Charge Transport Behaviours of End-Capped Narrow Band Gap Polymers in Bottom-Contact Organic Field-Effect Transistors

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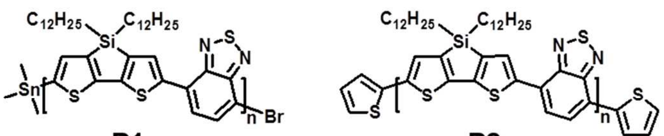
This report examines the influence of narrow band gap polymer end groups (bromine or thiophene) on the performance of field-effect transistors prepared using these polymers. The conjugated polymer chains that were capped with thiophene units enhanced the intermolecular packing structure and decreased device hysteresis by removing charge traps. The presence of the end-capping groups increased the hole mobility by a factor of 2 or 4, depending on the molecular weight of the polymer, in the bottom contact field-effect transistors.

The discovery that electrochemical doping can yield highly conductive π-conjugated polymers has led to significant investment in the development of π-conjugated polymers and small molecules by both academia and industry.[1,2] Certain emerging technologies would benefit from the polymers' unique optical and semiconducting properties.[3,4] Conjugated polymers can be used in organic field-effect transistors (OFETs) prepared by depositing the polymers on a substrate using solution printing techniques.[5,6] This technique has been broadly adopted to enable the low-cost fabrication of organic devices that display novel device functionalities, including flexibility and optical transparency, neither of which may be obtained easily using inorganic materials.[7] Conjugated polymers tend to be more highly disordered than inorganic materials, and their weak intermolecular interactions can reduce the charge carrier transport relative to the transport properties in crystalline inorganic semiconductors.[8] Over the last few decades, tremendous efforts have been applied toward understanding and enhancing the carrier mobility in polymeric semiconductors by testing new polymer structures, functional groups, and π-conjugated backbones, each of which can promote unique conformational and electrochemical properties.[9-11] Remarkable advances in OFET performances have been achieved by increasing the field-effect mobility of the organic polymers[12,13]; however, the severe hysteresis that develops during the operation of an OFET based on a conjugated semiconducting polymer presents a critical impediment to the development of organic integrated circuits.[14] Charge trapping in semiconductors determines the electrical properties of an OFET, including the threshold voltage, the field-effect mobility, the on-off current ratio, and the hysteresis.[15] Bromine groups in the conjugated polymer readily attract holes to create hysteresis during device operation. Few studies have thus far examined whether the nature of the end groups on the conjugated polymer chains affects the optoelectronic properties and device performance.[16,17]



P1
(10kg/mol and 30kg/mol)

P2
(10kg/mol and 30kg/mol)

Scheme 1. The molecular structures of the materials used in this study. The chains were terminated by Sn and Br (P1), or the chain end-capping thiophene reagents (P2).

It is recently demonstrated that low concentrations of structural defects, such as chemically reactive end groups, could influence the overall device performance.[18-20] We focused on the most common bromine end groups, which remain after polymerization via a dehalogenation synthesis. These defects may be removed by capping the chain ends with a conjugated segment, such as the thiophene group used in organic photovoltaic devices. In a previous report, which did not include a detailed analysis of the charge transport behaviors or the polymer molecular packing structure, we hypothesized that the end-capping chemical functional groups would adversely affect the electronic properties of the polymer by introducing charge carrier traps or by inducing undesirable chemical transformations during device operation. Jenekhe et al. studied the chain end-capping effects in several naphthalene diimide-based n-type polymers, revealing an enhancement in the OFET device performances.[21] Little is yet known about the degree to which such end group modifications affect the molecular structures of the semiconductor layer and benefit the device performance.

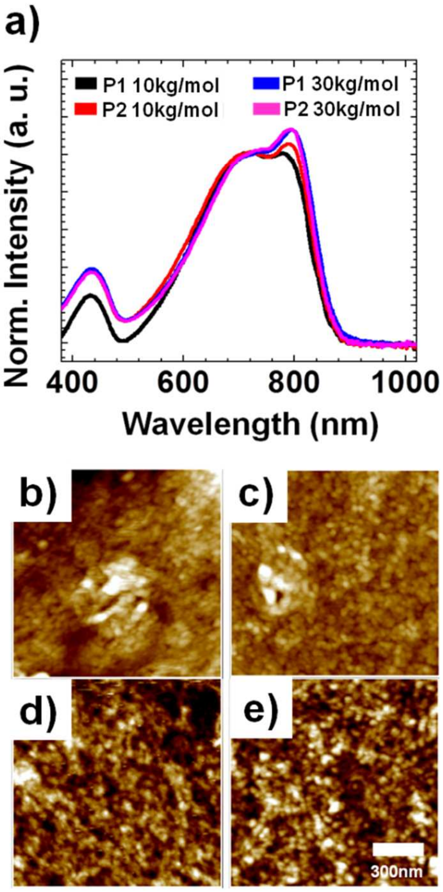


Figure 1. UV-vis. spectra of P1 and P2 films prepared from polymers with different molecular weights (a), and AFM height images of films corresponding to 10 kg/mol P1 (b), 10 kg/mol P2 (c), 30 kg/mol P1, (d) and 30 kg/mol P2 (e). The scale bars in the AFM images indicate 300 nm.

In this contribution, we compare the behaviors of OFETs fabricated with polymers having essentially identical chemical characteristics (structural units), except for the end group functionalities (Scheme 1). Two versions of the polymer targeted for study, poly[(4,4-didodecyldithieno[3,2-b:2',3'-d]silole)-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl] were prepared according to methods reported in the literature. P1 was functionalized with a stannyl and a bromide end group, whereas P2 was end-capped with thiophene groups. As reported in previous literature, the presence of stannyl and bromide end groups was evident in P1 by measuring x-ray photoelectron spectroscopy (XPS) whereas none can be detected in P2. Therefore, it is clearly demonstrated that the polymer chain was successfully end capped with thiophene units. [18]

We examined the influence of the bromine and thiophene end groups and the conjugated polymer molecular weight on the molecular packing and device performances. The two versions of the polymer synthesized here differed due to differences in the electrostatic interactions, stacking properties, and charge trapping properties of the bromine and thiophene units due to differences in the electronegativities, electronic structures, and steric effects. The effects of the molecular weights of the two versions of the polymer were investigated on the hypothesis that the density of the end group would increase as the molecular weight decreased, rendering the lower molecular weight polymer significantly sensitive to the identity of the end-capping group. A low molecular weight version of each polymer (M_n = 10 kg/mole with a polydispersity index (PDI) of 2.3) was prepared via Soxhlet extraction with THF from the large molecular weight polymer (M_n = 30 kg/mole with a PDI of 2.3) after removing the methanol-, acetone-, and hexane-soluble fractions.

Figure 1(a) shows the UV–vis absorption spectra of the P1and P2 films spin-cast onto a glass substrate from their neat chlorobenzene solutions. All spectra indicated a strong intramolecular charge transfer band ranging from 500 nm to 900 nm. The spectra of the high molecular weight polymers were nearly identical, regardless of the end-capping group, whereas the low molecular weight P2 displayed an enhanced aggregated phase, as indicated by an absorption band at 800 nm. The thiophene end groups on the P2 may have increased the chain packing density by strengthening the intermolecular stacking interactions among the chromophore units.[18-22] The positions of the absorption bands in both the P1 and P2 polymer films were indistinguishable, indicating that the end groups did not significantly alter the electronic structures of the polymers. The AFM images of the films, as shown in Figures 1(b) and 1(c), further supported this interpretation of the absorption spectra, as the root mean square (RMS) roughness increased from 2.39 nm to 3.42 nm, consistent with the presence of large ordered aggregates in the P2 film. The high molecular weight P1 and P2 films (Figure 1(d) and 1(e)) yielded indistinguishable RMS values (1.81 nm and 1.88 nm respectively).[18]

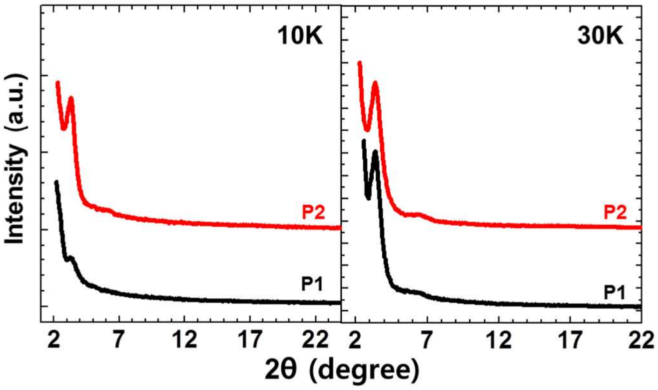


Figure 2. GIXRD measurements obtained from the P1 and P2 polymer films, for molecular weights of 10 kg/mol (a), or 30 kg/mol (b).

The molecular structures of thin films, prepared with the P1 and P2 polymers having either of the two molecular weights and bearing either of the end-capping groups, were examined using grazing incidence X-ray diffraction (GIXRD) measurements. These experiments focused on the molecular packing structures that resulted from each end-capping group. The results further elucidated the structures that gave rise to the UV-vis and AFM measurements presented in Figure 1. The one-dimensional out-of-plane plots shown in Figure 2 reveal that all films produced a first Bragg peak (100) at 2 θ = 3.5° due to the lamellar layer structure (22.1 Å), and no other diffraction patterns were observed. This result indicated that the polymer alkyl groups were preferentially oriented toward the substrate surfaces (in an edge-on orientation).[23] Dramatically distinct behaviors were observed, however, among the low molecular weight polymers with different end-capping groups. The (100) peak intensity of the P2 film was stronger than the corresponding peak in the P1 film. On the other hand, the differences between the high molecular weight P1 and P2 films were not as pronounced as for the low molecular weight films. These results suggested that the thiophene end groups enhanced the ordering and sizes of the polymer crystallites, presumably due to the π-π and sulfur–sulfur (S-S) intermolecular interactions[24] upon eliminating residual bulky end groups such as stannyl and/or bromide by the introduction of planar aromatic rings to the chain ends.

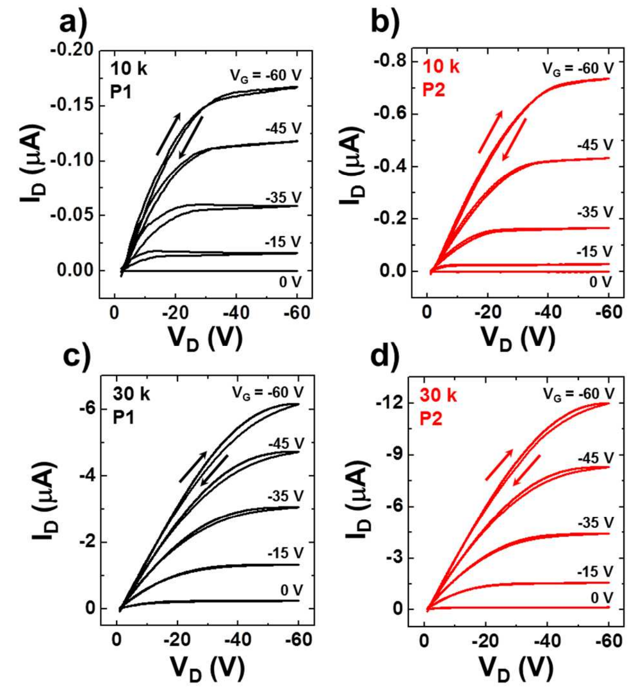


Figure 3. The output characteristics of OFETs prepared using the P1 or P2 polymers with either low or high molecular weights, with operation at various gate voltage (V_G) between 0 V and –60 V. The arrows represent the scan directions.

Bottom-contact (BC) OFET device structures can be manufactured at low cost, and they provide a geometry that is practical for a variety of applications.[25,26] BC OFETs were prepared to test the impact of the polymer chain end modifications on the electrical properties. The charge carrier mobilities and hysteresis were measured in OFETs prepared from each of the polymer films tested here.[27,28] Devices were fabricated using gold bottom contacts, a doped Si bottom gate, and SiO_2 dielectric treated with hexamethyldisilazane (HMDS).[29] The P1 and P2 semiconductor layers were spin-coated from a 0.5 wt% solution in chlorobenzene on an HMDS-treated SiO_2 substrate. The average mobility was calculated from the average of more than 10 devices prepared from P1, and P2 solutions. Typical source–drain current (I_D) vs. source–drain voltage (V_D) plots at five different gate voltages (V_G) are shown in Figure 3 as a function of the molecular weight and end-capping group. All devices showed typical p-type dominant transistor behavior at a negative V_G. The saturation current reached a value of –0.78 μA at V_G = –60 V for the BC OFETs prepared using a low molecular weight P2 film (Figure 3 (b)), whereas the maximum current obtained from the P1 film with the same molecular weight was –0.18 μA (Figure 3 (a)). In addition, the highest saturation current measured was obtained from the OFETs prepared with the high molecular weight P2: –12 μA at V_G = –60 V (Figure 3 (d)). This value was only twice the value obtained from OFETs prepared using the high molecular weight P1, –6 μA (Figure 3 (c)). A clear progression toward higher currents was observed as the polymer was chemically modified with end-capping groups prior to film deposition. The electrical properties of the low molecular weight polymers were highly sensitive to the identity of the end-capping group because the end groups made a larger contribution to the molecular properties in the low molecular weight polymers than in the high molecular weight polymers.

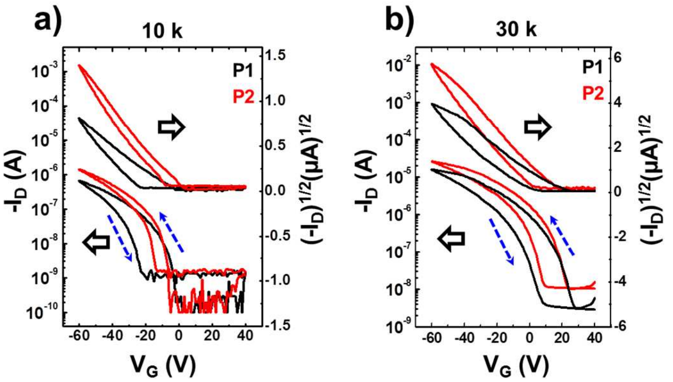


Figure 4. Plot of I_D versus V_G at a fixed V_D of –60 V, on both the linear (right axis) and log (left axis) scales, for P1 and P2 OFETs prepared with polymers having two different molecular weights: 10 kg/mole (a) or 30 kg/mole (b).

The charge trapping effects and field-effect mobility were calculated based on the transfer characteristics, shown in Figure 4. The extracted electrical parameters are summarized in Table I.[30] An OFET driven under a gate voltage displayed hysteresis that could usually be interpreted as a shift in the threshold voltage as a function of the gate voltage sweep direction.[31] Hysteresis is typically indicative of a reduction in the back sweep current in the device, which is often attributed to charge carrier trapping close to the channel. An increase in the back sweep current hysteresis usually results from the presence of mobile ions in the dielectric or from (ferroelectric) polarization in the dielectric film.[29,32] The observed hysteresis suggested charge trapping at the chemically reactive end functional groups, such as bromine or tin, because the applied gate bias was sufficiently large to polarize the end groups at the organic/dielectric interface and stabilize the charges in the channel.[29,33] The low molecular weight P1 polymer (10 kg/mol) displayed a large negative shift in the threshold voltage and a decay in I_D over consecutive scans, as shown in Figure 4(a). These results suggested that the P1 chain ends terminated with bromine attracted mobile holes that induced charge trapping and interfered with the intrinsic charge transport. Transfer characteristics hysteresis in the end-capped polymer, P2, was surprisingly lower than that observed in the uncapped polymer, P1. The hysteresis was reduced by end capping, which replaced the polarizable end groups with groups capable of participating in π-stacking interactions. This effect was more pronounced in low molecular weight polymers, 10 kg/mol than in the high molecular weight polymers, 30 kg/mol. The chain end concentration in the backbone, which varied with the molecular weight, significantly affected the trap density (Table I).

The average field-effect mobility in each device was calculated in the saturation regime by plotting the square root of the drain current versus the gate voltage, and by fitting the data to a standard model, as described previously.[30] The electrical characteristics depended strongly on the molecular weight. The P2 polymer exhibited excellent on-current values and a small degree of hysteresis during operation. The highest average field-effect mobility (6.5×10^{-3} $cm^2V^{-1}s^{-1}$) was observed in the high molecular weight P2 films. These performance characteristics were more than 2-fold greater than those of the P1 films cast from the same molecular weight (2.9×10^{-3} $cm^2V^{-1}s^{-1}$). Likewise, the mobility of the OFETs prepared using the low molecular weight P2 film (6.0×10^{-4} $cm^2V^{-1}s^{-1}$) was approximately 4 times the value obtained from OFETs prepared using the low molecular weight P1 (1.5×10^{-4} $cm^2V^{-1}s^{-1}$). The average mobility in an OFET prepared using P2 was several times greater than the value obtained from P1, and the end-capping effects were larger in the low molecular weight polymers than in the high molecular weight polymers, consistent with the trend in the hole trapping. The nature of the end group could influence the device performance in several ways, for instance, by producing chemical traps that directly trapped charges, by disrupting chain packing through steric or electrostatic interactions, or by accelerating degradation through enhanced chemical reactivity. In this study, the field-effect mobility enhancement and small degree of hysteresis were attributed to a reduction in the trap sites at the polarizable end groups and the improved interchain ordering as a result of the end cap interactions.[10,25]

Table 1. The summary of BG-BC OFET characterization

Polymers	M_n (kg/mol)	Mobility ($cm^2V^{-1}s^{-1}$)	ΔV_{th}	Charge trap density [a] (cm^{-2})
P1	10	$2.0\times10^{-4}\pm0.0002$	24	3.0×10^{12}
P2	10	$5.7\times10^{-4}\pm0.0003$	9	1.1×10^{12}
P1	30	$2.9\times10^{-3}\pm0.0005$	21	2.6×10^{12}
P2	30	$6.5\times10^{-3}\pm0.0007$	16	2×10^{12}

[a] The charge trap density was calculated according to the following equation: $N = C \times\Delta V_{th} /e$, where C is the gate channel capacitance per unit area, *e* is the elementary charge, and ΔV_{th} is the threshold voltage change.[34,35]

Conclusions

The electrical properties of BC OFETs prepared using the P1 and P2 polymers, in which the end groups were modified with bromine or thiophene units, respectively, were investigated. The charge carrier mobilities were found to increase due to an enhancement in the internal ordering and sizes of the crystallites, possibly as a result of S-S and π-π interactions among the chain ends by removing steric hindrance. Concomitant with the improved ordering, the device performance was enhanced and hysteresis was reduced by eliminating possible charge trap sites that could be easily polarized under the bias applied through the gate dielectric layer. These end-capping effects significantly impacted the OFET performances under conditions in which the semiconducting polymers had a sufficiently low molecular weight because the end-capping groups were present in a higher effective concentration than in the high molecular weight polymers. Understanding and controlling hysteresis in OFETs is crucial for the design of organic semiconductors that provide improved device performances. In practical application, hysteresis must be avoided in transistors used in standard integrated circuits, except in certain nonvolatile memory device applications. Studies designed to understand the physical attributes of the organic components used in field of organic electronics are important for transitioning fundamental research efforts into commercially viable technologies.

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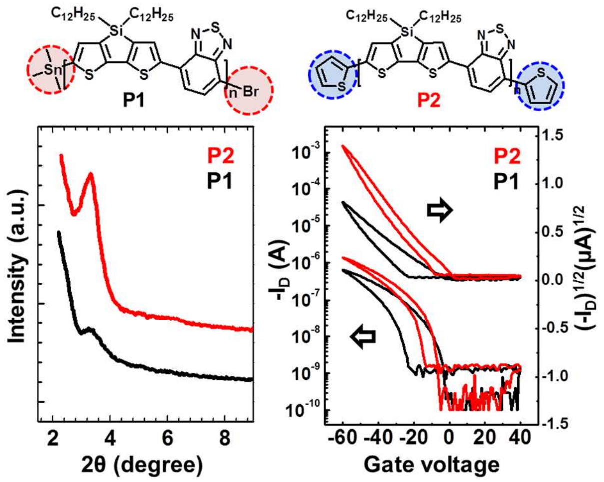
Table of Content



The ends of conjugated polymer chains were capped with thiophene units to enhance intermolecular packing and decrease device hysteresis by removing charge trap sites.