

# Toward Practical Useful Polymers for Highly Efficient Solar Cells via a Random Copolymer Approach

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## Supporting Information

**ABSTRACT:** Using benzo[1,2-*b*:4,5-*b'*]dithiophene and two matched 5,6-difluorobenzo[2,1,3]thiadiazole-based monomers, we demonstrate that random copolymerization of two electron deficient monomers, alternating with one electron rich monomer, forms a successful approach to synthesize state-of-the-art semiconducting copolymers for organic solar cells. Over a range of compositions, these random copolymers provide impressive power conversion efficiencies (PCEs) of about 8.0%, higher than those of their binary parent polymers, and with little batch-to-batch variation. A PCE over 8% could also be achieved when the active layer was deposited from nonhalogenated solvents at room temperature.

Polymer solar cells (PSCs) with an active layer consisting of a semiconducting polymer as electron donor and a fullerene derivative as electron acceptor have attracted considerable attention as a next-generation photovoltaic technology.<sup>1</sup> Significant progress has resulted in power conversion efficiencies (PCEs) exceeding 11% in single-junction and multijunction devices.<sup>2</sup> These achievements benefited from innovative semiconducting polymers with superior properties, next to significant improvements in morphology control, interface, and device engineering.<sup>1b,2b,3</sup> Generally, developing high-performance photovoltaic polymers relies on creating novel building blocks using an alternating donor–acceptor polymer design and exercising precise control over the regularity of the polymer chain.<sup>4</sup> This involves tedious multiple-step organic synthesis.<sup>5</sup> Hence, facile and reliable approaches that produce high performance polymers are desirable.

Additionally, fabricating high efficiency PSCs generally involves the use of halogenated solvents such as chlorobenzene (CB), *ortho*-dichlorobenzene (*o*-DCB), and additives such as 1,8-diiodooctane (DIO).<sup>2b,3a,6</sup> These solvents are hazardous to human health and environment and unsuitable for mass production.<sup>7</sup> In pioneering attempts in using nonhalogenated solvents for processing PSCs,<sup>2a,8</sup> most successful examples were achieved by trial-and-error, and there is no general strategy toward this goal mainly because of the poor solubility of the polymers in nonhalogenated solvents. Reducing the regularity of

polymers via random copolymerization improves their solubility in nonhalogenated solvents.<sup>9</sup> However, a common viewpoint is that the irregular polymer backbone in a random copolymer hampers the formation of ordered microstructures and deteriorates charge transport by creating energetic and structural disorder.<sup>10</sup> High sensitivity of electrical and morphological properties to composition variation is another misgiving.<sup>11</sup> Earlier studies on random copolymers mainly focused on tuning optical and electronic properties.<sup>12</sup> The largely changed optoelectronic properties can influence charge generation dynamics significantly, which obscured the real potential of random copolymers.<sup>10b</sup> Hence, few successful random copolymers were reported despite the fact that numerous examples were developed for PSCs.<sup>11d,12</sup>

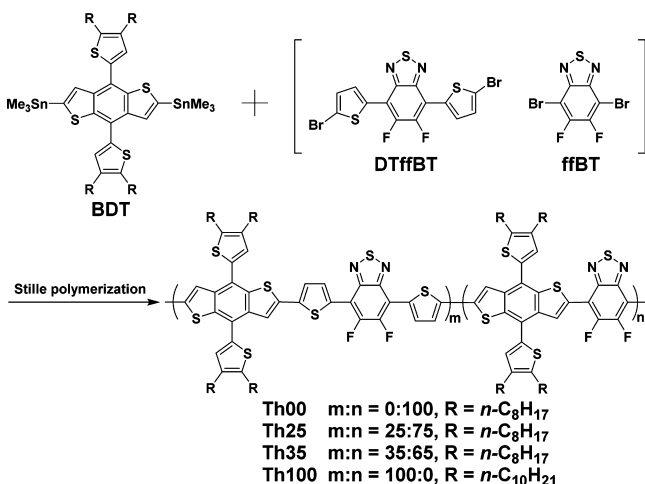
Herein, we demonstrate that random copolymerization is a promising synthetic strategy for developing state-of-the-art semiconducting polymers. Our results show that random copolymers outperform their binary parent polymers, show no batch-to-batch variations, and enable highly efficient PSCs with low sensitiveness to processing history. More importantly, random copolymers allow fabricating high performance PSCs from nonhalogenated solvents at room temperature.

To demonstrate the potential of random copolymers we use 5,6-difluoro-4,7-dithieno[2,1,3]thiadiazole (DTfBT) and 5,6-difluorobenzo[2,1,3]thiadiazole (fBT) as complementary acceptor units in a copolymer with thienyl-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) donor units (Scheme 1). Although the fBT and DTfBT monomers differ structurally, their parent binary copolymers with BDT (Th00 and Th100) have very similar band gaps and frontier orbital energy levels, evidencing that they are electronically alike. Because a carefully adjusted solubility is important for achieving optimized bulk-heterojunction morphologies in PSCs,<sup>13</sup> we applied octyl side chains for Th00, Th25, and Th35, while decyl side chains were applied for Th100. Stille polymerization produced the random copolymers Th25 and Th35 in 70–80% yield. Gel permeation chromatography (GPC, at 140 °C) suggests similar number-average molecular weights ( $M_n$ ) of ~40 kDa for all polymers (Figure S1 and Table S1, Supporting Information), ensuring a fair

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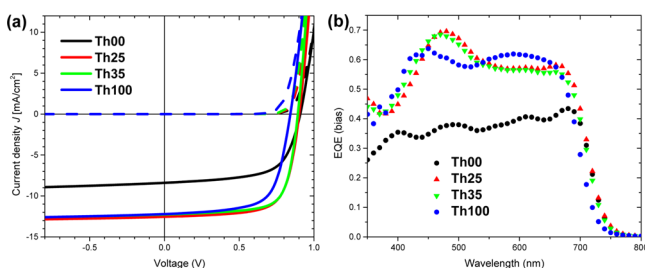
## Scheme 1. Chemical Structures and Preparation of the Polymers



comparison in PSCs. Th00, Th25, and Th35 are soluble in aromatic hydrocarbons (such as *o*-xylene and 1,2,4-trimethylbenzene (TMB)) and in chlorinated aromatics (such as CB and *o*-DCB) in concentrations of >8 mg mL<sup>-1</sup> at room temperature, while Th100 can only be dissolved in warm chlorinated aromatics.

The optical absorption spectra of thin films of Th25 and Th35 show maxima in between those of Th00 and Th100 (Figure S2), but the absorption onsets of all polymers are almost identical (Table S1). The energy levels of the polymers determined by cyclic voltammetry reveal that the differences in both the highest occupied and lowest unoccupied molecular orbital levels between different polymers are moderate (<0.15 eV) (Figure S3 and Table S1).

Photovoltaic properties were evaluated with an ITO/PEDOT:PSS(35 nm)/polymer:[70]PCBM/LiF(1 nm)/Al(100 nm) device structure under AM1.5G illumination (100 mW cm<sup>-2</sup>). Device optimization was first performed with halogenated solvents. The current-density–voltage (*J*–*V*) curves of the best devices (Figure 1) and device metrics (Table 1) reveal that Th25



**Figure 1.** (a) *J*–*V* curves of the polymer:[70]PCBM solar cells optimized from halogenated solvents in dark (dashed lines) and under illumination (solid lines). (b) Corresponding EQE.

and Th35 afford PCEs of 8.0% and 7.9%, higher than those of Th00 (4.9%) and Th100 (6.9%). Th25 and Th35 show a slightly lower open-circuit voltage (*V*<sub>oc</sub>) than Th00, but a significantly enhanced short-circuit current density (*J*<sub>sc</sub>) and a modestly improved fill factor (FF). Compared to Th100, the random polymers have higher *V*<sub>oc</sub> (~0.90 V vs 0.84 V) and FF (~0.71 vs 0.67), although the *J*<sub>sc</sub> is similar. External quantum efficiency (EQE) spectra confirm that the photoresponse of Th25 and Th35 is similar to that of Th100 but considerably higher than that

**Table 1.** Characteristics of Optimized Polymer:[70]PCBM Solar Cells from Halogenated Solvents

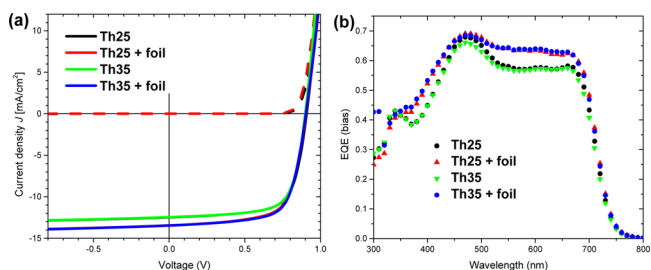
polymer	solvent	<i>J</i> <sub>sc</sub> <sup>a</sup> (mA cm <sup>-2</sup> )	<i>V</i> <sub>oc</sub> (V)	FF	PCE (%)
Th00	CF (3% DIO)	8.4	0.91	0.64	4.9
Th25	CB (3% DIO)	12.6	0.90	0.70	8.0
Th35	CB (3% DIO)	12.3	0.89	0.72	7.9
Th100	<i>o</i> -DCB	12.2	0.84	0.67	6.9

<sup>a</sup>Determined by integrating the EQE spectrum with the AM1.5G spectrum.

of Th00 (Figure 1b). Noticeably, the two random copolymers, Th25 and Th35, which differ considerably in composition, both afford high PCEs, suggesting that high performance materials can be developed within a reasonable composition range via random copolymerization. Random copolymers with higher DTffBT content were also synthesized and characterized. Longer side chains were introduced to these polymers to afford sufficient solubility. The chemical structure and device data of these polymers in solar cells are provided in Figure S4 and Table S2.

The batch-to-batch variation in device performance represents an important concern for random copolymers because the composition and sequence of monomer building blocks may differ significantly from batch to batch. To assess this concern, a second batch of Th35 was synthesized. Similar *M*<sub>n</sub> and polydispersity index (PDI) were obtained for the new polymer batch (Figure S1 and Table S3). Encouragingly, the two batches afford similar results with the same maximum PCE of 7.9% (Figure S5 and Table S3).

The PSCs performance of the random copolymers is relatively insensitive to the processing history. Th25 and Th35 afford robust PCEs upon changing the ratio of DIO/CB (v/v) from 2% to 4% (Figure S6 and Table S4). Interestingly, Th25 and Th35 provide highly efficient PSCs when processed from an environmentally benign TMB and diphenyl ether (DPE) solvent mixture (Figure 2, Table 2, and Table S5). The PCE of 7.9% is



**Figure 2.** (a) *J*–*V* curves of the polymer:[70]PCBM solar cells optimized from nonhalogenated solvents with and without retro-reflective foil in dark (dashed lines) and under illumination (solid lines). (b) Corresponding EQE.

virtually identical to those of devices processed from halogenated solvents. To further improve the performance, a retroreflective foil was applied.<sup>14</sup> The enhanced light in-coupling effectively enhances the EQE of the devices over the whole absorption region (Figure 2b). As a result, maximum PCEs of 8.3% and 8.4% were achieved for Th25 and Th35, respectively, which belong to the highest levels of the PSCs that processed from non-halogenated solvents at room temperature.<sup>8</sup>

The performance of PSCs is closely related to bimolecular charge recombination kinetics, which can be determined qualitatively by analyzing the ratio between the EQE measured with light bias equivalent to AM1.5G illumination and the EQE

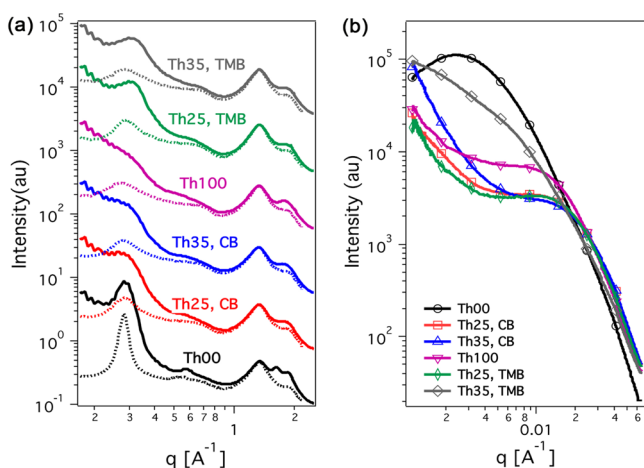
**Table 2. Characteristics of Optimized Polymer:[70]PCBM Solar Cells from Nonhalogenated Solvents with and without Retroreflective Foil**

polymer	solvent	$J_{sc}^a$ ( $\text{mA cm}^{-2}$ )	$V_{oc}$ (V)	FF	PCE (%)
Th25	TMB (3% DPE)	12.5	0.91	0.70	7.9
Th25 + foil		13.5	0.91	0.68	8.3
Th35	TMB (2% DPE)	12.5	0.90	0.71	7.9
Th35 + foil		13.5	0.90	0.69	8.4

<sup>a</sup>Determined by integrating the EQE spectrum with the AM1.5G spectrum.

measured without light bias (denoted as  $\rho = \text{EQE}_{\text{bias}}/\text{EQE}_{\text{nobias}}$ ). Because the bimolecular recombination efficiency scales with  $1 - \rho$ , a higher  $\rho$  implies less bimolecular recombination.<sup>15</sup> PSCs based on the random copolymers provide  $\rho$  average values near unity (0.994 for Th25 and 0.995 for Th35, see Figure S7), which are close to Th100, but are clearly larger than Th00. The PSCs processed from nonhalogenated solvents show a slight decrease in  $\rho$  (0.989 for Th25 and 0.991 for Th35), but are still near unity.

The crystalline order of the polymers in pure form and in blends was characterized by grazing incidence X-ray diffraction (GIXD, Figure 3a and Figure S9). The polymers adopt a face-on



**Figure 3.** (a) GIXD of the polymer:[70]PCBM blends (solid line, out-of-plane; dotted line, in-plane). (b) RSoXS of the polymer:[70]PCBM blends.

orientation, which is beneficial for charge transport. In the pure film Th00 exhibits the highest crystalline order, evidenced by the sharp and intense (100) diffraction. The  $\pi$ - $\pi$  stacking distance for Th00 is seen at  $q = 1.70 \text{ \AA}^{-1}$ , corresponding to a distance of 0.369 nm; random copolymer Th25 shows a  $\pi$ - $\pi$  stacking distance of 0.373 nm; Th35 shows a  $\pi$ - $\pi$  distance of 0.369 nm; Th100 shows a  $\pi$ - $\pi$  of 0.359 nm. Hence, the random copolymerization leads to a slightly larger cofacial stacking distance of the conjugated backbone, which can be rationalized by considering that the disorder disturbs the quadrupolar interchain interactions. The reduced crystallinity and  $\pi$ - $\pi$  stacking in the random copolymers improve the solubility of the resulting materials and thus enable better processability. From the line cut profiles of blend thin film (Figure 3a), it can be seen that Th00 possesses the most prominent (100) reflection peak, located at  $0.28 \text{ \AA}^{-1}$ , thus the alkyl-to-alkyl distance for this polymer is 2.24 nm. The crystal coherence length (CCL) estimated from in-plane line cut is 24.6 nm. The azimuthal

spreading of this peak is broad, and thus, the crystal orientation decreased in blend thin film. For Th25 and Th35 a similar behavior is seen in blends. The (100) CCL is estimated to be 7.4 and 6.6 nm, respectively (CB/DIO processed films). These random copolymers showed quite similar behavior when processed from TMB/DPE; thus, these new designed materials were insensitive to the specific solvent used.

The morphology of the polymer:[70]PCBM films was characterized by resonant soft X-ray scattering (RSoXS, Figure 3b) and transmission electron microscopy (TEM, Figure S10). The blend film of Th00 shows a clear phase separation with large domain size. The center-to-center distance in RSoXS was calculated to be  $\sim 250$  nm. Blend films of Th25, Th35, and Th100 show finely dispersed fibrillar microstructures and bicontinuous networks. This sharp contrast in morphology explains the large difference of  $J_{sc}$  and EQE between the PSCs made of Th00 and the other polymers. In scattering, a quite similar phase separation length scale of  $\sim 50$  nm was obtained, which correlated well with TEM characterizations. In TEM films of Th25 and Th35 processed from TMB/DPE exhibit similar fibrillar microstructures and bicontinuous networks as those processed from CB/DIO, although the fibril width seems to be slightly larger. In RSoXS scattering, these features were well recorded and the fibril network mesh size was also  $\sim 50$  nm. We note that the Th35 blend processed from TMB/DPE showed new scattering of a large size, which came from PCBM aggregation, also seen as the dark areas in TEM images.

In conclusion, the results demonstrate that semiconducting random copolymers offer a significant prospect for application in highly efficient PSCs. The beneficial effect originates from the fact that the random polymers possess structurally different monomers, but these do not result in strong variations of the energy levels along the chain. The random polymers do not suffer from batch-to-batch variation or strong dependence on the precise composition. The reduced crystallinity and  $\pi$ - $\pi$  stacking provides the random copolymers with good solubility and processability. As a result, random copolymers allow fabricating highly efficient PSCs with low sensitiveness to processing history, even from nonhalogenated solvents at room temperature. The successful demonstration of these random copolymers for PSCs represents a reliable methodology for developing practical useful photovoltaic polymers in future manufacturing of PSCs.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b06418.

Experimental details, synthetic procedures, GPC, UV/vis spectra, cyclic voltammograms,  $J$ - $V$  curves and EQE of the devices made under different conditions and different polymer batches, GIWAXS of neat polymers, and TEM images of the blends (PDF)

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### Notes

The authors declare no competing financial interest.

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