Phase segregation mechanisms of small molecule-polymer blends unraveled by varying polymer chain architecture

Jihua Chen1 | Sanjib Das2 | Ming Shao3 | Guoliang Li4 | Huada Lian5 | Jian Qin5 | James F. Browning6 | Jong K. Keum1,6 | David Uhrig1 | Gong Gu2 | Kai Xiao1

1Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA
2Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, Tennessee, USA
3Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan, China
4Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee, USA
5Department of Chemical Engineering, Stanford University, Stanford, California, USA
6Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

Correspondence
Jihua Chen and Kai Xiao, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. Email: chenj1@ornl.gov and xiaok@ornl.gov
Gong Gu, Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN 37996, USA.
Email: ggu1@utk.edu

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Abstract
As phase separation between the small-molecule semiconductor and the polymer binder is the key enabler of blend-based organic field-effect transistors (OFETs) fabricated by low-cost solution processing, it is crucial to understand the underlying phase separation mechanisms that determine the phase morphology, which significantly impacts device performance. Beyond the parameter space investigated in previous work, here we investigate the formation of blends by varying the branch architecture of the polymer binder and by shortening the solvent dry time using ultrasonic spray casting. The phase morphologies of the resulting blend films have been thoroughly characterized with a variety of techniques in three dimensions over multiple length scales, including AFM, energy-filtered transmission electron microscope, and neutron reflectivity, and have been correlated with electrical transport performance. From the results, we have inferred that the phase morphology is kinetically determined, limited by the inherent slow movement of polymer macromolecules. The kinetic picture, supported by molecular dynamics modeling, not only consistently explains our observations but also resolves inconsistencies in previous works. The achieved mechanistic understanding will guide further optimization of blend-based organic electronics, such as OFETs and organic photovoltaics.

Keywords
neutron reflectivity, organic field-effect transistors, phase separation, polymer binders

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1 | INTRODUCTION

Significant progress in the development of organic field-effect transistors (OFETs) has enabled a promising alternative to those based on amorphous silicon, in a wide range of applications, such as display backplanes, electronic sensors, memories, and radio-frequency identification tags.\(^1\)–\(^6\) In comparison with semiconducting polymers, organic small molecules allow for higher purity, crystallinity, and charge carrier mobility.\(^7\)–\(^8\) Solution processible small-molecule semiconductors, such as 6,13-bis(triisopropylsilylethynyl)pentacene (TIPS-PEN), that have demonstrated high mobility and good environmental stability,\(^9\)–\(^10\) further opens the potential for low-cost manufacture, once considered advantageous for polymers, but the solution-based processing suffers from thin-film dewetting, inherently due to strong intermolecular $\pi$–$\pi$ interaction that is behind good crystallinity and charge transport,\(^8\)–\(^11\)–\(^13\) and from poor film formation due to low solubility and low solution viscosity, especially in certain processes, such as inkjet printing,\(^14\)–\(^15\) resulting in nonuniform film morphology and thus large device-to-device performance variation. To overcome these drawbacks, binder polymers have been added to the solutions to boost viscosity for good film formation, yet do not negatively impact electrical transport of the resulting blend films if proper phase separation of the small-molecule semiconductor and the polymer is achieved.\(^12\)–\(^16\)–\(^20\)

As previous works on solution-deposited blend films of small molecule organic semiconductors and polymers have focused on the morphology of the separated phases, with attention also on the crystallinity of the small-molecule phase, the exact role played by and the behavior of the polymers has not been sufficiently understood. In nature, tough molluscan shells and brilliant pearls and nacres are the results of proteins (biopolymers) regulating the crystallization of CaCO$_3$ to form thermodynamically unfavored mineral-biopolymer composites with exceptional nanoscale regularity, which is behind the beautiful appearance and the mechanical strength approximately 3000 times that of either polymorph of the mineral,\(^21\) attracting active research to uncover the exact mechanisms.\(^22\) While engineered small molecule-polymer blend film formation is much less complex than molluscan biomineralization, honed by half billion years of evolution, and obviously lacks the chemical aspects of synergistic interactions of multiple biopolymers with mineral ions, the active role played by the polymers, probably beyond thermodynamics, is worth investigating.

Previous studies used insulating and semiconducting polymer binders to improve the charge transport performance of small-molecule OFET channels.\(^9\)–\(^12\)–\(^15\)–\(^17\)–\(^18\)–\(^23\) Desirable vertical phase segregation of small molecules and polymer binder is the primary mechanism behind the improvement, while lateral phase separation needs to be controlled in order not to affect percolated conducting pathways.\(^18\) The small molecules tend to segregate to the top surface (air interface) of the blend film, favoring top-gate OFET geometries, although in some cases\(^10\)–\(^18\)–\(^24\)–\(^26\) small molecules crystallize at both the bottom (substrate) and top interfaces; exceptions are rare where a small molecule species segregates to the bottom.\(^19\) This tendency has not been understood. Lee et al.\(^13\) attributed it to the lower surface energy of the small molecule crystal than that of the polymer thin film in their experiments.\(^13\) In systems where the polymer is more hydrophobic than the small molecule crystal, however, the small molecules still segregate to the top, even with the blend film on a hydrophobic substrate\(^23\) (in contrast to the hydrophilic substrate used by Lee et al.\(^13\)). There must be other factors driving this trend, and the segregation of small molecules to both sides of the blend film needs to be explained.

With regard to optimization of detailed blend composition and processing, previous studies elaborated on the importance of the polymer binder molecular weight and solvent effects on blend film morphology and device performances. Kang et al.\(^26\) found that the molecular weight of insulating polymer binder strongly affects the phase separation in blend films. Madec et al.\(^15\) studied the effect of molecular weight of polymer binder and binary solvents on film growth and crystallinity of TIPS-PEN. Furthermore, Kaimakamis et al.\(^27\) reported the effect of small molecule-polymer ratio on device performance. Nevertheless, a mechanistic understanding of the phase separation and small molecule crystallization is needed to guide process optimization.\(^18\) A three-dimensional investigation into the phase morphology across multiple length scales is required to sort out the interplay between the often coexisting vertical and lateral phase separations.

Beyond the parameter space investigated in previous work, here we study the effects of the polymer binder chain architecture on blend film phase morphology and the concomitant charge transport performance. Surprisingly, different chain architectures of the same polymer, polystyrene (PS), with nearly the same molecular weight yield small molecule segregation at opposite interfaces (top vs. bottom), as well as different extents of lateral separation and different gradients in vertical segregation, all revealed by a variety of in-plane and out-of-plane (through thickness) characterization techniques across multiple length scales. In the case of linear PS, we obtained vertical phase separation with a TIPS-PEN-rich layer only at the bottom side, in contrast to previous reports where small molecules prefer the top surfaces of
blend films. Taking into account the compactness of the three types of PS macromolecules with similar molecular weights but different branch architectures, the mechanistic understanding of the phase segregation kinetics, inferred from experimental results and supported by molecular dynamics (MD) simulation, not only explains all our observations but also resolves inconsistencies in previous works.

2 EXPERIMENTAL SECTION

2.1 Materials and solution preparation

TIPS-PEN, as purchased from Sigma Aldrich, was separately blended (weight ratio 1:1) with three polymer binders of similar molecular weights but different chain architectures, namely linear PS ($M_w = 486$ kg/mol), 4-arm-star PS ($M_w = 483$ kg/mol), and centipede PS ($M_w = 540$ kg/mol), synthesized by D. Uhrig using anionic polymerization. Each blend was dissolved in toluene at a total solid concentration of 5 mg/ml. Each solution was sprayed on SiO$_2$/Si$^{++}$ substrates using the ultrasonic technique reported elsewhere. Briefly, each substrate was tilted at a small angle (3°) during coating to enhance the orientation of the TIPS-PEN crystals. The optimized spray-coating parameters were: an atomizing gas pressure of 0.4 psi, a solution flow rate of 1.2 ml/min, a nozzle-to-substrate distance of 4.6 cm, and nozzle moving speed of 8 mm/s. For reference, 8 mg/ml neat TIPS-PEN solution in toluene was sprayed with similar conditions.

2.2 Device fabrication and testing

Before the deposition of organic thin films, $n^{++}$ doped type silicon substrates with 250 nm thermally grown silicon dioxide (capacitance $C_i = 12.5$ nF/cm$^2$) were cut into $20 \times 20$ mm pieces and cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol using an ultrasonic bath, followed by baking at 80°C for an hour. TIPS-PEN solutions with or without polymer binder were directly coated onto the SiO$_2$ surface by ultrasonic spray under ambient conditions. Finally, 50-nm thick Au source and drain electrodes were deposited through a shadow mask by thermal evaporation at 1 Å/s under a $4 \times 10^{-6}$ mbar vacuum. Channel lengths of the devices were 25, 50, 75, or 100 μm, while the width was 2000 μm. The electrical characteristics of OFETs were measured under ambient conditions using a Keithley 4200 semiconductor parameter analyzer. The field-effect mobility is extracted in the saturation regime by finding the slope of transfer curves $I_{DS}^{1/2}$ versus $V_{GS}$, using the gate capacitance $C_i$ measured by an Agilent E4980A precision LCR meter.

2.3 Thin-film characterization

The optical micrographs of thin films were collected using a Nikon Opti Phot 2-POL microscope with a cross-polarizer. Neutron reflectivity (NR) experiment was conducted at the beamline-4B (BL-4B) in Spallation Neutron Source, Oak Ridge National Laboratory using the Liquids Reflectometer (Beamline-4B). A neutron beam with a bandwidth of 3.5 Å (2.5 Å < $\lambda$ < 6.0 Å) was applied, where $\lambda$ is the wavelength of incident neutron. To account for the instrumental smearing of NR data, the instrumental resolution provided from the beamline was convoluted with the calculated NR curves. Atomic force microscope (AFM) images were acquired with a Bruker Dimension Icon operating in tapping mode. Transmission electron microscopy was performed using a Zeiss Libra 120 with an in-column energy filter.

2.4 Molecular simulation and calculations

The nonbond interaction is the WCA Lennard-Jones (L-J) potential, which is purely repulsive with a cut-off radius $r_c = 2^{1/6} \sigma$. The strength of the L-J potential is $\varepsilon = k_B T$, where $T$ is temperature. The harmonic bond interaction is $k (r_{ij} - \sigma)^2/2$, where $r_{ij}$ is the instantaneous distance between bonded beads $i$ and $j$ and the spring constant is set to be $k = 2000 k_B T/\sigma^2$, sufficiently high to suppress bond length fluctuation. A cubic box with periodic boundary conditions (PBCs) is filled with $M = 250$ polymers. The number of beads on each polymer is $N = 64$ for linear PS. For the 4-arm star, $N = 65$, with the 16-bead arms linked at a central bead. The centipede polymer is modeled by 10 four-bead side chains attached to a 29-bead main chain, thus $N = 69$. While the side chain junction intervals are much smaller than in the actual centipede PS, the model just intends to capture a more branched polymer than the 4-arm star PS. The simulation box size is chosen such that the bead number density is $\rho = 0.7 \sigma^{-3}$, previously shown to reliably represent the behavior of dense polymer melts. To prepare for the MD simulations performed using the NVT ensemble and Nosé-Hoover thermostat, initial molecular configurations are first generated for each PS type by random walks and folded back into the simulation box by applying PBCs, and then undergo Monte Carlo bead displacement ($3 \times 10^9$ moves), followed by elimination of unphysical bead
overlap. To ensure a good statistical average, all results are averaged over 10 independently simulated replicas for each PS architecture. The MD integration step unit is 0.005τ, where \( \tau = \sigma(m/\varepsilon)^{1/2} \), \( m \) being the bead mass. The temperature \( T \) is held constant such that \( k_B T = \varepsilon \). With \( \sigma \sim 0.9 \text{ nm} \) and 4 monomers each bead for PS, \( \tau \sim 1 \text{ ps} \). Here, a monomer refers to the chemical repeat unit, whereas the term is often used in the polymer physics literature for the bead.

3 | RESULTS AND DISCUSSION

Ultrasonic spray-coated blend films of TIPS-PEN with three PS binders (Table S1) of similar molecular weights (480–540 kg/mol) and narrow polydispersity (1.03–1.07) but distinct chain architectures, namely linear, 4-arm star, and centipede, as well as reference neat TIPS-PEN films, form active channels of bottom-gate, top-contact (BG/TC) OFETs (Figure S1). The ultrasonic spray technique is described in detail elsewhere. Figure 1 compares the saturation-regime field-effect hole mobility statistics of more than 20 OFETs from each type, extracted from transfer characteristics (fabrication and characterization details in Experimental Section). So far, in the case of TIPS-PEN, both linear and centipede PS additives demonstrated high levels of improvement, while the centipede version is statistically favored. Blend-based OFETs exhibit average mobilities of 0.26, 0.37, and 0.45 cm²/(V·s) for 4-arm-star, linear, and centipede PS binders, respectively, over the 0.10 cm²/(V·s) value for the neat TIPS-PEN reference (Table S2), with the centipede PS binder leading to a remarkable greater than fourfold increase in average mobility and an eightfold boost in the ratio of average mobility to the SD, indicating a significant enhancement in not only average performance but also device-to-device uniformity, further visualized by the device performance histogram, Figure 1A. This simultaneous improvement of average mobility and uniformity surpasses those achieved by using only linear polymer binders. Furthermore, from neat TIPS-PEN to the centipede PS blend, subthreshold swing drops threefold, indicating a trend of decreasing charge carrier trap density associated with that of increasing mobility. Good ambient stability of the devices, attributed to the intrinsic stability of TIPS-PEN, shows no significant difference among types of devices (Figure S2).

To understand the large but differing performance enhancements, we first compare the crystallinity of various TIPS-PEN:PS blends. Out-of-plane X-ray diffraction patterns of all blend films exhibit similarly sharp (001), (002), and (003) reflections (Figure S3), with average crystal domain sizes 155, 136, and 132 nm calculated from (001) peak widths for the linear, star, and centipede PS blends, respectively, indicating similar crystallinity for all blends.

Next, we examine the phase morphologies of the blend films using in-plane and out-of-plane (through thickness) characterization techniques on multiple length scales. On the 100-μm scale, polarized optical microscopy (Figure S4) shows the expected irregularly shaped ribbon crystals with random orientations and poor coverage for the neat TIPS-PEN film, due to the de-pinning of the contact lines during solvent evaporation. Blending with each of the PS binders improves both TIPS-PEN crystal alignment and film coverage. Furthermore, the centipede PS blend film exhibits large triangular TIPS-PEN crystals. Clearly, the PS binder

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

**FIGURE 1** Simultaneous improvements in OFET mobility average and uniformity, achieved by TIPS-PEN:PS blends using three different PS binders. (A) Saturation-regime field-effect hole mobility mean values and standard deviations. (B) Typical transfer characteristics curves.
branch architecture significantly influences the crystal growth, film formation, and millimeter-to-micron-scale morphology of TIPS-PEN.

AFM further reveals the blend film surface morphologies on the micrometre scale (Figure 2). The neat TIPS-PEN film shows a step-terrace geometry, indicative of its 3D crystal growth. The step height was about 1.65 nm, which is in agreement with the vertical intermolecular spacing of the (001) plane, reported previously. The centipede PS blend exhibits height variations reminiscent of the terrace-step topography, and the 4-arm-star PS blend appears smoother and less terrace-step-like. Distinctively, the diffused overall height map and the largely homogeneous topography revealed by a finer grayscale of the TIPS-PEN:linear PS film suggest a polymer top surface absent of small-molecule crystallites.

To investigate the lateral (or in-plane) phase morphology of TIPS-PEN:polymer blend films on the 10-nm scale, each blend film was imaged by energy-filtered transmission electron microscopy (EFTEM) at 0 ± 5 eV and 20 ± 5 eV electron energy loss (Figure 3). Here, the 0 eV (elastic) image contrast signifies mass thickness variation since regions of larger mass per area are less transparent to electrons. The 20 eV (low loss due to plasmons of the p-type organic semiconductor) images visualize TIPS-PEN and PS-rich domains as brighter and darker areas, respectively. The reversed contrast at 0 and 20 eV energy losses for each blend indicates larger mass thickness (i.e., mass per area) in the TIPS-PEN-rich regions. The 4-arm-star blend film exhibits distinctive domains with well-defined boundaries reminiscent of crystal edges (Figures 3B and 3E), indicating predominantly in-plane phase separation between 4-arm-star PS and TIPS-PEN (labeled as II phases). In contrast, smeared domain boundaries in the linear PS blend film (Figure 3A) suggest the dominance of vertical phase separation (referred to as = phases). In between,
recognizable domains with internal variations and slightly smeared boundaries in the TIPS-PEN:centipede PS film (Figure 3C) signal a combination of vertical and lateral phase separation modes (gradient phase separation or $\Delta$ phases).

The above results are corroborated by through-thickness concentration profiles of Si-containing TIPS-PEN, visualized by cross-section EFTEM Si element mapping based on the Si L$_{2,3}$ edge core loss near around 105 eV. The clear stratification of the linear PS blend film into Si-rich lower and Si-poor top layers unambiguously confirms vertical ($\equiv$) phase separation (Figure 4A, where the air interface as Au/Pt because the top surface is coated with Au for electrode fabrication or Pt for FIB processes). This through-thickness phase separation is previously reported as a reason for increased charge transport in TIPS-PEN/polymer-based OFETs with a BG/TC architecture.\textsuperscript{26} This observation is in agreement with the AFM imaging of a smooth surface attributable to a polymer top layer. Complementing the lateral imaging in Figures 3B and 3E, The cross-section Si element map of a TIPS-PEN-rich domain in the 4-arm-star PS blend film (Figure 4B) shows an ultrathin (~10 nm) TIPS-PEN-rich layer at the top of the 250-nm blend film with observable Si concentration. Distinctively, the TIPS-PEN:centipede PS film shows a clear through-thickness nanoscale gradient structure. Without an abrupt stratification interface, TIPS-PEN concentration continuously increases toward the top surface (Au/Pt side).

NR provides further insights into out-of-plane phase separation. Figure 5 shows the TIPS-PEN volume fraction as a function of depth normalized against blend film thickness for each blend. Experimental NR curves (Figure S5A) were fitted using the Parratt formalism,\textsuperscript{36} to obtain neutron scattering length density (SLD) distributions (Figure S5B), which are subsequently converted to volume fraction profiles, using a method reported elsewhere.\textsuperscript{37} Here, for linear and centipede blends, the composition profiles are in general consistent with cross-section EFTEM images (Figure 4): The TIPS-PEN:linear PS blend film has a bi-layer structure with high TIPS-PEN concentration at the dielectric interface and polymer-rich layer at the air interface, while the TIPS-PEN:centipede PS film has a reversed volume fraction profile and yet...
maintains a moderate TIPS-PEN fraction (~50%) at the dielectric interface. The NR-derived composition profile of the TIPS-PEN:4-arm-star PS film represents an average over TIPS-PEN-rich and -poor regions, displaying a TIPS-PEN volume fraction peak at the top, consistent with cross-section ETEM (Figure 4C).

Although centipede PS leads to a smaller TIPS-PEN volume fraction at the gate/dielectric interface compared with linear PS, the TIPS-PEN-rich upper part of this blend film facilitates charge carriers injection, as indicated by less current crowding at low drain voltages in output characteristics (Figure S6), resulting in higher apparent field-effect mobility. Furthermore, phase morphologies, captured by a multitude of characterization means over length scales from 10^{-8} to 10^{-2} m, consistently correlate to electrical transport performance of all four types of TIPS-PEN FET channels. The lowest apparent mobility of the neat TIPS-PEN film is directly attributed to the large voids and un-aligned ribbon crystals, leading to poor percolation and low effective channel width/length (W/L) ratio. The vertical phase segregation facilitated by linear PS giving rise to well-connected ribbon crystals (smallest voids, Figure S4) at the bottom is suitable for bottom-gate, bottom-contact OFETs, although the top-contact device here is injection-limited. While the average TIPS-PEN volume fraction profile obtained by NR of the 4-arm star PS blend is similar to that of the centipede PS blend, its lateral phase separation, visible as ribbon crystals often separated by ribbon voids in optical images, leads to poor percolation and low effective W/L ratio thus low apparent mobility, relative to the centipede PS blend. Overall, the gradient phase segregation afforded by the centipede PS gives rise to a TIPS-PEN-rich injection layer at the top and reasonably well-connected large-area crystals, with triangular rather than ribbon shapes leading to insensitivity to the current direction, together resulting in the highest apparent mobility for the BG/TC device geometry. In addition, subthreshold swing improves in the same trend as mobility, with the lowest corresponding to the centipede PS, since boundaries between conducting domains are usually associated with charge trapping.

To understand the mechanisms underlying our results, we note the following: (1) The major difference caused by different chain architectures is in the compactness of the three types of PS macromolecules of nearly the same molecular weight. (2) The uniqueness of our spray-coating process must play a role in the TIPS-PEN segregation to the bottom of the linear PS blend film, in contrast to small molecule segregation to both sides of spin-coated or drop-coated blend films using linear poly(α-methylstyrene) (PolyMS), similar to linear PS, as the binder. Aggregation of small molecules at top surfaces of previously reported blend films, regardless of
time for TIPS-PEN molecule aggregates to connect laterally, resulting in lateral phase segregation with TIPS-PEN-rich top layers in TIPS-PEN-rich lateral domains. Even faster movement of the more compact centipede PS molecule allows TIPS-PEN molecules to aggregate into a laterally connected top layer, while a decreasing amount of remaining TIPS-PEN molecules precipitate as the solvent drying front moves down, giving rise to the gradient vertical segregation.

While the previous work\(^\text{18}\) has recognized that the interplay between process kinetics and formulation thermodynamics determines the phase segregation, the driving force behind the preferential top-surface segregation of small molecules was solely attributed to surface energy differences, inconsistent with experiments using small-molecule semiconductors less hydrophobic than the polymer binders.\(^\text{23}\) In contrast, this work identifies the important role of the dynamics of the polymer macro-molecules in the process dynamics. To our best knowledge, the TIPS-PEN:linear PS blend represents the first observation of small molecule phase segregation to the bottom of a blend film made of a small molecule semiconductor and a polymer binder with comparable surface energies. We note that significantly higher surface energy of the small-molecule semiconductor with regard to the polymer can also lead to small-molecule segregation at the bottom,\(^\text{19}\) as the influence of thermodynamics becomes more important with longer solvent drying time.

The above mechanisms are supported by MD simulation, which focuses on the radius of gyration and diffusivity of polymer melts for simplicity, to capture the most relevant kinetic behavior at the solvent drying front. Details of the simulation, based on the standard coarse-grained bead-spring model\(^\text{30,31,42}\) are described in the Experimental Section. Briefly, each PS segment of one persistence length (~4 chemical monomers, ~0.9 nm) is modeled as a bead interacting with two nearest neighbors on the chain via a harmonic potential modeled as a spring of Hooke constant \(\kappa\). Nonbonded beads interact by the pairwise WCA potential, which is a purely repulsive, cut off, and shifted L-J potential,\(^\text{42}\) with the interaction range \(\sigma\) being the bond rest length. To manage computational cost, \(N \approx 65\) beads are included in a polymer molecule. Notice that \(N \lesssim N_e \approx 73\), the number of entangled beads, meaning that the model polymer molecule is barely one entangled blob in the tube model.\(^\text{40-42}\) Nevertheless, the small-scale simulation captures the key differences between the types of PS in the kinetics of individual beads (near joining junctions for branched variants). The radius of gyration \(R_g = 19.2\sigma, 12.4\sigma,\) and \(10.8\sigma\) for the linear, 4-arm star, and centipede PS, respectively, consistent with the expectation that more compact molecules are nimbler. The mean-squared displacement (MSD) for the central bead in each type of PS molecule (Figure 6), as a function of time \(t\) of the simulated MD, started from initial configurations (see experimental section), follows the usual transition from the Rouse dynamics (log (MSD) = \(t/2 + \) constant) to the free diffusion regime (log (MSD) = \(t + \) constant). After \(t = 5000\tau\), all three PS types are in the free diffusion regime. Here, the characteristic time \(\tau\) is estimated to be approximately 1 ps, therefore, the free diffusion regime behavior is relevant. The calculated diffusivity ratio is \(D_{\text{linear}}:D_{\text{Star}}:D_{\text{centipede}} = 1.0:1.1:1.3\). In summary, the simulation supports the foundational hypothesis on which our mechanistic understanding of phase segregation in solution-cast small molecule-polymer blends is based, namely that individual chain segments, one persistence length each, in more compact PS chain architectures move more rapidly due to less interchain blocking, thus facilitating small-molecule aggregation and therefore

![Figure 6](image-url)
small-molecule-polymer phase segregation. However, since the molecular weight and polydispersity of the three PS additives are not exactly the same, it is possible that the results reported here are generated by a combined effect of molecular weight and chain architecture. The slight difference and effect of molecular weight, however, are not expected to be mainly responsible for the different phase separation modes discussed here.

4 | CONCLUSION

We have gained a mechanistic understanding of small molecule-polymer phase segregation in solution cast blends, by investigating phase morphologies and electrical transport properties of spray cast TIPS-PEN:PS blend films using three PS variants with different branch architectures but nearly the same molecular weights. Besides polymer branch architecture, another key parameter is the shorter solvent drying time afforded by ultrasonic spray casting, not explored in the previous work. The slow movement of polymer macromolecules is the rate-limiting factor in the phase segregation process in which the polymer must move out of the way for small molecules to aggregate at the solvent drying front. Slow solvent drying leaves sufficient time for even sluggish linear polymers to move, giving rise to the formation, early in the process, of top small-molecule-rich layers invariably observed in the previous work (except the rare case where the small-molecule crystal has significantly higher surface energy than the polymer). In our spray cast film, a short drying time does not allow small-molecule aggregation in the early stage, forcing the formation of a sole small molecule-rich layer at the bottom, which has not been observed before. Consistent with this understanding, relatively nimble 4-arm star PS leads to a thin TIPS-PEN-rich top layer and decreases TIPS-PEN fraction toward the bottom, yet lateral phase segregation is observed because the polymer chains do not move out of the way sufficiently fast for aggregated TIPS-PEN domains to laterally percolate. More telling is the more agile centipede PS, which lends enough time for TIPS-PEN domains to laterally connect, resulting in gradient phase separation with a better lateral connection between TIPS-PEN domains. The achieved mechanistic understanding will guide further optimization of blend-based OFETs, considering the appreciable variation due to phase morphology we have demonstrated here.

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CONFLICT OF INTERESTS

The authors declare that there are on conflict of interests.

DATA AVAILABILITY STATEMENT

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

ORCID
Sanjib Das 🌐 https://orcid.org/0000-0002-5281-4458
James F. Browning 🌐 https://orcid.org/0000-0001-8379-259X
Gong Gu 🌐 https://orcid.org/0000-0002-3888-1427
Kai Xiao 🌐 https://orcid.org/0000-0002-0402-8276

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AUTHOR BIOGRAPHIES

Dr. Jihua Chen obtained a PhD in Macromolecular Science and Engineering from the University of Michigan-Ann Arbor in 2006. He authored and coauthored 150 scientific publications in the field of organic electronics, hybrid nanomaterials, and polymer ionics. He is an R&D staff member at the Center for Nanophase Materials Sciences (CNMS), Oak Ridge National Laboratory since 2011.

Dr. Sanjib Das is currently working as a Process Technology Development Engineer at Intel Corporation. He received his BS degree in Electrical Engineering from Bangladesh University of Engineering and Technology in
2009 and his PhD degree in Electrical Engineering from the University of Tennessee at Knoxville in 2015. After that, he worked as a postdoctoral fellow at Northwestern University in Prof. Bruce Wessels’ group, where he worked on developing radiation detectors at room and low temperatures. His research interests include advanced semiconductor chip design and nanofabrication.

Dr. Ming Shao is now a professor at Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, China. He received his PhD in Materials Science and Engineering from the University of Tennessee, Knoxville. After that, he worked as a postdoctoral fellow at Oak Ridge National Laboratory. His current interests have included organic and hybrid optoelectronics (e.g., photovoltaics, thin-film transistors etc.), spintronics, and flexible/stretchable electronics.

Dr. Gong Gu is a Professor of Electrical Engineering at the University of Tennessee, Knoxville. His research interests are in novel materials for electronic device applications. He received his PhD degree in 2000 from Princeton University and his Bachelor’s from Tsinghua University, Beijing.

Dr. Kai Xiao is a senior staff scientist at the Center for Nanophase Materials Sciences of Oak Ridge National Laboratory and a joint faculty at the Department of Computer Science and Electrical Engineering and Bredesen Center, the University of Tennessee at Knoxville. He received his PhD in Physic Chemistry from the Institute of Chemistry, Chinese Academy of Sciences in 2004. His research focuses on understanding and controlling the synthesis and processing of functional nanomaterials, including 2D quantum materials, organic semiconductors, and halide perovskites for new generation electronic and quantum devices for energy conversion, nanoelectronics, and flexible electronics. More information can be found on his website: https://kaixiao.ornl.gov.

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