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# Thermally Stable Bulk Heterojunction Solar Cells Based on Cross-Linkable Acrylate-Functionalized Polythiophene Diblock Copolymers

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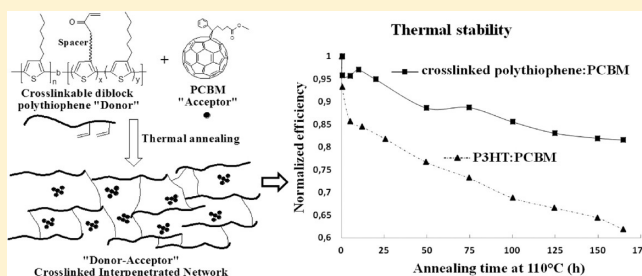
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## S Supporting Information

**ABSTRACT:** We report on the synthesis of new thermally cross-linkable all-conjugated diblock copolymers composed of a poly(3-hexylthiophene) (P3HT) block and an acrylate-functionalized polythiophene block. These copolymers are then used in bulk heterojunction (BHJ) solar cells with [6,6]-phenyl C61-butyric acid methyl ester (PCBM), and their photovoltaic performances are compared with standard P3HT/PCBM devices. Thermal cross-linking of the functional copolymers/PCBM blends is performed to improve the thermal stability of the active layer. BHJ photovoltaic cells with cross-linkable copolymers and PCBM show initial power conversion efficiencies slightly lower than that of P3HT devices. However, solar cells with cross-linkable copolymers retain more than 85% of their initial power efficiency value after 165 h of thermal annealing (accelerated aging test), whereas the same devices with P3HT retain less than 65% of their initial power efficiency. This improvement of the thermal stability of BHJ photovoltaic cells is the result of the polymer network that hampers PCBM diffusion and phase separation, as confirmed with TEM and AFM analysis of the microscopic morphology. Such an improvement is mostly observed when using a cross-linkable P3HT with a short spacer between the acrylate group and the polythiophene backbone.



## 1. INTRODUCTION

Polymer bulk heterojunction (BHJ) solar cells have attracted much attention in the past decade and appear to be one of the most promising candidates for the development of low-cost solar energy.<sup>1–3</sup> Recently, a power conversion efficiency (PCE) higher than 6–8% was demonstrated by several groups<sup>4–9</sup> and constitutes a significant breakthrough in the field of organic solar cells (OSCs). In the BHJ concept, interpenetrated networks are formed between the donor (D, conjugated polymers) and the acceptor (A, fullerene derivatives) components.<sup>10–12</sup> This concept relies on the formation of a large interfacial area between the donor and the acceptor, leading to efficient photoinduced charge separation in the device. The control of the phase separation between the two components is therefore of crucial importance for achieving efficient charge separation and transport.<sup>13,14</sup> The scientific literature is very rich in describing BHJ devices that use poly(3-hexylthiophene) (P3HT) as donor material and [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) as the acceptor material.<sup>15</sup> Among others, some of these studies report on the effect of molar mass of P3HT and the microscopic morphology of the blend on the photovoltaic performances.

For instance, PCE of 5% has been reached for OSC based on P3HT/PCBM after appropriate thermal treatment.<sup>16</sup> However, P3HT/PCBM blends suffer from two major drawbacks: a poorly controlled D/A domain size distribution and an inherent morphological instability. The P3HT polymer and the PCBM species are chemically incompatible, and their blends tend to undergo uncontrolled macrophase separation with time.<sup>17</sup> The resulting domain size can ultimately become much larger than the exciton diffusion length, consequently decreasing the device performance.

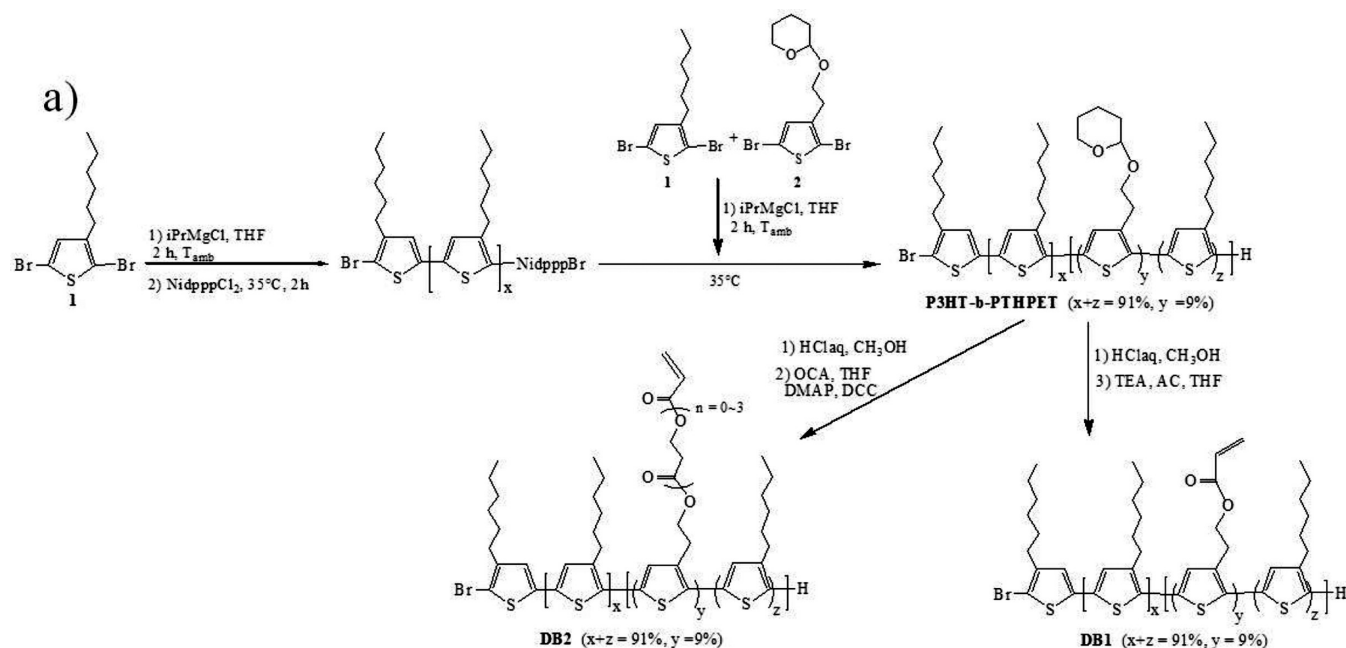
The optimal morphology in such polymer/fullerene BHJ solar cells can be controlled by process optimization involving the vapor pressure of the solvent,<sup>17</sup> the rate of solvent removal,<sup>18</sup> the addition of chemical additives,<sup>19–22</sup> thermal annealing treatments, and solvent annealing.<sup>23–26</sup> Although all of these strategies are efficient to improve the morphology of the BHJ blend, they do not solve the intrinsic problem of

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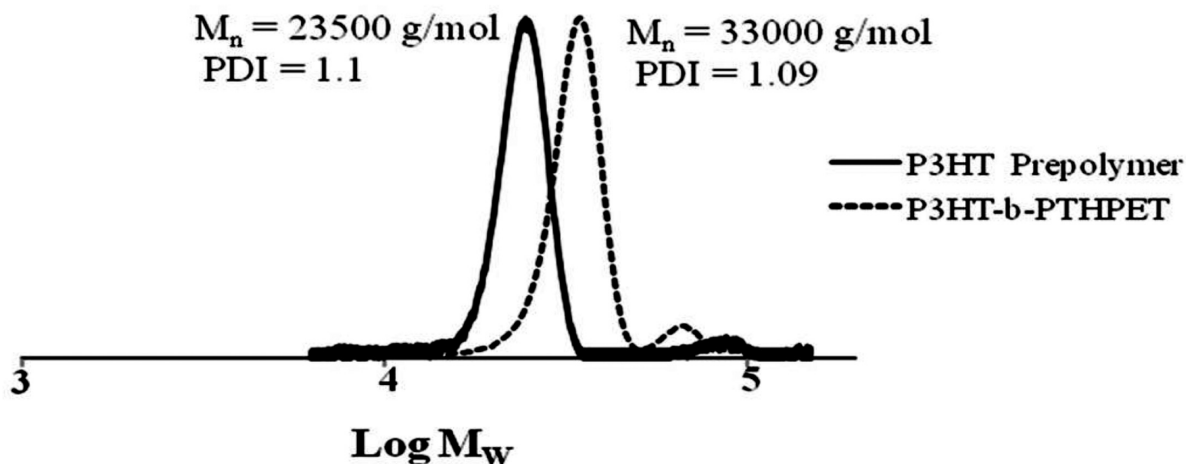
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Scheme 1. (a) Synthetic Route to the Diblock Copolymers and (b) SEC Profiles of P3HT-*b*-PTHPET and the Corresponding P3HT First Block



$i\text{PrMgCl}$ : isopropylmagnesium chloride,  $\text{Ni(dppp)Cl}_2$ : 1,3-bis(diphenylphosphino)propane]dichloronickel(II), OCA: 2-ethylcarboxyacrylate oligomer, DMAP: dimethylaminopyridine, DCC: dicyclocarbodiimide, TEA: Triethylamine, AC: Acryloylchloride.

b)



spontaneous macrophase separation that occurs over time, so that the durability of the PV performances is not guaranteed.

Numerous works are now dealing with improving the morphological stability and the long-term performances of these OPV cells.<sup>27–30</sup> One main strategy consists of cross-linking the active layer to maintain the morphology and avoid the migration of the fullerene species inside the film.<sup>31,32</sup> Recent studies reported on the effect of stabilizing the film morphology using thermal cross-linkable P3HT-azide.<sup>33,34</sup> They demonstrate that the use of a P3HT-azide random copolymer, as compatibilizer and cross-linker, suppresses the macrophase separation between P3HT and PCBM and stabilizes the morphology of the active layer by cross-linking. These cross-linkable P3HT-azide copolymers allow to obtain OPV cells with stable efficiency for 40 h of heating at  $110\text{--}150^\circ\text{C}$ .

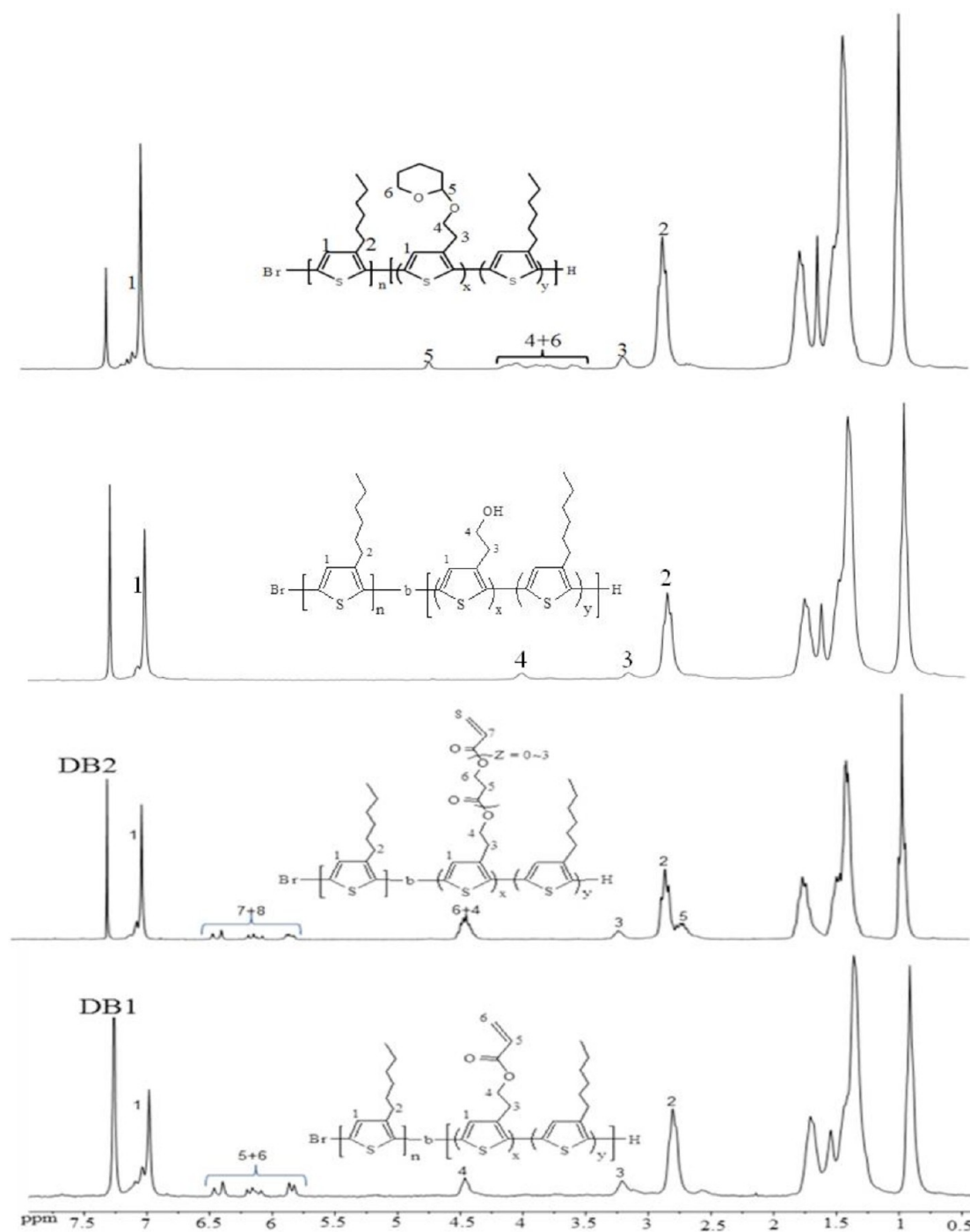
Another strategy to control phase separation between conjugated polymers and fullerene consists of using block-conjugated copolymers (BCPs) containing polythiophene segments with different functionalities. The self-assembly ability of these BCPs into nanodomains with controllable dimensions, on the order of the exciton diffusion length, makes them particularly promising for OPV applications.<sup>35–39</sup> Recently, Lin and coworkers have reported the cooperative self-assembly of BCPs containing polythiophene derivatives in both segments and functionalized fullerenes to yield solar cells with well-defined nanostructures.<sup>40</sup> However, the thermal stability of these types of systems remains lower than that of cross-linkable active layers.

In this work, we investigate the combination of cross-linkable polymers with well-defined block conjugated copolymers for controlling the microscopic morphology and thermal stability

Table 1. Molecular Weight and Composition of P3HT-*b*-PTHPET

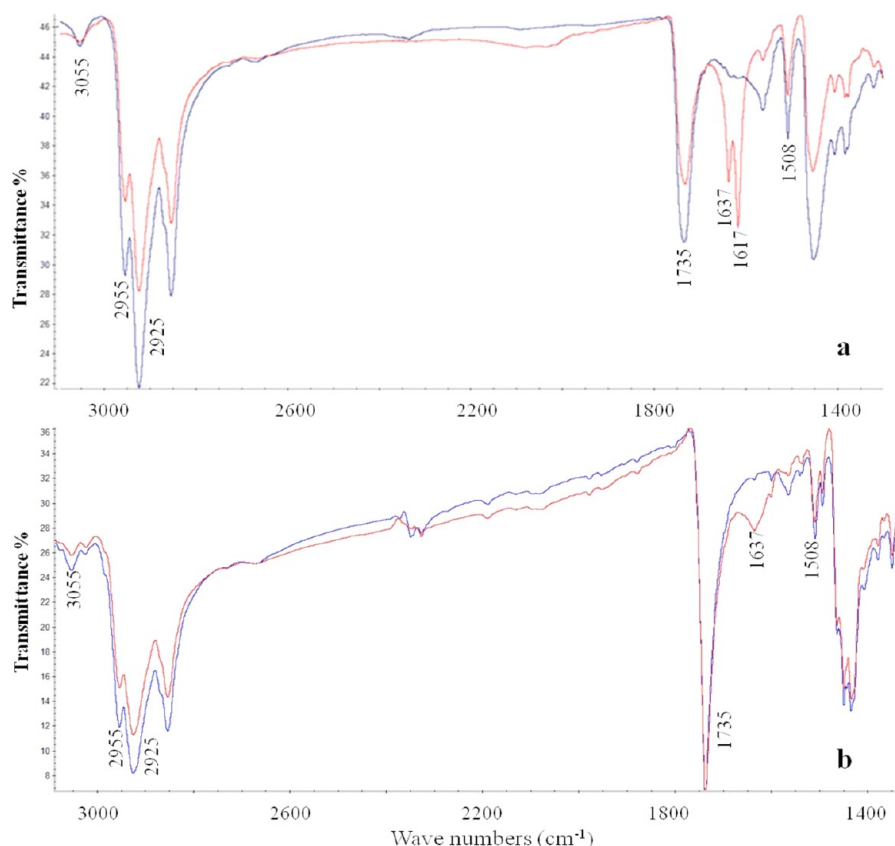
polymer	theoretical feed monomer molar ratio (3HT%/THPET%) <sup>a</sup>	feed monomer molar ratio (3HT%/THPET%) <sup>b</sup>	$M_n(\text{theor})^a$ (g/mol)	$M_n$ <sup>c</sup> (g/mol)	$M_w/M_n$	P3HT/PTHPET molecular weight ratio <sup>c</sup>
P3HT- <i>b</i> -PTHPET	88.5/11.5	91/9	22 200	33 000	1.09	~5/2

<sup>a</sup>From the monomer:catalyst ratio. <sup>b</sup>Calculated by <sup>1</sup>H NMR spectroscopy. <sup>c</sup>Estimated by SEC against PS standards.

Figure 1. <sup>1</sup>H NMR spectra of P3HT-*b*-PTHPET, P3HT-*b*-PHET, DB1, and DB2 in CDCl<sub>3</sub>.

of BHJ polymer/PCBM solar cells. We report the synthesis of cross-linkable diblock-conjugated copolymers composed of a P3HT block and a poly(thiophene) block bearing cross-linkable groups (acrylates). The diblock architecture is searched for (i) forming semicrystalline domains of the P3HT phase that is required for high charge mobility and (ii) for cross-linking

the polythiophene domains bearing acrylates to ultimately stabilize the morphology of the active layer. We then study the long-term performances of OSCs made of these copolymers as electron donors in combination with PCBM as acceptor and compare them to the standard P3HT/PCBM system. In parallel, we analyze with transmission electron microscopy



**Figure 2.** FTIR spectra of (a) DB1 before (red) and after (blue) treatment at 140 °C and (b) the DB1/PCBM blend (60:40 wt %) before (red) and after (blue) treatment at 140 °C.

(TEM) and atomic force microscopy (AFM) the evolution of the microscopic morphology upon thermal annealing. We demonstrate that cross-linking the film is not the only parameter required to improve the durability of the cell; the length of the spacer between the cross-linkable groups and the polymer backbone is also of prime importance.

## 2. RESULTS AND DISCUSSION

**2.1. Synthesis and Characterization.** Scheme 1 represents the synthetic route for two diblock copolymers, noted DB1 and DB2, composed of a P3HT block and a polythiophene block functionalized with acrylate groups. DB1 and DB2 differ only by the spacer between the P3HT backbone and the acrylate group: in DB1, it is a simple ethylene unit whereas in DB2 it is an oligocarboxylate group. We first synthesized diblock copolymers poly[3-hexylthiophene-block-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene] (P3HT-*b*-PTHPET) containing a P3HT block and a polythiophene block with alcohol-protected groups via a Grignard metathesis (GRIM) process.<sup>41,42</sup> These copolymers are obtained from the corresponding monomers, 2,5-dibromo-3-hexylthiophene (**1**) and 2,5-dibromo-3-tetrahydropyranylmethylthiophene (**2**). The GRIM method is particularly attractive to lead to high regioregular polythiophene blocks with predetermined molecular weight.<sup>36,43</sup> The product of the transmetalation of 2,5-dibromo-3-hexylthiophene is polymerized by addition of the [Ni(dppp)Cl<sub>2</sub>] catalyst. The reaction medium is heated to 35 °C during 2 h to yield the first P3HT block. In a second step, the mixture of 2-bromo-5-chloromagnesium-3-hexylthiophene and 2-bromo-5-chloromagnesium-3-(2-(2-tetrahydropyranyl-2-

oxy)ethyl)thiophene, prepared in situ by transmetalation of monomer **1** and **2**, is added to the P3HT solution (after quantitative consumption of the monomer) to form the second block (PTHPET) composed of 3-hexylthiophene units (3HT) and 3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene units (3THPET). The polymerization of the second block occurs for 4 h at 35 °C until quantitative conversion of the two monomers. The molar masses of the P3HT first block (quenched with HCl 37%) and the final diblock copolymers are determined by SEC in THF against polystyrene (PS) standards. Table 1 summarizes the results of the synthesis of the diblock copolymers noted P3HT-*b*-PTHPET.

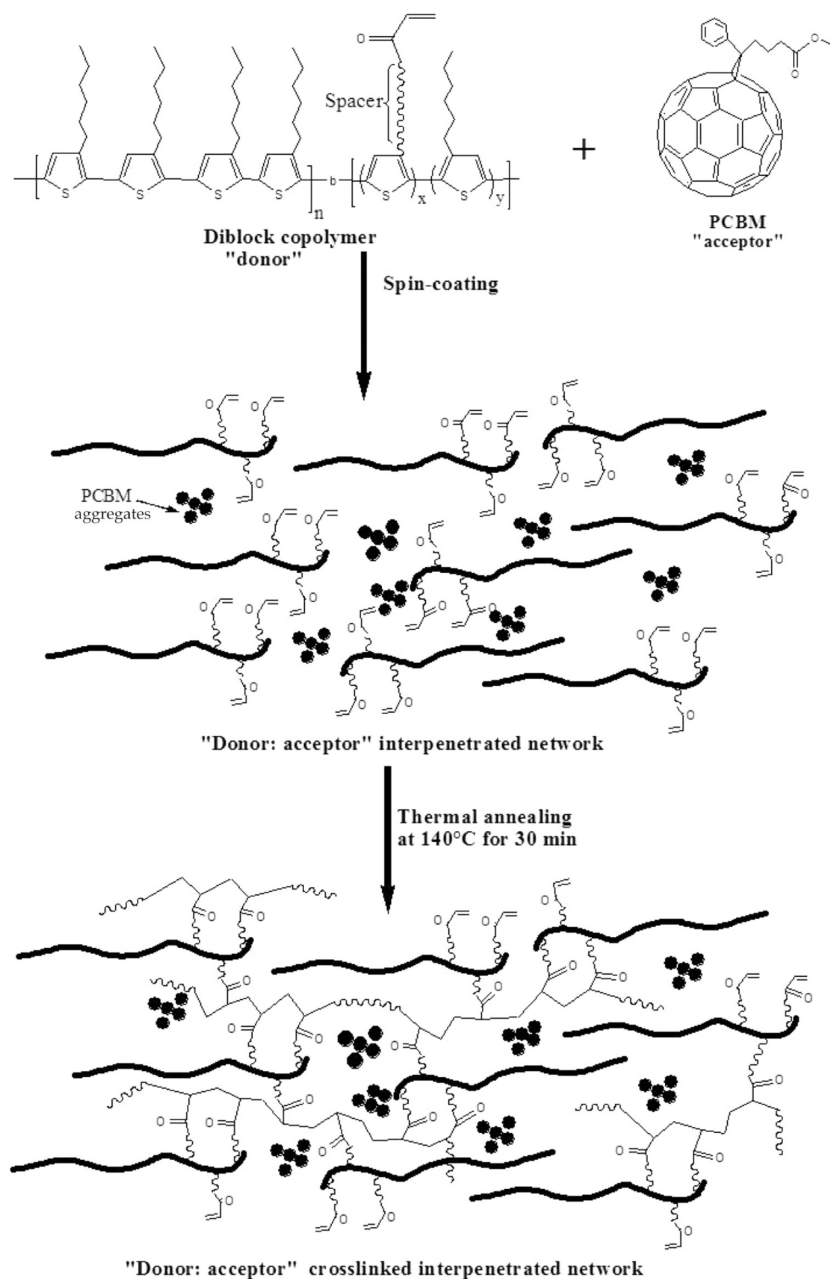
The SEC profiles of the P3HT first block and the diblock copolymer (P3HT-*b*-PTHPET) are shown in Scheme 1b. The SEC peak of P3HT is fully shifted toward higher molar masses during the block copolymerization, whereas the polydispersity remains low ( $M_w/M_n = 1.1$ ), indicating the formation of a well-defined diblock copolymer. We also observe a small amount (~5%) of a high-molecular-weight fraction that presents twice the molar mass of the main SEC peak ( $M_p = 34\,000$  vs  $66\,000$  g/mol). This product results from some coupling reactions between two P3HT-*b*-PTHPET active chains, as already observed in a previous work.<sup>39</sup>

The composition of the obtained diblock copolymer is calculated by <sup>1</sup>H NMR spectroscopy, taking the integral ratio between the P3HT methylene resonance groups at 2.80 ppm and the PTHPET methylene groups at 3.12 ppm (Figure 1). As reported in Table 1, P3HT-*b*-PTHPET presents 91% of 3HT units and 9% of THPET units.

The diblock copolymer P3HT-*b*-PTHPET is then modified according to the reaction presented in Scheme 1 to yield the



Scheme 2. Stabilization of the "Polymer/PCBM" Network by Crosslinking of the Acrylate-Functionalized Polythiophenes



final copolymers noted as DB1 and DB2. First, the THPs groups were transformed into alcohol groups by heating under reflux the suspensions of the copolymer in acidified methanol.<sup>44</sup> The  $^1\text{H}$  NMR spectrum of the obtained copolymer (P3HT-*b*-PHET) shows the complete deprotection of alcohol groups (Figure 1). This is confirmed by the disappearance of the peaks characteristic of alcohol-protected groups (4.6, 4.1, 3.7, and 3.5 ppm) and the appearance of the peak at 3.9 ppm attributed to  $\alpha$ -methylene groups of alcohol functions. Part of the product collected after deprotection of P3HT-*b*-PHTPET is reacted with acryloyl chloride in the presence of triethylamine to yield to the corresponding acrylate-functionalized copolymer (DB1).<sup>45</sup> The second part of deprotected alcohol P3HT-*b*-PHTPET is reacted with acid-functionalized 2-carboxyethyl acrylate oligomer (OCA) in the presence of dimethylaminopyridine (DMAP) and dicyclocarbodiimide (DCC) to form the

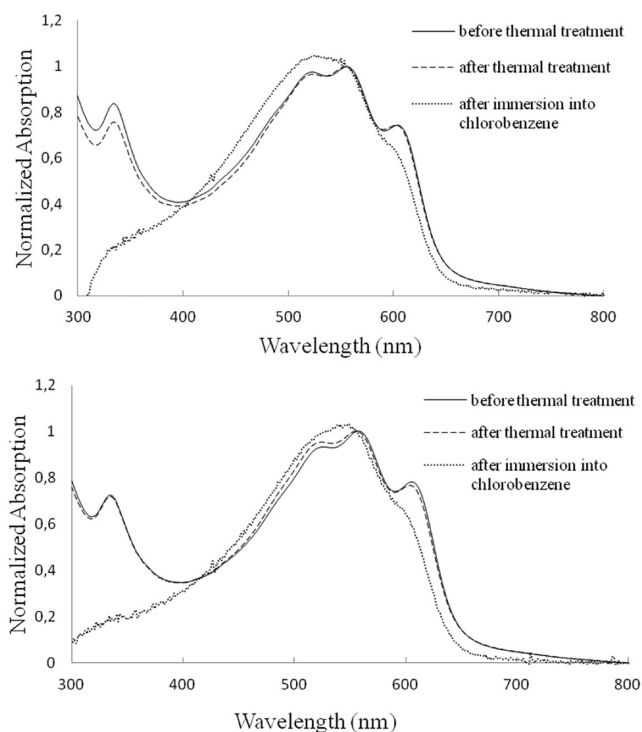
corresponding carboxyacrylate-functionalized copolymer (DB2).<sup>46</sup> The structure and the composition of DB1 and DB2 are checked by  $^1\text{H}$  NMR (Figure 2). DB1 and DB2 both contain 9% of acrylate groups.

**2.2. Cross-Linking of Polymer Films.** Polymers bearing acrylates can be easily cross-linked by thermal annealing or under UV irradiation.<sup>47</sup> In this work, the cross-linking was performed by thermal annealing of DB1 and DB2 films (or DB1/PCBM and DB2/PCBM blends) at 140 °C for 30 min (scheme 2). IR and UV spectroscopies are then used to demonstrate the cross-linking of the film.

The thermal cross-linking of acrylate groups is confirmed by FTIR analysis. Figure 2 shows the FTIR spectra of DB1 and its blend with PCBM (1/0.8 wt %) before and after the thermal treatment at 140 °C for 30 min. The spectra show the characteristic peaks of poly(3-hexylthiophene) at 3055  $\text{cm}^{-1}$

(for aromatic CH stretching), 2925 and 2950  $\text{cm}^{-1}$  (asymmetric C–H stretching of  $-\text{CH}_3$  and  $-\text{CH}_2-$ ), and 1508  $\text{cm}^{-1}$  (for thiophene ring stretching).<sup>48</sup> The peak at 1735  $\text{cm}^{-1}$  is typical of the vibration of the carbonyl group of both the acrylate functions of the diblock copolymer and the ester group of PCBM. After the thermal treatment at 140  $^{\circ}\text{C}$ , the intensity of the peaks at 1617 and 1637  $\text{cm}^{-1}$ , attributed to the double bond C=C of the acrylate groups, is strongly reduced, consistent with its consumption during cross-linking. It is important to note that the cross-linking also proceeds in the PCBM/DB1 blend. The same experiment was made for DB2 and DB2/PCBM blend, leading to the same conclusions.

The solid-state UV–vis absorption spectra of blends of diblock copolymers DB1 and DB2 with PCBM (1:0.8) before and after thermal annealing are shown in Figure 3. The films



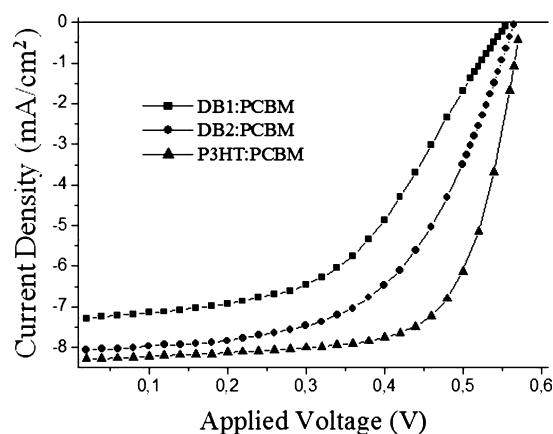
**Figure 3.** UV–vis absorption spectra of spin-coated films. Top: DB1/PCBM (1:0.8); bottom: DB2/PCBM (1:0.8); as cast (solid line), after thermal treatment at 140  $^{\circ}\text{C}$  (30 min, dashed line), and after immersion into chlorobenzene (dotted line).

were prepared by spin-coating DBx/PCBM solutions in *o*-dichlorobenzene (ODCB) onto glass substrates. The absorption spectra provide evidence of extensive  $\pi$ -conjugation and  $\pi$ – $\pi$  stacking of the polythiophene backbone, as indicated by the absorption peaks at  $\sim 510$ , 550, and 620 nm,<sup>49</sup> along with the absorption characteristic peak of PCBM at 330 nm. After the thermal annealing, the absorption spectra of the blends remain unchanged, indicating that cross-linking does not significantly reduce the degree of  $\pi$ -electron conjugation in the polythiophene chains.

The efficiency of the cross-linking of the polymer chains is evaluated by checking the solubility of the films deposited onto glass substrates using a good solvent of the polymers.<sup>12</sup> The annealed films are therefore immersed in chlorobenzene for 1 min. After drying the substrate, UV–vis absorption spectroscopy (Figure 3) evidences the absorption of the polymer, whereas that of PCBM disappears completely. This shows that

PCBM is extracted from the film while the polymer remains on the substrate. When the same experiment is carried out on a surface coated by P3HT/PCBM or with non annealed DBx/PCBM blends, no material remains on the substrate after immersion in chlorobenzene, clearly demonstrating the presence of a cross-linked matrix of polymer after thermal treatment of the BHJs containing DBx polymers.

**2.3. Solar Cell Performances.** The blends of the acrylate-functionalized polymers (DB1 and DB2) and PCBM were incorporated into BHJ OPV as active layers in devices with the following architecture: ITO/PEDOT:PSS/polymer:PCBM(1:0.8)/Ca/Al. Figure 4 and Table 2 show the



**Figure 4.** *J*–*V* curves of the devices with DB1, DB2, and P3HT combined with PCBM. The films were annealed at 140  $^{\circ}\text{C}$  for 30 min before Ca and Al deposition.

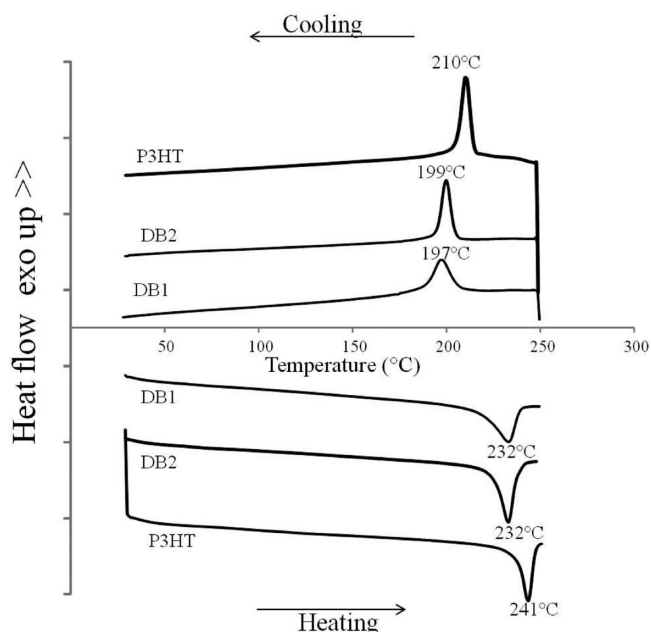
**Table 2.** Parameters of the Initial Performance of Devices with DB1, DB2, and P3HT Combined with PCBM (The Films Were Annealed at 140  $^{\circ}\text{C}$  for 30 min before Ca and Al Deposition)

name	Voc (V)	Jsc ( $\text{mA}/\text{cm}^2$ )	FF	PCE %
DB1/PCBM	0.560	7.310	0.504	2.065
DB2/PCBM	0.565	8.070	0.568	2.593
P3HT/PCBM	0.575	8.298	0.696	3.322

performances of these devices after thermal annealing at 140  $^{\circ}\text{C}$  for 30 min. For the sake of comparison, similar devices were built with P3HT in place of DB1 and DB2. The devices with DB1 and DB2 show similar values for open circuit voltage (Voc), whereas the short-circuit current density (Jsc), the fill factor (FF), and thus the PCE are lower for the DB1 cell compared with its DB2 counterpart. By comparing the photovoltaic parameters of P3HT and DB1, it is evident that the most affected parameter is the FF, reduced by almost 30% (from 0.7 to 0.5). The presence of acrylate groups may affect the crystalline morphology of P3HT, reducing the amount and the quality of P3HT fibers present in the blend. The reduced crystallinity may also hinder the transport in the cells, reducing the FF.

Differential scanning calorimetry (DSC) analyses of the different P3HT-based copolymers are thus performed to give any clue to these hypotheses. This technique is used to compare the thermal transitions and the degree of crystallinity of P3HT with those of DB1 and DB2. DSC thermograms obtained during the heating and cooling between 25 and 250  $^{\circ}\text{C}$  (heating rate rate of 10  $^{\circ}\text{C}/\text{min}$ ) of DB1, DB2, and P3HT

are presented in Figure 5. The thermograms of the polymers exhibit a single endothermic peak during the heating attributed



**Figure 5.** Heating and cooling DSC thermograms (10 °C/min) of DB1, DB2, and P3HT.

to the melting of crystalline phase and a single exothermic peak during the cooling attributed to the crystallization of the polythiophene chains. The melting temperature ( $T_m$ ), crystallization temperature ( $T_c$ ), enthalpy of melting ( $\Delta H_m$ ), and enthalpy of crystallization ( $\Delta H_c$ ) are reported in Table 3.

**Table 3.** Melting Temperature ( $T_m$ ), Crystallization Temperature ( $T_c$ ), Enthalpy of Melting ( $\Delta H_m$ ), and Enthalpy of Crystallization ( $\Delta H_c$ ) of P3HT, DB1, and DB2 Obtained from DSC Measurements

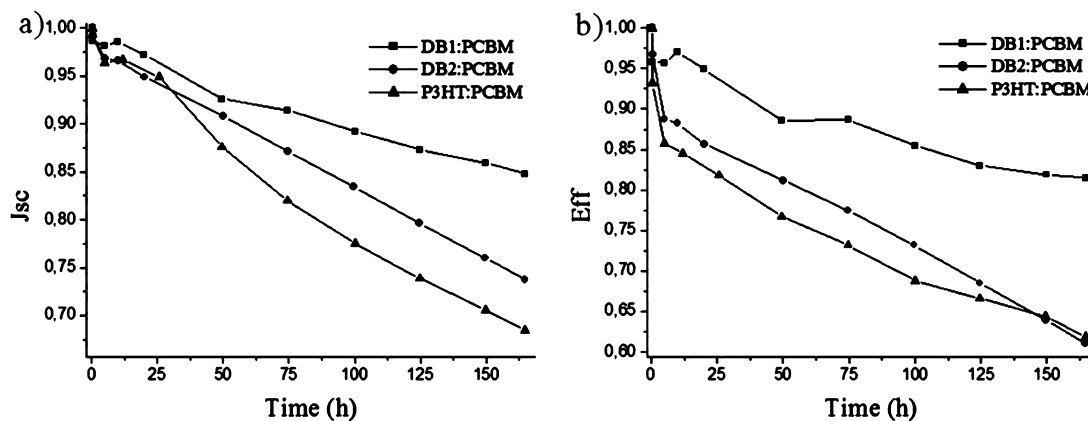
	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_c$ (°C)	$\Delta H_c$ (J/g)
P3HT	241	17	210	17.3
DB1	232	10	197	8.1
DB2	232	15.2	199	15.1

P3HT presents higher  $T_c$ ,  $T_m$ , and  $\Delta H_m$  and ( $c$ ) than DB1 and DB2 as the result of its higher molecular weight ( $M_w = 77\,500$  g/mol) compared with the block copolymers. This difference of crystallinity between P3HT and the diblock copolymers accounts for a higher PV performance for P3HT/PCBM device (PCE = 3.32%) compared with DB1(DB2)/PCBM ones ( $2.06 \leq \text{PCE} \leq 2.59\%$ ). It is in line with reports of several authors who demonstrated the correlation between the crystallinity<sup>50</sup> (but also the molar mass)<sup>51,52</sup> of P3HT and the PV performance.

**2.4. Thermal Stability of the Devices.** After measuring the initial device performances, we subjected the devices to an accelerated aging test. The test consists of a thermal annealing of the device at 110 °C for 165 h. DB1 and DB2 polymers were cross-linked in the BHJ films before carrying out this aging test. During aging at 110 °C,  $J_{sc}$  decreases, as shown in Figure 6a. In the case of P3HT and DB2 devices, the initial  $J_{sc}$  value decreases by 31 and 27%, respectively, upon aging. Importantly, this value decreases by only 15% when DB1 is used in the active layer. Interestingly, the power efficiency of solar cell based on DB1 retains more than 85% of its initial value after 165 h of thermal treatment, whereas devices with DB2 or P3HT retain less than 65% of their initial power efficiency (Figure 6b).

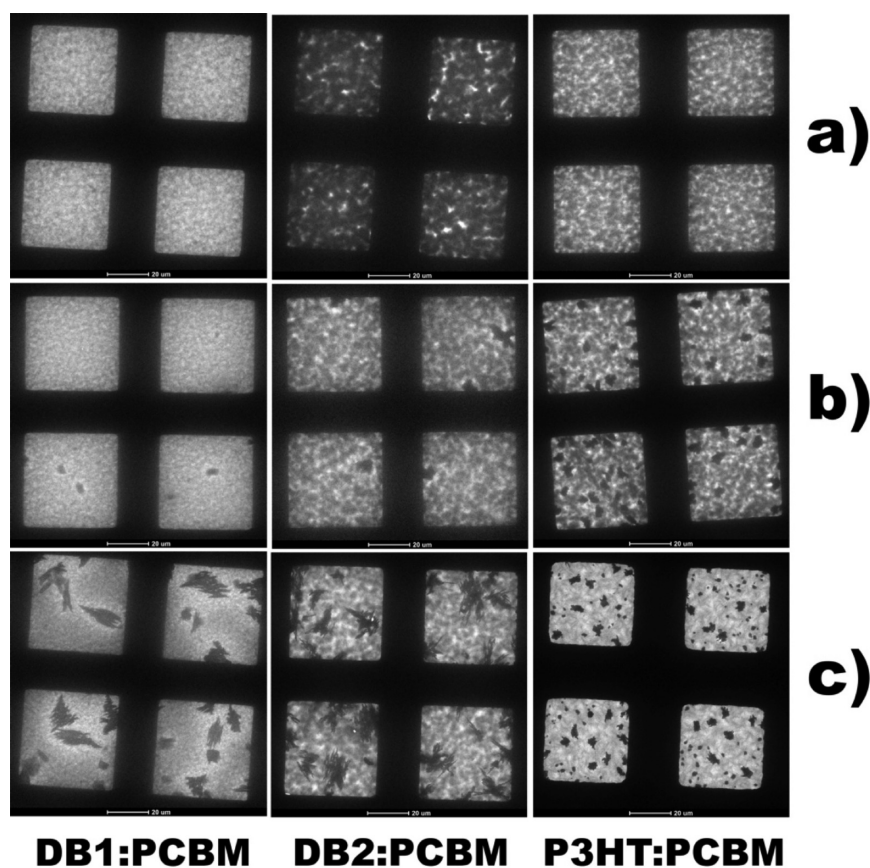
From these results, it is clear that the efficiency and  $J_{sc}$  of solar cells based on DB1 are significantly more stable compared with those based on P3HT and on DB2. The difference of behavior between DB1 and DB2 cells indicates that a shorter spacer between the acrylate groups and the polymer backbone leads to increased device stability. In the following, we shall demonstrate that the photovoltaic performance degradation is due to thermally induced phase separation and the formation of large PCBM clusters, as observed before for MDMO-PPV:PCBM solar cells.<sup>29</sup> Here we assume that the observed difference in stability for the DB1-, DB2-, and P3HT-based devices is the result of a decreased diffusion of PCBM due to the smaller mesh size of the polymer network in the case of DB1 compared with DB2, which hampers the diffusion of PCBM.

To investigate the morphology changes of the active layer, a microscopic analysis was carried out with TEM and AFM on the polymer/PCBM films. As shown in Figure 7a, the TEM images of as-cast films present a bicontinuous polymer/PCBM network. After thermal annealing at 140 °C for 30 min (Figure 7b), the morphology of the DB1:PCBM sample remains



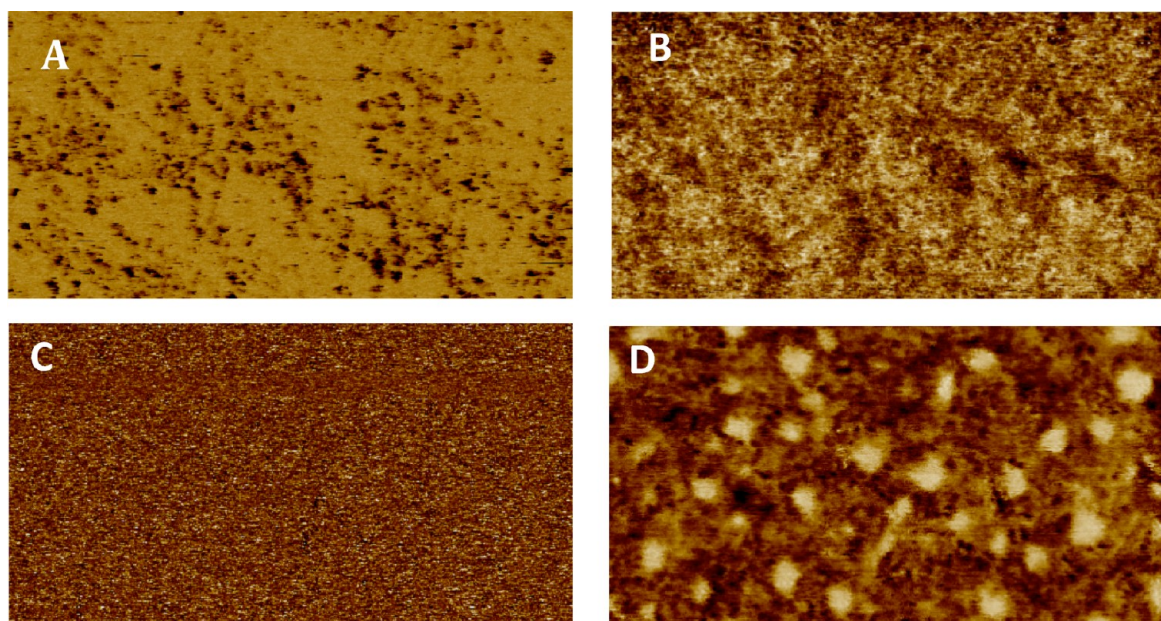
**Figure 6.** Device performance of DB1/PCBM and DB2/PCBM devices during thermal annealing at 110 °C compared with thermal annealing of P3HT/PCBM. (a)  $J_{sc}$  and (b) relative efficiency.





**DB1:PCBM DB2:PCBM P3HT:PCBM**

**Figure 7.** TEM images of DB1/PCBM, DB2/PCBM, and P3HT/PCBM (a) as cast, (b) after cross-linking the polymer at 140 °C for 30 min, and (c) after thermal aging at 110 °C for 40 h under a nitrogen atmosphere (scale bar corresponds to 20  $\mu\text{m}$ ).



**Figure 8.**  $2 \times 1 \mu\text{m}^2$  C-AFM current images, recorded with a sample bias of  $-2 \text{ V}$ : DB1/PCBM before (A) and after (B) annealing and DB2/PCBM before (C) and after (D) annealing. The current scales are: (A)  $-24$  to  $14 \text{ pA}$ ; (B)  $-78$  to  $18 \text{ pA}$ ; (C)  $-2.0$  to  $6.2 \text{ pA}$ ; and (D)  $-134$  to  $167 \text{ pA}$ . (The large differences in the absolute values of the current cannot be directly related to the intrinsic electrical properties of the materials; they are rather due to extrinsic factors, for example, tip shape, contact force, relative humidity, and so on.)

homogeneous, whereas DB2:PCBM and P3HT:PCBM both begin to show PCBM clusters with the latter being the worst. After thermal aging at 110 °C for 40 h (Figure 7c), clearly all

samples show PCBM crystals. However, the DB1 sample shows, quite clearly, bright borders around the clusters, which indicates that the PCBM is still present outside these borders in

the area in between the clusters.<sup>29</sup> A quite homogeneous texture is observed in the region between DB1 clusters, similar to the situation before the aging (Figure 7b), indicating that still fine intermixing between DB1 and PCBM is present. This region appears to be less homogeneous for DB2:PCBM film and even less in the case of P3HT:PCBM, indicating the lower presence of PCBM. These results confirm that the use of acrylate-functional copolymers with a short spacer allows stabilizing the morphology of the active layer and prevents the aggregation of PCBM.

It has to be noted that the bright borders observed around the PCBM in the TEM images of Figure 7 are attributed to a decrease in PCBM contents around the clusters. The gray regions correspond to a blended region of PCBM and polymer. Induced by thermal annealing, the PCBM from the originally blended diffuses toward PCBM clusters. These PCBM clusters are therefore surrounded by a PCBM-depleted region (i.e., almost pure polymer), which in TEM images gives a brighter image than the blended regions.

Figure 8 shows the Conductive-AFM (C-AFM) current images of the DBx/PCBM blends (1:0.8) before and after thermal annealing at 140 °C for 30 min. Before annealing (images A and C), the current response is quite homogeneous for both systems. Inhomogeneities in the current distribution can be observed only on the scale of a few nanometers, which is consistent with the fact that the two materials are finely dispersed into each other. The comparison of the C-AFM images of the blends after annealing (images B and D) confirms the clear difference in the thermal behavior between the two systems: the morphology of the DB1/PCBM blend remains stable and homogeneous, whereas a major morphological change has occurred for DB2/PCBM. The layer is now made of a homogeneous matrix containing rather large islands (from 100 to 200 nm) with a very different current response. Such a morphology is the signature of the occurrence of phase separation: the matrix is the polymer-rich phase, with the islands most probably consisting of PCBM aggregates (consistently, inverting the bias voltage leads to the reversal of the current contrast; see Figure SI-1). These observations are in agreement with the PV stability results and confirm that the cross-linked film with a shorter spacer between the acrylate groups and the polythiophene backbone, that is, DB1, allows obtaining a highly compact cross-linked active layer in which the PCBM diffusion is suppressed.

### 3. CONCLUSIONS

Cross-linkable diblock copolymers containing a P3HT block and an acrylate-functionalized polythiophene block were synthesized via the Grignard metathesis process. Two copolymers were prepared with different spacer lengths between the acrylate functions and the polythiophene backbone. Thermal annealing of the copolymers/PCBM blends at 140 °C for 30 min induces their cross-linking, which can stabilize the polymer/PCBM blend morphology. BHJ photovoltaic cells were then built using these cross-linkable polymers/PCBM blends, and their performances were compared with P3HT/PCBM cells. Although the initial PV performances are slightly lower for the devices with the copolymers, the thermal stability is strongly increased for the devices that contain the cross-linkable polymer with the shorter spacer between the acrylate groups and the polythiophene chain. The loss in efficiency after accelerated thermal aging tests is kept down to 15% in this optimal case, whereas 35% in

efficiency is lost for the conventional P3HT/PCBM devices. TEM and AFM microscopy studies suggest that the cross-linked polymer network hampers the diffusion of PCBM inside the film and therefore limits the phase separation of the photoactive blend. A suitable cross-linking of the copolymers/PCBM blend thus allows for significantly improving the performances of the photovoltaic cells.

### 4. EXPERIMENTAL SECTION

**4.1. Materials.** 2,5-Dibromo-3-(2-(2-tetrahydropyranyl-2-oxy)-ethyl)thiophene (BTHPET) was synthesized according to the literature.<sup>33</sup> 2,5-Dibromo-3-hexylthiophene was purchased from Aldrich. OCA with  $M_w = 170$  g/mol was purchased from Aldrich and used as received. P3HT ( $M_w = 77\,500$  g/mol and 96.3% of regioregularity) and PCBM utilized for the preparation of the devices were purchased from Sigma-Aldrich, whereas the PEDOT:PSS from Bayer and used as received. All other chemicals were obtained from Aldrich and used as received. Solvents were distilled over standard drying agents under dry nitrogen.

**4.2. Techniques.** The 250 MHz  $^1\text{H}$  NMR were recorded on a Bruker AVANCE 250 MHz spectrometer. Size exclusion chromatography (SEC) of polythiophene copolymers was carried out in tetrahydrofuran (THF) (flow rate 1 mL min) at 40 °C with a Waters 600 liquid chromatograph equipped with a 410 refractive index detector and styragel HR columns (four columns HP PL gel 5  $\mu\text{m}$  10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 10<sup>2</sup> Å). The molar mass and polydispersity were determined by SEC with PS calibration. Optical absorption spectra were recorded on Cary 500 scan UV-vis spectrometer. FT-IR spectra were obtained using a Perkin-Elmer FT-IR spectrometer. DSC measurements were acquired with a TA Instruments Q1000 DSC using standard aluminum pans, an indium standard for calibration, and nitrogen as the purge gas. Melting and crystallization temperatures were determined by taking the peak values of second heating and cooling scans.

Morphological and electrical AFM measurements were performed using a Dimension Icon microscope equipped with a Nanoscope V controller from Bruker-Nano. All images were recorded under ambient conditions. In Intermittent Contact AFM (tapping-mode) mode, Si cantilevers with a resonance frequency in the 150–300 kHz range were used. In Conductive AFM (TUNA mode), Pt/Ir-coated probes with a spring constant around 0.5 N/m were used for very soft contact between the tip and the sample. For the electrical measurements, the samples were connected to the sample holder with silver paint so that the ITO substrate is directly wired to the sample holder.

TEM: The morphology of the active layer was studied with a transmission electron microscope (FEI Tecnai G2 Spirit Twin) operating at 120 kV. Using the same procedure as for preparing the solar cell, this layer was deposited on a cleaned glass substrate. Afterward the film was isolated from the glass by etching with 40% hydrofluoric acid and transferred onto a copper TEM-grid.

**4.3. Synthesis of Diblock Copolymers.** Poly[3-hexylthiophene-block-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene] (P3HT-*b*-PTHPET-A). In a 250 mL round-bottomed flask, 2,5-dibromo-3-hexylthiophene (3HT) (2.450 g, 7.515 mmol) was dissolved in THF (100 mL) under an inert atmosphere. A 2 M solution of isopropylmagnesium chloride (iPrMgCl) in THF (3.133 mL, 7.515 mmol) was added, and the mixture was stirred at room temperature for 2 h. Ni(dppp)Cl<sub>2</sub> (39 mg, 0.072 mmol) was added in one portion, and the reaction mixture was stirred at 35 °C for 2 h. A sample was picked out of the reactor for determining the conversion (>95%) and the molecular parameters of P3HT ( $M_n = 23\,500$  g/mol and  $M_w/M_n = 1.1$ ). A mixture of 2-dibromo-5-chloromagnesium-3-hexylthiophene and 2-dibromo-5-chloromagnesium-3-(2-(2-tetrahydropyranyl-2-oxy)-ethyl)thiophene (prepared by reacting 306 mg (0.939 mmol) of 3HT and 349 mg (0.939 mmol) of THPET with 1 mL of iPrMgCl in 30 mL of THF for 2 h at room temperature) was then added; the feed molar ratio of 3HT to THPET was 9/1 and the feed molar ratio of Ni(dppp)Cl<sub>2</sub> to the total monomers was 1/130. The reaction was then quenched by pouring aqueous HCl (2 mL, 37 wt %) into the solution.



The polymer was precipitated in methanol, then washed with methanol in a Soxhlet apparatus and recovered by dissolution in THF. Removal of the solvent and drying under reduced pressure for 24 h at 40 °C yielded a purple solid, P3HT-*b*-PHTPET (960 mg, yield 69%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7.1–6.9 (q, 1H), 4.7 (t, 1H), 3.8 (m, 4H), 3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 14H), 0.9 (m, 3H). (See Figure 1.)  $M_n = 33\,000$  g/mol,  $M_w/M_n = 1.09$ . (See Scheme 1b and Table 1.)

**4.4. Deprotection of the Alcohol Function.** Poly[3-hexylthiophene-*b*-3-(2-hydroxyethyl)thiophene] (P3HT-*b*-PHTET). A solution of P3HT-*b*-PHTPET (900 mg) in 20 mL of chloroform was added to methanol (100 mL) to give a deep purple suspension. 25 mL of an aqueous hydrochloric acid solution (2 M) was added, and the suspension was stirred at reflux for 16 h. The precipitate was filtered and washed with methanol. The obtained copolymer, P3HT-*b*-PHTET, was dried under reduced pressure (790 mg, yield 93%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7.1 (m, 1H), 3.8 (m, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 8H), 0.9 (m, 3H). (See Figure 1.)

**4.5. Functionalization of the Block Copolymers by Acrylate Groups.** Poly[(3-hexylthiophene)-*b*-(3-(2-acryloyloxyethyl)thiophene)] (DB1). To a mixture of P3HT-*b*-PHTET (400 mg) and triethylamine (0.53 mL, 3.8 mmol) in 50 mL of dry THF was added dropwise a solution of acryloyl chloride (0.308 mL, 3.8 mmol) in 5 mL of dry THF at 0 °C. The mixture was stirred at room temperature for 16 h, and the obtained polymer DB1 was filtered and precipitated in methanol. The precipitate was filtered and dried at reduced pressure (307 mg, yield 76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7 (s, 1H), 6.4 (d, 1H), 6.1 (dd, 1H), 5.8 (d, 1H), 4.5 (t, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 1.8 (m, 8H), 0.9 (m, 3H). (See Figure 1.)  $M_n = 31\,000$  g/mol,  $M_w/M_n = 1.2$ .

Poly[3-hexylthiophene-*b*-3-(oligocarboxyacrylate)ethylthiophene] (DB2). To a solution of P3HT-*b*-PHTET (450 mg) in 50 mL of dry THF was added 100 mg DMAP and 180 mg of DCC and 320 mg of OCA. The mixture was stirred at room temperature for 16 h, and the obtained copolymer noted DB2 was filtered and precipitated in methanol. The precipitate was filtered and dried at reduced pressure (426 mg). <sup>1</sup>H NMR (CDCl<sub>3</sub>, ambient temperature): 7 (s, 1H), 6.4 (d, 1H), 6.1 (dd, 1H), 5.8 (d, 1H), 4.4 (t, 2H), 3.2 (t, 2H), 2.8 (t, 2H), 2.6 (m, 2H), 1.8 (m, 8H), 0.9 (m, 3H). (See Figure 1.)  $M_n = 34\,000$  g/mol,  $M_w/M_n = 1.3$ .

**4.6. Thermal Cross-Linking.** A solution of 10 mg/mL pure DBx or DBx:PCBM (1:0.8) in ODCB was spin-coated on glass substrate or ITO-coated glass substrate at 750 rpm for 20 s. After spin-coating and slow drying, the films were then cross-linked by thermally annealing at 140 °C for 30 min under a nitrogen atmosphere.

**4.7. Devices Fabrication and Characterization.** The photovoltaic devices were fabricated according to the following procedure: ITO-coated glass was cleaned with detergent, followed by ultrasonication in water, acetone, and isopropyl alcohol. After complete drying, ITO-coated glass was treated with UV ozone. As a buffer layer, the conductive polymer, PEDOT:PSS, was spin-coated onto ITO-coated glass substrates, followed by annealing at 120 °C for 15 min to remove water. The thickness of the PEDOT:PSS layer was ~30 nm. The active layer consisting polymers (DB1, DB2, and P3HT) and PCBM was spin-coated from ODCB solution (DBx:PCBM 1:0.8 (by weight) in ODCB [15 mg/mL] and P3HT:PCBM 1:0.8 in ODCB [10 mg/mL]) onto PEDOT:PSS layer at 750 rpm for 20 s. Spin-coated films were slowly dried and annealed at 140 °C for 30 min in a nitrogen atmosphere. After annealing, the cathode was deposited by thermal evaporation of 20 nm Ca and 50 nm Al layers. Devices with 3 and 5 mm<sup>2</sup> area were obtained. All subsequent device preparation steps have been performed in a glovebox system under a nitrogen atmosphere. PCE was calculated from *J*–*V* characteristics recorded by a Keithley 2400 under AM1.5 supplied by a Newport class A solar simulator (model 91195A).

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Bias-dependent C-AFM images. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Notes

The authors declare no competing financial interest.

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