Sub-Micrometer Structure Formation during Spin Coating Revealed by Time-Resolved In Situ Laser and X-Ray Scattering

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Solution-processed thin polymer films have many applications, such as organic electronics and block-copolymer nanofabrication. These films are often made by spin coating a solution that contains one or more solids and can show different phase-separated structures. The formation mechanism of the droplet-like morphology is studied here by processing polystyrene (PS) and a fullerene derivative ([6,6]-phenyl-C71-butyric acid methyl ester, [70]PCBM) from o-xylene. The final structure consists of [70]PCBM droplets partially embedded in a PS-rich matrix showing interdomain distance of 100–1000 nm as determined from transmission electron microscopy and grazing incidence small angle X-ray scattering (GISAXS). To elucidate the formation of these morphologies in real time, ultrafast in situ GISAXS coupled with laser interferometry and laser scattering is performed during spin coating. In situ thickness measurements and laser scattering show that liquid–liquid phase separation occurs at ≈70 vol% solvent. Subsequently, in only 100–400 ms, almost dry [70]PCBM domains start to protrude from the swollen PS-rich matrix. These results are used to verify the ternary phase diagram calculated using Flory–Huggins theory. The discussed multitechnique approach can be applied to study fundamental aspects in soft matter such as phase separation in thin films occurring at very short time scales.

1. Introduction

Solution processing is greatly appreciated in many device manufacturing fields due to its ease, flexibility, and capability for high-throughput device fabrication. Fields that use solution processing to their advantage are, for example, organic photovoltaics,[1] polymer/nanoparticle hybrids,[2] and block-copolymer nanolithography.[3] Independent of the technological application, control over the structure and feature size that characterize the formed morphology is required. For example, in organic photovoltaic cells, it has been shown that the morphology has a profound effect on the solar cell efficiency.[4] A large variety of morphologies are encountered depending on the used materials, solvents, and processing conditions. Possible morphologies include bicontinuous phases, with length scales above 1 µm,[5] droplets dispersed in a continuous phase with size of several micrometers,[6] or...
below 1 µm, fibrous networks, and homogeneously mixed films. To control the morphology it is crucial to understand the mechanisms that govern the phase-separation process, which is often determined by the occurrence or the absence of liquid–liquid phase separation. As this process occurs during the drying of the wet film, it is essential to investigate the dynamics of these processes in real time with in situ tools.

Although the fundamental physics of liquid–liquid phase separation in systems with evaporating solvents is very relevant, many theoretical and experimental questions remain still unsolved. The theoretical aspects are mainly related to the complexity of the system, which requires thorough 3D models, including the evaporation of one of the three components and a free liquid/air interface. Experimentally, similar difficulties are encountered. Ideally, one would record the full 3D structure on length scales of 100–1000 nm and on time scales in the order of milliseconds. These dimensions are complicated to analyze by visible light scattering, because the feature size is similar to the wavelength of visible light. Similarly, they are too small to be studied by optical microscopy, although real-space imaging has been successfully used to study in situ the phase separation on >1 µm length scale. Among the available in situ techniques, synchrotron X-ray-based methods like grazing-incidence wide-angle X-ray scattering (GIWAXS) and grazing-incidence small-angle X-ray scattering (GISAXS) are ideal to investigate structure evolution in thin films. In particular, GISAXS can provide structural information on 10–1000 nm length scales. When performed at synchrotrons, GISAXS becomes one of the best techniques to follow in situ structural evolution in thin films. Up to now, in situ GISAXS and GIWAXS studies have been mostly conducted on length scales <50–100 nm with moderate as well as fast time resolution, while examples of in situ GISAXS investigations on length scales up to 1000 nm with subsecond time resolution are rare, especially in soft matter.

An interesting model system giving features with size in the range of 100–1000 nm is the blend of polystyrene (PS) and [6,6]-phenyl-C_{71}-butyric acid methyl ester ([70]PCBM) in o-xylene. When mixtures of PS and [70]PCBM are cast into thin films from a dilute o-xylene solution, the increase in concentration and the consequently enhanced interaction between the PS and [70]PCBM solutes during evaporation of the solvent cause spinodal decomposition of the liquid. This mode of phase separation renders an eventual dry film morphology consisting of a [70]PCBM-rich droplet-like phase dispersed in a continuous PS-rich matrix. Apart from the mentioned fundamental aspects, potential applications of such droplet-forming systems include ferroelectric memories and microporous membranes, and construction of diffuse reflectors. Similar droplet-like features also form in solution-processed films for organic solar cell applications and have been relatively well studied. As observed for many other demixing blends, thin films of these droplet-like morphologies have a significant surface topography, which is often determined by the occurrence or the absence of such morphologies can differ. Droplet-like protrusions may, for instance, result from strong solvent partitioning across the phases or the presence of dynamic asymmetry imparted by a difference in molecular size between the solutes or a difference in glass temperature between the phases. Because these features inherently impart surface topography and form within seconds, these systems are challenging to investigate in situ.

In this contribution, we develop a multitechnique approach to meet these experimental challenges. We combine in situ high-resolution ultrafast GISAXS measurements (time resolution: 33 ms) with simultaneous laser scattering and thickness measurements by laser interferometry to study the formation and time evolution of [70]PCBM droplet-like domains in a PS-rich matrix during spin coating. For the final layer morphology, there is an excellent agreement between the GISAXS scattering features (probed area >10 mm²) and the local structure investigated by transmission electron microscopy (TEM) and atomic force microscopy (AFM) (probed area <100 µm²). Extensive simulations of GISAXS scattering patterns facilitate the identification of scattering contributions from both the embedded and the surface structures. The multitechnique in situ approach allows analyzing the temporal evolution of the film formation during drying in terms of thinning of the liquid layer, followed by phase separation and the formation of liquid droplet-like domains in a liquid matrix. Solvent fractionation results in dry films characterized by surface features caused by [70]PCBM domain protrusion, because the [70]PCBM-rich and the PS-rich liquid phases contained different amounts of solids. Using our multitechnique approach, we show how this complex sequence of events occurs within a temporal window of only 100–400 ms.

2. Results and Discussion

The aim of this work is to elucidate the mechanism of formation of small-molecule-rich droplet-like domains inside a polymeric matrix as a result of spinodal liquid–liquid phase separation occurring during spin coating. To achieve this goal, we use here a multitechnique approach, based on a combination of laser light and X-ray scattering techniques. Although the main focus is on the in situ study, it is first necessary to analyze the final film morphology in order to understand the in situ results. We therefore start this section with the real-space morphological analysis by microscopy techniques, followed by the analysis of the final morphology by GISAXS. We then introduce GISAXS modeling which is essential to interpret the in situ results. In the remaining part of the paper, we will discuss the in situ results of our multitechnique approach.

2.1. Dry-Layer Morphology by TEM and AFM

Blends of PS and [70]PCBM (concentrations: 3:6, 6:12, and 9:18 mg:mg mL^{-1}) in o-xylene have been spin-coated on a silicon substrate covered by a 30–40 nm thick layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS). The hygroscopic PEDOT:PSS layer is primarily used because it allows the blend films to be removed from substrate by floating in water, which is necessary to prepare the samples for TEM. Additionally, PEDOT:PSS is often used as an interface layer and a substrate for spin coating photoactive layers of organic solar cells for which PS:[70]PCBM serves as a model system.
TEM and AFM images shown in Figure 1 indicate that droplet-like morphologies are formed. The darker contrast in the cross-sectional image indicates that the domains are [70]PCBM rich, while the matrix phase is PS rich. This morphology is virtually identical to the one observed in photoactive blends of semiconducting polymers and [70]PCBM.\textsuperscript{[7,11]} The height of the domains is about 65 nm as shown by cross-sectional TEM (Figure 1c). Higher-magnification images of the cross-sectional sample are shown with detailed dimensions in Figure S1 (Supporting Information.). The average interdomain distance \(d_{\text{interdrop}}\) is extracted from low-magnification TEM images by Fourier transformation and detected as a peak in the radially averaged Fourier transform (FT; Figure 1d).\textsuperscript{[11]} In order to characterize the curvature of the top surface of the domains, we have extracted the slope at the edge of the domains from the AFM images (Figure 1e; see Section S2 in the Supporting Information). The dominant slope corresponds to an angle of \(\approx 16^\circ\), which is smaller than \(\approx 25^\circ\) measured in the cross-sectional TEM image in Figure 1c. However, the latter value is only based on a very small amount of domains. A more reliable value will be calculated further in the manuscript by GISAXS.

2.2. Dry-Layer Morphology by GISAXS

In addition to the real-space analysis by microscopy, the morphology of the [70]PCBM domains can be studied in great detail by 2D GISAXS. Previous studies have shown how GISAXS can be used to study the dewetting of thin polymer films, being able to resolve objects with dimensions up to several hundreds of nanometers.\textsuperscript{[36,37]} A GISAXS pattern for a sample prepared in exactly the same way, as those shown in Figure 1, is shown in Figure 2a as a function of the in-plane scattering angle \(2\theta\) and the vertical

![Figure 1](image1.png)

**Figure 1.** Analysis of the final morphology for PS:[70]PCBM thin films obtained by spin coating a 6:12 mg:mg mL\(^{-1}\) solution in \(\alpha\)-xylene at 2900 rpm. a) TEM image. b) AFM height image. c) Cross-sectional TEM image. All layers are clearly visible, starting from the bottom: Si | SiO\(_2\) | PEDOT:PSS | PS:[70]PCBM | Pt. Pt is used as a protective layer when making the cross-sectional sample. d) Power spectral density function as a function of the inverse length \(s\) obtained by radially averaging the Fourier transform of a low-magnification TEM image, which shows a clear peak (indicated by the red arrow) that corresponds to an average interdomain spacing of \(\approx 550 \text{ nm}\).\textsuperscript{[11]} e) Analysis of the AFM images, the steepest slope at the edge of all domains calculated and plotted in the histogram.

![Figure 2](image2.png)

**Figure 2.** a) GISAXS image for PS:[70]PCBM thin films obtained by spin coating a 6:12 mg:mg mL\(^{-1}\) solution in \(\alpha\)-xylene at 2900 rpm. S represents the specular beam; Y the Yoneda peaks; and RoS the inclined rods of scattering. The intensity map is displayed on a logarithmic scale with arbitrary units. b) In-plane GISAXS intensity as a function of the lateral scattering momentum \(q_y\) calculated at \(q_z = 0.38 \text{ nm}^{-1}\) (\(\alpha_f = 0.12^\circ\)), that is at the Yoneda peak position of the material. c) Vertical GISAXS intensity as a function of the normal scattering momentum \(q_z\) calculated at \(q_y = 0.011 \text{ nm}^{-1}\). The angle of incidence was \(\alpha_i = 0.24^\circ\), larger than the critical angles for the studied materials.
scattering angles $\alpha$. Five main features are detected for all analyzed PS:[70]PCBM thin films (Figure 2a; see also Figure S3 in the Supporting Information). (i) Along the specular direction ($2\theta_i$ and $q_y = 0$), a bright specular rod is detected together with the specularly reflected beam (indicated with S). The reflected beam is located at an exit angle equal to the angle of incidence $\alpha_i = 0.24^\circ$ and it is blocked by the beam stop. (ii) The region around $\alpha_i = 0.1^\circ$ is dominated by multiple maxima along the vertical direction, the so-called Yoneda peaks (denoted with Y), that are given by the maximum in the Fresnel transmission function and are located at exit angles equal to the critical angles $\alpha_c$ of the materials. Since the critical angle depends on the sample density, the Yoneda peak position is an indication of the material density. For all the prepared films, the Yoneda peaks are located at the same exit angles. (iii) The in-plane intensity along the $q_y$ direction (with $q_y = 2\pi/\lambda\sin(2\theta_i)\cos(\alpha_i)$) is dominated by one main scattering peak located at small $q_y$ values and indicated as $q_y^{\text{max}}$ in Figure 2b. The scattered intensity is the Fourier transform of the pair-distance distribution function, the presence of a main correlation peak located at $q_y^{\text{max}}$ in the in-plane direction is related to the existence of an average interdomain distance that can be derived using Bragg's law as $d_{\text{interdom}}^{\text{max}} = 2\pi/q_y^{\text{max}}$. The broad nature of this scattering peak and the lack of any higher-order reflections denote an in-plane lattice without long range order for the [70]PCBM domains. This is in agreement with the TEM image in Figure 1a. For the sample obtained by spin coating a 6:12 mg-mL$^{-1}$ solution in o-xylene at 2900 rpm an interdomain distance of 560 nm is observed in agreement with the value extracted from the TEM images (580 nm). This Bragg peak associated with the positional order of the [70]PCBM domains is described by the structure factor of the system, as it will be described in the next session. (iv) Several modulations of the intensity are observed in the intensity cut along the vertical $q_y$ direction and taken at $\alpha_i = 0.12^\circ$ (with $q_y = 2\pi/\lambda\sin(\alpha_i) + \sin(\alpha_i)$). These intensity oscillations present in the vertical cuts (Figure 2c) are related to the characteristic length scales of the objects in the direction perpendicular to the substrate. In particular, two main modulations are observed in Figure 2c: one low-frequency modulation at high $q_y$ values, which is related to the [70]PCBM domains, and another one at higher frequency immediately after the Yoneda peaks, which is related to the existence of intermediate layers between the substrate and the droplet-like domains. A detailed analysis of these modulations is challenging due to the presence of more than one layer, and as such modeling is required to understand these modulations (see Section S4 in the Supporting Information). (v) Finally, the out-of-plane scattering intensity is dominated by several inclined streaks or rods of scattering (indicated with RoS in Figure 2a). Inclined RoS are usually expected and have been observed for faceted islands, where the tilt angle between the RoS and the normal to the surface gives directly the tilt angle between the facet and the substrate. Inclined RoS are also expected in GISAXS from objects with curved surfaces like the hemispherical shape of the droplet-like domains as shown in the next section and confirmed by GISAXS pattern simulations in Section S4 of the Supporting Information. Since the inclined RoS are related to the statistical dependence of the particle diameter and height, their inclination is directly related to the curvature of the objects. The tilt angle between the RoS and the surface normal in Figure 2a is about $22^\circ$. This compares well to the domain curvature angle extracted from the AFM/TEM.

2.3. Modeling of the GISAXS Scattering

A detailed analysis of the GISAXS images using different morphological models is reported in Section S4 of the Supporting Information. In order to reproduce the X-ray scattering features, such as correctly shaped RoS, it is essential to use the correct shape of the scattering objects in the GISAXS simulations. We found that the system is qualitatively well described by an ensemble of flattened hemispheroids supported on a substrate with two intermediate layers (PEDOT:PSS and SiO$_2$), in agreement with cross-sectional TEM images (Figure S4d, Supporting Information). However, more extensive analysis was not possible using such a simplified model. The real system features a [70]PCBM domain consisting of a bottom part embedded in a PS matrix and a top protruding part, as shown by cross-sectional TEM. Thus, the scattering from both the embedded and the protruding part is expected to contribute to the final GISAXS intensity. The question that rises is if the contrast from the embedded part is sufficient to be detected with respect to the signal from the protruding part. Based on the theoretical atomic scattering factors and the densities of the pure materials, we can estimate the expected contrast terms for the embedded part and the protruding part, assuming the phases consist of pure materials. For both SAXS and GISAXS, the scattered intensity is proportional to the contrast of the dielectric constants between the scatterer and the embedding medium, and it can be expressed as the difference between the respective index of refraction. For X-rays, the index of refraction is $n = 1 - \delta - i\beta$, where $\delta$ is the dispersion and $\beta$ is the absorption term. The theoretical values of $\delta$, $\beta$, and $n$ for the [70]PCBM and PS are listed in Table S1 (Supporting Information). The ratio between the contrast factors for the protruding part $(n_{\text{PS}}/n_{\text{Xr}} - 1)$ and the contrast factor for the embedded part $(n_{\text{Xr}}/n_{\text{PS}} - n_{\text{Xr}} - 1)$ is about 6. This difference in scattering contrast will make it challenging, but not impossible to resolve internal phase separation. We have thus introduced a model capable of describing the scattering from a semiembedded [70]PCBM cylinder with a hemi-}

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both the embedded part and the protruding part of the objects (Figure 3c, and more details in Section S4 of the Supporting Information). The different simulations performed demonstrate that the effect of only the protruding part of the [70]PCBM domains (surface topography) would produce a scattering peak centered at the same $q_y^\text{max}$ value as the full model simulations (see Figure 3b and Figure S5 in the Supporting Information). The same holds for the isolated effect of the embedded part. However, only the full model reproduces the correct shape of the in-plane scattering curve, suggesting that the GISAXS data are sensitive to the overall object shape, given by both the embedded and the protruding part. As expected, modeling of the isolated contributions shows that the experimental signal intensity is dominated by the scattering contribution from the protruding part of the [70]PCBM domains (the surface topography).

In summary, crucial morphological information can be extracted from the GISAXS images. The main in-plane scattering peak is the strongest signal, and its position measures the interdomain distance, while its intensity is most sensitive to the surface features. The shape of the in-plane intensity is related to the diameter of the embedded part. The less intense out-of-plane signals are related to the shape and height of the surface features (inclined RoS).

2.4. In Situ Measurements

The droplet-like morphologies originate from liquid–liquid phase separation.[7,30] This droplet-like domain formation thus occurs in a layer that is still wet, i.e., there is still a significant amount of solvent present. To study the process of domain formation in situ, we have to focus on the real-time dynamics, shortly before the spin coating film dries. We have thus used a combined multitechnique approach to study the system evolution in real-time over different length scales by performing laser interferometry, laser scattering, and GISAXS. The experimental setup is shown in Figure 4. In short, the intensity of the specular reflection of the laser light is used to calculate the wet layer thickness at each point in time via interferometry once the final thickness is known.[11] Laser scattering detects lateral variations in the complex refractive index, and as such is very sensitive to the onset of liquid–liquid phase separation. However, because the scattered light intensity is only measured for one specific angle, it does not contain any information on the size and shape of the scattering features.[11] This lack of length scale and shape sensitivity is compensated by GISAXS that provides a complete morphological picture. Moreover, in our specific case, GISAXS will clearly detect when the surface topography is established, and the domains start to protrude from the film surface. It should be stressed that all three in situ measurements are acquired simultaneously during spin coating with high temporal precision. The spinning motor of the spin coater device is started at time $t = 0$ s, which triggers both laser-based experiments and GISAXS acquisition to start simultaneously. Details on how the three measurements are performed simultaneously and discussion about temporal resolution are reported in Section S7 of the Supporting Information. The three measurements are discussed separately and in more detail in the following sections.
Measuring the time evolution of the layer thickness is essential as it allows us to calculate the volume fraction of solvent and solids over time. Laser interference is chosen to study the time evolution of the wet-layer thickness, as this is relatively easy to implement experimentally and is very fast.[11,43,44] The incident laser is reflected both on top of the wet film and on the film–substrate interface. The decreasing layer thickness (because of solvent evaporation) causes a repetitive occurrence of constructive and destructive interferences between these two reflections. This results in an oscillation of the intensity of the specularly reflected laser beam, as shown in Figure 4 (red curve). By measuring the dry-layer thickness with profilometry and using a backcalculation algorithm, we extract the thickness evolution during spin coating. In the second panel of Figure 5a, two different calculation algorithms are used. First, a peak-counting method is employed. For a better reconstruction in the final portion of the interference curve, a transfer-matrix method is used to solve the Fresnel equations;[45,46] see Section S6 of the Supporting Information for more details. It must be stressed that both methods assume a perfectly flat layer, which is evidently not true for the final film. This will cause a discrepancy in absolute values of solvent content calculations. However, we believe that all trends which we observe are real and not significantly affected by this assumption.

Apart from the specular reflection of the laser, a significant fraction of the incident light is scattered onto off-specular angles.[11,44] A fraction of this scattered light is measured by...
a second photodiode and displayed as well in Figure 5a (third panel, blue curve). Note that because of the high intensity of specular reflected light, some of the interference signal is also collected by the scattering photodiode and superimposed to the scattered signal. However, the onset of light scattering can be clearly seen at $t_{\text{onset}}^{LS} \approx 4.78\text{ s}$. Light scattering can be caused by both surface topography and differences in the complex refractive index between different domains. The large difference in the complex refractive index between the two solid materials ($n_{\text{PS}} = 2.07 + 0.09i$ and $n_{\text{PCBM}} = 1.59$) will result in significant light scattering as soon as large-scale phase-separated domains of these materials are formed, even when no surface topography appears. Second, because the angle of incidence of the laser ($\approx 45^\circ$) is much larger than that of the X-rays, laser scattering will be much more sensitive to embedded phase separation. However, no particular length scale can be extracted from laser light scattering, as we only probe the intensity at a single scattering angle and not the angular distribution of the scattered light.

With the aim to associate a length-scale with the laser results and to follow the structural evolution of the film in real time, GISAXS experiments have been simultaneously carried out. Full 2D GISAXS images have been recorded with a time resolution of 0.033 s (see Section S9 and Figure S11 in the Supporting Information). The evolution of the integrated horizontal in-plane intensity (along $q_y$) and of the vertical (along $q_z$) GISAXS intensity is reported in Figure 5a (bottom panel). As a result of the enhanced scattering intensity at the Yoneda peak position ($q_y = q_{\text{Y}}$), the GISAXS signal along the $q_y$ direction (in-plane) can be collected with sufficiently high time resolution to follow the ultrafast domain formation. The evolution of a selection of in-plane GISAXS intensity cuts as a function of time is reported as a map in Figure 5b and as intensity versus $q_y$ over time in Figure 5c. At first, the GISAXS intensity is given by the incoherent X-ray scattering due to the absence of any structural features in the solution directly after starting the spin coating. In the first stage of the spin-coating process ($t < 0.3\text{ s}$), a large portion of the solution is ejected laterally. As the scattered $X$-ray intensity is proportional to the amount of sample crossed by the X-rays, the diffused GISAXS intensity first decreases strongly. The intensity subsequently decreases with time as a result of the drying of the wet layer, which further decreases the thickness. Following that, the onset of laser scattering ($t_{\text{onset}}^{LS} \approx 4.78\text{ s}$) indicates that separated phases are formed. The PS-rich and the [70]PCBM-rich domains are highly swollen and are most likely still embedded in the wet film, i.e., there is not yet any significant protrusion of the [70]PCBM-rich domains from the film surface. At the same time, first, a small increase of the in-plane GISAXS scattering intensity is observed without the presence of a clear Bragg peak, as a consequence of the weak X-ray scattering from the embedded highly swollen domains and the absence of a well-defined interdomain distance. Conversely, a sharp intensity increase of the in-plane GISAXS signal is detected at $t_{\text{onset}}^{GISAXS} \approx 4.95\text{ s}$, and it is associated with the appearance and growth in intensity of a clear Bragg peak centered at $q_y = \pm 0.011\text{ nm}^{-1}$. The presence of a Bragg peak from the structure factor of the system is associated with the appearance of a well-established nearest neighbor distance of about 570 nm among the [70]PCBM domains. This value is in agreement with static GISAXS measurements and TEM. In time, the in-plane intensity rapidly increases, reaching its final values in about 0.15 s. On the basis of GISAXS simulations (Figure 3b), we attribute this sharp increase of the GISAXS signals to the formation of surface features caused by the [70]PCBM domain protrusion. We propose that the establishment of the surface topography is associated with a faster drying of the [70]PCBM domains, which causes the [70]PCBM domains to start to protrude from the PS-rich matrix in the final stage of drying. This mechanism is explained in detail below in Section 2.6. Interestingly, no significant peak shift is observed for all the spin coating conditions used, i.e., once observed by GISAXS the interdomain distance does not change with solvent evaporation. This indicates that the number of domains does not change after the appearance of the surface topography, and thus no further ripening or coalescence of domains is observed.

The evolution of the integrated vertical GISAXS intensity (along $q_z$) follows very close that of the horizontally scattered one. Interestingly, within the period of time between the laser scattering onset ($t_{\text{onset}}^{LS} \approx 4.78\text{ s}$) and the GISAXS onset ($t_{\text{onset}}^{GISAXS} \approx 4.95\text{ s}$), only a moderate increase in the vertical scattered GISAXS intensity is observed, while a clear Yoneda peak and the oscillations due to the [70]PCBM domains are absent. However, laser scattering and in-plane GISAXS both indicate beginning of the phase-separation process (see Figure S12 in the Supporting Information). The absence of a clear Yoneda peak can be explained by the presence of a liquid film covering the substrate and decreasing the electron density fluctuations at the interfaces. At $t_{\text{onset}}^{GISAXS} \approx 4.95\text{ s}$, the Yoneda peak and at least one oscillation relative to the [70]PCBM droplet scattering in the direction perpendicular to the substrate start to appear and evolve rapidly with time (Figure S12b, Supporting Information). Unfortunately, due to their weak nature (about 100 times lower than the in-plane one) and the short exposure time, the out-of-plane scattering features (i.e., inclined RoS) cannot be properly resolved in real time, preventing quantitative analysis of the evolution of the droplet dimension with time (see Figure S11 in the Supporting Information).

### 2.5. Influence of Drying Rate

We have shown previously that the evolution of the interdomain distance scales with the normalized drying rate (the drying rate divided by the final film thickness) rather than the drying rate or the film thickness.

Here the drying rate is defined as the rate of the wet-layer thickness change during spin coating (nm s$^{-1}$). In the final part of the solvent evaporation, this drying rate is constant. We have thus plotted our results for the interdomain distance of the PS:[70]PCBM films as a function of the normalized drying rate (Figure 6a).

As expected, the evolution of the interdomain distance obtained by both GISAXS and TEM scales with the normalized drying rate $\alpha$ according to the equation $d_{\text{interdom}} = \alpha^b$ (Figure 6a). A slightly different value of exponent $b$ is found ($b = -0.35 \pm 0.04$ from TEM and $b = -0.26 \pm 0.04$ from GISAXS). A considerable discrepancy between GISAXS and TEM results is observed for the lowest drying rates used. This could be due
The solvent content can be approximated as $\phi_{\text{dry}} = 1 - \frac{\text{dry layer thickness}}{\text{wet layer thickness}}$. At the onset of the laser scattering, the solvent content is calculated to be $70 \pm 5$ vol% (Figure 6b), independently of the normalized drying rate. Due to the fast drying rate, small feature size, and thin layers, we do not observe any light scattering for the fastest-dried films. On the other hand, the steep increase in the GISAXS intensity at the $t_{\text{onset GISAXS}}$ always occurs shortly before the final film thickness is reached, i.e., when most of the solvent has evaporated. The GISAXS signal levels off exactly when the final film thickness is reached, as all the solvent has evaporated and the system morphology cannot further evolve. The solvent content at the onset of the strong GISAXS signal is always below 60 vol%. We do not observe a clear relation with drying rate. As the time resolution of GISAXS is lower than that of laser scattering and the solvent content is low, the solvent content at the GISAXS onset is subject to a larger uncertainty. However, the difference in the onset time (i.e., in the solvent content) measured by laser and GISAXS is well above the experimental errors. Thus, we always observe internal phase separation with laser scattering before we observe the formation of surface features with GISAXS. The results in Figure 6 extend the findings discussed in the previous sections to multiple solution concentrations and drying rates.

2.6. Mechanism of Droplet Formation

Based on the in situ results shown here from the three different applied techniques, the following mechanism for the droplet-domain formation can be inferred (Figure 7a). (I) In the beginning, the ternary PS:PCBM:o-xylene mixture is homogeneous, and only a change in film thickness occurs. Accordingly, the scattered GISAXS intensity (Figure 5a) decreases with time as a result of the decreasing thickness. (II) At the onset of laser scattering ($t = t_{\text{onset LS}}$), the system undergoes internal phase separation into [70]PCBM-rich and PS-rich domains which are highly swollen (average $\phi_{\text{dry}} = 70\%)$. This is most probably the point where the unstable region of the phase diagram is entered and where liquid–liquid phase separation occurs. [70]PCBM-rich droplet-like domains phase separate from a PS-rich matrix, which causes an increase in the laser light scattering signal as governed by the difference in the complex refractive index. This stage of the phase separation process occurs in a liquid film covering the substrate (as evidenced by the absence of a clear Yoneda peak) whose thickness is of the order of a few hundreds of nanometers. At this point, the electron density contrast between the two phases is quite small due to the high solvent content and because of a possibly incomplete phase separation between PS and [70]PCBM. Therefore, the contrast for X-rays is still low. (III) At the large increase in scattering intensity for GISAXS ($t = t_{\text{onset GISAXS}}$), the average solvent content is well below 60%. Solvent fractionation is expected to occur, i.e., the solvent content in the [70]PCBM-rich domains which are highly swollen becomes lower than the solvent content in the PS-rich matrix due to the larger affinity of o-xylene for PS (see Section S10 in the Supporting Information). Due to solvent fractionation, the [70]PCBM-rich domains will dry earlier than the PS-rich

![Figure 6](https://www.afm-journal.de)

**Figure 6.** a) The interdomain distance of dry-layer morphologies as a function of the normalized drying rate. b) Solvent content at the onset of the laser scattering (due to internal phase separation, blue squares) and at the onset of the strong GISAXS signal (due to surface topography, orange circles). For laser scattering, the error bars indicate the difference between the peak-counting method and the transfer-matrix approach. For the orange points, the transfer-matrix approach is used, and error bars are based on the time uncertainty in the GISAXS onset.

to several reasons like (a) the limited GISAXS resolution at the very small angles (larger distances are detectable at lower angles where the detector pixel size becomes critical and also the signal overlaps with the bright specular rod) and (b) a larger error in computing the FT of TEM images containing lower amount of large droplets. However, considering the limited range of drying rates in this experiment, we can consider that exponent $b$ calculated from both the results of TEM and GISAXS is in agreement with previously reported data ($b = -0.35 \pm 0.04$).\(^{[11]}\) Physically, an exponent of $b = 0.3$ is indicative for droplet coarsening being diffusive and occurring predominantly via Ostwald ripening, for which the growth rate of the average droplet radius inversely scales with the domain surface area. Hence, the typical domain size scales as $x^1$. If the evaporation rate determines the time available for coarsening, a similar exponent is expected from a plot expressing domain size as a function of evaporation rate.

\[ \phi_{\text{dry}} = 1 - \frac{t_{\text{dry layer thickness}}}{t_{\text{wet layer thickness}}} \]
matrix. Because of continued solvent evaporation from the PS-rich phase, the [70]PCBM-rich domains start to protrude from the PS-rich matrix. A scattering peak appears, centered at $q_{\text{max}}$ and related to the appearance of a well-established interdomain distance. The peak intensity rapidly increases, while $q_{\text{max}}$ is time independent. (IV) The solvent evaporation is finished and the final morphology is reached. Although we cannot provide quantitative estimation, at the end of the phase separation process some molecularly dissolved [70]PCBM and very small aggregates could be present in the PS phase.

At moment III, where we expect the [70]PCBM domains to start protruding from the PS-rich matrix, we assume that there is $\approx 50\%$ solvent left in the PS-rich phase. From the onset of intense GISAXS signal, we know that the average solvent content at that moment is below 60% (Figure 6b). We then make the rough assumption that the [70]PCBM-rich domains are fully dry when they start to protrude from the PS-rich matrix. Then we can extract a value of $\approx 50\%$ solvent content from the thickness difference between the [70]PCBM domains and the PS-rich matrix in the cross-sectional TEM (Figure S1, Supporting Information). The same thickness difference of $\approx 50\%$ can be extracted from the combination of the AFM data with the total layer thickness as measured by profilometry.

Despite the fact that the film formation process during spin coating of a blend solution occurs too fast to render a dry-layer morphology corresponding to global thermodynamic equilibrium, the in situ results reported here can be used to verify the theoretical ternary phase diagram. This is understood as follows: because early-stage decomposition is very fast, thermodynamic equilibrium is reached at a local scale, with fullerene- and PS-rich phases at corresponding binodal compositions, i.e., being at the same chemical potential. In the subsequent late-stage regime, the only dynamic processes further minimizing the free energy toward global equilibrium are those that reduce liquid–liquid interface, such as coalescence and ripening. As these processes are driven by composition gradients, they are not directly related to the ternary phase diagram, which is obtained by taking derivatives of the homogeneous mixing free energy expressed in terms of the composition defined as a local quantity.

We have calculated the approximate isothermal phase diagram of the ternary blend PS:[70]PCBM:o-xylene by means of Flory–Huggins theory (Figure 7b). As discussed in Section S10 in the Supporting Information, the driving force for liquid–liquid phase separation is given by the repulsion between PS and [70]PCBM. Despite the fact that the Flory–Huggins theory is expected to, at best, give a semi-quantitative description of the blend, the observed phase dynamics taking place during solvent evaporation is in good agreement with the calculated phase diagram. The red arrows indicate the approximate sequence of events occurring during drying (schematically depicted in Figure 7b): I $\rightarrow$ II entrance of the miscibility gap at about 70–80 vol% of solvent, resulting in composition bifurcation, including solvent fractionation. Then, from II $\rightarrow$ III further solvent fractionation occurs until moment III, when the domains start to protrude from the PS matrix. Note that domain coarsening can occur only in the narrow time window between moments II and III. However, we were not able to measure any domain coarsening or the absence thereof due to the low X-ray contrast at this stage. Finally, from III $\rightarrow$ IV the system approaches the dry state, where the PS-rich matrix also dries completely.

The onsets of the laser scattering and low-intensity GISAXS signals are in excellent agreement with the location of the miscibility gap. The fact that upon bifurcation the solvent resides
preferentially in the PS-rich phase, as demonstrated by the tilt in the tie lines (in brown), is in agreement with the observation of protruding [70]PCBM-rich domains. Note that the present diagram suggests demixing to take place at the moment the spinodal is crossed. However, due to the approximate nature of the Flory–Huggins equation and the uncertainty in the values of the binary interaction parameters (see Section S10 in the Supporting Information), we cannot exclude that demixing already starts in the metastable region.

The shape and size of the miscibility gap, indicated by the binodal (blue) as well as the region of instability, indicated by the spinodal (green), are reminiscent of those calculated earlier for the photoactive blend of PDPPST, [70]PCBM, and CHCl3. Due to the asymmetry resulting from the considerable size difference between the solid blend components, demixing yields a PS-rich phase containing a significant fraction of [70]PCBM and a virtually pure fullerene-rich phase. This good correspondence between the phase diagrams of these two blends is perhaps surprising given the fact that PDPPST probably has a higher chain stiffness than polystyrene. On the other hand, a quick calculation (see Section S10 in the Supporting Information) reveals that the contour length of our PDPPST polymer considerably exceeds its (estimated) persistence length, which rules out a rigid rod conformation and associated influence on blend phase behavior. We must stress that the morphology formation via liquid–liquid spinodal demixing as observed for PS:PCBM and PDPPST:PCBM is not ubiquitous for photovoltaic blends. For instance, in poly(3-hexylthiophene) (P3HT):PCBM blends, subdomains of crystallization-induced phase separation have been reported upon drying following the first solvent evaporation stage. This crystallization-induced aggregation results in a morphology that is dominated by the length scales of the P3HT crystals pushing apart the PCBM molecules and forcing them to aggregate, regardless of the processing method employed (spin coating or slot-die printing).

3. Conclusions

The PS:[70]PCBM mixture used in this study phase separates into sub-micrometer-sized [70]PCBM droplet-like domains inside a PS-rich matrix when spin-coated from o-xylene. As a result of solvent partitioning, the final morphology of dry films is composed of [70]PCBM droplet-like domains protruding from the PS-rich matrix, with the [70] PCBM height approximately twice the PS-rich matrix height. GISAXS simulations inspired by the structures observed in cross-sectional TEM show that the [70]PCBM domains can be well described as consisting of a cylindrical part embedded in a PS-rich matrix with a protruding hemispherical cap. The [70]PCBM domains are polydispersed in size, especially in the in-plane direction, and arranged in a 2D disordered manner (i.e., no long range order). The interdomain distance ranges from 100 to 1000 nm and scales, as expected, with the normalizing drying rate (drying rate/film thickness). GISAXS simulations indicate that the contribution to the GISAXS intensity of the embedded [70]PCBM domains is small, and most of the X-ray scattering signal arises from the formation of surface features due to the protruding part of the [70]PCBM domains.

Studying the mechanism of formation of such droplet-like domains during spin coating represents a challenging task because of their sub-micrometer dimensions and the very short processing time. To tackle this challenge, the mechanism of sub-micrometer domain formation has been investigated here by using a multitechnique approach providing ultrafast time resolution. Using laser-based thickness measurements and laser scattering during spin coating, we detect a first onset of phase separation at ~70 vol% solvent. This onset is attributed to liquid–liquid demixing of PS-rich and [70]PCBM-rich phases. The PS-rich and the [70]PCBM-rich domains are highly swollen and probably still embedded in the wet film (i.e., there is no significant surface topography). Due to the weak nature of the GISAXS scattering intensity and, probably, the lack of spatial correlation between the [70]PCBM domains, we are unable to resolve a clear scattering peak at this stage. At a solvent content below 60 vol%, there is a striking increase in the GISAXS scattering intensity that we attribute to the appearance of surface features; the [70]PCBM-rich domains start to protrude from the PS-rich matrix. Together with the rapid increase in scattered intensity, the appearance of a Bragg peak associated with the existence of a well-defined distance among neighboring domains is observed. Surprisingly, we do not see any change in the interdomain distance after the first observation of the scattering peak. This indicates that the entire morphology formation occurs in a very narrow time window (100–400 ms) between the first laser scattering onset and the first appearance of an in-plane GISAXS scattering peak. We propose that this narrow time window should be the focus point of further research in order to elucidate the evolution of domain shape and size during spin coating. To elucidate the processes in such a narrow time window, proper material systems have to be chosen, and sophisticated techniques with sufficiently high time resolution have to be employed. Our data clearly suggest that selecting a slower-evaporating solvent will greatly enlarge the time window for the morphology evolution. It is clear that the formation of surface features together with internal phase separation complicates the analysis, because two different factors contribute to the X-ray signals. However, many technologically relevant applications of phase-separating systems inherently exhibit surface structures. As such, it is essential to understand the contribution of both factors. Here, we have clarified the effect of both embedded phase separation and the formation of surface topography, and introduced a model which is able to simulate the effect of both factors on the GISAXS scattering intensity.

The collected data have been used to verify a theoretical ternary phase diagram using Flory–Huggins theory. Thus, the presented multitechnique experimental approach can be employed to experimentally study the thermodynamics of multicomponent systems occurring during the ultrafast development (~400 ms) of thin film morphologies with features on the 10–1000 nm length scale. Finally, the simultaneous combination of GISAXS, laser interferometry, and laser scattering is of general application and can be utilized in the future to elucidate morphological development in situ and in real time occurring during ultrafast solution processing of fundamentally and technologically relevant materials, like organic photovoltaic, block-copolymers, and polymer/nanoparticle hybrids.
4. Experimental Section

**Substrate Preparation:** Silicon substrates (Si-Mat, 525 µm thickness, 200 nm SiO2 layer, ultraflat, <1 µm total thickness variation) were cut into pieces of 1 × 1 to 2 × 2 cm. These substrates were cleaned by scrubbing with a sodium dodecyl sulfate (Acros, 99%) solution in water, then rinsed with deionized water, and finally sonicated in 2-propanol. PEDOT:PSS ( Heraeus Clevios P VP AI 4083) was filtered with a 0.45 µm poly(vinylidene fluoride) (PVDF) filter before use, and spin-coated at 3000 rpm to form a 30–40 nm thick layer.

**Solution Preparation:** [70]PCBM (Solelone, 90–95%) and poly styrene (Sigma-Aldrich, Mw = 280 kg mol⁻¹) were dissolved in a 2:1 weight ratio in o-xylene with a polystyrene concentration of 3, 6, and 9 mg mL⁻¹. These solutions were stirred for 1 h at 90 °C to dissolve all materials, and then left stirring at room temperature until use.

**Spin Coating:** A home-build spin coating setup was used to facilitate the integration in the beam line. The setup was built in air without cover or additional airflow. A brushless motor (McLennan BLDC 48) was used, which was able to reach a maximum spin speed of ~5000 rpm. The spin speed was set by applying a 0–5 V control signal. The nominal rotational velocity generated by the frequency generator signal was calibrated to all spin speeds using the reflected laser beam. The authors declare no conflict of interest.

**Ex Situ Film Analysis:** PEDOT:PSS was dissolved in water to float the films on 200 square mesh copper grids. A Tecnai G2 Sphera TEM (FEI) was operated at 200 kV. AFM was done on a Veeco MultiMode in tapping mode with Nanosensor PPP-NCHR-50 tips. Film thicknesses were measured with a Veeco Dektak 150. The image analysis by FT has been described in ref. [11]. The cross-sectional TEM sample was prepared by the Ga focused ion beam milling using a Quanta 3D FEG (FEI) dual beam microscope.

**Laser Interference and Scattering:** A 635 nm diode laser (5 mW, LaserLyte Flex 635-5) was incident on the substrate under an angle of 45°. The specular reflected light was collected with a Thorlabs SM1P1D1A photodiode positioned behind a Thorlabs ED1-C50-MD diffuser and amplified by a Keithley 428 preamplifier. To collect the scattered light, a Hamamatsu S2281 photodiode was used. The signal was amplified with a Stanford Research System Model SR570 current preamplifier operated in high-bandwidth mode. Both signals were measured by a MUSST electronic module (http://www.esrf.eu/Instrumentation/DetectorsAndElectronics/musst). To calculate the layer thickness from the interference pattern, a previously published peak-counting method was used along with a script based on a transfer-matrix implementation of the Fresnel equations.[45] (Section S6, Supporting Information).

**Gracing Incidence Small Angle X-Ray Scattering:** GISAXS experiments were performed at the BM26B beamline DUBBLE at the ESRF,[48] particularly suited for soft matter investigation with millisecond time resolution.[49] The wavelength of the X-rays was 0.1 nm, and the beam size at the sample position was 1 × 0.25 mm (horizontal × vertical). Due to the small wavelength of the X-rays (0.1 nm), the scattering angle (2θ) of in-plane features with a typical length scale of ~500 nm was on the order of only 0.006° (Bragg’s law: nλ = 2 sinθ); thus, very large sample-to-detector distances were necessary to resolve such small scattering angles. To resolve scattering features from droplet-like morphologies with interdomain distances of 300–1000 nm, high-resolution GISAXS was used with a sample-to-detector distance of 7.5 m to cover the in-plane range qy = 0.0007–0.9 nm⁻¹ (i.e., 890–7 nm), with qy being the modulus of the in-plane scattering vector. A 1702516 pixel size of 172 µm × 172 µm. An angle of incidence of 0.2°, which is above the critical angle of the materials, was used for the following reasons: to separate the Yoneda peaks from the reflected beam, which allows the use of a double beamstopper and thus detect scattering at very low angles; to allow full penetration of the film; to be less sensitive to the very small but possible substrate waviness caused by a slight misalignment of the spinning substrate. No background subtraction was performed as the background from the air, and the empty substrate was orders of magnitude lower with respect to the [70]PCBM domains. Image acquisition was hard triggered together with the laser reading triggering by a MUSST electronic module as soon as the spin coating motor started to rotate. Image framing rate was 30 Hz (exposure time of 30 ms and readout time of 3 ms). Static images were acquired after each spin-coating process with an exposure of 60 s. The large dimension of the Pilatus 1M detector allowed this study to cover a large range in scattering angles. Due to the large object dimensions (100–1000 nm), most of the scattering was concentrated in the low-angle region. Thus, zoomed portions of the total GISAXS images covering the angular range qy = 0.0–0.9° (qz = 0.25–1.2 nm⁻¹) and 2θ = −0.25°–0.25° (qz = 0.15–0.15 nm⁻¹) relevant to this study were reported here. GISAXS in-plane cuts ((qy) vs qz) were calculated at the Yoneda peak height at an exit angle equal to the material critical angle (qy = 0.12°), where the scattering of the material has its maximum. For the in situ data, the in-plane intensity cuts were fitted using a sum of a Gaussian peak (to describe the peak at qy = 0 given by the Yoneda peak) and two Lorentzian peaks (to fit the left and right scattering peaks from the domain in-plane structure). The GISAXS vertical cuts ((qz) vs qy) were calculated at 2θ = 0.01°. In order to have a better signal-to-noise ratio, an integration interval of 5 adjacent pixels was used to obtain the intensity cuts along the horizontal (qy) and the vertical (qz) direction. Simulations of the GISAXS images were performed by means of the FitGISAXS package for the IgorPro software (v.6.3.7.2 from WaveMatrix[52] using the indices of refraction for pure [70]PCBM (density of 1.5 g cm⁻³) and PS (density of 1.05 g cm⁻³).

**Supporting Information**

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

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**Conflict of Interest**

The authors declare no conflict of interest.

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