Stabilization of the Film Morphology in Polymer:Fullerene Heterojunction Solar Cells with Photocrosslinkable Bromine-Functionalized Low-Bandgap Copolymers

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ABSTRACT: Novel bromine-functionalized photocrosslinkable low-bandgap copolymers, PBDTTT-Br25 and PBDTTT-Br50, are synthesized via Stille cross-coupling polymerization for the purpose of stabilizing the film morphology in polymer solar cells (PSCs). Photocrosslinking of PBDTTT-Br25 and PBDTTT-Br50 copolymers dramatically improves the solvent resistance of the active layer without disrupting the molecular ordering and charge transport, which is confirmed by the insolubility of the films washed by organic solvents and by their thermal behavior. As a result, the formation of large aggregations of fullerene is suppressed in polymer:fullerene blend films even after prolonged thermal annealing, and the stability of the

INTRODUCTION Solution-processable polymer solar cells (PSCs) have attracted considerable attention over the past two decades because of the advantages of cost-effective fabrication and the potential physical flexibility.¹ Bulk heterojunction (BHJ) is the most successful device structures, in which the photoactive layer is a blend of a p-type conjugated polymer (electron donor) and an n-type fullerene derivative (electron acceptor).^{2,3} Controlling the BHJ morphology within the active layer is critical for achieving and maintaining high performance. In optimized BHJs, the network of the donor and acceptor materials should be bicontinuous, and the domain size of the phase-separated donor and acceptor network should be comparable with that of the exciton diffusion length to facilitate charge separation and transportation.^{4–6}

Thermal annealing,⁷ solvent annealing,^{5,8} and adding highboiling-temperature additives⁹ are the most used approaches to control phase separation of the donor and the acceptor materials. However, even if such a phase-separated nanostructure is constructed, this morphology only represents a metastable state and may gradually undergo changes over device is enhanced when compared with cells based on noncrosslinkable PBDTTT. The power conversion efficiency of the PSCs based on PBDTTT-Br25 and PBDTTT-Br50 reaches 5.17% and 4.48%, respectively, which is improved obviously in comparison with that (4.26%) of the PSCs based on the control polymer PBDTTT. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 3123–3131

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long operation time, as the polymer and the PCBM ([6,6]phenyl-C61-butyric acid methyl ester) thermodynamically prefer to segregate from each other.^{10–12} Improving the robustness of the BHJ with respect to thermal stability is critical, as any heat generated by solar irradiation could be detrimental to the performance of these devices due to the relatively low $T_{\rm g}$ of polymers and the strong immiscibility of components in the active layer.¹³

To improve the thermal stability of the PSCs, several strategies have been proposed, which include the use of diblock copolymer compatibilizers,¹⁴ corsslinkable fullerene-attached diblock copolymers,¹⁵ and crosslinkable acceptor¹⁶ and donor¹³ materials within the active layer. Crosslinking has proven to be a promising approach to stabilize the nanoscale morphology of the blended active layer. Most approaches of crosslinking conjugated polymers focus on crosslinking the specific functional groups such as pendant acrylates,¹⁷ peripheral oxetane groups,¹⁸ alkyl bromide,¹⁹ azide,²⁰ vinyl,²¹ and diacetylene moieties,²² with the crosslinking reactions being activated by either heat (thermal) or ultraviolet (UV) light. Although the crosslinking concept is simple and

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SCHEME 1 Synthetic route of the polymers.

powerful, the development of materials with both stable morphology and high performance remains a challenge. To minimize the disturbance to the π - π stacking of the conjugated polymers thus maintaining high charge mobility and light absorption, the crosslinking units should be small in size and efficient enough to freeze the BHJ morphology.

Nowadays, the copolymerization of electron-rich and electron-deficient monomers, building a conjugated backbone with donor-acceptor (D–A) structure, has proven to be an effective way to tune the optical and electronic properties of low-bandgap conjugated polymers. The power conversion efficiency (PCE) of PSCs based on the low-bandgap D–A copolymer has exceeded 7%.²³ However, the morphology stability of PSCs based on D–A copolymers has not been intensively investigated.

In this study, we have developed novel photocrosslinkable conjugated polymers with D–A conjugated backbone and bromine-functionalized side group (see Scheme 1), which can be crosslinked by UV light with minimal impact on the packing of conjugated polymers and electronic properties, thus enabling high-performing and thermally stable PSCs. Devices based on copolymers with various amounts of Br units [0% Br-units (PBDTTT), 25% Br-units (PBDTTT-Br25), and 50% Br-units (PBDTTT-Br50)] were investigated. The best PSC performance was obtained with photocrosslinked PBDTTT-Br25. In contrast to the sharp PCE decrease observed for PBDTTT devices, the PSCs based on PBDTTT-Br25 demonstrated remarkable long-term thermal stability.

EXPERIMENTAL

Materials

Pd(PPh₃)₄ (tetrakis(triphenylphosphine)palladium(0)) was purchased from Frontiers Scientific. 4,6-Dibromothieno[3,4*b*]thiophene-2-carboxylic acid and bis(trimethyltin)-BDT ((4,8bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b0]dithiophene-2,6-diyl)bis(trimethylstannane)) monomers were purchased from Solarmer Materials. Patterned Indium Tin Oxide (ITO) glass with a sheet resistance of 10 Ω/sq was purchased from CSG Holding (China). PC₇₀BM was purchased from Nano-C. PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) Clevious P VP AI 4083) was purchased from H. C. Stark. 1,8-Diiodooctane was purchased from Sigma-Aldrich. All these commercial available materials were used as received without further purification.

Synthesis

8-Bromooctan-1-ol (1)

To a mixture of octane-1,8-diol (7.3 g, 50 mmol) and toluene (150 mL), concentrated HBr [18 mL of a 48% (9 M) aqueous solution, 0.162 mol] was added.²⁴ The heterogeneous mixture was stirred and heated at reflux for 36 h. The reaction mixture was allowed to cool to room temperature, and the phases were separated. The organic layer was diluted with ether and washed with 1 M NaOH, brine, and phosphate buffer (3 M, pH 7). Drying (Na₂SO₄) and concentration of the organic layer gave a yellow oil, which was purified by silica gel column chromatography using ethyl acetate/hexane (1:10) as eluent. After the removal of the solvent, 9.29 g (yield 89%) of Compound $1\ \mbox{was}$ obtained.

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 3.65 (s, 1H), 3.62 (t, 2H), 3.40 (t, 2H), 1.87 (quintuple, 2H), 1.54 (d, 2H), 1.31–1.41 (m, 8H).

8-Bromooctyl 4,6-dibromothieno[3,4-b]thiophene-2carboxylate (2)

The 4,6-dibromothieno[3,4-*b*]thiophene-2-carboxylic acid (5.13 g, 15 mmol), DCC (Dicyclohexylcarbodiimide, 3.7 g), and DMAP (4-Dimethylaminopyridine, 640 mg) were added to a 250-mL round-bottomed flask with CH₂Cl₂ (100 mL).²⁵ 8-Bromooctan-1-ol (15.68 g, 75 mmol) was added to the flask and then stirred for 20 h under N₂ protection. The reaction mixture was poured to 100 mL of water and extracted with CH₂Cl₂. The organic phase was dried by sodium sulfate, and then the solvent was removed. Column chromatography on silica gel using hexane/CH₂Cl₂ = 10/1 yielded the title compound as red solid (3.39 g, 42%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.53 (s, 1H), 4.33 (t, 2H), 3.43 (t, 2H), 1.87 (m, 2H), 1.76 (m, 2H), 1.36–1.47 (m, 8H). ¹³C NMR (CDCl₃, 400 MHz), δ (ppm): 162.49, 145.73, 141.22, 140.57, 123.33, 102.42, 97.30, 66.21, 34.06, 32.89, 29.15, 28.75, 28.67, 28.20, 25.95.

Octyl 4,6-dibromothieno[3,4-b]thiophene-2-carboxylate (3) The 4,6-dibromothieno[3,4-*b*]thiophene-2-carboxylic acid (3.42 g, 10 mmol), DCC (2.47 g), and DMAP (427 mg) were added to a 250-mL round-bottomed flask with CH_2Cl_2 (70 mL). 8-Bromooctan-1-ol (6.5 g, 50 mmol) was added to the flask and then stirred for 20 h under N_2 protection. The reaction mixture was poured to 100 mL of water and extracted with CH_2Cl_2 . The organic phase was dried by so-dium sulfate, and then the solvent was removed. Column chromatography on silica gel using hexane/CH₂Cl₂ = 10/1 yielded the title compound as red solid (1.62 g, 35.7%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.53 (s, 1H), 4.33 (t, 2H), 1.87 (m, 2H), 1.75 (m, 2H), 1.26–1.44 (m, 8H), 0.87–0.90 (t, 3H). ¹³C NMR (CDCl₃, 400 MHz), δ (ppm): 162.51, 145.75, 141.31, 140.60, 123.28, 102.37, 97.30, 66.21, 31.92.06, 29.32, 29.30, 28.71, 26.04, 22.78, 14.24.

General Procedure for the Stille Cross-Coupling Polymerization

PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 were prepared with the same procedure as coupling dibromide compounds with bis(tributylstannyl)-substituted compounds. In a 50-mL flask, (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (0.386 g, 0.5 mmol) and different amount of monomer (**2**) and monomer (**3**) were dissolved in toluene (10 mL) and flushed with argon for 10 min. Then, Pd(PPh₃)₄ (30 mg) was added into the flask, which was then flushed by argon for another 20 min. The solution was heated to reflux and stirred for 15 h under inert atmosphere. Then, the reactant was cooled to room temperature, and the polymer was precipitated by the addition of 50 mL of methanol and

filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol and hexane. The solid was dissolved in chloroform (150 mL) and passed through a column packed with alumina, Celite, and silica gel. The column was eluted with chloroform. The combined polymer solution was concentrated and was poured into methanol.

Polymerization of PBDTTT

Without monomer (2), monomer (3) (0.114 g, 0.25 mmol), yield = 210 mg (54.7%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.50–8.10 (br, 4H), 6.52–7.16 (br, 2H), 4.42 (br, 2H), 3.96 (br, 4H), 0.88–1.92 (br, 45H).

Polymerization of PBDTTT-Br25

Monomer (2) (0.067 g, 0.125 mmol) and monomer (3) (0.170 g, 0.375 mmol), yield = 220 mg (57%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.50–8.10 (br, 4H), 6.52–7.16 (br, 2H), 4.42 (br, 4H), 4.02 (br, 8H), 3.47 (t, 1H), 0.70–2.49 (br, 89H).

Polymerization of PBDTTT-Br50

Monomer (2) (0.133 g, 0.25 mmol) and monomer (3) (0.114 g, 0.25 mmol), yield = 220 mg (56%).

¹H NMR (CDCl₃, 400 MHz), δ (ppm): 7.50–8.10 (br, 4H), 6.52–7.16 (br, 2H), 4.42 (br, 4H), 4.02 (br, 8H), 3.47 (t, 2H), 0.70–2.49 (br, 88H).

Measurements

 $^{1}\mathrm{H}$ and $^{13}\mathrm{C}$ NMR spectra were measured on a Bruker Arx-400 spectrometer using chloroform-d as a solvent and tetramethylsilane as an internal standard. Absorption spectra were taken on a Hitachi U-3010 UV-vis spectrophotometer. The molecular weight of polymers was measured by the Gel Permeation Chromatography (GPC) method, and polystyrene was used as a standard by using tetrahydrofuran (THF) as eluent. Thermogravimetric Analysis (TGA) measurements were performed on a TA Instruments TGA-2050. The electrochemical cyclic voltammetry experiments were conducted on a CHI650D Electrochemical Workstation with glassy carbon disk, Pt wire, and a Ag/Ag⁺ electrode as the working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. The hole mobilities of the obtained polymers were derived from the space-charge limited current model with a structure of ITO/PEDOT:PSS/polymer:PC70BM/Au.²⁶ The optical microscopy images of the blend films were obtained using an Olympus Fluoview Fv1000.

Fabrication and Characterization of PSCs

The PSCs were fabricated with the structure of glass/ITO/ PEDOT:PSS/blend layer/Ca/Al. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone, and isopropanol. The precleaned ITO substrate was treated in an UV-ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company) for 20 min. PEDOT:PSS aqueous solution was filtered through a 0.45-µm filter and





FIGURE 1 TGA thermograms of the polymers.

spin-coated at 2000 rpm for 60 s on the ITO electrode. Subsequently, the PEDOT:PSS film was baked at 150 °C for 10 min in air. The thickness of the PEDOT:PSS was around 30 nm. Subsequently, the photosensitive blend layer was prepared by spin coating (2000 rpm) the 1,2-dichlorobenzene solution of polymer and PC70BM (1:1.5 weight ratio, polymer concentration of 10 mg/mL) with 3% volume ratio of 1,8-diiodooctane additive on the ITO/PEDOT:PSS electrode for 60 s. Photocrosslinking was carried out for PBDTTT-Br25- and PBDTTT-Br50-based films in a nitrogen-filled glove box using 254 nm UV light from a low-power handheld lamp for 10 min. The photoactive layer thickness of all these devices was about 90 nm as determined by Ambios XP-2. Finally, a 10 nm Ca and 100 nm Al was thermally deposited in vacuum under a pressure of 5 \times 10⁻⁵ Pa. The active area of the device is about 4 mm^2 .

The current density-voltage (*J*-*V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. Device characterization was done in a glove box under simulated AM 1.5 G irradiation (100 mW/ $\rm cm^2$) using a xenon lamp-based solar simulator (from Newport). The input photon to converted current efficiency (IPCE) was measured using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with a WDG3 monochromator and 500-W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell. The IPCE measurement was performed under ambient atmosphere at room temperature.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The obtained polymers, PBDTTT, PBDTTT-Br25, and PBDTTT-Br50, were easily prepared by Stille cross-coupling method as shown in Scheme 1 and identified by ¹H NMR spectroscopy. The synthesized polymers are easily soluble in common organic solvents, such as chloroform, toluene,

chlorobenzene, and dichlorobenzene at room temperature. The weight-average molecular weight (M_w) of PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 are 3.3×10^4 , 3.1×10^4 , and 3.0×10^4 with the polydispersity index of 2.3, 2.0, and 1.8, respectively. The TGA curves of the polymers reveal a relatively high thermal stability as shown in Figure 1. The initial weight loss (5%) temperatures of PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 are found to be 327, 335, and 345 °C, respectively. The high thermal stability of the photovoltaic polymers is closely related to the long-term stability of the PSCs, which prevents morphological change, deformation, and degradation of the photoactive layer by heat during the operation of photovoltaic devices.¹⁰

Optical and Electrochemical Properties

As shown in Figure 2(a), the ultraviolet-visible (UV-vis) absorption spectra of PBDTTT-Br25 and PBDTTT-Br50 in dilute chloroform solution exhibit three maxima (412, 623,



FIGURE 2 Absorption spectra of the polymers (a) in diluted chloroform solution and (b) in solid-state film as cast.



FIGURE 3 Cyclic voltammograms of PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 drop-cast on glassy carbon working electrode in 0.1 M Bu_4NPF_6 in CH_3CN at a scan rate of 50 mV/s.

and 673 nm) between 400 and 700 nm, which are almost identical to that of PBDTTT. It illuminates that the conjugation length of the main chain in the solution was not affected by the introduction of bromine groups at the side chains.

From solution state to solid film, a red shift of about 10 nm can be observed from the absorption peaks of PBDTTTs [Fig. 2(b)]. These changes indicate the extension of the π -conjugation lengths and the interchain interaction between the backbones in the films.²⁷ Furthermore, no major differences can be observed between the absorption spectra of the three polymers, indicating that the addition of bromine units to the polymer does not significantly affect its optical properties in solid films.

Electrochemical cyclic voltammetry is used to measure the molecular energy levels of the polymers.²⁸ The cyclic voltammogram curves of PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 are shown in Figure 3. Based on the onset potentials, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the control polymer, PBDTTT, are estimated to be -5.02 and -2.92 eV, respectively. After functionalized with bromine groups at the side chains, the LUMO levels for PBDTTT-Br25 and PBDTTT-Br50 are almost unchanged, whereas the HOMO levels are slightly changed to -5.06 eV for PBDTTT-Br25 and -5.04 eV for PBDTTT-Br50, indicating that the addition of bromine units to the polymer does not significantly affect π - π coupling between polymer backbones. These findings are in good agreement with the aforementioned optical absorption studies.



FIGURE 4 Photocrosslinking behaviors of the polymers. Absorption spectra of (a) PBDTTT, (b) PBDTTT-Br25, and (c) PBDTTT-Br50 films under UV treatment for 5 min before and after flushing with chlorobenzene at 2000 rpm for 1 min. (d) Insoluble film fraction as a function of UV exposure times is measured for PBDTTT, PBDTTT-Br25, and PBDTTT-Br50.





FIGURE 5 (a) *J–V* curves of the polymer solar cells based on PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 under the illumination of AM 1.5 G, 100 mW/cm². (b) Absorbance of the blend films and IPCE curves of the corresponding PSCs.

Photocrosslinking Behavior of the Polymers

After spin coating of the active layer, photocrosslinking was carried out in a nitrogen-filled glove box using 254 nm UV light from a low-power hand-held lamp with exposure times ranging from 0 to 30 min. The photocrosslinking behaviors of the polymers are shown in Figure 4. As given in Figure 4(a), the control polymer PBDTTT without crosslink group shows no solvent resistance, and the film retains less than 3% of the initial integrated optical absorbance after flushing with chlorobenzene at 2000 rpm for 1 min. In contrast, the functionalized polymers, PBDTTT-Br25 and PBDTTT-Br50, which were crosslinked via a radical mechanism initiated by the photochemical cleavage of the C-Br bonds under deep-UV irradiation,¹⁹ show excellent solvent resistance with UV treatment for 5 min, as shown in Figure 4(b,c). No major differences in the

absorption spectra of as-cast and photocrosslinked films are observed, indicating that the photocrosslinking process does not significantly affect the optical properties of the solid-state polymer.

To calculate the insoluble fraction after photocrosslinking, the irradiated polymer films were flushed with chlorobenzene by spin coating at 2000 rpm for 1 min. We compared the integrated optical absorbance of the films before and after washing with chlorobenzene, as shown in Figure 4(b,c). After 10 min of UV irradiation, the films of PBDTTT-Br25 and PBDTTT-Br50 are insoluble, whereas the control PBDTTT is not photocrosslinked at all. The trend of photocrosslinking behavior as a function of Br content is clearly evident in Figure 4(d).

Photovoltaic Properties

The performance of the corresponding PSC devices was investigated using the ITO/PEDOT:PSS/polymer:PC₇₀BM/Ca/ Al device architecture. Photocrosslinking was carried out for PBDTTT-Br25- and PBDTTT-Br50-based films after spin coating in a nitrogen-filled glove box using 254 nm UV light from a low-power hand-held lamp for 10 min. Figure 5(a) shows the *I-V* characteristics of devices made from PBDTTT, crosslinked PBDTTT-Br25, and crosslinked PBDTTT-Br50 copolymers, which achieve PCE (average of 10 devices) of 4.26, 5.17, and 4.48%, respectively. The devices based on PBDTTT-Br25 and PBDTTT-Br50 without photocrosslinking show similar Voc, Jsc, FF, and PCE as PBDTTT-based devices, indicating that introduction of bromine groups at the side chains does not affect the electron properties of PBDTTT. The photovoltaic performances of the devices are summarized in Table 1. Because of the small difference of the HOMO levels (Fig. 3), all devices based on PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 show similar (around 0.60 V) open-circuit voltage ($V_{\rm oc}$), which is determined by the gap between the HOMO level of the polymer and the LUMO level of the fullerene in the blend film.^{29,30} In comparison with PBDTTT-based devices (12.97 mA/cm²), crosslinked PBDTTT-Br25- and PBDTTT-Br50-based devices show higher short-circuit current density (J_{sc}) of 14.88 and 14.97 mA/cm², respectively. The improvement of J_{sc} should attribute to the enhanced hole motilities (Table 1) via crosslinking between the side chains, in which the C-H bond energies in alkyl chains are weaker than those in the conjugated rings,31 thereby preserving the main polymer chain backbone integrity and polymer conjugation length, increasing transverse hole conductivity in the solid films.³² In comparison with PBDTTT-Br25, PBDTTT-Br50 with more Br units of 50 mol % shows similar $V_{\rm oc}$ and $J_{\rm sc}$ but lower FF of 50.0%. The possible reason should attribute to the higher crosslinking sites in PBDTTT-Br50 to create higher conformational defects, which give rise to localized charge traps.³³

Figure 5(b) shows the IPCE of the PSCs based on the PBDTTT, PBDTTT-Br25, and PBDTTT-Br50. The shape of the IPCE curves of the devices based on the three polymers is very similar to their absorption spectra, which indicates that



FIGURE 6 (a) The J-V output characteristics and (b) the evolution of device performance with annealing time for the PBDTTT- and PBDTTT-Br25-based devices.

all the absorption of the polymers contributed to the photovoltaic conversion. Furthermore, the IPCE curves can be simply divided into two regions of 300-500 nm and 500-800 nm due to the contribution of PC₇₀BM and polymers,

respectively. The major difference between the three polymers in IPCE curves located at the region of 500–800 nm might be attributed to the difference of the charge mobility and the absorbance of the films.

Long-Term Thermal Stability of the Devices

To examine the use of photocrosslinkable conjugated polymers for enhancing the stability of BHJ devices, devices made from PBDTTT and PBDTTT-Br25 (UV exposed for 10 min) undergoing postproduction annealing at 150 °C in nitrogen-filled glove box for 0.5-24 h were compared. The *I*-V output characteristics and the evolution of device performance with annealing time for the two systems are shown in Figure 6(a,b), respectively. At early stage, an increase in the $V_{\rm oc}$ is observed for both devices after annealing at high temperature. The increased $V_{\rm oc}$ should attribute to that thermal annealing potentially causes the morphological rearrangement of the fullerene molecules adjacent to the polymer chains, which induces the change in the energy of the interfacial charge-transfer states between the polymer and fullerene.34,35 However, the control device made from PBDTTT without crosslinking units undergoes a significant decrease in $J_{\rm sc}$ and $V_{\rm oc}$ after long-time annealing, which results in a sharp decrease (60%) in PCE with respect to the initial values. Conversely, the J_{sc} and V_{oc} of PBDTTT-Br25 device remain 80% and 95% of its initial value even after 24 h of annealing at 150 °C. This result clearly shows that the photocrosslinking is a promising approach for thermally stable high-performance devices.

To further understand the extreme contrast in thermal stabilities observed above, we examined the active layer morphology via optical microscopy. Figure 7(a-c) shows the optical microscopy images of as-prepared polymer:PC₇₀BM (1:1.5) blend film for PBDTTT, PBDTTT-Br25, and PBDTTT-Br50, respectively. Obviously, all the films are uniform without fullerene aggregation, indicating no large-scale phase separation between the polymer and the fullerene. The microscopy images for the blended films without UV crosslinking after 24 h of annealing at 150 °C are shown in Figure 7(d-f) for PBDTTT, PBDTTT-Br25, and PBDTTT-Br50 blend films, respectively. These images demonstrate that thermal annealing induces the formation of many dot-like PCBM crystals that are near 1 μ m in diameter in all blend film, indicating that there is severe macrophase separation

TABLE 1 Photovoltaic Performance and Hole Mobility of PBDTTT	-, PBDTTT-Br25-, and PBDTTT-Br50-Based PSCs
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Polymer	$V_{\rm oc}$ (V)	J _{sc} (mA/cm²)	FF (%)	PCE (%)	Mobility [cm ² /(V s)]
PBDTTT	0.59	12.97	55.7	4.26	$1.56 imes10^{-4}$
PBDTTT-Br25 ^a	0.61	13.13	53.8	4.31	$1.87 imes10^{-4}$
PBDTTT-Br25 ^b	0.61	14.88	57.0	5.17	4.67×10^{-4}
PBDTTT-Br50 ^a	0.60	12.85	53.5	4.13	$1.68 imes 10^{-4}$
PBDTTT-Br50 ^b	0.60	14.97	50.0	4.48	$3.74 imes 10^{-4}$

^a Without UV crosslinking.

^b UV crosslinking for 10 min.





FIGURE 7 Optical microscopy images of polymer:PC₇₀BM (1:1.5) blend film for PBDTTT (a, d, and g), PBDTTT-Br25 (b, e, and h), and PBDTTT-Br50 (c, f, and i) as prepared, as prepared-after thermal annealing, and UV treated after thermal annealing, respectively.

driven by the crystallization of the polymer and PCBM molecule. Figure 7(g) shows the morphology of control sample PBDTTT blend film with UV treatment after 24 h of annealing at 150 °C, in which severe phase separation of $PC_{70}BM$ crystals is observed. Uncrosslinked films undergo macrophase separation on further thermal annealing, and thus their performance is quickly degraded. In contrast, the optical micrograph of the PBDTTT-Br25 [Fig. 7(h)] and PBDTTT-Br50 [Fig. 7(i)] blend films crosslinked by UV treatment show homogeneous films with only a few dark $PC_{70}BM$ crystals. These optical micrographs confirm that the photocrosslinking of the polymers dramatically suppresses phase segregation, thus producing stable performance in solar cell devices.

CONCLUSIONS

Novel photocrosslinkable low-bandgap D–A copolymers, PBDTTT-Br25 and PBDTTT-Br50, for using in PSCs were developed. The UV-sensitive Br unit attached at the side chain does not appear to disturb the π - π stacking of the backbone. Careful adjust of the photocrosslinking Br content in the side chain was found to be critical in order to achieve optimal device performance. The formation of large fullerene aggregations at elevated temperate for a long time was suppressed by the photocrosslinking of the polymer, which led to a more stable device performance in the case of PBDTTT-Br when compared with that of PBDTTT. This approach might be useful for the development of stable PSCs. The insolubility of the photocrosslinkable PBDTTT-Br is also considered to be useful for the fabrication of multilayers by subsequent solution processes, which can enable the fabrication of efficient multilayer or tandem PSCs.

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