Slow drying has been proposed as a way to improve the performance of polymer solar cells (PSCs) where the drying time for the coated films is increased using a condensed solvent vapor atmosphere. This work investigated the slow drying mechanism by using PSCs consisting of poly(3-hexylthiophene-2,5-diyl) (P3HT) and bis-[6,6]-phenyl-C61-butyric acid methyl ester (bis-PCBM) and focusing on the phase-separated morphology of bulk heterojunction films. With conventional spin casting, the power conversion efficiency (PCE) of the cells was very low (0.83%). The application of slow drying resulted in notable improvements in the short-circuit current density ($J_{sc}$) and fill factor (0.12 → 0.55). Optimization of the thermal annealing and cathode interfacial conditions resulted in a high PCE of 4.05%. As the drying time was increased, the P3HT domains changed from connected band-like shapes to small separated ball-like shapes. The mechanism for this effect of slow drying on the bis-PCBM/P3HT cell characteristics is understood as follows: The slow drying causes the P3HT domains to separate into small pieces, which causes the area of the p–n interfaces to increase, resulting in an increase in free carrier generation and increased the short-circuit current density of PSCs.

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Organic photovoltaics have been actively studied as a major candidate for use in next-generation solar cells due to the several advantages they possess, including lightweight, thin film, and low material cost. In particular, polymer solar cells (PSCs) can be made by applying a solution of p-type polymers and n-type fullerene-based small molecules, meaning that PSCs do not require expensive vacuum equipment, which can potentially reduce processing costs. The efficiency of PSCs has been drastically improved over the past decade. A cell efficiency of more than 10% has already been reported. However, further improvement in efficiency is crucial for practical use.

The performance of PSCs depends not only on the materials used but also on their processing conditions. Thermal annealing and solvent annealing are representative techniques for improving solar cell performance. These methods have been extensively studied, and their effects on the short-circuit current density ($J_{sc}$) of PSCs have been clarified. They enhance the crystallinity of the constituent materials and thereby increase the carrier mobility, leading to higher $J_{sc}$.

Unfortunately, these methods are problematic. Thermal annealing can only be applied to certain polymers, and solvent annealing requires an extremely long processing time (normally several hours). Another proposed method is “slow drying,” in which the drying time of the coated films is reduced by increasing the solvent vapor pressure of the film coating atmosphere. This method also effectively increases the $J_{sc}$ of PSCs. While this method resembles solvent annealing, it has a much shorter treatment time (10–20 min). Therefore, from the viewpoint of mass-manufacturing, slow drying has great potential for improving the performance of PSCs.

The slow drying method is sometimes referred to as the “solvent annealing method” since these methods are very similar. To avoid confusion, we distinguish these methods as follows. “Solvent annealing” means that the films are subjected to lengthy solvent vapor exposure after they are dried using the conventional fast spinning method, and “slow drying” means that the film drying process itself is controlled using solvent vapors, which increases the drying time.

Unfortunately, the number of reports on slow drying is limited, and it is not widely used for fabricating PSCs. Moreover, the mechanism of slow drying is not fully understood. A suggested mechanism is that the crystallization of polymers and fullerenes is promoted, and the mobilities of holes and electrons are thereby increased.

The active layers of PSCs have a phase-separated morphology, i.e., a bulk heterojunction (BHJ) morphology. After the constituent molecules absorb photons, excitons form in the individual domains. The excitons diffuse and, when they reach the polymer-fullerene domain interfaces, they decompose into free carriers (holes and electrons). Both the holes and electrons are transported through the domains and reach the two electrodes, anodes and cathodes respectively.

The morphology of BHJ films is considered to play a key role in achieving highly efficient PSCs. The size of the phase-separated domains is particularly important. It has been suggested that they should be smaller than the exciton diffusion length so that the photo-generated excitons in the domains can diffuse into the p–n interfaces before deactivation. Since the exciton diffusion length in organic films is typically around 10–20 nm, the domains should be 20 nm at most. Moreover, the total interfacial area is very important for efficient carrier generation. Domain size is also closely related to the interfacial areas: smaller domains increase the interfacial areas and thus enhance carrier generation.

It is natural to assume that a difference in drying time changes the phase-separated morphology of BHJ films. Although the BHJ morphology greatly affects cell performance, the effect of the drying time on the morphology is not well understood. It has been reported that slow drying or solvent annealing causes fibril-like P3HT crystallization growth. Since P3HT is a high crystalline polymer, large crystalline segregates sometimes appear during the drying process. However, crystalline segregation differs from the micro phase separation that occurs in the film bulk. To the best of our knowledge, there have been no studies that clarified the relationship between the drying time and phase-separated morphology in detail (domain size, shape, mutual connectivity, etc.).

In this study, we investigated the effect of drying time on the performance of PSCs consisting of bis-[6,6]-phenyl-C61-butyric acid methyl ester (bis-PCBM) and poly(3-hexylthiophene-2,5-diyl) (P3HT) and focusing on the phase-separated morphology of BHJ films. We selected bis-PCBM/P3HT cells because previous reports have suggested that the $J_{sc}$ of these cells depends significantly on the film preparation conditions. The lowest unoccupied molecular orbital (LUMO) level of bis-PCBM (3.64 eV) is shallower than that of PCBM (3.75 eV). It is known

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Effect of Drying Time on Morphology and Photovoltaic Characteristics of Polymer Solar Cells of Bis-PCBM/P3HT Composites

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that the maximum open circuit voltage ($V_{oc}$) of PSCs is correlated with the difference between the donor polymers' highest occupied molecular orbital (HOMO) level and the acceptor fullerene's LUMO level.\textsuperscript{18} The $V_{oc}$ of cells consisting of bis-PCBM and P3HT was shown to be higher ($\sim 0.7$ V) than that of PCBM/P3HT cells ($\sim 0.6$ V).\textsuperscript{19,20} However, there was a problem in the bis-PCBM/P3HT cells: only an extremely low $J_{sc}$ could be obtained.\textsuperscript{19}

Subsequently, it was found that the $J_{sc}$ of bis-PCBM/P3HT cells can be increased by controlling the fabrication process. Yun et al. reported that the $J_{sc}$ of bis-PCBM/P3HT cells was increased from 6.84 to 7.97 mA/cm$^2$ by applying the solvent annealing method.\textsuperscript{16} The reported power conversion efficiency (PCE) was 3.75%. Ogo et al. attained a higher $J_{sc}$ of 8.66 mA/cm$^2$ by using a solvent mixture consisting of a high-boiling-point one (dichlorobenzene) and a low-boiling-point one (chloroform).\textsuperscript{37} The maximum efficiency of their cell was 4.0%.

Before the phase morphology of spin-cast BHJ films often tends to freeze before the phase separation process is completed.\textsuperscript{8} In contrast, the morphology of the films formed using the methods above may approach a thermodynamic equilibrium state due to the use of a high-boiling-point solvent (mixed solvent method) or reabsorption of solvent (solvent annealing method). If the thermodynamic equilibrium morphology is better for increasing $J_{sc}$, it should be possible to achieve similar effects by increasing the drying time during film formation. Therefore, a single solvent (chlorobenzene) was chosen and slow drying was used to increase $J_{sc}$ in this study.

Using grazing-incidence wide-angle X-ray scattering (WAXS), we previously investigated the effect of film drying time on the crystallinity of the constituent materials of BHJ films.\textsuperscript{21} The major differences between this and the previous work are as follows. 1) The previous study used PCBM as an acceptor while this study used bis-PCBM. 2) The previous study looked at the crystallization of BHJ films by varying the volume of the solvent in the cup. The details of the experimental set-up can be found elsewhere.\textsuperscript{21}

In this work, we considered the nature of the difference between bis-PCBM and PCBM, including the phase separation behavior, processing conditions, and material characteristics. Various types of fullerene derivatives have been examined for PSCs to improve the $V_{oc}$.\textsuperscript{22} Unfortunately, most of the candidate materials resulted in failure. Bis-PCBM is one of the few materials proven to be an effective replacement for PCBM. Understanding the difference between bis-PCBM and PCBM would thus be very helpful for future research work.

Method

Cell fabrication.—Solar cells were fabricated by first preparing indium-tin oxide (ITO)-patterned glass substrates (a 15 mm × 15 mm ITO film was formed on a 15 × 15 mm glass substrate) and spin coating them with poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT/PSS) buffer (~30 nm thick). They were then annealed at 135°C for 15 min.

A sample solution was prepared by dissolving 14 mg of regioregular P3HT (Merck, $M_w = 20,000$) and 14 mg of bis-PCBM (Solaris Co., Ltd.) into 1 mL of chlorobenzene.

The films were coated and slow dried in a sealed chamber installed in a glove box (GB). The chamber was equipped with a doctor blade and syringe to enable the films to be coated without breaking the seal. A quartz glass window enabled observation of the film formation process. The substrate to be used was placed in the chamber, and a small cup of solvent (chlorobenzene) was placed beneath the substrate. The chamber was then sealed. The syringe was used to drop the solution onto the substrate, and the doctor blade was used to form the film. The presence of the solvent in the cup increased the vapor pressure in the chamber, resulting in slow drying of the film. The solvent vapor pressure and thus the film drying time was controlled by varying the volume of the solvent in the cup. The details of the experimental set-up can be found elsewhere.\textsuperscript{21}

The substrates were then thermally treated with either pre- or post-annealing. The pre-annealing was carried out immediately after the active layer was formed using a hot plate installed in the same GB. An Al cathode was then evaporated onto the active layer to form a solar cell. The post-annealing was carried out using the same hot plate after the Al cathode was formed. The annealing temperature ranged from 130 to 160°C, and the annealing time was fixed at 15 min in all cases. A non-annealed cell was prepared as a reference. The performance of each cell (10 × 10 mm) was estimated under AM 1.5 solar simulated illumination.

Cross-sectional analysis.—Scanning transmission electron microscopy (STEM) and focused ion beam (FIB) were used to analyze the BHJ phase-separated morphology.

Thin sliced specimens for observation were cut from the substrates using Ga\textsuperscript{+} ion irradiation with an FIB instrument (FEI, Strata DB235M). Liquid nitrogen was used during the cutting process to cool the substrates. Cutting damage was minimized by processing the substrates in multiple steps while gradually reducing the ion current, which was set to 5200 pA for the crude processing and 80 pA for the finish processing. The acceleration voltage was a constant 10 kV. The prepared specimens were 50 μm wide, 80 μm long, and 30 nm thick.

The prepared specimens were attached one by one onto a holder for STEM observation. The holder with an attached specimen was inserted into the STEM instrument (Hitachi, S5500). The observation was done by scanning an electron beam over the cross-sectional surfaces of the specimen, using an acceleration voltage of 30 kV. Electron energy loss spectroscopy (EELS) was used to analyze the sulfur (S) and carbon (C) elements to elucidate the main components of the individual phase-separated domains. Since only P3HT contains S atoms, the distribution of S atoms represents the distribution of P3HT. Since fullerene molecules contain more C atoms, the distribution of C atoms is used as an index of the fullerene distribution.

Results

Drying time and cell characteristics.—Drying time during the phase separation process is thought to greatly affect the morphology formation of BHJ films. From this point of view, we divided the film formation process into two periods: 1) starting point (solution dropped onto substrate) to phase separation completed and 2) phase separation completed to ending point (substrate removed from chamber). The times for each period, $t_1$ and $t_2$, respectively, were measured, and their effects on the cell characteristics were examined.

The occurrence of phase separation was determined on the basis of the UV/visible absorption peak shift of the P3HT from 440 to 510 nm (Fig. 1). This shift corresponds to the π-π stacking formation from polymer chains\textsuperscript{23} and is thus considered to be a sign of P3HT

![Figure 1](https://example.com/figure1.png)

**Figure 1.** Absorbance spectra of BHJ coated film before and after phase separation.
aggregation. The timing of the phase separation could be visually determined since the color of the solution changed from transparent to opaque black.

For comparison, a cell fabricated by conventional spin casting was also examined. Its $J_{sc}$ was low (5.85 mA/cm²), its fill factor (FF) was extremely low (0.21), its PCE was very low (0.83%). The cell film thickness was 140 nm.

Figure 2 shows the relationship between $J_{sc}$ and $t_1$ when $t_2$ was fixed at a very high value (720 min) and all the cells were post-annealed at 130 °C for 15 min. The cell film thickness was 280 ± 30 nm. The $J_{sc}$ values for the slowly dried cells were clearly larger than those for the spin-cast cell although the comparison is not straightforward due to the difference in film thickness. The $J_{sc}$ increased to 6.62 mA/cm² when $t_1$ was set to 60 s and to slightly above 8 mA/cm² when it was set to 700 s.

The FF drastically improved to 0.51 at 60 s, but further improvement was not evident for $t_1 ≥ 60$ s. There was no correlation between $t_1$ and $V_{oc}$, which remained almost constant at 0.53 ± 0.02.

Figure 3 shows the relationship between $J_{sc}$ and $t_2$ when $t_1$ was fixed at 500 s. Note that the unit for the x-axis is minutes. All the cells were post-annealed under the same conditions described above. Unlike for $t_1$, the effect of $t_2$ on $J_{sc}$ was very limited. Moreover, $J_{sc}$ gradually decreased for $t_2 ≥ 10$ min, meaning exposing BHJ films at high vapor pressure for too long adversely affects performance.

These results show that slow drying is effective for increasing the $J_{sc}$ of bis-PCBM/P3HT cells and that the timing of the slow drying is important. Extending the drying time ($t_1$) during the phase separation process effectively increases the $J_{sc}$. However, once phase separation has completed, lengthy exposure of the films to the solvent vapor adversely affects the $J_{sc}$. The most effective slow drying treatment time for optimizing $J_{sc}$ was found to be around 15 min.

**Thermal annealing and cell characteristics.**—The $J_{sc}$ of unannealed slowly dried cells ($t_1 = 500$ s; $t_2 = 10$ m) was only 2.84 mA/cm², the FF was only 0.12, and the PCE was very poor (0.23%). Moreover, the series resistance ($R_s$) of the cells was extremely high (96.07 Ω). Thermal annealing significantly improved the photovoltaic characteristics of the slowly dried cells.

Figure 4 shows the relationship between the post-annealing conditions and cell characteristics. The vertical bars represent the PCE. The $J_{sc}$ values of the post-annealed cells ranged from 7.37 to 7.87 mA/cm², almost twice the value of an unannealed cell. The FF values were also significantly improved, and the $R_s$ values were reduced to 5.71–10.71 Ω. The maximum PCE was over 3%, which is the same level as for the optimized PCBM/P3HT cell.

Figure 5 shows the relationship between the pre-annealing conditions and cell characteristics. All the characteristics of the pre-annealed cells were inferior to the post-annealed cells. The $J_{sc}$ values ranged from 6.13 to 6.48 mA/cm², and the $V_{oc}$ values were around 0.55 V. The maximum PCE was below 2%.

The cells described above were made by forming cathodes directly on organic layers. It is known that the introduction of a cathode buffer layer effectively improves the characteristics of PSCs. To investigate the effect of a buffer layer, we deposited a lithium fluoride (LiF) buffer layer (nominal thickness of 0.3 nm) on the organic layer, which had undergone pre-annealing treatment at 160 °C for 15 min. The conditions for slow drying were $t_1 = 500$ s and $t_2 = 10$ m. Introducing the LiF buffer layer dramatically increased the $J_{sc}$ of the cells to 10.1 mA/cm², 1.6 times greater than without a LiF buffer. The $V_{oc}$ also improved greatly, to 0.68 V. As a result, a high PCE of 4.05% was attained.

In short, we succeeded in obtaining high efficiency bis-PCBM/P3HT cells with a short processing time (~15 min) by using...
slow drying combined with thermal annealing and a cathode buffer layer.

Table I summarizes the relationship between the cell fabrication conditions (including the drying time, annealing timing, annealing temperature, and cathode buffers) and the photovoltaic characteristics of the PSCs.

As highlighted in the table, the combined effect of the slow drying and the thermal annealing is clearly shown in the $R_s$ values. The $R_s$ values of the cells without slow drying or thermal annealing are extremely high ($>80 \ \Omega$). Contrary, the cells those were treated with a combination of slow drying and thermal annealing have very low $R_s$ values (<12 $\Omega$).

Phase-separated morphology.—Figure 6 shows representative cross-sectional STEM bright-field images of slowly dried films. The bright portions in the BHJ films represent P3HT-rich domains, and the dark ones represent bis-PCBM-rich domains.

Figure 6a shows a cross-sectional image of a cell that was treated with a combination of shorter drying times ($t_1 = 50 \ \text{s}$; $t_2 = 0 \ \text{m}$) and post-annealing ($150 \ ^\circ \text{C}$ for $15 \ \text{m}$). The P3HT domains have mutually connected band-like shapes, which is a characteristic of a percolation-type phase-separated morphology. The film also exhibited features of vertical phase separation:25–28 the P3HT domains were gathered around both electrodes, and the bis-PCBM domains were localized in the bulk center of the film.

Figure 6b shows a cross-sectional image of a cell that was treated with a combination of longer drying times ($t_1 = 500 \ \text{s}$; $t_2 = 10 \ \text{m}$) and post-annealing ($150 \ ^\circ \text{C}$ for $15 \ \text{m}$). The phase-separated morphology differed from that of the one with shorter drying times. The P3HT domains were separated into small ball-like shapes, $\sim 15 \ \text{nm}$ in diameter. These spherical-shaped domains were widely distributed in the film. The film thus had a phase-separated morphology in which small P3HT domains were spread among the bis-PCBM continuous phases.

**Table I. Cell fabrication conditions and photovoltaic characteristics of PSCs.**

| Drying time $t_1$ (s) | 60 | 500 | 700 | 500 |
|-----------------------|----|-----|-----|-----|
| Annealing temp. (°C)  | Pre | None | 130 | Post |
| $t_2$ (m)             | 720 | 0   | 10  | 60  | 720 |

| Cathode buffer | none | LiF |
|----------------|------|-----|
| $J_{sc}$ (mA/cm$^2$) | 5.9 | 6.8 |
| $V_{oc}$ (V)   | 0.7 | 0.5 |
| FF             | 0.2 | 0.3 |
| Rs (Ω)         | 84.5 | 456 |
| PCE (%)        | 0.8 | 4.1 |

Figure 4. Relationship between cell characteristics and post-annealing conditions: (a) $J_{sc}, V_{oc}$ vs. Temp. and (b) photocurrent vs. applied voltage.

Figure 5. Relationship between cell characteristics and pre-annealing conditions: (a) $J_{sc}, V_{oc}$ vs. Temp. and (b) photocurrent vs. applied voltage.
 Though increasing the drying time causes the shape of the P3HT domains from connected ones to small separated ones. This means that the area of the p–n interfaces increased greatly. Therefore, the following slow drying mechanism can be assumed. The slow drying causes the P3HT domains to separate into small pieces, which causes the area of the p–n interfaces to increase, resulting in an increase in free carrier generation.

The domain distribution can also affect cell performance. In the films treated with a shorter drying time, the P3HT domains were gathered around both electrodes, and the bis-PCBM domains were localized in the bulk center of the film. The P3HT domains gathered around the cathodes clearly had an adverse effect on electron injection into the cathodes. On the other hand, the films treated with a longer drying time had a morphology in which small P3HT domains were widely scattered in the film, so the bis-PCBM domains were distributed near the cathodes. Such a morphology would help electron injection through the formation of carrier connection paths reaching the cathodes.

In addition, slow drying apparently enhanced domain purity. Increasing the drying time promotes the separation of the individual components, which improves domain purity. Purified domains would promote exciton separation into free carriers at the domain boundaries and thereby increase $J_{sc}$. Previous studies have shown that slow drying of a PCBM/P3HT cell enhances its crystallinity, which increases $J_{sc}$ without thermal annealing. Our bis-PCBM/P3HT cell differed on this point: thermal annealing was needed to increase $J_{sc}$. Various types of thermal annealing effects have been proposed, including crystallinity improvement, cathode interface segregation, domain coalescence, and domain distribution changing. Among these candidate effects, the improvement of crystallinity is particularly important for our bis-PCBM/P3HT cells.

Our previous work demonstrated that there is an appropriate drying time for PCBM/P3HT cells. Our data showed that extended drying degrades P3HT crystallization, leading to a significant reduction in cell performance. Our current results for bis-PCBM/P3HT cells also suggest the existence of an optimal drying time. As shown in Fig. 3a, the $J_{sc}$ of the bis-PCBM/P3HT cells increased up to a certain drying time ($t_2 \approx 10$ m) and then gradually decreased. However, the decrease was not as significant as in previous work. A difference between this work and previous work is that the dried films were thermally annealed in this work. Apparently, the thermal annealing enhanced the P3HT crystallization and thereby compensated for the potential drawback of slow drying, i.e., degradation of P3HT crystallization after extended drying.

In the case of our bis-PCBM/P3HT cells, post annealing was better than pre-annealing (at the same temperature) for improving performance. Furthermore, introducing a LiF buffer layer into the cathode interfaces dramatically increased the $J_{sc}$ and improved the FF of a pre-annealed cell. That post annealing is better for improving performance is well known for PCBM/P3HT cells. It has been explained by the difference in component segregation at the cathode interfaces. In a post-annealed cell, PCBM, which segregates at the cathode interfaces, can control the leakage current by blocking holes and promotes electron injection into the cathodes. In the other hand, in a pre-annealed cell, the leakage current is larger since P3HT segregates at the cathode interfaces. If a suitable buffer layer is introduced into the cathode interfaces and the leakage current is controlled, a pre-annealed cell could achieve the same level of efficiency as that of a post-annealed cell, as demonstrated in previous studies.

From these comparisons, as well as in the case of bis-PCBM/P3HT cells, it is presumed that current leakage through the cathode interfaces caused the $J_{sc}$ reduction in the pre-annealed cell. However, it is rather difficult to explain this from the cell’s phase-separated structure. This is because there was no clear difference in the segregated state between the post-annealed cell (Fig. 6b) and pre-annealed cell.
Morphology formation mechanism under slow drying conditions.—We first briefly review previous work on the morphology formation mechanism of PCBM/P3HT cells and then consider the case of bis-PCBM/P3HT cells under slow drying conditions.

Since molecules of PCBM are much smaller than those of P3HT, PCBM molecules have larger diffusion coefficients. It is thus natural to assume that the diffusion of actively moving PCBM molecules plays an essential role in the morphology formation of BHJ films. This means that PCBM-rich domains are formed by the diffusion and subsequent aggregation of PCBM molecules. The escape of PCBM molecules results in an increase in the P3HT concentration in these regions, which then gradually transform into P3HT-rich domains.

The PCBM diffusion and P3HT crystallization compete with each other during the BHJ morphology formation. If the P3HT crystallization speed is sufficiently high to disturb PCBM diffusion, the phase separation process is suppressed. Comparison of the speed between PCBM diffusion and P3HT crystallization is thus important to understand the BHJ morphology formation. We previously demonstrated that P3HT crystallization is completed much sooner than PCBM diffusion under slow drying conditions. The time to complete PCBM diffusion at room temperature was not negligible, around 300 s. On the other hand, Su et al. reported that PCBM diffusion dominated P3HT crystallization in the thermal-annealing process.

Our previous WAXS data showed that, when the drying time was relatively short, only P3HT crystallization peaks were observed. As the drying time was increased, signs of PCBM crystallization appeared, and the intensity of the P3HT crystallization peaks decreased. When the drying time was very long, the P3HT crystallization peaks disappeared, and only the PCBM crystallization peaks were left. Evaluation of cell performance revealed that the best performance was attained by balancing the crystallization between PCBM and P3HT. This means there is an optimal drying time for fabricating PCBM/P3HT cells.

The appearance of the crystallization peaks in our previous WAXS data indicated that the PCBM molecules strongly aggregated during the drying process. After they diffused from the mixed regions, they came together and formed aggregates. This was also the case for P3HT. The crystallization peaks showed that the P3HT molecules formed aggregates in the solution as the drying process progressed. The increased molecular concentration apparently caused the aggregation of the individual components.

Most previous work on the BHJ morphology formation process, including ours, investigated PCBM/P3HT composites. We believe that the phase separation of bis-PCBM/P3HT composites has a similar mechanism since these two fullerene derivatives have nearly the same molecular size. This means that the phase separation process of bis-PCBM/P3HT composites is governed by the diffusion and subsequent aggregation of bis-PCBM molecules.

Figure 7 shows the proposed mechanism of the phase-separated morphology formation of bis-PCBM/P3HT composites. Initially, the coated BHJ film is a homogeneous mixture of bis-PCBM, P3HT, and solvent. In the early stage of phase separation, the bis-PCBM molecules diffuse and aggregate. As the bis-PCBM molecules escape, the polymer concentration in the mixed phase increases (Fig. 7a).

As more bis-PCBM molecules escape, the polymer-rich domain (continuous phase) shrinks and form mutually connected slender shapes (Fig. 7b). The mutually connected morphology observed for cells treated with a shorter drying time apparently corresponds to this stage of phase separation. Although bis-PCBM molecules might not have fully escaped, their diffusion is stopped by the rapid removal of the solvent. The morphology is thus frozen at this stage, in the middle of the process.

Under lengthy drying time conditions, the bis-PCBM molecules diffuse further, and the polymer-rich domains greatly shrink until finally they separate into small domains (Fig. 7c). The small separated domains observed for the cells treated with a longer drying time apparently formed as a result of strong domain shrinking.

Not only the domain shapes but also their spatial distributions differed between the films treated with shorter and longer drying times. In the former, the domain distribution exhibited features of vertical phase separation. In the latter, the small separated polymer domains were dispersed widely in the film. These differences can be explained as follows.

The occurrence of vertical phase separation has been reported for various types of polymer blend films, including BHJ films. We recently reported the occurrence of a vertical phase separation in spin-cast PCBM/P3HT films and proposed a formation mechanism based on the depletion effect of polymer chains. We considered that the same type of mechanism, the depletion effect, acted on the bis-PCBM/P3HT films and caused vertical phase separation.

The depletion effect is well-known in the field of colloidal science. It sometimes appears in systems in which colloidal particles coexist with isolated polymer chains. If the polymer chains cannot penetrate the colloid accumulation regions, osmotic pressure occurs in the system due to the localized depletion of polymer chains. This osmotic pressure forces out the solvent molecules from the colloid regions, leading to an effective attractive force between the colloids.

During the drying process, a gradient of P3HT concentration forms in the film perpendicular to the film’s surface, with a higher density near the film surface and a lower density in the bulk. Near the film’s surface, polymer aggregation advances due to the increased concentration and the isolated polymer chains are depleted in this region. The bulk region contains a higher density of polymer chains since aggregation has not yet occurred.

The large difference in the concentration of isolated polymer chains can cause osmotic pressure between the near-surface region and the bulk region. This osmotic pressure creates solvent flow from the near-surface region toward the bulk region. Many bis-PCBM molecules are thereby removed from the near-surface region, and P3HT domains gather near the surface. A concentration gradient thus occurs in the coated film: there is a P3HT-rich region near the surface with an adjacent PCBM-rich region. Because the drying time is short, the distribution of the domains is fixed at this stage, resulting in a compositional gradient in the dried film.

In contrast, the films dried for a longer period of time exhibited small separated polymer domains uniformly dispersed in the film. In our previous results for PCBM/P3HT cells, the domain distribution became uniform when the film was formed using drop casting, which has a long drying time. This suggests that a uniform domain distributed morphology is thermodynamically stable at room temperature. In bis-PCBM/P3HT cells, if the coated films have sufficient fluidity after the P3HT domains separate into small domains, the small domains will take a random distribution with minimum free energy (Fig. 7d).

Moreover, thermal annealing after drying enhances the domain dispersion. Thermal annealing has the potential to change the domain distribution of BHJ films. Our previous results demonstrated that thermal annealing at a higher temperature (160 °C) can effectively change the polymer domain distribution so that it becomes more uniform.

Since the contribution of entropy to the free energy is higher at higher temperature, the tendency toward a random distribution is higher. Since the annealing temperature used in the present study was also rather high (150 °C), it apparently changed the P3HT domain distribution so that it became more random. Although this effect would also act on the films dried for a shorter period of time, their domains were difficult to move since they were mutually connected. In contrast, the polymer domains in the films dried for a longer period of time were separated into small domains, so they could easily move and change their distribution.
Finally, it is interesting to compare BHJ morphology formation with the phase separation of polymer solutions. These two systems resemble each other in that they are a mixture of polymer and small molecules (fullerenes, solvents). Many studies have been done on the phase separation of polymer solutions, and it is widely accepted that the diffusion and subsequent aggregation of small solvent molecules determine the phase-separated morphology.31,32 A morphology with mutually connected percolation-type polymer domains often appears in the middle of the phase separation of polymer solutions. Since these connected polymer domains are not stable, they are usually separated into small domains, leading to a final morphology. These two types of phase-separated morphologies greatly resemble those observed in our study: the percolation-type one corresponds to the films dried for a shorter period of time, and the small-domain dispersed one corresponds to the films dried for a longer period of time.

**Solubility parameters.**—Our finding that the performance of bis-PCBM/P3HT cells can be improved using slow drying led to a question: “why do bis-PCBM/P3HT cells require a special treatment like slow drying to improve their performance?” With bis-PCBM/P3HT cells, the efficiency was poor when spin film formation was used. In contrast, with PCBM/P3HT cells, even when conventional spin film formation was used, an efficiency of about 3% was easily attained. In our case, the performance of the PCBM/P3HT cells did not improve with slow drying compared to the performance of cells formed using spin film (the same P3HT lot was used).

This suggests that, if a PCBM/P3HT cell was used, the phase-separated morphology could reach a stable equilibrium state with fast drying of the spin film. On the other hand, to reach an equilibrium phase-separated morphology for a bis-PCBM/P3HT cell, the drying time must be increased. These differences suggest that phase separation is more difficult with bis-PCBM/P3HT film than with PCBM/P3HT film.

From the viewpoint of material design, it is very important to know the key material characteristic that determine the phase separation behavior. In phase separation, the most important characteristic is the affinity between materials. If the affinity is low, the tendency toward phase separation of a mixed system is high, and if the affinity is high, the tendency toward phase separation is low.

We next discuss the effect of the molecular interaction on phase separation and attempt to clarify the origin of the difference in phase separation behavior between bis-PCBM/P3HT and PCBM/P3HT solutions.

According to Flory-Huggins theory, which describes the phase separation phenomenon of polymers, the effect of the interaction on the phase separation is determined by the Flory-Huggins interaction parameter, which is a measure of the affinity between two different components in a mixture.
phase separation can be expressed using interaction parameter $\chi$:

\[
\chi = U_{XY} - \frac{1}{2}(U_{XX} + U_{YY}),
\]

where $U_{ij}$ is the potential between the $i$ and $j$ components.\(^{33}\) When one side is a polymer, only a single polymer segment needs to be considered. The $\chi$ indicates the local potential difference (exchange energy) between a mixed state and a separated state. When the molecule polarity is small, it can be approximated by using the solubility parameter $\delta$:

\[
\delta = \frac{\Delta E}{vRT},
\]

where $\Delta E$ is the cohesive energy and $v$ is the volume. $\chi$ is the most important index of phase separation. If it is large, the affinity is low, and phase separation proceeds easily. In contrast, if it is small, the affinity between materials is high, and phase separation proceeds with difficulty.

There is a problem in applying approximation formula 2. The conventional solubility parameter, defined by Eq. 3, does not take into account the difference in molecular size. This is a problem when the solubility parameter is used to compare molecules with substantially different sizes. Although the solubility parameter concept has already been introduced in the field of PSC,\(^{14,25}\) the effect of volume is seldom taken into consideration.

Flory-Huggins theory uses a lattice model for the calculation. In this model, a solvent molecule or a polymer segment is assigned to a unit lattice, and the difference in free energy between before and after mixing is considered. It is assumed that the molecules allocated to each unit lattice have the same size. If the sizes of a polymer segment and a solvent molecule are substantially different, the number of molecules (segments) assigned to each unit lattice need to be arranged so that the sizes of the molecule (segment) groups per unit lattice are equal.

In our case, the sizes of the thiophene unit of P3HT and chlorobenzene were almost the same. However, the difference in volume between a thiophene unit and a fullerene molecule cannot be ignored. The volume of fullerene is about four times that of a thiophene unit. Some adjustment is thus required to unify the sizes of the individual unit lattices.

Here, we consider a unit lattice with the size of a fullerene molecule. One fullerene molecule and four thiophene units are assigned to a single unit lattice. Therefore, in the application of approximation formula 2, the definition of the conventional solubility parameter cannot be used as is. The use of a solubility parameter that makes four thiophene units one unit is required. It could be said that “the solubility parameter per unit lattice” should be used instead of the solubility parameter defined per thiophene unit.

The value of the solubility parameter defined for a thiophene lattice is smaller than the value defined for a thiophene unit. Because a solubility parameter is determined by the cohesive energy density, the interactions between the four thiophene units constituting one unit lattice is considered to be internal energy that does not contribute to the cohesive energy. This discussion is thus applicable to the solubility parameter for a solvent lattice. Since the solvent molecule has nearly the same size as a thiophene unit, four solvent molecules are assigned to one unit lattice.

Table II summarizes the values of the solubility parameter based on our new lattice definition and the conventional molecular definition. The values were calculated using the atomic group contribution method. Correction of the volume factor was evaluated as being inversely proportional to the molecular volume. The correction value for a thiophene unit lattice was thus obtained by dividing the conventional value for a thiophene unit by two. The lattice solubility parameter for chlorobenzene was obtained using the same method.

As shown in the table, the values of the lattice solubility parameter for thiophene and chlorobenzene were very close. This means that their affinity is very high; in other words, chlorobenzene is a very good solvent for P3HT and the effect of the solvent on phase separation is limited. In contrast, the values of the lattice solubility parameter for fullerene were much different. This suggests that there is a strong repulsive force between fullerenes and P3HT molecules. Such a repulsive force would naturally promote phase separation. Therefore, from the viewpoint of molecular interaction, we can say that the repulsive force between fullerene and P3HT molecules is the driving force for the phase separation of BHJ solutions.

Moreover, the lattice solubility parameter of bis-PCBM was closer to the value of P3HT than that of PCBM. More specifically, the difference between PCBM and P3HT (PCBM–P3HT) was 11.21 and the difference between bis-PCBM and P3HT (bis-PCBM–P3HT) was 6.97. This shows that bis-PCBM has higher affinity for P3HT than PCBM. This means that the phase separation process of bis-PCBM/P3HT is slower than that of PCBM/P3HT.

In addition to the molecular interaction, steric hindrance of molecules affects the diffusion behavior. Bis-PCBM molecules have a disadvantage in terms of phase separation from this point of view. Bis-PCBM molecules have two substituents, so their steric hindrance effect is higher than that of PCBM. This means that bis-PCBM experiences more diffusion disturbance during phase separation.

The difference in phase separation behavior between bis-PCBM and PCBM can be understood by considering the solubility parameter, including the concept of volume factors. The procedure presented here can be used to predict the phase separation behavior for other types of molecular matrixes. Investigation of the use of this method for other matrixes as well as more precise estimation of the molecular interaction remain for future work.

| Molecule | P3HT | CB | bis-PCBM | PCBM |
|----------|------|----|----------|------|
| Molecule | 20.22 | 20.67 | 17.08 | 21.32 |
| Lattice  | 10.11 | 10.34 | 17.08 | 21.32 |

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