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Synthesis of Terminally Dendronized Poly(3-hexylthiophene)s as a Platform for Functional Conjugated Polymers

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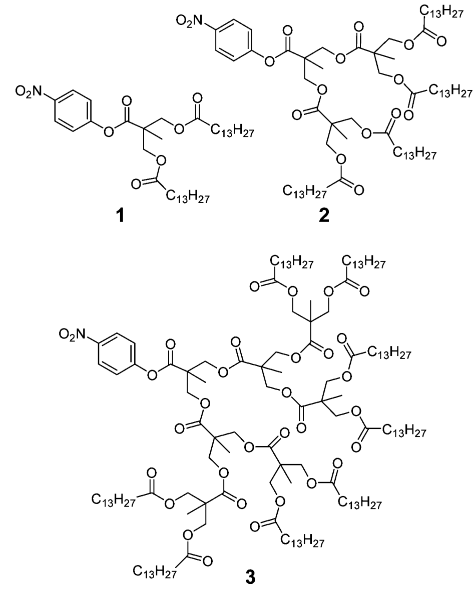
The preparation of well-defined block copolymers containing one or more semiconducting blocks is the subject of intense research due to their potential for application in plastic-based electronics.[1−5,6−9] Among various semiconducting polymers, regioregular poly(3-hexylthiophene) (RR−P3HT) is known to be the most successful material for use in plastic-based electronic devices due to its high conductivity and processability.[10−14] Appending crystalline or amorphous polymer segments to P3HT permits control of the physical properties including film morphology.[15−17] Although the chemical modification of P3HT at its polymer backbone or its termini generally disrupts the effective crystal packing and decreases the hole mobility, functionalized P3HTs are nevertheless attractive materials as "functional surfactants" for use in applications that do not require high mobility. For example, a RR−P3HT end-functionalized with an amine improves the film morphology of P3HT/CdSe solar cells by increasing the dispersion of CdSe nanocystals, and enhances the power conversion efficiency.[18] Block copolymers of P3HT with fullerenes are useful as compatibilizers for P3HT/fullerene bulk heterojuction solar cells which stabilize the active layer of the device.[4] Additionally, block and random copolymers of P3HTs appear to be promising materials for use in volatile organic compound (VOC) chemresistor sensors.[19] In this paper, we report on the synthesis and characterization of a dendron-modified P3HT, in which one terminus of a RR−P3HT is linked to the focal point of a polyester-type dendron. This dendron structure allows the placements of multiple functionalities at one extremity of the macromolecule for further elaboration. Despite the insulating nature of the polyester dendron, a device made with this dendron-modified P3HT functions as a transistor, and shows moderate field effect mobilities. In earlier work, dendrons have been used as solubilizing groups for oligo- and polythiophenes.[20−23]

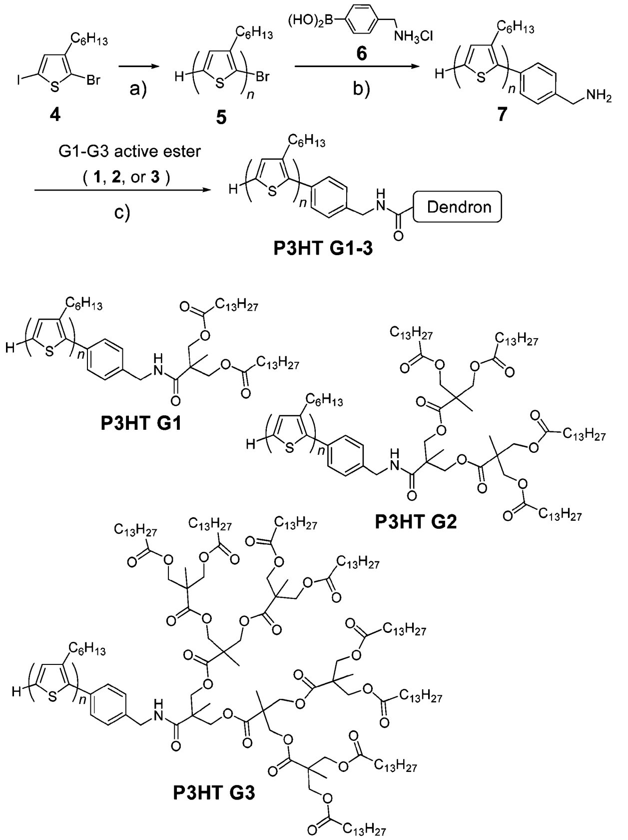
The structures of the generation 1 to 3 (G1−3) aliphatic polyester dendrons **1**−**3**, used as the building blocks for the preparation of the dendronized P3HTs, are shown in Chart 1. The polyester-type dendrons were synthesized by iterative divergent growth as previously described.[24,25] A key advantage of such dendrons is the high reactivities of both the single focal point moiety and the multiple peripheral functionalities In this study, the peripheral hydroxy groups were end-capped by long-chain alkyl (myristic) esters, while the focal point was activated with a 4-nitrophenyl ester for coupling to a reactive terminus of P3HT.

Chart 1. Chemical Structures of G1 Dendron 1, G2 Dendron 2, and G3 Dendron 3 with Active Ester



RR−P3HT was prepared from 2-bromo-3-hexyl-5-iodo thiophene (**4**) through the Grignard metathesis (GRIM) reaction (Scheme 1).[26−30] Polymerization via GRIM affords highly regioregular (RR) P3HT **5** with a 5-bromothiophene end group. Detailed characterization of the P3HT produced through GRIM and the reaction mechanism are described elsewhere in the literature.[27,30] The number-average molecular weight (M_n) and polydispersity (PDI) of the RR−P3HT used throughout this

Scheme 1[a]



[a] Conditions: (a) *i*-PrMgCl, THF, 0 °C, 1 h, then Ni(dppp)Cl_2, room temperature, 1 h, 44%; (b) **6**, Pd(PPh_4)$_3$, toluene/EtOH/H_2O, Na_2CO_3, 90 °C, 3 h, 55%; (c) **1**, **2**, or **3**, diisopropylethylamine, THF, reflux, 12−24 h, 59−64%.

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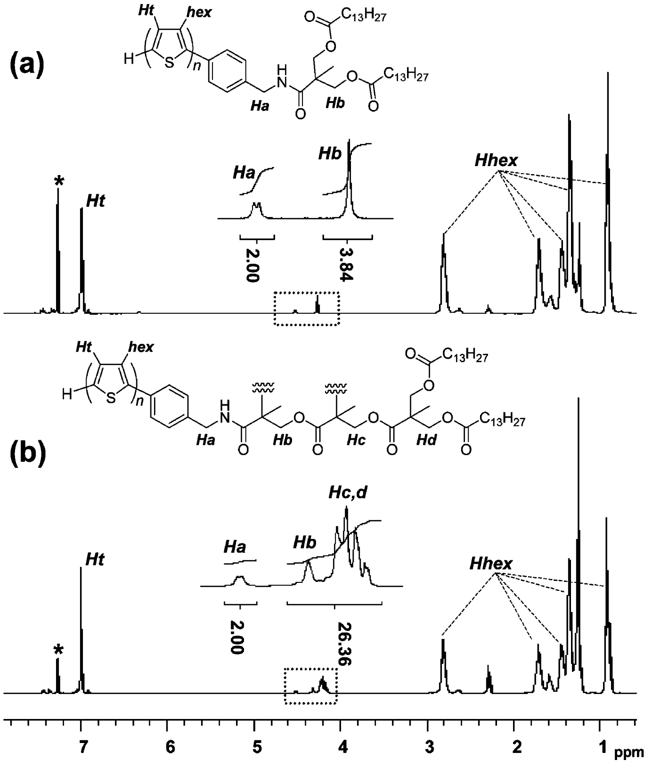

Figure 1. ^{1}H NMR spectra (400 MHz, in CDCl$_3$) of (a) **P3HT-G1**, and (b) **P3HT-G3**. The peaks with an asterisk (*) indicate the residual solvent.

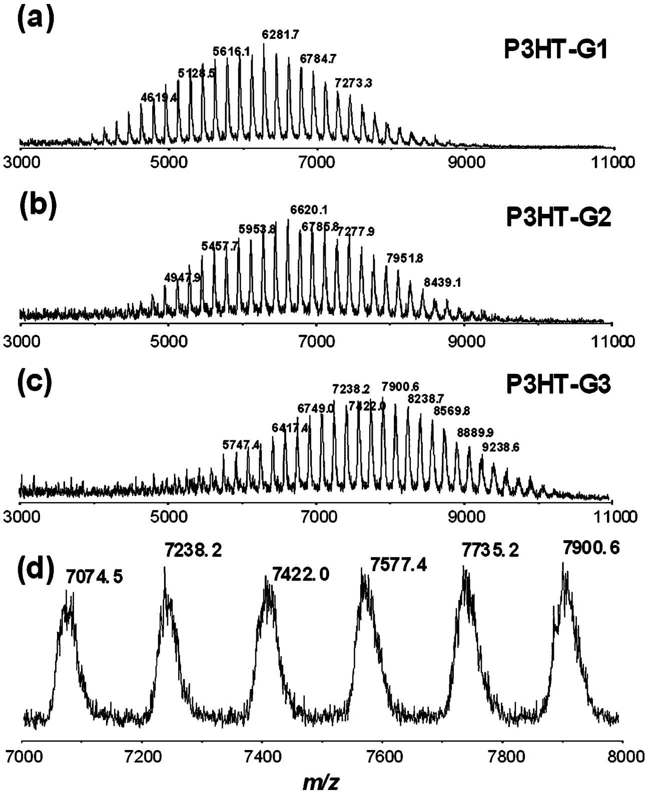

Figure 2. MALDI mass spectra (matrix; terthiophene) of (a) **P3HT-G1**, (b) **P3HT-G2**, and (c) **P3HT-G3** and (d) the magnified figure of Figure 2c from 7000 to 8000 mass (*m/z*) range.

Table 1. Field Effect Mobility of P3HT G1−G3

		wt % of dendron		
	MW of dendron	by NMR[a]	by SEC[b]	mobility (μ)[c]
P3HT G1	643	10	6	2.5E−4
P3HT G2	1296	19	11	1.1E−4
P3HT G3	2602	32	21	3.5E−5

[a] Determined based on the degree of polymerization (DP) of P3HT which is calculated by integral ratio of P3HT and dendron protons in ^{1}H NMR spectra. [b] Determined based on the M_n of P3HT (M_n = 10 000) (SEC (THF), polystyrene standards). [c] Averaged saturation mobilities (cm^2/(V s)) of three experiments for a bottom contact device.

study were 10 000 and 1.15, respectively, as measured by SEC in THF using polystyrene standards. End-functionalization of P3HT was carried out by Suzuki coupling with 4−aminomethylphenylboronic acid hydrochloride **6**, to afford the benzylamine functionalized P3HT **7** in 55% yield. Introduction of this benzylamine moiety in **7** serves a dual purpose: first it introduces a polar group into the polymer thus facilitating its purification; second, it provides a highly reactive handle for attachment of the active ester dendon. Purification of **7** is readily achieved by silica chromatography which affords a pure product as evidenced by ^{1}H NMR and MALDI mass spectrometry. The amino-functionalized P3HT **7** was then treated with G1-G3 active ester (**1**−**3**) in the presence of base under reflux in THF, affording **P3HT G1—G3** in 59−66% yield. In all cases the **P3HT G1—G3** block copolymers were purified by Soxhlet extraction followed by silica gel chromatography.

The structures of the dendron-modified P3HTs were confirmed by ^{1}H NMR (Figure 1). Definitive assignments of the individual peaks were made by comparison with the protons of P3HT (Ht and Hhex) and of the dendrons (Ha, Hb, Hc, Hd, and protons of myristic ester). Further, the integral ratios are also consistent with the assignment.

Much information on the quality of the end-functionalization process could be garnered from a detailed examination of the MALDI mass spectra. Figure 2 shows the MALDI-mass spectra of **P3HT G1-G3**. As the size of the dendron increases from G1 to G3, the expected shift of the peak distribution toward higher mass is readily observed (Figure 2a−c). For the **P3HT G3** block copolymer, the molecular mass of a specific macromolecule with *n* hexylthiophene units is calculated as $M = 166.3$ *n* (poly(hexylthiophene unit) + 1 (hydrogen end-group) + 2602 (**G3** dendron unit). A close examination of an expanded portion of the mass spectrum shown in Figure 2d reveals molecular masses (m/z = 7422.0, 7577.4 and 7735.2) that are in good agreement with the calculated mass (7417.4, $n = 29$; 7583.4, $n = 30$; 7749.5, $n = 31$). Each peak of **P3HT G1—G3** is monodisperse, and no specific peaks that could be attributed to side products are seen in the MALDI−MS.

In order to verify that the presence of the dendrons did not destroy the conductivity of the various **P3HT G1—G3** block copolymers, organic field effect transistors (OFETs) were fabricated in bottom-contact geometry (thin film of **P3HT G1—G3**/1000 Å SiO$_2$ dielectric/*n*-doped Si gate) with gold electrodes. Thin films were deposited from chloroform solutions of the various **P3HT G1—G3** copolymers by spin-casting, and the devices were tested without annealing (see Supporting Information for details). The hole mobility and the weight ratio of the dendrons in **P3HT G1—G3** are summarized in Table 1. Devices made from **P3HT G1—G3** showed hole conductivity with averaged saturation mobilities of 2.5 × 10^{-4} cm^2/(V s) (**P3HT G1**), 1.1 × 10^{-4} cm^2/(V s) (**P3HT G2**), and 3.5 × 10^{-5} cm^2/(V s) (**P3HT G3**), respectively. As expected, the size of the dendron affects mobility and as dendron size increases from G1 to G3, the mobility decreases by an order of magnitude. However, it is worth noting that even with 32 wt % of insulating polyester dendron attached to RR−P3HT,[31] the device made from **P3HT G3** operates effectively as a field effect transistor.

It should also be emphasized that the relatively low mobilities of **P3HT G1—G3** can also be attributed in part to the low molecular weight of the P3HT.[32]

In conclusion, we have demonstrated a strategy for the synthesis of block copolymers consisting of RR−P3HT with dendrons attached at on terminus of the P3HT. Each dendron-modified P3HT can be purified by chromatography, affording a pure and well-defined material. The dendritic structure at the P3HT terminus can be further functionalized at the periphery to endow specific properties to the overall assembly. While the size of the dendron increases from **G1** to **G3**, the OFET device performance gradually decreases in terms of mobility. However, high hole mobilities are not necessarily required for specific purposes such as use as compatibilizers in bulk heterojuction solar cells[4] and chemresistor sensor polymers.[19] In addition, the unique structure of the terminally dendronized P3HT is useful not only for devices but also for applications involving properties such as adhesion[33] and light harvesting.[34−36] We are currently exploring additional functionalization reactions of these block copolymers at the peripheral points of the polyester dendron for a variety of polymer-based devices.

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Supporting Information Available: Text giving complete experimental procedures including reaction schemes, a table of OFET data, and figures showing the electrical characterization of OFETs and NMR spectra, and text describing the calculation of weight percent for dendrons. This material is available free of charge via the Internet at http://pubs.acs.org.

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