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Molecular Weight Dependent Charge Carrier Mobility in Poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene)

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Poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene), a polymer recently used for the fabrication of organic field effect transistors, has been fractionated into five fractions distinctly differing in their molecular weights (M_n), with the goal of determining the influence of the degree of polymerization (DP_n) on its principal physicochemical parameters. It has been demonstrated that within the M_n range studied (from 1.5 kDa to 10.5 kDa by SEC), corresponding to DP_n from 10 to 38, the polymer band gap steadily decreases with growing molecular weight, which is clearly manifested by an increasing bathochromic shift of the band originating from the $\pi-\pi^*$ transition. The same trend is observed for the HOMO level, determined from the onset of the p-doping in cyclic voltammetry, which shifts from −5.10 eV to −4.90 eV for the lowest and the highest molecular weight fractions, respectively. The most pronounced influence of DP_n has been found for the charge carriers' mobility—one of the most important parameters of field effect transistors (FETs) fabricated from this polymer. A fourfold increase in DP_n results in an increase of the carriers' mobility by more than 3 orders of magnitude. Comparison of these results with those obtained for fractionated regioregular poly(3-hexylthiophene) shows a strikingly similar behavior of both polymers with respect to the molecular weight.

Solution-processible derivatives of polythiophene have been extensively studied in the past decade in view of their application as semiconductor materials in organic field effect transistors (OFETs). A large majority of this research has been focused on regioregular poly(3-alkylthiophene)s;[1−5] however, very recently, a few other polymers have also appeared as excellent candidates for this purpose, namely, poly(2,5-bis(3-alkyl-thiophen-2-yl)thieno[3,2-*b*] thiophene)s[6] or poly(3,3′-dialkyl-2,2′:5′,2″-terthiophene)s,[7,8] to name a few. One of the attractive features of the polythiophene-based semiconductors is the possibility of tuning their electronic properties by an appropriate design of their chain microstructure. However, fabrication of polythiophene-based OFETs is a delicate matter in which two sets of parameters should be considered: molecular and supramolecular ones. The former depend on the chosen polymer preparation method and embrace the type of chain microstructure and, in particular, its regioregularity, the chemical nature of the chain ends, and the molecular weight and its distribution. It is known that, for a given polymer, the electrical transport properties worsen with the increasing content of the coupling defects lowering its regioregularity.[9] Electron-donating (accepting) properties of the polymer end groups may also influence the electrical properties of the polymer;[10] however, their effect must decrease with the increasing chain length. Finally, the influence of the molecular weight, M_n, must be taken into

account.[10−12] Electrical properties of a semiconductor polymer are also dependent on its supramolecular organization in the solid state which embraces such supramolecular parameters as the type of crystal structure, coherence length, degree of crystallinity, and the morphology of the polymer layer.[13] All these parameters depend on the processing conditions, for example, on the type of solvent used for casting[4] or on the selected annealing process.[14] Finally, the type and the quality of the electrode/polymer interfaces must be taken into account.[15]

In a series of recently published papers, it has been clearly demonstrated that in the case of regioregular poly(3-alkyl-thiophene)s the molecular weight, M_n, of the polymer is the dominant parameter determining the mobility of charge carriers, μ, in the fabricated OFETs.[10−12] The value of μ is, in turn, crucial for the performance of OFETs. It seems therefore interesting to verify whether a similar type of dependence exists for other families of polythiophene derivatives used in organic electronics.

In this communication, we present, for the first time, the effect of M_n and more precisely the degree of polymerization, DP_n, on selected physicochemical properties of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (PDOTT) with special emphasis on charge carrier mobility. The formula of the polymer investigated is schematically depicted in Scheme 1, whereas the synthetic pathway used for its preparation can be found in the Supporting Information. The polymer was fractionated into five fractions of reduced polydispersity using a sequence of extracting solvents as recommended in ref 16. Their macromolecular parameters

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TABLE 1: Macromolecular and Electrochemical Parameters of PDOTT and PHT Fractions Studied

sample	M_n (SEC) (kDa)	PI	M_n^{corr} (kDa)	PD$^{corr\ a}$	HOMO^b	LUMO^b	E_{gap}^{el} (eV)
PDOTT fraction CHCl$_3$	10.5	1.69	5.9	38	−4.90	−2.51	2.39
PDOTT fraction CH$_2$Cl$_2$II	6.62	1.77	4.3	27	−4.95	−2.59	2.36
PDOTT fraction CH$_2$Cl$_2$I	5.5	1.53	3.7	24	−4.97	not measured	not determined
PDOTT fraction hexane	2.4	1.23	1.9	12	−4.99	−2.57	2.42
PDOTT fraction acetone	1.54	1.16	1.6	10	−5.10	−2.56	2.54
PHT high mass (Merck)	120	2.25	27	163	not measured	not measured	not determined
PHT fraction THF	27.4	1.98	10.8	65	not measured	not measured	not determined
PHT fraction CH$_2$Cl$_2$	10	2.07	5.6	34	−4.88	−2.50	2.38
PHT fraction hexane	2.5	1.45	1.9	12	not measured	not measured	not determined

^{a} Expressed per one 2,5-thienylene ring. ^{b} Calculated by assuming the position of the Fc/Fc$^+$ redox couple to be −4.80 eV with respect to the vaccum level.

SCHEME 1: Repeat Units of the Polymers Studied: (a) Poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) (PDOTT), (b) Poly(3-hexylthiophene) (PHT)
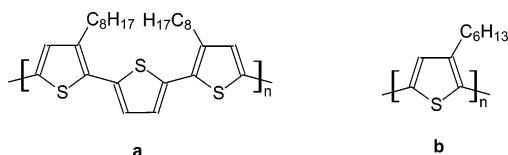
are collected in Table 1. In parallel, investigations of fractionated regioregular poly(3-hexylthiophene) (PHT; see Scheme 1 for the formula)—the polymer most frequently used for fabrication of FET—were carried out, with the goal of exposing similarities and differences between both polymers. Commercially available PHT (electronic grade) was purchased from Rieke Metals and fractionated is the same manner as PDOTT (see Supporting Information); the highest molecular weight fraction was provided by Merck UK. Although the dependence of M_n has already been reported for PHT,[10−12] the investigations presented here cover a much larger, previously unexplored M_n range.

PDOTT can formally be considered an alternate copolymer of tail-to-tail coupled dioctyl bithiophene with thiophene. Despite different lengths and distribution of alkyl side chains along the conjugated backbone, PDOTT and PHT exhibit strikingly similar supramolecular organization. The structure of both polymers can be described as consisting of planes of π-stacked conjugated chains separated by interdigitated alkyl side chains.[17,18] For the same substituent, the distance between the planes of π-stacked conjugated chains in poly(3,3″-dialkyl-2,2′:5′,2″-terthiophene)s is shorter than in poly(3-alkyl-thiophenes) as a result of a significantly stronger interdigitation in the former. For this reason, the interchain distance in poly-(3,3″-dihexyl-2,2′:5′,2″-terthiophene) (13.0 Å) corresponds to that of poly(3-butylthiophene) (12.7 Å), whereas this distance in poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) is almost the same as that in poly(3-hexylthiophene) (15.7 and 16.6 Å, respectively). Thus, despite apparent structural differences, both polymers are, in reality, similar as far as the conjugated chains and the distances between them are considered.

It is interesting to verify whether these structural similarities are also reflected in physicochemical properties of both polymers and, in particular, whether their dependence on the molecular weight is of similar nature. Both polymers differ in the number and the mass of the side substituents. Their comparison should therefore be carried out in terms of degree of polymerization (DP$_n$) rather than molecular weight (M_n). Moreover, it is known that molecular weights of poly(alkylthiophene)s determined by size exclusion chromatography (SEC) are overestimated. With this in mind, we have calculated the corrected molecular weights M_n^{corr} and, consecutively, DP$_n^{corr}$ using the correlation between the MALDI TOF data and the SEC data presented in ref 19.

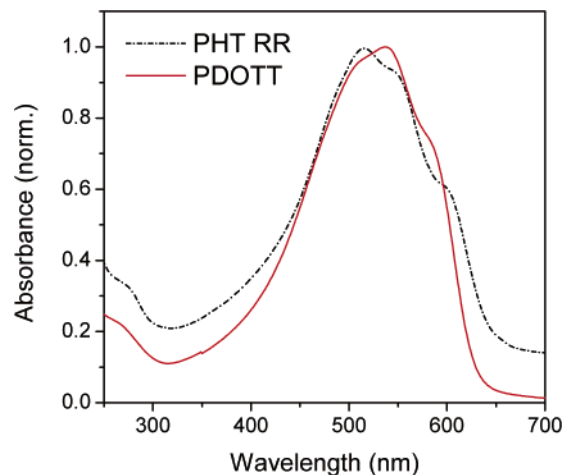**Figure 1.** Solid-state UV−vis absorption spectra of PDOTT (DP$_n^{corr}$ = 38) and PHT (DP$_n^{corr}$ = 34).

UV−vis absorption spectra of thin films of PDOTT and PHT, showing similar DP$_n^{corr}$ and cast in identical conditions, are shown in Figure 1. Typical of conjugated polythiophene derivatives in both spectra, an absorption band associated with the π−π* transition, i.e., the transition from the valence (π) band to the conduction (π*) one, appears. It must also be noted that both spectra show a clear vibrational structure. Such structure in the solid-state spectra of conjugated polymers is always a manifestation of the electron lattice coupling. The energy of the 0−0 transition, i.e., the transition from the ground state to the relaxed state, is inversely proportional to the conjugation length. Second-derivative analysis of the spectral lines presented in Figure 1 gives the maxima of $-d^2A/d\lambda^2$ for the 0−0 transition at 608 nm (2.04 eV) and 598 nm (2.07 eV) for PHT and PDOTT, respectively. Thus, for comparable DP$_n^{corr}$, PHT is slightly more conjugated than PDOTT, but the difference is small. Similar trends are observed for both polymers studied: with decreasing DP$_n^{corr}$, the maxima of the peaks corresponding to the 0−0 transitions shift hypsochromically, and for the lowest DP$_n^{corr}$ fractions, they merge with bands originating from other transitions (not shown here).

The positions of the HOMO and LUMO levels (corresponding to the highest state of the valence band and the lowest state of the conduction band, respectively) are important parameters determining the electronic properties of conjugated polymers. They can be extracted from properly designed chronovolta-mperometric experiments covering the potential range of both p and n doping of the polymer under investigation. If the π−π* transition in polythiophene derivatives really reflects the extent of conjugation and by consequence the width of the band gap, the potential difference between the oxidative (p-type) and
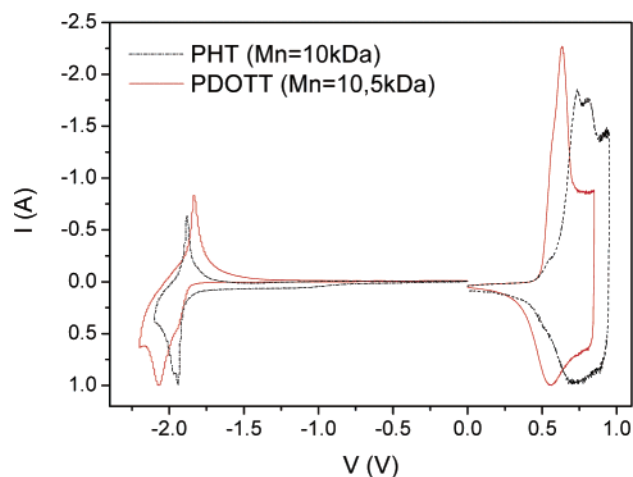
Figure 2. Cyclic voltammograms of PDOTT (DP_n^{corr} = 38) and PHT (DP_n^{corr} = 34). Potential vs Ag pseudoreference electrode, whose potential measured versus Fc/Fc+ was 0.395 V; scan rate 15 mV/s.

Figure 3. Bottom-gate, bottom-contact transistor used for the studies.

Figure 4. (a) Output and (b) transfer characteristics of a typical OTFT fabricated with PDOTT (CH_2Cl_2 I fraction, DP_n^{corr} = 24). The channel length is 20 μm, and the channel width is 9 mm.

Figure 5. Saturation mobility (V_{ds} = −60 V) versus DP_n^{corr} (SEC) for spin-coated films of PDOTT and PHT.

reductive (n-type) dopings should be very close in PDOTT and in PHT. Moreover, if the positions of the bands are similar with respect to the vacuum level, the p-doping and n-doping redox couples should appear at similar potentials. In Figure 2, cyclic voltammograms of both polymers, exhibiting very close DP_n^{corr} values, are compared. The potentials first determined vs Ag pseudoreference electrode were then calibrated using ferrocene/ ferricenium (Fc/Fc+) in the same electrolytic solution as recommended by IUPAC.[20] The so-called "electrochemical band gap" can be determined from the onset of the electrochemical p-doping peak (removal of an electron from the HOMO level) and from the onset of the n-doping peak (introduction of an electron to the LUMO level). It is clear that, although the shapes of the p-doping peaks are different for PDOTT and PHT, their p-doping starts at very similar potentials. The same applies to the n-doping. The double-peak character of the voltammetric p-doping of PHT is typical of fractions with DP_n^{corr} > 30.[16] Electrochemical parameters of PDOTT and PHT fractions being compared are collected in Table 1. The energy values of the HOMO and LUMO levels were calculated by assuming the ferrocene couple level being −4.8 eV below the vacuum level.[21] It can be noticed that for very similar DP_n^{corr} the HOMO levels determined for PDOTT and PHT are very close, being only slightly higher for the latter. Similar to the case of PHT,[16] for PDOTT the position of the HOMO level systematically changes from −4.90 eV to −5.10 eV when DP_n^{corr} M_n decreases from 38 to 10.

FET mobility of charge carriers, μ, is one the most important technological parameters of any polymeric semiconductor used for the fabrication of OFETs. For PHT, μ significantly increases with increasing DP_n.[10−12] We have been tempted to verify whether similar dependence can also be observed for PDOTT. To elucidate this problem, we have fabricated, in identical conditions, a series of FETs from all polymer fractions listed in Table 1. The carriers' mobilities have been measured on a specially prepared bottom gate, bottom contact field effect transistor, schematically depicted in Figure 3. All details concerning its fabrication can be found in Supporting Information.

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
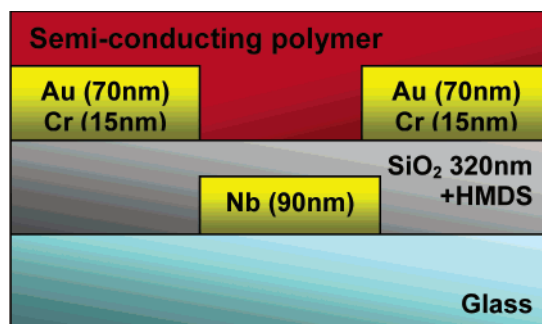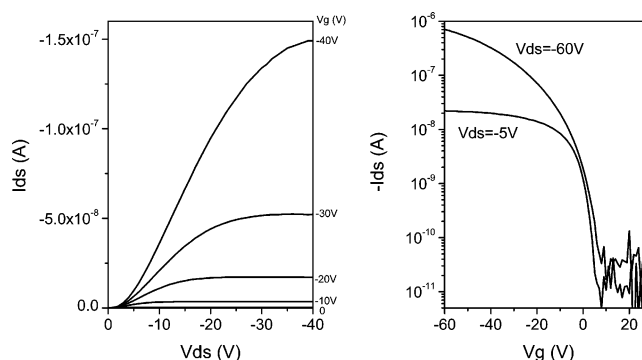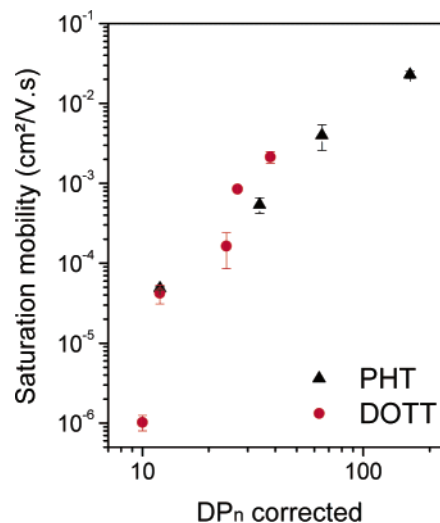
in the saturation regime (V_{ds} = −60 V) using the standard equation[22,23]

$$I_{ds} = \frac{W}{2L} C_{ox}\mu_{sat}(V_g - V_t)^2 \qquad (1)$$

where W is the channel width, L is the channel length, C_{ox} is the dielectric capacity, μ_{sat} is the saturation field mobility, and V_g and V_t are the gate voltage and threshold voltage, respectively. The reported results are average values obtained from three different transistors fabricated with the same polymer fraction. A typical transistor characteristic is shown in Figure 4.

The dependence of the saturation FET mobility on DP_n^{corr} measured for different fractions of PDOTT and for PHT is shown in Figure 5. It should be noted here that for the latter we
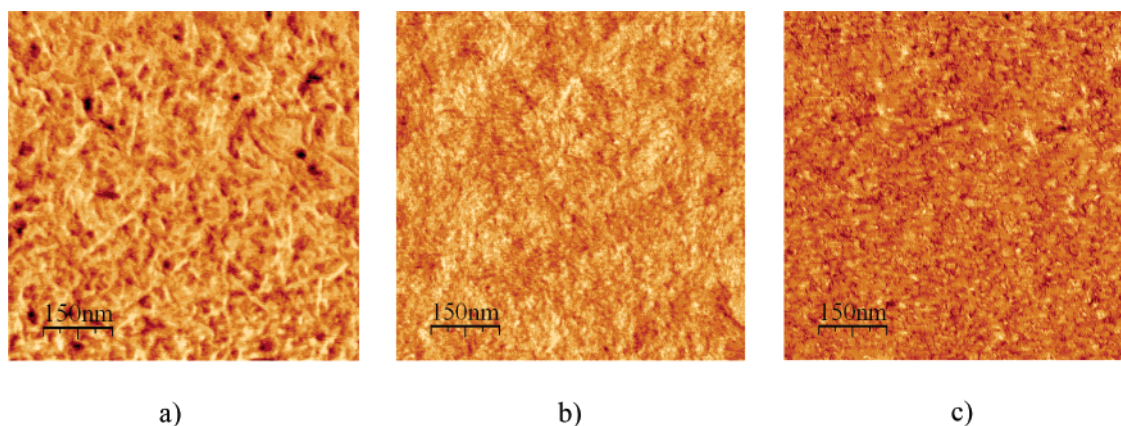
Figure 6. AFM measurements (phase image) of spin-coated films of (a) PHT ($DP_n^{corr} = 34$), (b) PDOTT ($DP_n^{corr} = 38$), and (c) PHT ($DP_n^{corr} = 163$). The measurements are made in the transistor channels.

have extended the range of DP_n^{corr} studied as compared to previous reports.[10−12] Although the ranges of molecular weights of the PDOTT and PHT fractions studied only partially overlap, it is clear that similarly strong dependence of carriers' mobility on the molecular weight is observed in both cases, proving that M_n is a critical factor influencing the electrical transport properties in both polymers. The charge carriers' mobility determined in the FET configuration embraces several contributions such as the transport of the carriers along an individual chain, their interchain hopping within a given supramolecular aggregation, and finally their transfer between different aggregations. DP_n can interfere at all these levels. First, it is clear from the spectroscopic studies that in both polymers studied the conjugation length increases with increasing DP_n facilitating the carriers' transport along an individual chain. Second, the increasing chain length should improve the interchain hopping of charge carriers, since the probability of this hopping depends on the density of low activation energy pathways for the crossing between chains whose number should increase with the chain length. Finally, longer chains can serve as connectors facilitating the charge transport between different supramolecular aggregations. Thus, chains of increasing DP_n should improve the connectivity and lower the density of charge traps.

Interestingly, for intermediate DP_n^{corr} values, carriers' mobilities measured for PDOTT exceed those obtained for PHT. We attribute this phenomenon to morphological differences, since electronic properties of both polymers, exhibiting close DP_n^{corr} values, are very similar (vide supra). It is known that DP_n strongly influences the morphology of thin polymer films obtained by spin-coating.[12] In particular, the use of fractions of low molecular weight leads to nanorod-like morphology with clear grain boundaries, whereas high molecular fractions give isotropic nodular morphology with no distinguishable grain boundaries. It is believed that for short chain length, the grain boundaries limit the mobility of charge carriers leading to lower mobility values.[24] In Figure 6a,b, AFM images of thin PDOTT and PHT films, fabricated from fractions of essentially the same DP_n^{corr}, are compared. The image of the PHT film still shows the presence of nanorods with clear grain boundaries, whereas the PDOTT film shows isotropic nodules, i.e., the morphology typical of PHT films of much higher molecular weight (see Figure 6c).

To summarize, we have demonstrated that a very strong dependence of electrical transport properties on the degree of polymerization (DP) previously reported for regioregular poly-(3-hexylthiophene) is also observed for poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene)—another promising candidate for the use in organic electronics. Moreover, close similarity of the behavior of both polymers, as far as the effect of DP is concerned, has been found for other physicochemical properties such as the onsets of n- and p-dopings and others. The obtained results seem to indicate that, at least in the polythiophene family of electroactive polymers, the DP dependence of the crucial electrical parameters persists to relatively high molecular weights and underline the importance of the macromolecular parameters control in the fabrication of polymer-based electronic and electrochemical devices.

Note Added after ASAP Publication. This Letter was published on Articles ASAP on June 10, 2006. Changes were made to eq 1 and the surrounding text. The corrected Letter was reposted June 14, 2006.

Supporting Information Available: Details of the synthesis of poly(3,3″-dioctyl-2,2′:5′,2″-terthiophene) and transistor fabrications. This material is available free of charge via the Internet at http://pubs.acs.org.

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Letters

J. Phys. Chem. B, Vol. 110, No. 27, 2006 **13309**

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