

Received 18th April 2006, Accepted 25th May 2006
First published as an Advance Article on the web 14th June 2006
DOI: 10.1039/b605504d

Poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene), obtained from its corresponding monomer by oxidative polymerization with $FeCl_3$, has been fractionated into five fractions of reduced polydispersity, covering the M_n range from 1.50 kDa to 10.50 kDa (measured *vs.* polystyrene standards). The effect of M_n on spectroscopic, electrochemical, spectroelectrochemical and electrical transport properties has been investigated. Fractions of growing M_n show an increasing bathochromic shift of the band originating from the π–π* transition in the neutral polymer with the appearance of a clear vibrational structure for the two highest molecular fractions. The onset of oxidative doping determined from the cyclic voltammogram shifts towards lower potentials with increasing molecular weight. A similar trend is observed for doping induced near infrared bands, which shift towards lower energies (higher wavelengths) with increasing molecular weight and appear at lower potentials in spectroelectrochemical experiments. Finally, a comparison of the FET mobility in two transistors fabricated under identical conditions from polymer fractions differing in their molecular weight shows that a *ca.* fourfold increase of M_n (from 2.40 kDa to 10.50 kDa) results in a two orders of magnitude increase in the carriers' mobility (from $\mu_{sat} = 4 \times 10^{-5}$ cm^2 V^{-1} s^{-1} to $\mu_{sat} = 2 \times 10^{-3}$ cm^2 V^{-1} s^{-1}). The obtained results underline the importance of the control of the macromolecular parameters in the preparation of electronic and electrochemical devices from poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene).

Introduction

Attractive properties of poly(alkylthiophene)s have stimulated, in the past two decades, extensive, multidisciplinary research aimed at the elucidation of their electrical transport, electrochemical and spectroscopic properties as well as their application as active components in various types of organic electronic devices.[1,2]

A technologically interesting property of this family of electroactive polymers is their solution processability, which is rare in polyconjugated macromolecular systems. Moreover, several structural features of these polymers such as chain planarity, extent of π-stacking, type of supramolecular aggregation *etc.* can controllably be tuned by changing the type of macromolecule regioregularity. Since all these structural parameters govern the electronic and electrochemical properties of polymer solid films, poly(alkylthiophene)s are very well suited for testing new molecular design concepts in the fabrication of modified electrodes, electrochemical sensors or organic electronic devices.[3,4]

The effect of the type of the regioregularity on various properties of poly(alkylthiophene)s was first pointed out by Souto Maior *et al.*[5] and Zagorska and Krische,[6] who demonstrated that structural, spectroscopic and electrochemical features of head to head–tail to tail (HH–TT) coupled poly(3,3′-dialkyl-2,2′-bithiophene)s and poly(4,4′-dialkyl-2,2′-bithiophene)s are significantly different from those of their predominantly head to tail–head to tail (HT–HT) coupled regioisomers. These findings were then additionally corroborated by comparison with "purely" regioregular poly(3-alkylthiophene)s developed by Rieke[7] and McCullough.[8] Regioregular HT–HT poly(3-alkylthiophene)s were found to be promising candidates for the fabrication of field effect transistors[9–14] and, in a bulk heterojunction configuration with fullerene derivatives, for the preparation of photovoltaic cells.[15] To the contrary, they show one order of magnitude lower electroluminescence quantum efficiency as compared to their HH–TT coupled regioisomers.[16] These examples merely indicate the importance of molecular design in the development of new organic electronic or electrochemical devices.

Basic electronic, spectroscopic and electrochemical properties are not only dependent on the type and degree of polymer regioregularity but also on its molecular weight. The effect of

---

[a] *Faculty of Chemistry, Warsaw University of Technology, Noakowskiego 3, 00-664, Warsaw, Poland. E-mail: zagorska@ch.pw.edu.pl*
[b] *CEA Liten-DTNM-LCH, 17 rue des Martyrs, 38054, Grenoble cedex 9, France*
[c] *CEA DRFMC, UMR 5819-SPrAM (CEA-CNRS-Univ. J. Fourier-Grenoble I), 17 rue des Martyrs, 38054, Grenoble cedex 9, France. E-mail: adam.pron@cea.fr*

† Electronic supplementary information (ESI) available: A diagram of the transistor structure, synthetic details and product characterization. See DOI: 10.1039/b605504d

molecular weight on spectroscopic, electrochemical and spectroelectrochemical properties of HT–HT coupled poly(3-alkylthiophene)s was first reported by Trznadel *et al.*,[17] who showed that this dependence persisted to relatively high M_n values. The authors rationalized the observed behavior by identifying the types of propagation errors and chain termination mechanisms which led to lower chain regioregularity in lower molecular weight fractions. More recent papers have shown that M_n influences the supramolecular organization in poly(3-alkylthiophene)s and their crystallinity[18,19] and by consequence charge carrier mobilities in HT–HT poly(alkylthiophene) based organic field effect transistors[14,20] and photovoltaic cells.[21]

The use of dialkylterthiophenes as macromonomers in the preparation of poly(alkylthiophene)s constitutes an interesting route to the preparation of processible, electroactive polymers with tunable properties since it increases the number of possible regioisomers of different chain microstructure. Among them poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) has recently been tested in the fabrication of organic field effect transistors with promising results.[3,4] This polymer can formally be considered as an alternate copolymer of tail to tail (TT) coupled dialkylbithiophene and thiophene. Due to a different chain microstructure its optical and electrical transport properties are distinctly different from those reported for HT–HT and HH–TT coupled poly(alkylthiophene)s.[4] In this paper, we explore in detail: electrical transport, redox, spectroscopic and spectroelectrochemical properties of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) as a function of the polymer molecular weight. Such studies, to the best of our knowledge never reported to date, are important not only from the basic research point of view but should also constitute the starting point for the design of better poly(alkylthiophene) based electronic devices, modified electrodes and electrochromic devices.

Experimental

Characterization techniques

Both the monomer and the resulting polymer were characterized by ^{1}H NMR, ^{13}C NMR, FTIR and elemental analysis. NMR spectra were recorded on a Varian Mercury 400 MHz spectrometer with chloroform-d ($CDCl_3$) solvent. FTIR spectra were obtained on a FTIR Bio-RAD FTS 165 spectrometer (wavenumber range: 400–4000 cm^{-1}, resolution: 4 cm^{-1}) either on free standing films cast from chloroform or using the KBr pellet technique. UV-vis-NIR spectra of thin solid films or solutions in chloroform were recorded on a Cary 5000 (Varian).

Molecular weights of the fractionated polymer were measured using size exclusion chromatography (SEC), on a LabAlliance chromatograph equipped with a Jordi Gel DVB Mixed Bed column, using refractometric detection by RI-2000-F refractometer, $CHCl_3$ was used as the eluent. The column temperature and the flow rate were fixed to 35 °C and 1 mL min^{-1}, respectively. The column was calibrated using polystyrene standards provided by the Polymer Standards Service.

For cyclic voltammetry investigations, a thin layer of the polymer was deposited on a platinum disc or plate electrode by casting from chloroform solution. The experiments were carried out in a one compartment electrochemical cell, in 0.1 M Bu_4NBF_4 in acetonitrile solution, using a Pt counter-electrode, and Ag/0.1 M $AgNO_3$ in acetonitrile as a reference electrode. In the case of UV-vis-NIR spectroelectrochemical studies, a thin polymer film was deposited on an ITO transparent working electrode, the electrolyte and the counter and reference electrodes remaining the same.

Fabrication of transistors and electrical measurements

The active semiconducting layer was deposited by spin-coating on a specially prepared substrate, which together with the poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) layer formed a bottom gate, bottom contact field-effect transistor (FET). Thus, it consisted of a 320 nm thick SiO_2 layer grown on a Nb gate. Interdigitated (L = 20 µm, W = 9 mm) source and drain electrodes, consisting of an adhesion layer of Cr (15 nm) covered with an Au (70 nm) layer, were prepared by photolithography. In the next step, the surface of SiO_2, not covered with the electrodes, was modified by exposure to hexamethyldisilazane (HMDS). Finally, the polymer layer was deposited from $CHCl_3$ solution. The fabricated device was pumped under dynamic vacuum with the goal to fully remove even minute amounts of the residual solvent and adsorbed oxygen from its polymer layer. The exact scheme of the transistors tested can be found in the Electronic Supplementary Information (ESI†).

All electrical measurements of the fabricated FETs were performed in an inert (N_2) atmosphere using a HP4156B Semiconductor Parameter Analyzer. The mobility was extracted from the saturation regime (Vds = −60 V) using the standard equation:[22]

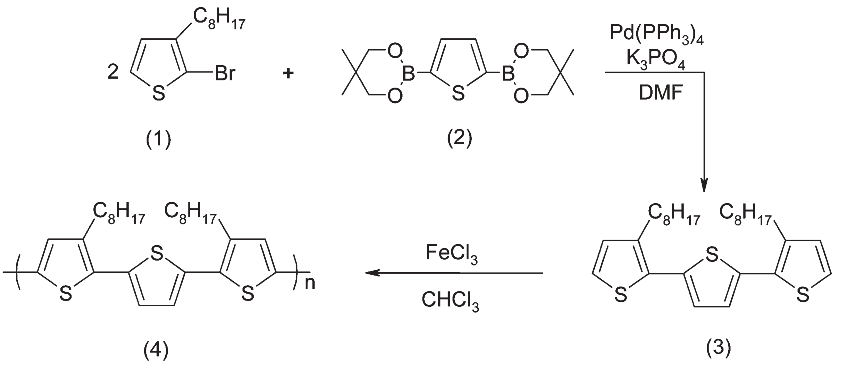
$I_{ds} = (WC_{ox}\mu_{sat}/2L)(V_g - V_t)^2$ where I_{ds} is the source–drain current, W the channel width, L the channel length, C_{ox} the dielectric capacity, μ_{sat} the saturation field effect mobility, V_g and V_t the gate voltage and the threshold voltage, respectively.

Synthesis

The applied synthetic pathway is depicted in Scheme 1. First, the monomer (**3**) is obtained from **1** and **2** by Suzuki coupling, it is then oxidatively polymerized to give poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (**4**). Full synthetic details and product characterization can be found in the ESI.†

Fractionation of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (4)

As prepared, crude polymer exhibits a rather high polydispersity index. In order to obtain sharper fractions we modified the fractionation procedure used for HT–HT poly(3-alkylthiophene)s.[17] This method consists of sequential extraction of fractions with increasing molecular weight using an experimentally established set of solvents. It turned out to be very effective not only for poly(alkylthiophene)s but also for copolymers of alkylthiophenes with other conjugated molecules.[23] The polymer was fractionated in a Soxhlet apparatus, by consecutive extractions using the following sequence of



Scheme 1

solvents: acetone, hexane, dichloromethane, chloroform. Two fractions were taken with dichloromethane, at the beginning and at the end of the extraction, with the goal of increasing the number of fractions with reduced polydispersity. Macromolecular parameters of the obtained fractions are listed in Table 1.

Results and discussion

Although tested only very recently, for application to the fabrication of organic field effect transistors (FETs),[3] poly(3,3″-dialkylterthiophene)s have been known for more than a decade.[24] This polymer offers a very attractive chain microstructure, at least concerning the extended conjugation, since two TT-coupled alkylthiophene units are always separated by an unsubstituted thiophene ring, which makes the spacing between the alkyl groups larger. All these structural features, combined with chain regioregularity, promote the formation of ordered supramolecular aggregation in the solid state, clearly seen in X-ray diffraction studies.[4,24]

As already mentioned, the effect of molecular weight on electronic, electrochemical and spectroscopic properties in regiochemically well defined poly(3-alkylthiophene)s persists to relatively high molecular weights.[14,17,18,20,21] We were tempted to verify whether a similar phenomenon can be observed for poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene). The determination of such a relationship is of crucial importance for any application of this polymer in organic electronics, electrochemical sensors or electrochromic devices. Poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) can be fractionated in a similar manner as regioregular HT–HT poly(3-alkylthiophene)s, giving fractions of distinctly different M_n and reduced polydispersity coefficient as demonstrated by size exclusion chromatography (SEC) (see Table 1). The "raw" SEC results of polythiophene derivatives should however be treated with caution, especially if polystyrene sharp fractions are used as standards. Because of the significantly different shape of the macromolecules, the exclusion mechanisms are different in the flexible σ-bonded main chain polymers and the conjugated ones. As a consequence, the SEC M_n data of polythiophene derivatives are underestimated for low molecular weights ($Mn < 2$ kD)[23] and overestimated for higher ones ($Mn > 2$ kD).[25] Assuming that the relationship between the M_n values determined by mass spectrometry (MALDI) and SEC is the same as for HT–HT poly(alkylthiophene)s and for poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) we have calculated the corrected M_n. The results are included in Table 1.

Conjugation length is the principal factor determining electronic and electrochemical properties of organic conductors and semiconductors. Better conjugation implies wider bands and a narrower band gap in the resulting semiconducting polymer. The latter should be reflected in the UV-vis spectra of thin solid layers of the neutral (undoped) polymer. It is convenient to establish the concept of an effective conjugation length as probed by UV-vis spectroscopy. In the visible part of the spectrum, oligo- and polythiophene derivatives show a strong absorption band originating from the π–π* electronic transition. For monodispersed regioregular oligoalkylthiophenes this absorption band is being red shifted, with increasing degree of polymerization (*DP*), up to a certain *DP* value above which no further shift is observed. This corresponds to the effective conjugation length. Further increase of the *DP* does not result in an increase of the effective conjugation length. As shown in ref. 26 for monodispersed oligoalkylthiophenes the limiting effective conjugation length corresponds to a *DP* of *ca.* 20.

Table 1 Macromolecular parameters of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) fractions studied in this research

Solvent	M_n(SEC)/kDa	M_w(SEC)/kDa	*PI*	Correction factor[a]	M_n corrected	DP_n[b] corrected	Content of the fraction[c]/wt%
Acetone	1.54	1.78	1.16	0.97	1.59	10	15.6
Hexane	2.40	2.96	1.23	1.3	1.84	12	24.4
Dichloromethane I	5.50	8.45	1.53	1.5	3.67	24	23.3
Dichloromethane II	6.62	11.74	1.77	1.55	4.27	27	4.4
Chloroform	10.50	17.75	1.69	1.77	5.93	38	17.9

[a] Calculated on the basis of the results presented in refs. 23, 25. [b] Degree of polymerization normalized per thiophene ring. [c] Insoluble part – 14.4 wt%.

Table 2 Absorption maxima (nm) determined for the bands corresponding to the π–π* transition in electronic spectra of fractionated poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (PDOTT) recorded for $CHCl_3$ solutions and for thin solid films[a]

Fraction	$CHCl_3$ solution	Solid state 0–0	0–1		0–2	0–3
PDOTT/acetone	441			463		
PDOTT/hexane	449			484		
PDOTT/CH_2Cl_2 (I)	460			516		
PDOTT/CH_2Cl_2 (II)	463	*594*	*547*		*507*	*474*
PDOTT/$CHCl_3$	466	*598*	*551*		*511*	*476*

[a] The maxima of $-d^2A/d\lambda^2$ are given in italics.

Polydispersed samples behave differently. For regioregular HT–HT poly(3-hexylthiophene) the dependence of the effective conjugation length persists for DP_n values exceeding 50, as shown by the comparison of the UV-vis spectra of fractionated samples.[20] Evidently, this difference of behaviour originates from the polydispersity phenomenon and reflects different distributions of the effective conjugation length for samples with increasing DP_n. A similar phenomenon is observed for poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (see Table 2 and Fig. 1). Spectral changes are observed for all DP_n studied, for the two highest molecular weight fractions being small but measurable. The spectra of these fractions also show a clear vibrational structure. The vibrational structure of the electronic spectrum, frequently observed for regioregular conjugated polymers, has its origin in electron-lattice coupling. In particular, the position of the band originating from the transition from the ground state to the relaxed excited state (0–0 transition) is indicative of effective conjugation. As expected, the energy of this transition is the smallest for the fraction DP_n = 38. It should also be noted that, for comparable DP_n values, the spectra of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) are very similar to those of regioregular HT–HT coupled poly(3-hexylthiophene) with the band of the 0–0 transition only slightly hypsochromically shifted (by <10 nm).[17]

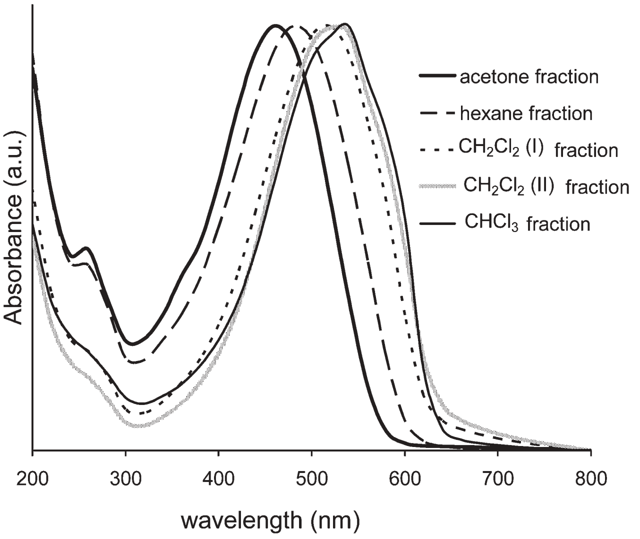


Fig. 1 UV-vis spectra of thin solid layers of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) deposited on quartz plate.

These conclusions concerning the effective conjugation length in fractionated poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) are also confirmed by FTIR spectroscopy (see Fig. 2).

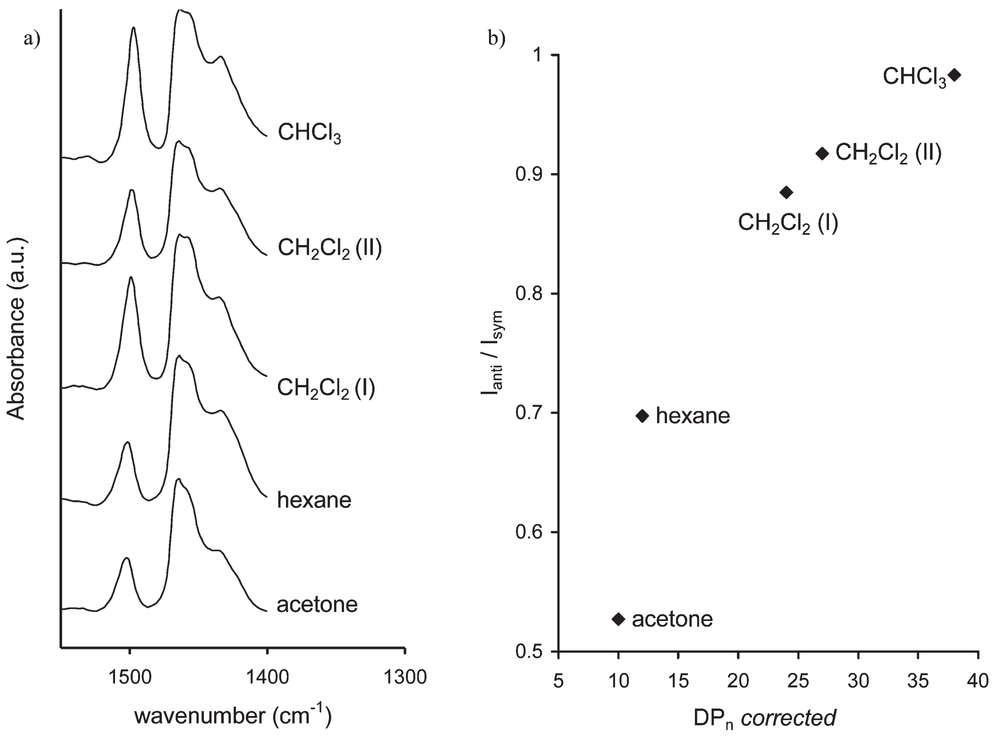


Fig. 2 a) FTIR spectra of different fractions of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) in the range of 1400–1550 cm^{-1}; b) I_{anti}/I_{sym} band ratio plotted against DP_n for different fractions of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene).

Fractions with increasing DP_n significantly differ in the spectral range 1400–1550 cm^{-1}. According to Furukawa[27] the ratio of the band at 1497–1502 cm^{-1} (C=C antisymmetric stretching) to that at 1463–1465 cm^{-1} (C=C symmetric stretching) is diagnostic of the conjugation length. The plot of I_{anti}/I_{sym} against DP_n, shown in Fig. 2, clearly indicates the increasing average effective conjugation length with increasing DP_n. One must add here that the band ascribed to the C=C symmetric stretching deformations embraces the contribution from the CH_2 bending deformations of the alkyl substituents. Since, to a first approximation, the oscillator strength of the latter is not dependent on DP_n and, for this reason remains constant for all fractions, the selected ratio properly describes changes in the effective conjugation length.

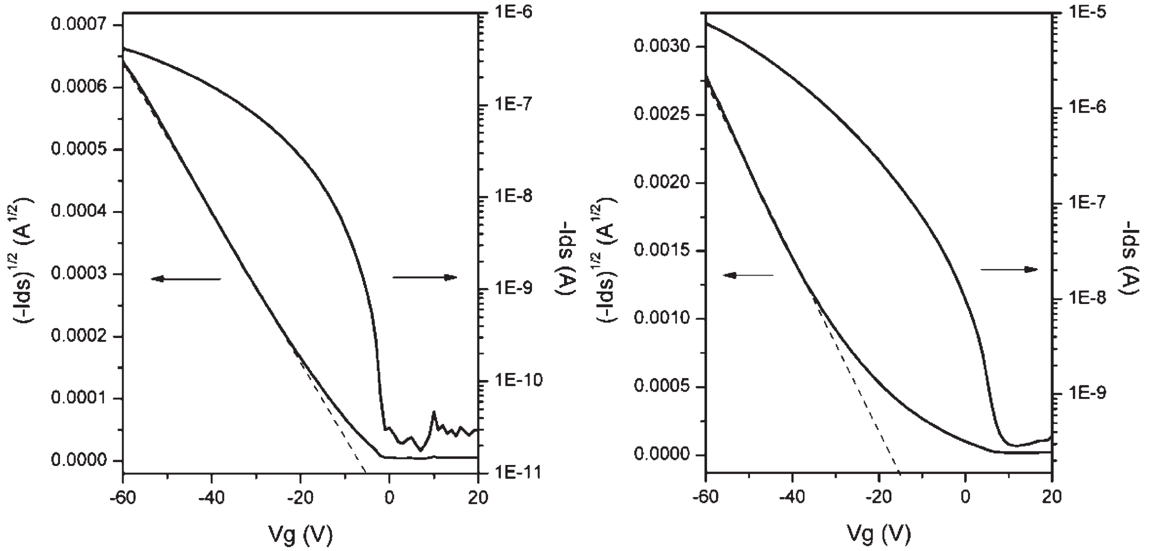
As it has already been stated, the changes in the average effective conjugation length persist in poly(alkylthiophene)s to high DP_n values. Moreover DP_n has been found to be the critical factor determining the charge carrier mobility in polymer based field effect transistors (FETs). In fact, the measured FET mobility in HT–HT poly(3-hexylthiophene) steadily increases with DP_n even for very high molecular weights where the changes in the average effective conjugation length are very small. This strong dependence was previously verified up to $DP_n = 85$[19] and more recently up to $DP_n = 163$.[28]

Inspired by the findings described above, we have decided to verify whether the same effect can be observed for poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene). We have fabricated two field effect transistors (FETs) under identical technological conditions (see Experimental and ESI† for details) in which the active semiconductor layer consisted of the hexane and the chloroform fractions of the polymer, respectively. The characteristics of these transistors obtained in the saturation regime (Vds = −60 V) are presented in Fig. 3.

The FET mobility, extracted from the above data, is almost two orders of magnitude higher for the higher molecular weight chloroform fraction ($DP_n = 38$, $\mu_{sat} = 2 \times 10^{-3}$ $cm^2\ V^{-1}\ s^{-1}$) compared to that measured for the lower molecular weight hexane fraction ($DP_n = 12$, $\mu_{sat} = 4 \times 10^{-5}$ $cm^2\ V^{-1}\ s^{-1}$). The obtained values slightly exceed those obtained for HT–HT poly(3-hexylthiophene) of similar DP_n value.[19,20] Thus, the molecular weight dependence of the charge carriers' mobility is not restricted to HT–HT-poly(alkylthiophene)s but seems to be a more common phenomenon in the polythiophene family of organic semiconductors. Moreover, this mobility strongly increases even for polymer fractions of high DP_n, where the observed increase of the effective conjugation length is very small. Two factors seem to determine this behaviour: i) evidently, independently of the effective conjugation length, the carriers' transport along an individual chain is easier than their transport *via* interchain hopping, leading to increased μ for fractions of higher DP_n; ii) as pointed out by Sirringhaus[29] the increasing chain length should also improve the interchain hopping of carriers since the probability of this hopping depends on the density of low activation energy pathways for crossing between chains whose number should increase with the chain length.

The above results seem to suggest that electrochemical properties of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) should vary for different fractions since the effective conjugation length and the charge mobility – critical parameters which determine electrochemical oxidative doping in thin solid films – are strongly molecular weight dependent.

In general, in polythiophenes the electronic spectra of their neutral (undoped) form which reflect their effective conjugation lengths, correlate well with the onset of the polymer oxidative doping process (p-doping). In particular, in poly(alkylthiophene)s of lower conjugation, whose π–π* bands are hypsochromically shifted, the oxidative electrochemical doping (p-doping) starts at higher electrode potentials.[6] With this in mind one should expect a lowering of the oxidative doping potential for fractions with increasing DP_n. Cyclic voltammetry is very well suited for this type of investigation since the



(a) (b)

Fig. 3 Transfer characteristics (Vds = −60 V) of field effect transistors fabricated from two different fractions of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene): a) hexane fraction, b) chloroform fraction.

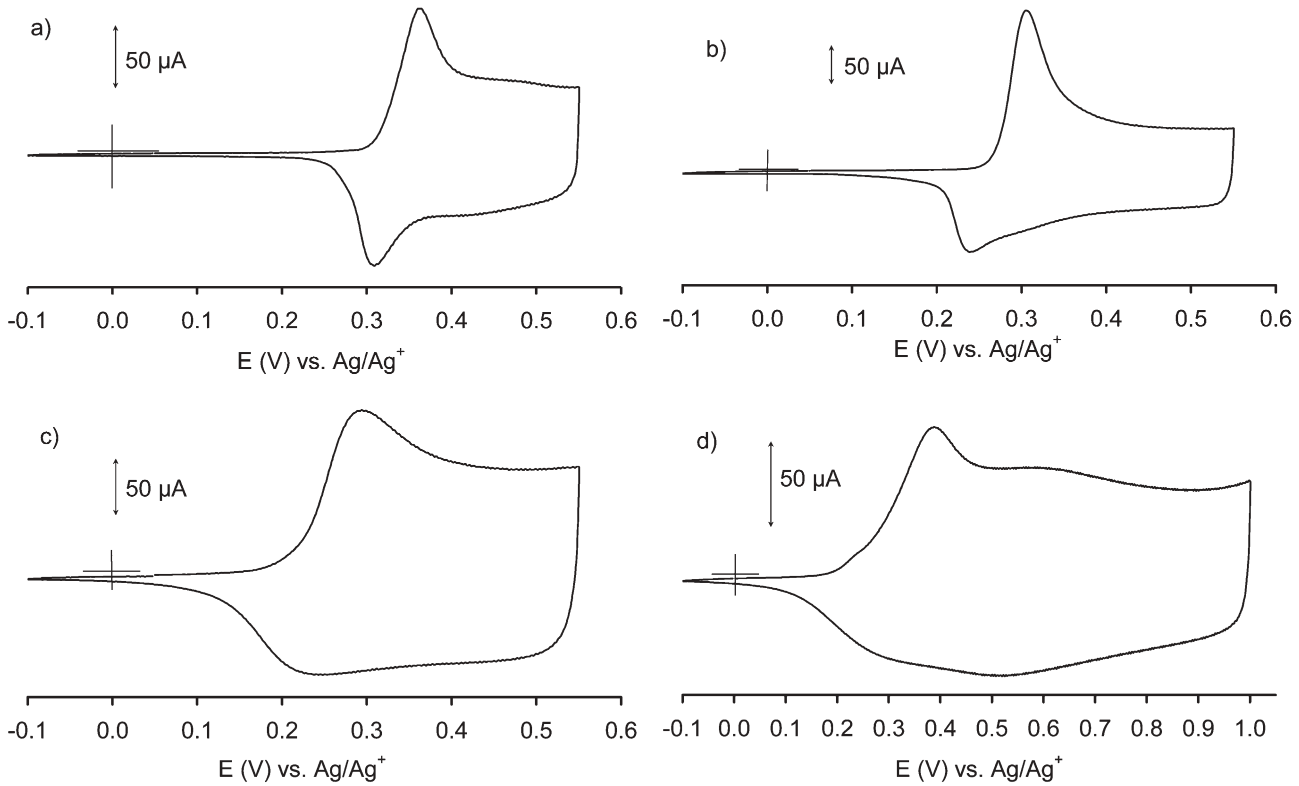


Fig. 4 Cyclic voltammograms obtained for different poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) fractions, in 0.1 M Bu_4NBF_4–acetonitrile solution at a scan rate of 50 mV s^{-1}: a) acetone fraction; b) hexane fraction; c) dichloromethane (I) fraction; d) chloroform fraction.

polymer oxidative doping gives rise to one (or more) anodic peaks, whereas consecutive reduction of the doped polymer results in the appearance of its (their) cathodic counterparts. In Fig. 4 cyclic voltammograms registered for four fractions of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene), distinctly differing in their molecular weight, are compared. First, it should be noted that with increasing M_n the onset of the p-doping anodic peak shifts to lower potentials with increasing DP_n (see Fig. 5). Second, significant changes in the shape of both anodic and cathodic peaks are observed with increasing molecular weight. For low molecular weight fractions (acetone, hexane), the p-doping anodic peak is relatively narrow and a significant potential difference is observed between the positions of the anodic doping and the cathodic dedoping peaks. These features are characteristic of the voltammetric behavior of poorly conjugated poly(alkylthiophene)s.[6] With increasing M_n, the shape of the voltammogram starts to resemble that of better conjugated derivatives of polythiophenes. For example, the CV curve of the chloroform fraction of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) is similar to that of the corresponding fraction of HT–HT coupled regioregular poly(3-hexylthiophene).[17] Two broad, strongly overlapping redox couples of higher electrochemical reversibility, superimposed on a pronounced capacitive current background, can be distinguished. For this fraction we have extended the cyclic voltammetry investigations to E = 1.05 V *i.e.* to the maximum potential at which the irreversible overoxidation phenomenon does not yet take place.

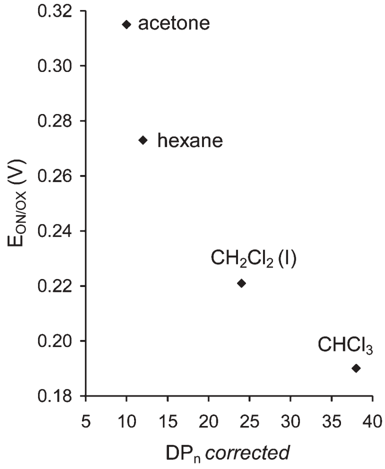


Fig. 5 The onset of the oxidative doping peak ($E_{on/ox}$) plotted against DP_n for different fractions of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene).

UV-vis-NIR spectroelectrochemistry is especially interesting in the study of conjugated polymers since the dominant doping induced spectral changes are observed in the near infrared spectral range. Figs 6a and b show the evolution of the UV-vis-NIR spectra of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene), imposed by increasing working electrode potential, recorded for the hexane (DP_n = 12) and the chloroform (DP_n = 38) fractions, respectively. The observed spectral changes can clearly be correlated with the registered voltammograms (Fig. 4), although some differences should be pointed out. The discussed spectroelectrochemical experiment is quasi-static *i.e.* the electrode potential is being changed step-wise in small increments. At each imposed potential the spectrum is

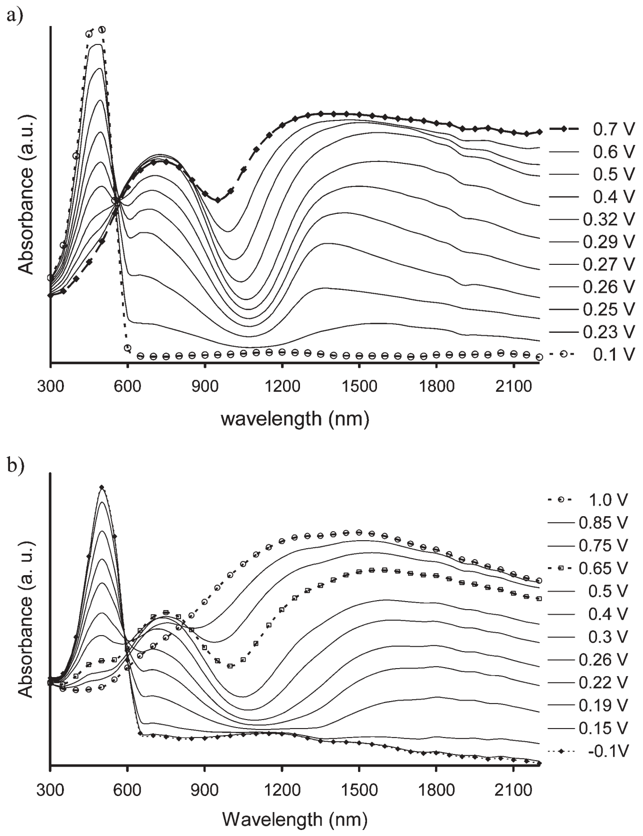


Fig. 6 UV-vis-NIR spectra of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) recorded for increasing electrode potential, *E vs* Ag/0.1 M Ag^+ reference electrode, in 0.1 M Bu_4NBF_4-acetonitrile solution: a) hexane fraction; b) chloroform fraction.

recorded after a certain time, when no more current and spectral evolutions are observed. This quasi-static character of the experiment causes the doping induced changes to appear at lower potentials compared to cyclic voltammetry investigations which are dynamic in nature. The first spectroscopic indication of the oxidative doping of the lower molecular weight fraction (hexane fraction) appears at $E = 0.23$ V *i.e.* at the potential 60 mV lower than the potential of the onset of the anodic doping peak in the cyclic voltammogram. The electrochemical doping gives rise to two doping induced bands with maxima at 722 nm and 1470 nm, attributed to the formation of bipolaronic states within the band gap, with simultaneous decrease of the band associated with the π–π* transition at 484 nm. The bipolaronic band of lower energy is being hypsochromatically shifted with increasing electrode potential. Note that the most pronounced spectral changes occur in a rather narrow potential range from 0.25 V to 0.4 V consistent with the shape of the corresponding cyclic voltammogram. For the higher molecular weight fraction (chloroform fraction) we have carried out UV-vis-NIR spectroelectrochemical investigations up to $E = 1.05$ V, as in the case of cyclic voltammetry. Spectroelectrochemical signatures of the oxidative doping appear in this case at $E = 0.18$ V, again at a slightly lower potential than that of the onset of the corresponding cyclic voltammetry curve. Contrary to the case of the hexane fraction, the doping induced spectral changes are extended over a much larger potential range, which is consistent with the broad nature of the cyclic voltammogram registered for this fraction. Two spectroscopically distinctly different doping steps can be distinguished. In the potential range from $E = 0.15$ V to $E = 0.65$ V the electrochemical doping results in the correlated increase of the two bipolaronic bands at 732 nm and 1850 nm, the latter being continuously hypsochromically shifted with increasing electrode potential. In the same potential range, the band originating from the π–π* transition of the neutral polymer decreases in intensity, being still visible, however, at $E = 0.65$ V. Above this potential the intensity of the band at 732 nm starts to decrease whereas the less energetic bipolaronic band continues to grow and to broaden. Finally at $E = 1.00$ V both bands merge giving an extremely broad, essentially featureless, absorption characteristic of the metallic state.[30]

It is clear from spectroelectrochemical studies that both polymer fractions are semiconductors of different band structures. The energy of the π–π* transition is higher for the hexane fraction (2.56 eV) as compared to the chloroform fraction (2.25 eV). The energies of the first and the second bipolaronic transitions, determined for low electrode potentials *i.e.* for low doping levels, are also more energetic for the hexane fraction (1.71 eV and 0.86 eV) than for the chloroform one (1.69 eV and 0.67 eV). Note also that, in the case of the chloroform fraction, total disappearance of the π–π* band leads to the metallic state whereas no such state is observed for the hexane fraction, even after the disappearance of the π–π* band.

Small discrepancies between the potentials of the onset of the doping process as probed by dynamic (CV) and quasi-static (spectroelectrochemistry) methods has prompted us to perform experiments in which spectral changes are recorded simultaneously with the cyclic voltammogram. As a typical example, we show here the results obtained for the chloroform fraction. Five spectral lines were selected for these investigations: i) one line from the spectral range of the band corresponding to the π–π* transition (510 nm); ii) one line from the spectral range of the first doping induced band (750 nm); iii) three lines from the spectral range of the second doping induced band (1500 nm, 1700 nm, 2000 nm). The obtained absorbance–time responses were differentiated in the form of −dA/dt for the peaks decreasing in intensity with increasing potential and as dA/dt for those increasing in intensity with increasing potential. Their plot *vs.* *E* gives, so called, differential cyclic voltabsorptograms (DCVAs). In Fig. 7 five voltabsorptograms obtained for the chloroform fraction, in the potential range from $E = -0.3$ V to $E = +0.7$ V, are compared with the corresponding voltammogram. The double peak nature of the oxidative doping, clearly seen in the cyclic voltammograms is very well reproduced in all five voltabsoptograms with only minimal differences in the peak positions.

Conclusions

To summarize, we have demonstrated that by fractionation of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) into a few fractions differing in molecular weight and showing reduced

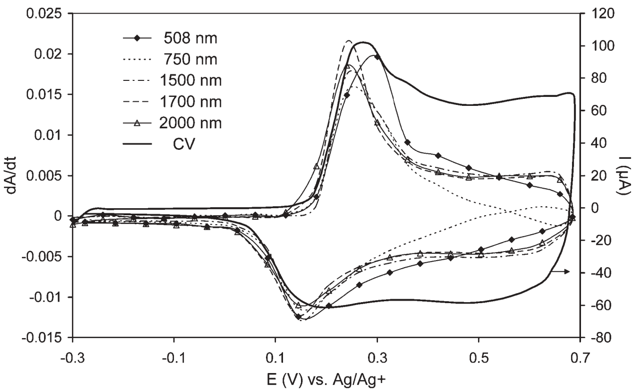


Fig. 7 Cyclic voltammogram (solid line) and voltabsorptograms obtained for the chloroform fraction of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) in 0.1 M Bu_4NBF_4–acetonitrile solution at the scan rate 5 mV s^{-1}.

polydispersity, it is possible to establish the effect of DP_n on several application-important properties of this polymer such as: the onset of electrochemical doping, the potential range of its spectroelectrochemical response and the FET charge carriers' mobility *etc*. Since in all cases the observed changes are monotonic in character, fractionation can be considered as a convenient tool for tuning the properties of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene).

Acknowledgements

This work was partially financed by the Polish Ministry of Education and Science in the years 2006–2007 as scientific project No. 1T09B04730.

References

1 Handbook of Oligo- and Polythiophenes, ed. D. Fichou, Wiley-VCH, Weinheim, 1999.
2 Handbook of Conductive Molecules and Polymers, ed. H. S. Nalwa, vol. 1–4, Wiley, Chichester, 1997.
3 I. McCulloch, C. Bailey, M. Giles, M. Heeney, I. Love, M. Shkunov, D. Sparrowe and S. Tierney, *Chem. Mater.*, 2005, **17**, 1381.
4 Y. Wu, P. Liu, S. Gardner and B. S. Ong, *Chem. Mater.*, 2005, **17**, 221.
5 R. M. Souto Maior, K. Hinkelmann, H. Eckert and F. Wudl, *Macromolecules*, 1990, **23**, 1268.
6 M. Zagorska and B. Krische, *Polymer*, 1990, **31**, 1379.
7 T.-A. Chen and R. D. Rieke, *J. Am. Chem. Soc.*, 1992, **114**, 10087.
8 R. D. McCullough and R. D. Lowe, *J. Chem. Soc., Chem. Commun.*, 1992, 70.
9 H. Sirringhaus, N. Tessler and R. H. Friend, *Science*, 1998, **280**, 1741.
10 Z. Bao, A. Dodabalapur and A. J. Lovinger, *Appl. Phys. Lett.*, 1996, **69**, 4108.
11 W. Fix, A. Ullman, J. Ficker and W. Clemens, *Appl. Phys. Lett.*, 2002, **81**, 1735.
12 J. F. Chang, S. Baoquan, D. W. Breiby, M. M. Nielsen, T. I. Sölling, M. Giles, I. McCulloch and H. Sirringhaus, *Chem. Mater.*, 2004, **16**, 4772.
13 B. H. Hamadani and D. Natelson, *Appl. Phys. Lett.*, 2004, **84**, 443.
14 R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu and J. M. J. Frechet, *Adv. Mater.*, 2003, **15**, 1519.
15 G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864.
16 P. Barta, F. Cacialli, R. H. Friend and M. Zagorska, *J. Appl. Phys.*, 1998, **84**, 6279.
17 M. Trznadel, A. Pron, M. Zagorska, R. Chrzaszcz and J. Pielichowski, *Macromolecules*, 1998, **31**, 5051.
18 A. Zen, M. Saphiannikova, D. Neher, J. Grenzer, S. Grigorian, U. Pietsch, U. Asawapirom, S. Janietz, U. Scherf, I. Lieberwirth and G. Wegner, *Macromolecules*, 2006, **39**, 2162.
19 R. J. Kline, M. D. McGehee, E. N. Kadnikova, J. Liu, J. M. J. Frechet and M. Toney, *Macromolecules*, 2005, **38**, 3312.
20 A. Zen, J. Pflaum, S. Hirschmann, W. Zhuang, F. Jaiser, U. Asawapirom, J. P. Rabe, U. Scherf and D. Neher, *Adv. Funct. Mater.*, 2004, **14**, 757.
21 P. Schilinsky, U. Asawapirom, U. Scherf, M. Biele and C. J. Brabec, *Chem. Mater.*, 2005, **17**, 2175.
22 G. Horowitz, *Adv. Mater.*, 1998, **10**, 365.
23 R. Demadrille, P. Rannou, J. Bleuse, J. L. Oddou, A. Pron and M. Zagorska, *Macromolecules*, 2003, **36**, 7045.
24 M. C. Gallazzi, L. Castellani, R. A. Marin and G. Zerbi, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 3339.
25 J. Liu, R. S. Loewe and R. D. McCullough, *Macromolecules*, 1999, **32**, 5777.
26 T. Izumi, S. Kobashi, K. Takimiya, Y. Aso and T. Otsubo, *J. Am. Chem. Soc.*, 2003, **125**, 5286.
27 Y. Furukawa, M. Akimoto and I. Harada, *Synth. Met.*, 1987, **18**, 151.
28 J.-M. Verilhac, G. LeBlevennec, D. Djurado, F. Rieutord, M. Chouiki, J.-P. Travers and A. Pron, *Synth. Met.*, in press.
29 H. Sirringhaus, *Adv. Mater.*, 2005, **17**, 2411.
30 T. C. Chung, J. H. Kaufman, A. J. Heeger and F. Wudl, *Phys. Rev. B*, 1984, **30**, 702.