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High-Mobility Semiconducting Naphthodithiophene Copolymers

Itaru Osaka,* Toru Abe, Shoji Shinamura, Eigo Miyazaki, and Kazuo Takimiya*

Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University, 1-4-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan

Received February 7, 2010; E-mail: iosaka@hiroshima-u.ac.jp; ktakimi@hiroshima-u.ac.jp

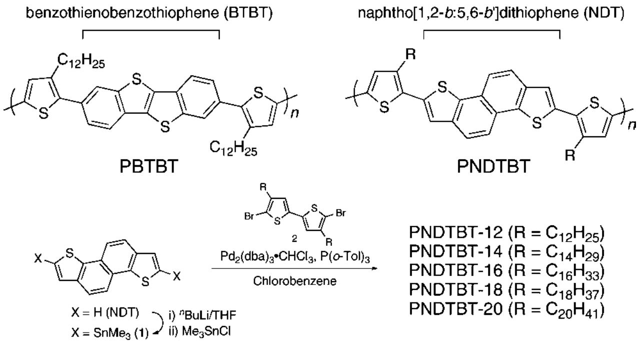
Semiconducting polymers are an important class of active materials in printable electronics. They offer great advantages, such as solution processability along with uniformity and thermal stability of the thin films, over small-molecule semiconductors.[1] Remarkable advances in this area have been realized through the development and numerous studies of regioregular poly(3-alkylthiophene)s in the past decade.[2] A key structural feature of such polymers is the strong π stacking of planar polymer chains, which facilitates charge-carrier transport. The introduction of thiophene-based fused rings (heteroarenes)[3] as well as donor−acceptor systems[4] into the polythiophene backbone is a promising approach for enhancing the intermolecular π overlap and thus the π stacking, leading to high charge-carrier mobilities of >0.1 cm^2 V^{-1} s^{-1} in organic field-effect transistors (OFETs).

An important design constraint on heteroarenes for such polymer systems is the fusion of thiophene rings at the end of the structure; it is necessary to avoid twisting between the adjacent thiophene rings, which would destroy the π stacking and thereby reduce the carrier mobility.[5] A preliminarily synthesized benzothienobenzothiophene (BTBT)−thiophene copolymer (PBTBT, Scheme 1) gave a highly twisted backbone (λ_{max} < 400 nm) and did not work in OFETs (see Supporting Information), despite the fact that BTBT has been successful in small-molecule systems.[6] Meanwhile, naphtho[1,2-*b*:5,6-*b*′]dithiophene (NDT), a recently developed BTBT isomer that has an electronic structure similar to that of BTBT,[7] is considered to be an excellent candidate heteroarene for semiconducting polythiophenes. With two thiophenes fused at the end of naphthalene, NDT is expected to provide a highly rigid planar backbone in the polythiophene system, enhancing the intermolecular π overlap. Furthermore, its zigzag motif induces curvature in the unit structure and thus offers sufficient solubility, which is a key parameter for printable materials and is often an issue for such polymers with heteroarenes.[8] In this communication, we present novel semiconducting polymers (PNDTBTs, Scheme 1) that incorporate NDT into a regiosymmetric polythiophene system;[9] these polymers exhibited among the highest values of field-effect mobilities observed to date for semiconducting polymers (>0.5 cm^2 V^{-1} s^{-1}).

The synthetic route to PNDTBTs is depicted in Scheme 1. PNDTBT-12 with dodecyl side chains precipitated from the reaction system because of its limited solubility, resulting in a low molecular weight (M_n = 7100). Meanwhile, PNDTBT-14−20 showed improved solubility and did not precipitate during the polymerization, leading to high molecular weights (M_n) of 24100−33400 (Table 1). The polymers are soluble in warm chlorinated benzenes, and the ones with longer side chains show better solubility, improving their processability.

All of the polymers afforded two absorption peaks at around 540 and 500 nm in the solid state (Figure S2 in the Supporting Information), which were greatly red-shifted relative to those of isomeric PBTBT and similar to those of polymers with thiophene-based heteroarenes.[3b,e] The ionization potentials (IPs) of the polymers were evaluated to be 5.0 eV by photoelectron spectroscopy in air (Figure S3), suggesting good oxidative stability. Thermal analyses showed no backbone melting or liquid-crystalline phase transitions up to 300 °C. Only broad peaks assignable to side-chain melting were observed in PNDTBT-16−20 (Figure S4).

Scheme 1. Chemical Structures of PBTBT and PNDTBT and the Synthetic Route to PNDTBTs



Top-contact OFET devices were fabricated using polymer thin films spin-coated from *o*-dichlorobenzene solutions onto hexamethyldisilazane-treated Si/SiO$_2$ surfaces, which were subsequently annealed at 150 °C. Although the PNDTBTs did not show phase-transition behavior, thermal annealing improved the mobilities by one order of magnitude. The devices exhibited excellent behavior: the transfer curves showed a small hysteresis, and the output curves showed almost no noticeable contact resistance (Figure 1), leading to a maximum mobility of 0.54 cm^2 V^{-1} s^{-1} and an average mobility of ~0.2 cm^2 V^{-1} s^{-1} for PNDTBT-16, which are among the highest observed to date for semiconducting polymers. Other alkyl-chain polymers also showed excellent mobilities as high as 0.4 cm^2 V^{-1} s^{-1}, whereas PNDTBT-12 showed one order of magnitude lower mobility, as often seen for low-molecular-weight polymers (Table 1).[10] Although no distinct alkyl-chain-length dependence of the mobility was seen in PNDTBT-14−20, longer-side-chain polymers apparently provided better reproducibility, perhaps because of their higher solubility. Interestingly, the far-superior OFET properties of NDT relative to BTBT in the polymer system contrast with the fact that NDT showed 1 order of magnitude lower mobility than BTBT in small-molecule systems.[6,7] In addition, the high on/off ratios of up to 10^8 imply that the polymers are stable under ambient conditions, reflecting the large IP. The devices were also environmentally stable in low-humidity air: the transfer characteristics did not show severe degradation over a 3 month period (Figure S6).

The out-of-plane X-ray diffraction (XRD) pattern of a PNDTBT-16 thin film (Figure 2a) afforded sharp peaks assignable to (*h*00),[11] indicating a highly ordered lamellar structure with a *d* spacing of 20.4 Å. The smaller *d* spacing than in a thienothiophene copolymer (pBTTT) with the same side chain (23.5 Å)[10c] is likely due to the

10.1021/ja101125p

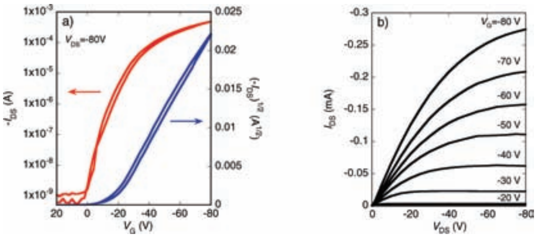


Figure 1. (a) Transfer and (b) output characteristics of a PNDTBT-16 device at $V_{DS} = -80$ V (50 μm length, 1500 μm width) after annealing.

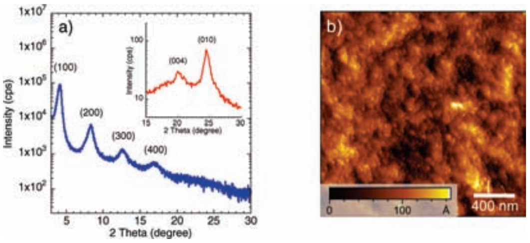


Figure 2. (a) Out-of-plane and (inset) in-plane XRD patterns and an (b) AFM topographic image of an annealed PNDTBT-16 thin film.

Table 1. Molecular Weights, OFET Characteristics, and XRD Results for the Polymers

polymer	M_n/M_w	μ (cm^2 V^{-1} s^{-1})^a	I_{on}/I_{off}^{b}	d (Å)^c l	d (Å)^c π
PNDTBT-12	7100/12900	0.05 (0.027)	~10^6	17.8	3.7
PNDTBT-14	24100/34500	0.37 (0.18)	~10^7	19.3	3.6
PNDTBT-16	28900/45800	0.54 (0.20)	~10^7	20.4	3.6
PNDTBT-18	28100/43500	0.20 (0.18)	~10^8	22.7	3.6
PNDTBT-20	33400/72600	0.32 (0.18)	~10^7	24.1	3.6

[a] Maximum mobilities; average mobilities from more than 10 devices are shown in parentheses. [b] Current on/off ratios. [c] Lamellar (l) and π stacking (π) distances determined by XRD studies.

wider free space between alternating alkyl chains in PNDTBTs that results from the longer molecular axis of NDT than of thienothiophene, which consequently allowing deeper side-chain interdigitation.[11] A striking structural feature of this system is the highly crystalline π stacking of the facing polymer chains with a narrow distance of 3.6 Å, as the in-plane data (inset of Figure 2a) gave an intense (010) peak at $2\theta = 24.5°$.[11] These highly ordered structures, particularly because of the closer π stacking relative to other polythiophene systems, which usually give spacings of 3.7−4.0 Å,[3,4a,8,9] are expected to determine the high mobility in this system. In addition, the relatively wide π stacking distance of 3.7 Å in PNDTBT-12, together with its low molecular weight, is consistent with the low mobility.

Figure 2b shows an atomic force microscopy (AFM) topographic image of a PNDTBT-16 device. The polymer formed rounded grains differing from the clear terrace structure observed for pBTTTs.[3b,10c,12] This may be due to the wider free space in PNDTBTs, which may give rise to somewhat looser side-chain packing and in turn weaker interlocking of the vertically adjacent polymer chains.

In summary, we have shown that the novel NDT-based semiconducting polymers designed and synthesized in this study achieve mobilities among the highest recorded to date (i.e., >0.5 cm^2 V^{-1} s^{-1}), most probably as a result of the strong π stacking evident from the structural studies. It is noteworthy that the choice of isomeric heteroarene (NDT vs BTBT) in the unit can dramatically change the physical and electronic structures and hence the OFET performance of the semiconducting polymers, even though the two isomers possess similar electronic structures; interestingly, this contrasts with the trend in small-molecule systems. We believe that these findings will give new insight into the design of new organic semiconducting materials and that the present polymers are promising materials for printable electronics.

Acknowledgment. Financial support was provided by the Strategic Promotion of Innovative Research and Development from the Japan Science and Technology Agency. We thank Sumitomo Chemical Co., Ltd. for the measurement of photoelectron spectra. We also thank Rigaku Corp. for the in-plane XRD measurement.

Supporting Information Available: Complete ref 10c and syntheses, properties, OFET characteristics, and structural data. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA101125P