Solvent-Free Transfer of Freestanding Large-Area Conjugated Polymer Films for Optoelectronic Applications

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Conventional processes for depositing thin films of conjugated polymers are restricted to those based on vapor, liquid, and solution-phase precursors. Each of these methods bear some limitations. For example, low-bandgap polymers with alternating donor–acceptor structures cannot be deposited from the vapor phase, and solution-phase deposition is always subject to issues related to the incompatibility of the substrate with the solvent. Here, a technique to enable deposition of large-area, ultra-thin films (=20 nm or more), which are transferred from the surface of water, is demonstrated. From the water, these pre-solidified films can then be transferred to a desired substrate, circumventing limitations such as solvent orthogonality. The quality of these films is characterized by a variety of imaging and electrochemical measurements. Mechanical toughness is identified as a limiting property of polymer compatibility, along with some strategies to address this limitation. As a demonstration, the films are used as the hole-transport layer in perovskite solar cells, in which their performance is shown to be comparable to controls formed by spin-coating.

1. Introduction

The ability to deposit thin films (<100 nm) with precise thicknesses and in a sequential order is a critical aspect of semiconductor device manufacturing. As modern optoelectronic devices continue to incorporate more organic components (e.g., organic light-emitting diodes), new processes are necessary that are compatible with a wide variety of hard and soft materials. In particular, there is demand for methods that yield homogeneous films on large substrates (>100 cm^2) that are compatible with previously deposited layers that may be sensitive to stressors such as heat, solvents, or other conditions.

Conjugated polymeric materials—defined by the delocalization of electrons through an extended system of π bonds—are of potential value in many such multi-layer devices, such as organic and hybrid perovskite photovoltaic cells. However, deposition of polymeric materials is generally limited to processing from vapor, liquid, or solution phases (e.g., chemical vapor deposition, spin-coating, or various printing methods). These classes of approaches have particular limitations. In the case of vapor-phase processing, the most significant drawback is that the monomers must be polymerized in situ in a reactive process (as in chemical vapor deposition of polymers). This requirement restricts the structural diversity that can be achieved. For solution-phase processing, perhaps the most significant limitation is ensuring the solvents used do not damage the underlying layers—that is, “solvent orthogonality.” Deposition of pre-solidified films has been shown to open up new processing opportunities such as avoiding solvent incompatibility or conformally coating textured structures.

Freestanding polymer films have been of significant scientific and technological interest over the last two decades, where they are used in service of fundamental studies and characterization, energy storage, sensing, separation membranes, tissue engineering and various other applications. Here, we have made use of freestanding films to fully circumvent the concerns of solvent orthogonality by enabling deposition truly free of liquid solvents. We named this process “solvent-free transfer” (SFT). A key step in SFT is to generate ultra-thin, freestanding films, for example, using the technique of interfacial spreading described by others. These films can then be drawn up onto a planar or cylindrical frame, which supports the edges of the films by van der Waals forces. These films can then be transferred directly onto a variety of substrates that are either bare or coated with other layers in a device stack in a manner that is compatible with roll-to-roll manufacturing. While the polymers are originally formed atop a water bath, they are highly hydrophobic and can be dried (for example, by vacuum) prior to the transfer such that the substrate is agnostic to the solvents used to form the film. We demonstrate that SFT has significant potential in depositing over large areas by forming and transferring free-standing films which are up to
10 × 10 cm² in area, with thicknesses of ≈20 nm. These films are characterized by various techniques and compared against spin-coated controls. Finally, we demonstrate the viability of the films as the hole-transport layers (HTL) in small area (0.07 cm²) perovskite solar cells (PSCs).

2. Results and Discussion

A summary of SFT, as it is applied in the fabrication of PSCs, is shown in Figure 1. The process begins by the interfacial spreading of a polymer solution on the surface of water held in a rectangular trough (step 1). The spreading of the polymer solution itself is driven by the Marangoni effect. Once the solvent evaporates, it leaves behind a polymer film suspended upon the surface of the water. The thickness of this film is determined by the concentration of the solution, the volume of the droplet, and the surface area of the trough (step 2). This film is then contacted at the edges by a supporting structure, in this case a cylindrical drum, to which the edges of the polymer film adhere. The drum is rotated to shear the polymer film off the surface of the water (step 3). The drum with suspended films can then be aligned (step 4) and rolled over appropriately shaped substrates to transfer the film, for example, to a perovskite half-cell (step 5). Once the films have been transferred, the device stack is ready for additional processing (step 6). Depending on the interfacial energies between the polymer and the desired substrate, the film will readily wet the substrate or it may benefit from additional treatment to promote complete contact. In the case of the perovskite/polymer pairings used in this work, we used chloroform vapor to promote the wetting process, but if the substrate surface is sufficiently hydrophilic, the wetting is rapid and effective. Footage of the film formation, drawing, and transfer using freestanding (P3AT) films (2.5 × 2.5 cm² in area, 15 nm thick) can be found in Video S1, Supporting Information.

In order to better assess the scope of SFT, we explored the survivability of films in the drawing step of the process, which we generally found to be the limiting factor. If a film could be drawn, then it could be transferred, but we did not find all films could be drawn. In our exploration, we found a variety of factors to play a significant role in the film survivability. These factors included intrinsic and extrinsic properties of the film (mechanical toughness and film thickness, respectively), as well as properties of the setup (the diameter of the roller drum). Conjugated polymers with high toughness were generally easy to draw. All of the P3ATs we tested had toughness over 1.5 MJ m⁻³ and we were able to consistently draw films spanning a wide range of thicknesses, from approximately 15 to 135 nm. Higher thicknesses were not tested. On the other hand, DPP-DTT was the polymer we tested with the lowest toughness (≈0.15 MJ m⁻³), and we were never able to produce a high quality film with this polymer. All films drawn would fracture as the film was sheared from the water. A summary of the polymers (toughness and ease of drawing) with which we attempted to form freestanding films is shown in Figure 2a. Tensile test data gathered for this study can be found in Figure S4, Supporting Information.

The most illuminating polymer we tested was PTB7-Th. We had two batches at our disposal that had dramatically different toughness, owing to their fracture strain, but similar tensile moduli and yield points. Representative stress versus strain curves of the two batches are show in Figure 2b, as measured by the film-on-water method. The batches, referred to as “57 k” and “47 k” (based on their molecular weights) had approximate toughness of 1.8 and 0.3 MJ m⁻³, respectively, which could be accounted for by the differences in their molecular weight, entanglement density, dispersity, or the presence of impurities. As expected, we were readily able to draw films made with 57 k, but 47 k was much more challenging. Using our typical drum diameter of 40 mm, no films were successfully drawn with 47 k at a thickness of ≈20 nm. However, increasing the drum diameter

Figure 1. Summary of the solvent-free transfer process. A polymer film is formed on the surface of water before being sheared from the water surface using a cylindrical drum. The freestanding film can then be subsequently transferred to a solid substrate.
to 60 mm appears to alleviate the stresses the film is subjected to, and some films were successfully drawn at a thickness of 20 nm. We hypothesize this difference originates from the adhesion of water to the polymer as the film ascends when the drum is rotated. The water remains partially adhered to the film at first. With the smaller drum, the film is rapidly raised and is subjected to stresses as it is made to raise the water with it. By increasing the drum radius these stresses are reduced, as the film is more effectively sheared, rather than peeled, from the water surface. On the other hand, when the film thickness of 47 kDa was increased to ~45 nm, we were able to draw high quality films with the 40 mm diameter drum. This increased survivability can be rationalized by considering that the stresses resulting from the drawing process (e.g., due to adhesion of the water) will be distributed over the greater thickness. This dilation of the stress reduces the maximum stresses, suppressing the formation and propagation of cracks.

Based on these results, we conclude that SFT is likely to be compatible with a broad range of polymers, but with some caveats. The toughness of the particular polymer and batch being drawn is a fundamental limiting factor. However, some strategies exist to mitigate the impact of the polymer toughness on the process. Here we explored the film thickness as well as the diameter of the rolling drum. The maximum thickness that can be produced using interfacial spreading, while retaining high film uniformity, is one factor that has not been well explored and that, in our experience, does vary between different polymers. The drum radius itself can be increased arbitrarily, keeping spatial restriction in mind. Beyond film thickness and increased drum radius, other strategies to expand the scope of SFT are expected to exist. Such strategies may pertain to the processing setup itself (e.g., other geometric aspects, drawing speed, and choice of liquid substrate) or polymer additives such as plasticizers which can alter the mechanical properties of the film itself.

When forming large area films (100 cm²), we replaced the rotating drum with a square planar frame (10 × 10 cm²) which shears the film from the water surface by translating laterally on a linear bearing. This approach is conceptually equivalent to a roller drum of infinite radius. The use of the planar frame (instead of a large drum) is expected to minimize the strain on the film, and the drawn films were of high quality (Figure 3a).

Figure 2. a) Chemical structures of the polymers with which we attempted to form freestanding films. Most could be readily drawn to form freestanding films. The 47 kDa batch of PTB7-Th required a larger drum radius or greater film thickness than other polymers. No freestanding films were successfully drawn with DPP-DTT. b) Characteristic stress versus strain curves of the two PTB7-Th batches (57 and 47 kDa) that were drawn using SFT.

Figure 3. a) Summary of the large-area SFT variant, where the floating film is sheared off the water surface by a planar frame, which translates horizontally. This film can then be applied directly to a substrate. b) Photographs of a 10 × 10 cm² area film made of P3BT, mounted on the drawing frame (left) as well as after the same film was transferred onto a sheet of glass (right). c) Thickness measurements by profilometry of the same P3BT film (left) as well as a separate P3HpT film (right).
The film can then be transferred to a large area substrate by lowering down the film at a gentle, off-horizontal angle such that one corner touches down first. Upon contact with a high energy surface, such as glass treated with air plasma, the film is quickly pulled down onto the surface as the triple interface (glass/polymer/air) propagates across the substrate. As this process evolves, air pockets sometimes form. We observed in most instances that these pockets deflated by themselves as the gas molecules diffused through the film, as was the case for the transferred film shown in Figure 3b. Otherwise, the elimination of the bubbles can be accelerated by exposing the substrate and film to solvent vapor.

The thickness uniformity of these films was assessed by contact profilometry (see Figure 3c), which we found to have a reasonably low standard deviation (<5 nm) for films with an approximate mean thickness of 20 nm. Additionally, the quality of the film formed also strongly depends on the local environment, control over which was limited in the ambient laboratory environment. Factors such as the presence (or absence) of air currents can influence the uniformity of the film. Generally, the last regions to dry are also the thickest. This non-uniformity can be attributed to increasing concentration of polymer in the liquid region as the film solidifies in an adjacent region. Therefore, the manner in which the film dries can have a significant impact on the uniformity of the film. For example, in the case of large area films (which were formed with the setup simply placed in the open air of a fume hood), the last region to dry was consistently one of the back two corners, and when drawn, this region would be slightly, but visibly, thicker than the others. In contrast, when the evaporation was allowed to proceed in an enclosed container without flowing air, the overall solidification of the film was much less predictable, as was the subsequent non-uniformity. It may be possible to create a channel where uniform laminar flow can be leveraged to produce films with greater uniformity than is shown in Figure 3c.

We then measured the roughness and pinhole density of the films produced by SFT compared to those produced by spin-coating (SC). Films produced by both methods were of the same thickness (~20 nm) and derived from the same solution. Atomic force microscopy (AFM) was used to generate a topographic map of the film surfaces before and after exposure to chloroform vapor, that is solvent-vapor annealing (Figure 4a). A

![Figure 4. a) Atomic force microscopy of P3BT films that were deposited by SFT (top row) and spin-coated (bottom row). Films were evaluated before solvent-vapor annealing (SA) (left) and after SA (right). b) Root-mean-squared (RMS) and mean roughness of the various films, before and after SA. c) Scanning electron micrographs of the same films. An InLens detector was used to enhance contrast from surface roughness. The horizontal feature at the top of each micrograph is an intentionally scratched region to demonstrate the contrast between the polymer and its underlying silicon substrate. d) Electrochemical chronoamperometry of P3BT films that were deposited by large-area SFT (blue), small-area SFT (yellow), and spin-coating (green). To compare the scalability of SFT, multiple small area films are compared to multiple regions of a single large area film.](image-url)
quantitative look at the surface roughness of the films shows that, overall, the SFT films were slightly smoother than their SC equivalents (Figure 4b). As expected, the chloroform vapor treatment reduced the roughness for both the SFT and SC films. To ensure that the minima shown in the AFM images were not pinholes, we obtained scanning electron microscopy (SEM) images of the films (Figure 4c); no pinholes were observed.

In addition to AFM and SEM, we tested for the presence of pinholes using electrochemical chronoamperometry. In this technique, we utilized a standard three-electrode system with 0.1 m tetrabutylammonium hexafluorophosphate (TBAH) in anhydrous propylene carbonate (PC) as the electrolyte and ferrocene/ferrocenium ($F_c/F_{c}^+$) as the outer sphere redox couple. The films were held at 0.8 V versus the standard hydrogen electrode for 30 s resulting in an exponential decay curve (Figure 4d). As detailed in our previous work, the ratio of the current density as time approaches zero between the P3BT-coated indium tin oxide (ITO) electrode and the bare ITO electrode (Figure S4, Supporting Information) approximates the pore density by which charge can be transported whether by defects, pinholes, conductive filaments, or impurities. Using this method, the surface coverage for films transferred by both SFT methods (small and large area) as well as SC controls was estimated. The results are tabulated in Figure S5, Supporting Information. We find that all of the films performed similarly with the large area SFT, small area SFT, and SC films exhibiting 97%, 96%, and 95% coverage, respectively. The large area SFT films all came from a single sequential filtered solution (0.45 and 0.2 µm pore sizes) and made in a Class 100 cleanroom in order to minimize the occurrence of pinholes.

Ultimately, we were interested in how films deposited by SFT perform in devices in comparison to films produced by spin-coating. In a typical perovskite solar cell (PSC), the absorber is sandwiched between two charge selective layers (the electron- and hole-transporting layers, ETL and HTL). In general, the selective layers must exhibit high electronic conductivity for the desired charge carrier, have favorable band alignments with the absorber, be chemically compatible with the absorber, have a high degree of stability against operational stressors, be optically transparent, and form interfaces with low levels of carrier traps. We reasoned that PSCs would be a good platform on which to test the viability of SFT of a conjugated polymer due to the lack of liquid solvents needed for SFT, which might otherwise damage the underlying perovskite absorber. Additionally, the stability of PSCs is often further negatively impacted by the additives incorporated into the other layers in the device stack, such as the dopants used in HTLs made from small-molecular (non-polymeric) organic semiconductors.

We made PSCs with a variety of P3ATs, and found the electronic performance of all P3ATs tested to be comparable, with a slight loss in $V_{oc}$ with increasing side-chain length. Ultimately, we settled on poly(3-heptylthiophene) (P3HpT) due to the favorable adhesion that we observed with the perovskite and this polymer, as opposed to that of glassier P3ATs with shorter alkyl chains. These films had free-standing dimensions of 2.5 × 2.5 cm², though the device active area was significantly smaller, at 0.07 cm², as defined by a stencil mask. Our findings are summarized in Figure 5. In general, we found the performance of the SFT films to be comparable to the SC ones. The open-circuit voltage, $V_{oc}$, of SFT devices were somewhat lower, and showed greater hysteresis, compared to those made with SC. However, the SFT devices displayed slightly increased short-circuit current density, $J_{sc}$ in both scan directions. The fill-factor (FF) was comparable between the two types of devices, with SC slightly outperforming SFT in the forward scan, but the opposite in the reverse scan. The underlying cause for these differences is unclear, but one possible explanation could be the difference in microstructure of the polymer which results from different processing conditions. For example, the preferential edge-on microstructure of films formed by interfacial spreading when compared to films formed by SC could slightly alter the energetics at the HTL/perovskite interface, therefore affecting the photovoltaic metrics.
3. Conclusions

In summary, we have introduced a novel processing method, SFT, that leverages the mechanical robustness of conjugated polymers to form exceptionally thin, freestanding films that can be transferred onto sensitive substrates without using liquid solvents. The scope of the process was explored by attempting to utilize it to form films from a variety of conjugated polymers. Most polymers were quite compatible, but we identified toughness as a critical material property in determining the applicability of SFT with a particular polymer. The process was also demonstrated to be amenable to large areas, and the quality of the films is assessed for uniformity by profilometry (where we found films of ≈20 nm thickness to have a standard deviation in thickness of 5 nm or less). The films were also compared against spin-coated controls. Film roughness was assessed using SEM and AFM (where we found SFT films to be slightly smoother than the controls), surface coverage was estimated by chronoamperometry (where SFT films yield slightly better coverage than the controls.) Last, we implemented SFT to produce the HTLs in PSCs, which performed very comparably to those in which the HTL was fabricated by spin-coating.

In SFT, after original solidification from solution, the subsequent processing occurs in the solid phase, allowing for deposition which is free of liquid solvents and therefore fully circumvents the usual need for solvent orthogonality. In principle, SFT could work with any polymer film that is floating on the surface of water or an alternative solvent, and interfacial spreading may be the most scalable method to produce such a film.[23] Additionally, because the polymers are initially processed from solution, SFT is expected to be compatible with the vast majority of conjugated polymers in use today. We believe this process holds additional potential in roll-to-roll application as well as in enabling other processing opportunities which leverage the ability to modify the film before applying them to the desired substrate.

4. Experimental Section

General: All polymer solutions were made with chlorobenzene as the primary solvent, were magnetically stirred for >12 h at ~60 °C, and were taken off the heat shortly before experiments and allowed to cool to room temperature. Air plasma treatments were done using a RF plasma cleaner from Harrick Plasma. The plasma cleans were done at 30 W for 120 s in a nitrogen-filled glovebox.

Preparation of the Freestanding Polymer Films: All film formations and drawing were performed on custom-built systems. All custom parts, such as roller drums, troughs, and substrate carriage were printed on a Form 3 SLA printer using Form Clear Resin. The troughs in particular were treated in air plasma for an extended period of time (>3 h) to crosslink the print surface and minimize leaching of the monomers and oligomers into the water used for interfacial spreading. Furthermore, a hydrophobic silane treatment was applied to the trough surface to modify the water contact angle and planarize the water surface in order to avoid pooling of the polymer solution.

Mechanical Properties of Polymers: The mechanical properties of the P3ATs were cited from ref. [28]. All other mechanical properties were measured using the pseudo-freestanding “film-on-water” tensile test, which has been described elsewhere.[29] All reported mechanical properties were from films prepared by interfacial spreading, and all gathered data can be found in Figure S4, Supporting Information.

Profilmetry: The initial thickness of transferred films was estimated by using the same “spreading parameters” (drop volume, polymer solution concentration, and dish size) to form films which were transferred to planar (glass) substrates. For P3HT and P3HT films, the concentrations used were 10 and 7 mg mL⁻¹, respectively. For the “small-area” trough (4 × 11 cm area) a droplet volume of 15 µL was used. For the “large-area” trough (13.5 × 15.5 cm area) a droplet volume of 70 µL was used. The thickness of these films was then measured using a Dektak XT profilometer.

Electrochemistry: For all electrochemical measurements, a standard three-electrode system with a bare coated ITO as the working electrode was used, a platinum (Pt) wire was used as the counter electrode, and a non-aqueous single junction silver (Ag) reference electrode (Pine Research, AKREF0033) filled with 10 mm of silver nitrate in acetone as the electrolyte. All voltages reported were corrected with 85% automatic and 15% manual IR compensation and all electrochemical measurements were performed on a BioLogic VSP 300 potentiostatic with EC-lab software. The reference electrode was calibrated using the ferrocene/ferrocerium redox couple whose redox standard potential in propylene carbonate had been determined to be 0.624 V versus SHE.[10] In cyclic voltammetry, the films were scanned five times at which point they stabilized with minimal differences between scans four and five. The scan rate was 20 mV s⁻¹. In the chronoamperometric measurements to determine pore density, the films were held at 0.8 V versus SHE for 30 s after a 2 s linear sweep from open-circuit voltage. In order to minimize the formation of pinholes, all samples were prepared in a Class 100 cleanroom using a sequentially filtered P3HT solution (0.45 and 0.2 µm pore sizes).

Atomic Force Microscopy: The polymer films were deposited by SFT or spin-coated onto polished silicon which had been rinsed in acetone, ethanol, isoproplyl alcohol, and deionized water, followed by treatment with air plasma. AFM measurements were taken using a Veeco atomic force microscope (AFM) in tapping mode and analyzed using NanoScope and Gwyddion software.

Scanning Electron Microscopy: SEM micrographs were captured on a Zeiss Sigma 500 SEM with an accelerating voltage of 3.00 kV and an InLens detector. The samples used were the same as AFM.

Substrate Preparation of Perovskite Solar Cells: Indium tin oxide (ITO) substrates were purchased pre-diced and pre-etched from Biotain Crystal Co. (TEC 8, 6-8 Ω/sq). They were cleaned by a series of sonication and washing steps as follows: sonicated in 2 vol% Hellmanex III in DI water for 15 min, rinsed with DI water, sonicated in DI water for 15 min, rinsed with DI water, sonicated in IPA (99.5% purity) for 15 min, rinsed with IPA, sonicated in acetone (99.9% purity) for 15 min, rinsed with IPA, and then dry with filtered dry air. Immediately prior to tin oxide deposition, the ITO substrates were UVO-treated for 20 min.

Tin Oxide Electron Transport Layer: The seed solution was prepared by diluting a colloidal dispersion of SnO₂ (15% in water, Alfa Aesar) with DI water (Alfa Aesar) in a 1:4 volume ratio. Prior to use, the solution was stirred at room temperature for 4 h then filtered with a 0.2 µm PTFE filter. Cleaned and UVO-treated substrates were prepared and 150 µL of the SnO₂ seed solution was spun atop the substrates at 4000 rpm for 30 s in air. The films were then sintered at 150 °C for 30 min also in air.

Perovskite Absorber: The selected perovskite composition had a nominal solution stoichiometry of Pb₃(MA)₉(PbI₃)₉(PbBr₃)₉(PbF₃)₉ dissolved in a 3:1 v/v mixture of DMF and DMSO at a 1:25 m concentration. Prior to the perovskite deposition, the tin oxide coated ITO substrates were treated again with UVO to improve the wettability of the perovskite solution resulting in better films. The films were spin-cast at 5000 rpm for 50 s with a 200 µL drop of methylacrylate 22 s into the spin. The resulting films were annealed at 100 °C for 30 min. All perovskite processing was conducted in a nitrogen-filled glovebox.

FAI was purchased from GreatCell Solar Materials, Csl (99.999% purity) and MACI (99.0% purity) from Sigma Aldrich, lead iodide...
11002 SunLite Solar Simulator, under AM 1.5G, at 100 mW cm \(^{-2}\), significantly improved the device fill factors by eliminating "double-
allowed to age in nitrogen for 15 days, as this was observed to
scan speed of 0.1 V s \(^{-1}\), the light intensity was calibrated using a standard silicon reference cell
from the author.

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

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
G.L.E. and M.K. contributed equally to this work.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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