Superiority of Branched Side Chains in Spontaneous Nanowire Formation: Exemplified by Poly(3-2methylbutylthiophene) for High-Performance Solar Cells

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One-dimensional nanostructures containing heterojunctions by conjugated polymers, such as nanowires, are expected to greatly facilitate efficient charge transfer in bulkheterojunction (BHJ) solar cells. Thus, a combined theoretical and experimental approach is pursued to explore spontaneous nanowire formation. A dissipative particle dynamics simulation is first performed to study the morphologies formed by rodlike polymers with various side-chain structures. The results surprisingly predict that conjugated polymers with branched side chains are well suited to form thermodynamically stable nanowires. Proof of this concept is provided via the design and synthesis of a branched polymer of regioregular poly(3-2-methylbutylthiophene) (P3MBT), which successfully demonstrates highly dense nanowire formation free from any stringent conditions and stratagies. In BHJ solar cells fabricated using a blend of P3MBT and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM), P3MBT polymers are self-organized into highly crystalline nanowires with a d_{100} spacing of 13.30 Å. The hole mobility of the P3MBT:PC71BM (1:0.5 by weight) blend film reaches 3.83×10^{-4} cm² V⁻¹ s⁻¹, and the maximum incident photon-to-current efficiency reaches 68%. The results unambiguously prove the spontaneous formation of nanowires using solution-processable conjugated polymers with branched alkyl side chains in BHJ solar cells.

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1. Introduction

Polymer solar cells (PSCs) based on solution-processable conjugated polymers are a promising candidate for the production of a low-cost renewable energy source.^[1] Such PSCs are light-weight and mechanically flexible, and the properties of the photoactive layer can be straightforwardly fine-tuned by device architecture and chemical composition. An outstanding configuration of PSCs should be credited to the bulk heterojunction (BHJ), which is based on the interpenetration of electron donor (D) and acceptor (A) phases and has been extensively exploited in the active layer.^[2-16] In blends of separate D and A phases, the characteristic sizes of D and A domains play a key role in the improvement of photovoltaic performance. To facilitate efficient charge transport prior to charge recombination, an ideal domain size is close to the exciton diffusion length (i.e., ~10-20 nm).^[17-19] Another attractive approach is to provide a direct pathway for charge transport through 1D nanostructures, such as nanowires^[20,21] and nanofibers.^[22] In general, more efficient transport of charge carriers is critical for creating more efficient solar cells.

BHJ devices require sensitive control over domain morphology on the nanoscale, which is largely affected by the choice of materials, solvents, and the D:A weight ratio. A prototypical polymer/fullerene system is the blend of regioregular poly(3-hexylthiophene) with [6,6]-phenyl-C61butyric acid methyl ester (P3HT:PC₆₁BM). Linear alkyl side chains are attached to increase the solubility of conjugated polymers in common solvents. In addition, the performance of P3HT:PC₆₁BM blend solar cells has been progressively improved by various annealing protocols, and the mechanism of enhanced performance is attributed to the improvement of the two-phase nanoscale morphology frozen in the metastable state associated with the phase separation of the blend. Evidently, the formation of 1D nanostructures greatly facilitates charge carrier mobility by the provision of a superhighway for charge carriers to travel along to the electrode. Although nanofibers and nanowires have been prepared from regioregular P3HT and poly(3-butylthiophene) (P3BT), respectively, the formation of stable 1D nanostructures remains elusive because the thermodynamics and kinetics of blend phase separation cannot be controlled due to the numerous variables involved.^[21,22] It is difficult to gain improvement in a systematic manner using current methods, which involve controlling the film morphology of the polymer/fullerene blend by annealing protocols and may cause poor stability and durability of BHJ PSCs. As a consequence, spontaneous formation of 1D nanostructures (i.e., without resorting to any stringent requirements) should be the most attractive approach. Comparative studies of regioregular poly(3-akylthiophene) indicate a large variation in morphology and mobility upon varying the length of the alkyl side chain.^[7,15] It is therefore anticipated that the film morphology will be influenced by the architecture of the side chain; the nanowires may eventually be a thermally favorable state if the side-chain structures are appropriately designed.

Thus far, efforts to obtain 1D nanostructures that enhance hole mobility have proceeded largely by trial and error rather

than systematic design. However, recent advancements in polymer simulations have enabled predictive studies of the dependence of morphology upon side-chain types. To explore the mesoscale morphology, a coarse-grained model of conjugated polymers must be employed. The dissipative particle dynamics (DPD) method, proposed by Hoogerbrugge and Koelman.^[23] is a genuine mesoscale approach for studying the behavior of complex fluids, including micelles, polymeric systems, liquid crystals, and colloidal suspensions.^[24-27] DPD incorporates the idea of coarse-grained beads, which are clusters of several atoms or molecules that have similar properties. The interaction potential between any pair of DPD beads is thus soft, allowing the system to evolve much faster. Therefore, DPD can treat a wider range of length and time scales compared to atomistic simulations such as classical molecular dynamics. Herein, conjugated polymers were modeled as rodlike chains with various side-chain structures, and DPD was performed to investigate the influence of the side-chain type on the morphology formed by polymers.

2. Results and Discussion

2.1. The Influence of Side-Chain Bulkiness on the Morphological Structure of Polymer Aggregates

Conjugated polymers with three types of side-chain structures were considered, as illustrated in Figure 1a. Polymer architectures labeled A to C are represented by a rodlike backbone with linear, double, and branched structures, respectively. Note that the rods are depicted in light gray, and the side chains are in black. The influence of side-chain bulkiness on the morphological structure of polymer aggregates was thus systematically studied. As a result, we found an interesting and perhaps previously unrecognized morphological transition. Figure 1a shows the overall morphology from the top, the cross-sectional view and isosurface of the domain formed by rods, and the aggregates of backbones for the three molecular architectures considered. For the linear type, the equilibrium morphology is a multishell, football-like aggregate. For the double type, the rod domain of the aggregate is formed by sticklike regions. When side chains further grow to a branched pattern, a bundle of distinct strings is formed in the cylindrical aggregate, as is clearly shown in the crosssection. This result can be accounted for by the bulkiness of the side chain. In the absence of solvophilic side chains, the solvophobic backbones cannot dissolve in the selective solvent. However, the presence of side chains aids in the dissolution of the rodlike polymers. Nonetheless, the polymers still form aggregates, similar to micelles formed by surfactant molecules.^[28,29] Due to the incompatibility between rods and side chains, they tend to aggregate with themselves and form rod and side-chain domains, respectively. In the rod domain, the steric interactions among rods lead to alignment of the rods to maximize the translational entropy, similar to liquid crystals, as clearly demonstrated in Figure 1b.

The morphology of the aggregates was then determined by the free energy competition between the interfacial



Figure 1. a) Architectures of the rodlike polymers with various types of side chains (**A**–**C**). From the top of each column, morphologies of the polymer aggregate in the simulation cell, cross-sectional view (left)/isosurface of the rod domain (right), and the aggregate of the backbones for three types of side chains. For the aggregate morphologies, the side chains are in black and the rods are in light gray. b) For the rodlike polymer with branched side chains, from left to right, the enlarged nanowire morphology, microscopic arrangement of rods, and the isosurface of the rod domain. The figure also shows a snapshot of a unit string and the pattern of the strings within a wire-like structure with side chains removed.

energy associated with unfavorable interactions (between the rod and side-chain domains) and the free-volume entropy associated with side chains. The linear side chains are less bulky, and their demand for free volume is thus easier to satisfy. The reduction of interfacial energy is dominant and can be fulfilled by the formation of a continuous shell of rod domain. Moreover, the interface between the rod and side-chain domains tends to be as smooth and as minimal as possible to minimize the interfacial energy increment, as shown in the isosurface of Figure 1a for the linear type. When the side chain becomes bulky, the entropic penalty increases. As a result, the isosurface of the rod domain becomes rough, and the stick-like regions appear, as depicted in Figure 1a for the double type. When the side chains become very bulky, as in the branched type, the entropic factor becomes dominant, and the interfacial energy must be sacrificed to provide more free volume. Consequently, a nanowire formed by a bundle of dispersed strings appears, which have much more interfacial area than the shell. Detailed arrangement of the rods belonging to a string within a nanowire is further presented in Figure 1b to illustrate its microscopic structure.

Note that polymer chains in conventional knowledge are expected to be perpendicular to the ribbons as in previous experiments for P3HT.^[30–32] However, our simulation results indicate a different scenario; our polymer chains (P3MBT; poly(3-2-methylbutylthiophene)) are clearly parallel to the long axis of the nanowire. It should be noted that nanoribbons formed by P3HTs are precipitated out into polycrystal-line material by a cooling process while P3MBT nanowires are spontaneously formed in solution through a self-assembly process at ambient temperature. The formation mechanisms are fundamentally different.

In previous works,^[30–32] P3HTs were first dissolved in their marginal solvents at high temperature. They were cooled down to room temperature to be deposited from their solutions and then crystallized dynamically into polycrystalline material upon solidification. In a crystallization process, it is known that chains tend to fold together to form ordered regions called lamellae. Therefore, it is anticipated that nanoribbons are the result of the layer-by-layer stacking of the lamellas. As a consequence, the width of the nanoribbon grows with concentration. In stark contrast, in our experiments, the nanowires are formed spontaneously in the selective solvents. Similar to micelle formation, these nanowires are thermodynamically stable, self-assembled structures. As a result, the polymer backbones prefer to orient parallel to the nanowire in order to increase the translational entropy and reduce the interfacial area between solvophobic backbones and solvents. The diameters of the nanowires are essentially independent of the solution concentration, which is notably different from the nanoribbons formed by P3HT^[32] (vide infra).

The above theoretical standpoints defy conventional wisdom regarding, for example, polythiophenes with linear alkyl side chains, for which the formation of 1D nanowires can occur under specific conditions (e.g., slow sedimentation in a selected solvent and at a specified temperature).^[21,22,30–32] Bearing this controversy in mind, we then carried out the synthesis of a conjugated polymer with branched side chains, namely, regioregular P3MBT (**Scheme 1**), via a facile synthetic route (see Supporting Information, SI). **Figure 2**a depicts the structures of P3MBT together with a sketch of the energy levels for P3MBT and [6,6]-phenyl-C71-butyric acid methyl ester (PC₇₁BM).

2.2. Morphology and Structure

Figure 3a,e show the morphological features and phasemode images, respectively, of pristine P3MBT by tappingmode atomic force microscopy (TM-AFM). The P3MBT film exhibits an extremely homogeneous nanowire structure, which is indicative of a relatively extended conformation of the polymer aggregate. **Figure 4**a reveals transmission



Scheme 1. Synthetic strategy for regioregular poly(3-2methylbutylthiophene) (1). NBS, THF, AcOH, dppp represent *N*-bromosuccinimide, tetrahydrofuran, acetic acid, and 1,3-bis (diphenylphosphino)propane.



Figure 2. a) Chemical structures and energy level diagram of P3MBT and PC₇₁BM. The highest occupied molecular orbital (HOMO) levels are taken from cyclic voltammetry (CV) measurements while the lowest unoccupied molecular orbital (LUMO) levels were calculated from UV–vis absorption spectroscopy. b) A schematic representation of P3MBT:PC₇₁BM morphology after annealing.

(b)



Figure 3. Morphology characterization of a–d) TM-AFM topography and e–h) phase images of P3MBT:PC₇₁BM blend films with various compositions: a,e) 1:0; b,f) 1:0.5; c,g) 1:1; and d,h) 1:2. The area is 1.5 μ m × 1.5 μ m.



Figure 4. TEM images in combination with selected-area electron diffraction (SAED) patterns and enlarged images of P3MBT:PC₇₁BM blend films with different P3MBT:PC₇₁BM compositions: a) 1:0, b) 1:0.5, c) 1:1, and d) 1:2.

small

electron microscopy (TEM) images and the corresponding selected-area electron diffraction (SAED) pattern for pristine P3MBT: the latter was used to identify the internal order of the polymer films. As shown by the SAED patterns, a large fraction of the film is occupied by nanowires, and these nanowire features are ascribed to the P3MBT crystallites originating from very tight stacks of several polymer chains. Figure 4a also reveals that the nanowire-based P3MBT film possesses an elongated shape with an average diameter of 12.5 nm, which is consistent with the TM-AFM observation. Note that the P3MBT nanowires are spontaneously formed in common solvents, such as ortho-dichlorobenzene (ODCB) or chloroform (see Figure S3 in the SI), simply by solvent evaporation in an open system at room temperature. This result unambiguously supports the prediction based on the DPD approach (vide supra).

Further fabrication of the solar cell requires blending P3MBT with an acceptor

(e.g., $PC_{71}BM$). It was thus imperative to examine whether the spontaneous formation of nanowire takes place in the presence of PC₇₁BM. Indeed, nanowires in P3MBT:PC₇₁BM blend films with various compositions (by weight) were also spontaneously formed, as shown in panels b-d and f-h of Figure 3. For the sake of clarity in the following discussion, a cartoon-like 3D schematic representation of the P3MBT:PC₇₁BM morphology is depicted in Figure 2b. The TM-AFM images (Figure 3b,f) show that the composite film of the P3MBT:PC71BM (1:0.5) blend has a relatively smooth surface, displaying densely packed nanowires. It suggests a relatively good mixing of the two components, which would not inhibit charge transfer. The TEM image in Figure 4b indicates that the nanowires have a lateral dimension ranging from 10 to 17 nm, which is approximately the same as the exciton diffusion length, and may effectively assist charge transport prior to recombination.^[17-19] The PC71BM molecules tend to homogeneously fill the spaces in the P3MBT network^[33-35] (as depicted by the TEM image in Figure 4b) and form an amorphous matrix, providing a continuous pathway for electron transport. Moreover, the enlarged image of the 1:0.5 blend (insert of Figure 4b) clearly suggests a lack of phase separation; this may be attributed to the fact that phase separation may only take place in tiny domains that are very small compared to the film thickness, resulting in no observable contrast. In comparison, the TM-AFM images of the 1:1 blend (Figure 3c,g) reveal larger nanowire diameters (c.f. 1:0.5 blend). Furthermore, beadlike clusters can be found sporadically, suggesting the formation of PC₇₁BM nanocrystals embedded in the amorphous PC71BM matrix. The TEM image shown in Figure 4c reveals the growth of large PC71BM crystallite domains with an average size of 31.6 nm. In Figure 3d, the surface of the 1:2 blend becomes increasingly uneven due



Figure 5. GIXRD diffraction patterns of $P3MBT:PC_{71}BM$ blend films with various compositions.

to the higher concentration of $PC_{71}BM$. The surface roughness of this blend is 12.3 nm, which is significantly greater than that of the other blends (~5–8 nm) as shown in Figure 3a–c. In addition, it is noteworthy that in Figure 3h, P3MBT nanowires are surrounded by large $PC_{71}BM$ clusters with an average size of 53.2 nm (Figure 4d). Evidently, the presence of $PC_{71}BM$ changes the morphology of P3MBT nanowires, which varies with the amount of $PC_{71}BM$ added, and may accordingly alter the crystallite size and absorption spectrum, which are pivotal to photovoltaic performance (vide infra).

The SAED patterns associated with the P3MBT:PC71BM blends of various compositions show sharp diffraction rings, implying crystalline formation of P3MBT. The crystallinity and crystalline size of nanowires can be further investigated through their diffraction patterns via grazing-incidence X-ray diffraction (GIXRD) measurements. Figure 5 shows that all of the blend films contain ordered structures. A strong (100) diffraction peak at $2\theta = 6.64^{\circ}$ with a d_{100} spacing of 13.30 Å corresponds to an ordered and self-organized lamellar structure, with an interlayer spacing between two P3MBT backbones separated by the branched alkyl side chains. The peaks at $2\theta =$ 13.28° and 19.70° correspond to the (200) and (300) reflections, respectively. The amorphous hump typically observed near 20° appears to be very weak. These results reaffirm that the spontaneously assembled P3MBT nanowires are highly crystalline. All of the P3MBT and PC71BM peaks and the corresponding d spacing values are listed in Table S2 in the SI. Furthermore, the crystal size of the nanowires (t) can be estimated through the full width at half maximum (FWHM) of the GIXRD diffraction peaks with the Scherrer formula:^[36]

$$t = 0.9 \times \frac{\lambda}{B \times \cos \theta_{\rm B}} \tag{1}$$

where *B* represents the FWHM of the XRD peak, λ is the wavelength of the X-rays, and $\theta_{\rm B}$ is the Bragg diffraction angle. For the (100) reflection of the P3MBT:PC₇₁BM films, the crystallite sizes are 15.20, 12.77, and 10.70 nm for the 1:0.5, 1:1, and 1:2 blends, respectively, and these values are consistent with those estimated by TEM. The smaller P3MBT crystallite sizes for the 1:1 and 1:2 blends imply that P3MBT interchain interactions are disrupted due to interfacial structure incompatibility between P3MBT and PC₇₁BM nanocrystals. This effect was further examined by UV–vis absorption spectra.

2.3. Optical Properties

All of the aforementioned samples were treated by annealing at 150 °C for 10 min to enhance crystallinity.^[6,14] Comparisons of the absorption spectra associated with the pristine P3MBT films before and after thermal annealing are shown in **Figure 6**a and demonstrate the crystallinity changes



Figure 6. a) Normalized absorption spectra for a pristine P3MBT film before and after thermal annealing. b) Normalized absorption spectra for P3MBT:PC₇₁BM blend films with different compositions. All of the films were dried slowly in a covered Petri dish and subsequently thermally annealed at 150 °C for 10 min.

of the nanowires. Before annealing, the absorption spectrum exhibits a maximum at 506 nm and two shoulders at 553 and 602 nm, which are assigned to the crystalline π -stacking structure of P3MBT.^[37,38] After thermal annealing, the maximum absorption peak is slightly red-shifted to 510 nm, and the shoulder bands are augmented in terms of absorption cross-section.^[6,14] The influence of PC71BM on the crystallinity of nanowires was also studied by examining the UV-vis spectra of the blend films, as depicted in Figure 6b. When the PC₇₁BM composition is low, the amorphous PC₇₁BM matrix only weakly perturbs the P3MBT nanowires, resulting in an extended conjugated P3MBT structure similar to that in the absence of PC71BM. Therefore, the absorption spectral feature remains essentially unchanged. As the PC71BM composition increases, the PC71BM nanocrystals, which are formed in proximity to the P3MBT nanowires, grow significantly and then interfere with the interchain stacking interactions in the nanowires. Because the crystallinity of the nanowires declines with increasing PC71BM concentration, the absorption peak undergoes a blue-shift from 506 to 487 nm, accompanied by decreases in the vibronic structures located at 553 and 602 nm. A similar behavior has also been reported for P3HT:PC₆₁BM and P3BT:PC₆₁BM blends.^[21,22,39] The P3MBT:PC₇₁BM (1:0.5) film enhances the red-light absorption due to its more organized chain packing, thus harvesting more photons for increased solar cell performance.[6,14,34,35]

2.4. Photovoltaic Properties

The transport of holes in conjugated polymers is often the rate-limiting step in PSCs. To demonstrate the advantage of nanowire morphology and the influence of $PC_{71}BM$, the hole mobility of the blends was measured using the space-charge-limited current (SCLC) model at low voltage.^[40–42] However, in the blend devices, the presence of Ohmic contacts at both interfaces could lead to a SCLC that is a combination of both hole and electron current. In order to measure SCLC of one type of charge carrier only, the SCLC of the other carrier has to be suppressed by a large injection barrier, resulting in a hole-only or electron-only diode device. The device characteristics were extracted by modelling the dark current under forward bias using the SCLC expression described by the Mott–Gurney law:

$$J = 9\varepsilon_0 \varepsilon_r \mu_h V^2 / 8L^3 \tag{2}$$

where J is current density, ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer, μ_h is the hole mobility, V is the voltage drop across the device, L is the polymer thickness, and $V = V_{appl} - V_r - V_{bi}$ (where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the difference in work function of the two electrodes). The resistance of the device was measured using a blank configuration ITO/PEDOT:PSS/Al and was found to be ~25 Ω (ITO: indium tin oxide; PEDOT: poly(3,4-ethylene-dioxythiophene); PSS: poly(styrenesulfonate)). The dielectric



Figure 7. Determination of the hole mobility from the dark current densities for P3MBT:PC₇₁BM diodes with various compositions (symbols). The solid lines are fits of the data points. The applied voltage was corrected for the built-in voltage ($V_{\rm bl}$) arising from the work function difference between the contacts and the voltage loss ($V_{\rm cl}$) due to contact resistance and series resistance across the electrodes. The thickness of the films is indicated in the plots.

constant was assumed to be 3 in our analysis, which is a typical value for conjugated polymers.

Figure 7 shows the experimental dark current densities $(J_{\rm D})$ of P3MBT:PC₇₁BM blends, which were measured in hole-only diode devices. When the applied voltage is greater than $V_{\rm bi}$, $J_{\rm D}$ throughout all devices scales quadratically with voltage (trap-free region), indicating the feasibility of spacecharge-limited (SCL) transport. In this range, SCL follows the SCLC model and its value allows for a direct determination of a constant mobility. When voltage is too high or too low, serious deviation takes place, and the result may no longer obey the SCLC model.^[41] Applying the Mott–Gurney law for SCLC, the hole mobility values were calculated to be 3.83×10^{-4} , 1.82×10^{-4} , and 7.95×10^{-5} cm² V⁻¹ s⁻¹ for the 1:0.5, 1:1, and 1:2 of P3MBT:PC71BM blends, respectively. As a consequence, P3MBT nanowires provide short pathways to the electrodes and thus offer efficient hole transport, superior to typical phase-separated blends. Although all of the P3MBT:PC71BM blend films possessed an electrically bicontinuous morphology, the 1:0.5 blend displayed a significantly higher hole mobility, the value of which is comparable to the reported values of highly efficient solar cell polymers.[3,16] This result is attributed to the higher crystallinity of the nanowires, as manifested by the crystalline size and red-shift of the absorption peak. As a result, the film with a blend ratio of 1:0.5 is capable of attaining a better balance between transport of electrons and holes across the device, which is advantageous to the fill factor^[43,44] and power-conversion efficiency of PSCs owing to the accumulated SCLC charges, and recombination processes were reduced by the increased hole mobility and enhanced charge collection efficiency.

The spontaneous formation of P3MBT nanowires facilitates efficient hole transport, while the presence of $PC_{71}BM$ may affect the nanowire crystallinity and the solar cell performance. For example, the incident photon-to-current



Figure 8. a) IPCE spectra of optimized devices made from different ratios of the P3MBT:PC₇₁BM blend illuminated by monochromatic light. b) Current density versus voltage (*J*–*V*) characteristics of optimized devices made from different blend ratios of P3MBT:PC₇₁BM measured under AM1.5 white light illumination at 100 mW cm⁻². For the 1:0.5 device (•): $V_{oc} = 0.72$ V, $J_{sc} = -9.15$ mA cm⁻², FF = 0.63, and PCE = 4.15%. For the 1:1 device (•): $V_{oc} = 0.65$ V, $J_{sc} = -7.98$ mA cm⁻², FF = 0.57, and PCE = 2.96%. For the 1:2 device (•): $V_{oc} = 0.63$ V, $J_{sc} = -7.06$ mA cm⁻², FF = 0.54, and PCE = 2.40%.

efficiency (IPCE) is closely related to the current of the minority carrier. According to the PSC devices fabricated with various P3MBT:PC₇₁BM blend ratios, very broad panchromatic spectra over the entire excitation spectral range were obtained from IPCE measurements, as shown in **Figure 8**a. The spectrum of the 1:0.5 active layer exhibited a maximum IPCE of ~68% in the 460–510-nm range and nearly 50% in the 388–570-nm range. Moreover, this result also demonstrates that the photon wavelength for the current generation extends to ~750 nm, as expected from the absorption spectrum of the active layer (Figure 6b). Regardless of the blend ratios, the data for these devices highlight the important fact that IPCE exceeds 45% for more than half of the visible region.

All of the photovoltaic parameters for $P3MBT:PC_{71}BM$ nanowire-based PSCs are summarized in **Table 1**. As anticipated, a PSC with a blend ratio of 1:0.5 exhibits the

P3MBT:PC ₇₁ BM blend ratios	V _{oc}	J _{sc}	FF	PCE	Hole mobility	R _s	R _{sh}
	[V]	[mA cm ⁻²]		[%]	[cm ² V ⁻¹ s ⁻¹]	$[\Omega \ { m cm}^2]^{ m a)}$	$[\Omega \text{ cm}^2]^{a}$
1:0.5	0.72	9.15	0.63	4.15	3.83×10^{-4}	3.2	635
1:1	0.65	7.98	0.57	2.96	$1.82 imes 10^{-4}$	6.1	582
1:2	0.63	7.06	0.54	2.40	$7.95 imes 10^{-5}$	12.2	560

Table 1. Optimized performance of P3MBT:PC71BM nanowire-based PSCs.

^{a)}R_s, series resistance; R_{sh}, shunt resistance. The series and shunt resistances were deduced by the inverse gradient of the J–V curves.

best performance, in which the open-circuit voltage (V_{oc}) of the device can reach 0.72 V, with a short-circuit current density (J_{sc}) of 9.15 mA cm⁻² and a fill factor (FF) of 0.63, resulting in a power-conversion efficiency (PCE) of 4.15% (Figure 8b). The high PCE may result from the short branched side chain of P3MBT, enhancing the charge separation efficiency. Note that regardless of the blend ratio, the results in Table 1 show that our nanowire-based devices have a higher Voc compared to that obtained from a P3HT:PC₆₁BM device (V_{oc} = 0.55–0.60). The high $V_{\rm oc}$ value is mainly due to the energy level difference between the highest occupied molecular orbital (HOMO) level of the donor (-5.23 eV) and the lowest unoccupied molecular orbital (LUMO) level of the acceptor (-4.02 eV). Moreover, upon further vertical phase separation, the top contact from the 1:0.5 nanowires to the electrode increases the shunt resistance by eliminating shorting paths present in the active layer. A similar effect on $V_{\rm oc}$ has been observed in other organic BHJ structures.^[45]

3. Conclusion

In summary, based on a DPD approach, we present the previously unrecognized feature that branched alkyl side chains on a rodlike polymer tend to form nanowire bundles that are more thermodynamically favorable than those with linear alkyl side chains. The theoretical prediction is exemplified by P3MBT, which successfully demonstrates highly dense nanowire formation spontaneously at room temperature, free from any stringent requirements. Subsequently, we fabricated BHJ solar cells using as-prepared, highly dense P3MBT nanowires blended with PC71BM to achieve short and continuous pathways in the photoactive layer, a key factor contributing to the high performance of PSCs by facilitating efficient hole transfer. The as-prepared BHJ solar cells offer several advantages such as relatively high V_{oc} (~0.72 V), high IPCE (~68%) and low P3MBT molecular weight ($M_n = ~16800$ with a polydispersity index (PDI) of 1.12). The optimum conversion efficiency of 4.15% for the P3MBT:PC₇₁BM device was mainly limited by absorption spectral coverage of P3MBT. Interestingly, it is recently shown that a PSC using diketopyrrolopyrrole with highly branched side chains has a PCE of 5.5% and also involves spontaneous polymer fiber formation,^[46] further reaffirming our theoretical prediction in this study. We hope this seminal concept and its demonstration will stimulate future work on the development of novel nanowire-based polymers, such as branched or dendritic side chains for photovoltaic applications.

4. Experimental Section

The P3MBT polymer was synthesized as reported in the Supporting Information. The molecular weight (M_n) of P3MBT was 16 800 with a PDI of 1.12. Details about the dissipative particle dynamics method are described in the Supporting Information.

Optimized solar cell devices used in this study were prepared by dissolving P3MBT and PC71BM (purchased from Nano-C) in ODCB in the weight ratios of 1:0.5, 1:1, and 1:2 with a P3MBT concentration of 20 mg mL⁻¹. For device fabrication, a solution was stirred for more than 48 h to ensure complete dissolution. Patterned ITO-coated glass substrates (Kintec Company, 15 Ω per square) were successively cleaned by ultrasonication in 1% neutral detergent in water, then deionized water, followed by acetone and finally ethanol for 20 min each. The substrates were then dried and O₂-plasma-cleaned immediately prior to the deposition of a 35-nmthick layer of PEDOT:PSS, as verified by a Dektak 3030 profilometer. Deposition of the PEDOT:PSS layer was followed by baking at 140 °C for 20 min. Substrates were subsequently transferred to an inert N₂-filled glove box (<0.1 ppm O_2 and H₂O), and the active layer was spin-coated. The wet film was slowly dried in a covered Petri dish for a certain time and subsequently annealed at 150 °C for 10 min in the glove box. The thicknesses of the P3MBT:PC₇₁BM composite films were adjusted to ~70-100 nm by controlling the spin-coating rate. The coated substrates were then transferred to a thermal evaporator and evacuated to $\leq 1 \times 10^{-6}$ Torr before a 30-nm-thick calcium layer followed by a 100-nm aluminum electrode layer were deposited. The thin interfacial layer of calcium has been reported to enhance the fill factor of the devices.[10,14,16]

TM-AFM images were taken on a NanoScope IIIa controller (Veeco Metrology Group/Digital Instruments, Santa Barbara, CA), using NanoScope software (version V6.13R1) to capture images. TEM images and SAED patterns were obtained using a Philips FEI Tecnai F20 G² field emission transmission electron microscope. GIXRD patterns were collected using a Rigaku-TTRAX III diffractometer, operating at an accelerating voltage of 50 kV and current of 300 mA. A Ni-filtered Cu K α radiation source (0.154 nm) was used. A 0.4° incident angle, a 0.01° sampling step, a 5° min⁻¹ scanning rate, and a ~4–30° of scanning range at 2 θ were carefully chosen to allow for complete X-ray penetration into the polymer film. The absorption spectra were obtained on a Hitachi U-4100 spectrophotometer. Hole mobility was measured according to a similar method described in the literature,^[40-42] using a diode configuration of ITO/PEDOT:PSS/ polymer/Al. The SCLC current was measured under dark conditions using a Keithley 2400 Source Meter. The fabricated device was encapsulated in a nitrogen-filled glove box with UV epoxy and cover glass. The J-V curves were measured with a Newport-Oriel AM 1.5 G light source operating at 100 mW cm⁻² and independently crosschecked using a 300-W AM1.5 G source operating at 100 mW cm⁻²

for verification. The light intensity was determined by a monosilicon detector (with KG-5 visible color filter) calibrated by the National Renewable Energy Laboratory (NREL) to minimize spectral mismatch. The IPCE spectra were measured using a lock-in amplifier with a current preamplifier under short-circuit conditions. The devices were illuminated by monochromatic light from a xenon lamp passing through a monochromator with a typical intensity of 30 μ W. A calibrated monosilicon diode with known spectral response was used as a reference.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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