

An interfacial instability in a transient wetting layer leads to lateral phase separation in thin spin-cast polymer-blend films

SASHA Y. HERIOT* AND RICHARD A. L. JONES

Department of Physics and Astronomy, Hicks Building, Hounsfield Road, University of Sheffield, Sheffield S3 7RH, UK

*e-mail: s.heriot@sheffield.ac.uk

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Spin-coating is a very widely used technique for making uniform thin polymer films. For example, the active layers in most experimental semiconducting polymer-based devices, such as light-emitting diodes and photovoltaics, are made this way. The efficiency of such devices can be improved by using blends of polymers; these phase separate during the spin-coating process, creating the complex morphology that leads to performance improvements. We have used time-resolved small-angle light scattering and light reflectivity during the spin-coating process to study the development of structure directly. Our results provide evidence that a blend of two polymers first undergoes vertical stratification; the interface between the stratified layers then becomes unstable, leading to the final phase-separated thin film. This has given us the basis for establishing a full mechanistic understanding of the development of morphology in thin mixed polymer films, allowing a route to the rational design of processing conditions so as to achieve desirable morphologies by self-assembly.

Spin-coating is a method used very widely in the creation of highly uniform, submicrometre polymer films. It is used widely in industry for making thin films of photoresists, sol-gel glasses and functional materials such as semiconducting polymers for use in polymer-based field-effect transistors, light emitting diodes and photovoltaics. Spinning a film of a single polymer generally produces a smooth, unstructured thin film, but if a mixture of polymers is used the two polymers will usually phase separate. Many possible morphologies result from this phase separation; it is a complex non-equilibrium process and the outcome is very sensitive to the details of the solvent used and the precise spinning conditions. At one extreme, phase separation can take place exclusively in the direction perpendicular to the plane of the film, resulting in a self-stratified film^{1,2}. Alternatively, phase separation can take place exclusively in the plane of the film, resulting in a laterally patterned film characterized by a length scale that depends in a complex way on the processing history³⁻¹⁰.

Important applications are emerging in which a better understanding and control of this process of phase separation in thin films would be highly desirable. Blends of semiconducting polymers can make efficient photodiodes and photovoltaic devices, owing to the importance of interfaces in the localization and separation of excitons¹¹⁻¹⁵. Similar considerations make bilayer geometries attractive for polymer photovoltaics¹⁶. It has now been shown that such bilayer structures can form spontaneously during spin-coating leading to efficient devices¹⁷⁻²⁰. The possibility of the self-assembly of a complex nanoscale morphology during an inexpensive and facile processing method is obviously very attractive. A further development has shown that the lateral phase separation could in some circumstances be templated by an underlying pattern created by, for example, soft lithography²¹.

So far, the many studies that have been made of phase separation in spin-coated films have been restricted to an analysis of the structure of the final films. It is obviously difficult to deduce the complex details of this non-equilibrium process from the end point alone. Nonetheless, in an important paper by Walheim and co-workers²² it was suggested that one important mechanism for lateral phase separation was the creation of a transiently layered

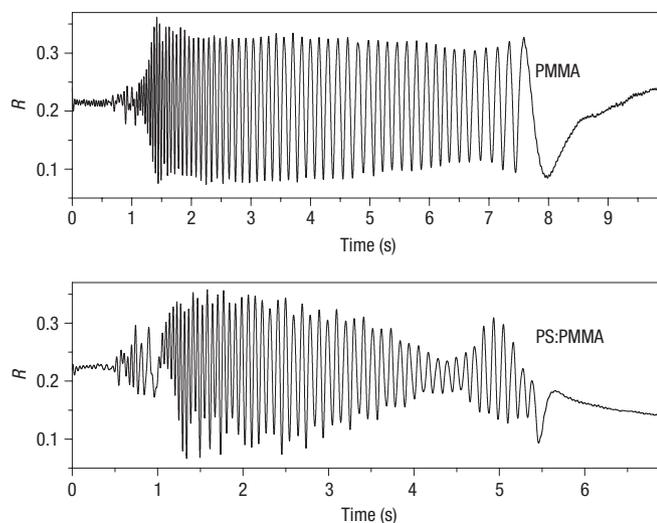


Figure 1 Specular reflectivity measured during the spin-coating process. The top graph is for a film of pure PMMA and the bottom graph is for a blend of 50% PMMA with 50% PS. At the beginning of the spin-coating process the peaks cannot be resolved.

film by a process of wetting, followed by the break-up of the layers because of an interfacial instability. We have developed a technique for studying the process of phase separation in spin-cast films *in situ* as it happens. Our results provide convincing direct evidence in favour of the Walheim hypothesis, and establish the full sequence of processes that lead to the final phase-separated thin film. This will give us the basis for establishing a full mechanistic understanding of the development of morphology in thin mixed polymer films, allowing a route to the rational design of processing conditions so as to achieve desirable morphologies by self-assembly.

We use time-resolved small-angle light scattering and light reflectivity during the spin-coating process to study the development of structure directly. The apparatus we have used to study the film-formation process *in situ* has been described elsewhere²³ and in the Supplementary Information. Briefly, a small amount of solution was deposited using a pipette onto a silicon substrate (approximate area 1 cm² and thickness 1 mm) mounted on a spin-coater chuck. This was spun at a speed of 1,500 r.p.m. for 20 s, during which time a laser (633 nm) was incident (at 40° to the normal) on the centre of the substrate. The reflected light was collected by two detectors simultaneously—a photodiode for specular reflection and a charge-coupled-device camera for off-specular reflection.

The polymers, polystyrene (PS) and polymethylmethacrylate (PMMA), were obtained from Polymer Laboratories and had molecular weights of 100,000 and 96,000, respectively, and narrow molecular weight distributions. Solutions were made up to 10% polymer and 90% toluene by weight.

Figure 1 shows the specular reflectivity (R) measured during the spin-coating process, both for a film of pure PMMA and for a blend of 50% PMMA with 50% PS. The most prominent features are the series of fringes, which arise from reflections from the front and back surfaces of the film coming in and out of constructive interference as the film thins. By measuring the final film thickness and counting back the fringes we can use these curves to reconstruct the profile of thickness as a function of time for the films; these are shown in Fig. 2. Further details about constructing thickness–time profiles are provided in the Supplementary Information.

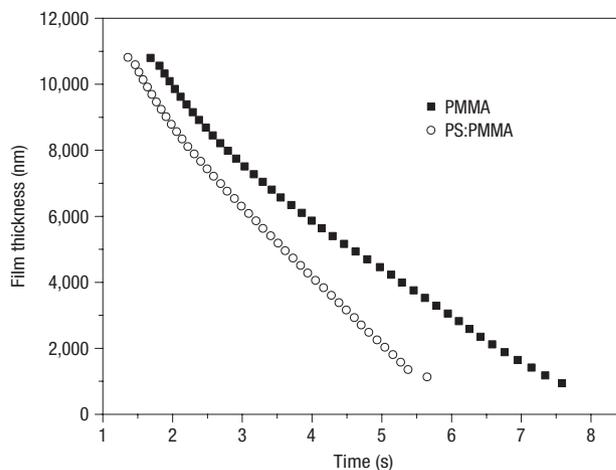


Figure 2 Film thickness as a function of time. Thickness–time profiles for PS and PMMA were determined by measuring the final film thickness and then counting back the fringes from the specular data.

Figure 3 is a contour plot showing the radially averaged light-scattering intensity out of the specular direction for the blend film. The pure PMMA film showed no features in the off-specular. A movie supplied in the Supplementary Information shows the light scattering in real-time. The data show the smooth appearance of a broad scattering peak, reminiscent of that observed in bulk systems undergoing spinodal decomposition. However, there are two key differences in the behaviour of this peak from that of a bulk phase-separating system. First, superimposed on the rise in scattering intensity is a periodic increase and decrease in overall intensity, with a period that matches that observed for the specular reflectivity. Second, there is a shift in peak position with time towards higher values of the scattering vector q . This is in marked contrast to the situation in bulk phase separation, in which the spinodal peak moves with time to a lower value of q , corresponding to a coarsening of the initial phase-separated structure.

The appearance of scattering with a well-defined peak scattering vector is indicative of the development of some kind of lateral structure within or at the surface of the film; for the example shown in Fig. 3 the length scale characterizing the lateral structure is around 30 μm . There are two obvious candidate mechanisms for producing such a peak. The first is the bulk mechanism of spinodal decomposition²⁴, in which thermal composition fluctuations are amplified by a process that selects a fastest-growing length scale. The second possibility is that the initial phase separation within the film is perpendicular to the plane of the film, resulting in a lateral interface between layers of different composition. This interface may become unstable^{22,25}, leading to the wavelength-selective amplification of a capillary wave in a process analogous to spinodal dewetting²⁶. In both cases, we expect a continuous increase in scattered intensity with the increase in amplitude of the fluctuations causing the scattering. The periodic modulation of intensity observed in our experiments arises because of the thin-film geometry. As the film continues to thin, interference effects cause a periodic variation with film thickness of the electric-field intensity at the position of the roughening interfaces from which the scattering is arising.

A more detailed analysis of the specular reflectivity offers support to the second suggestion. In Fig. 4, we show the fringe visibility, calculated as $(R_{\text{max}} - R_{\text{min}})/(R_{\text{max}} + R_{\text{min}})$ from the data

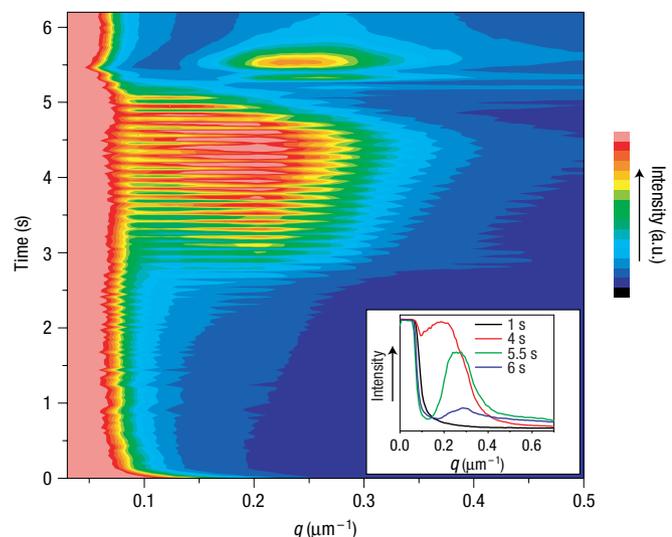


Figure 3 A contour plot showing the radially averaged light-scattering intensity out of the specular direction for the blend film. The colours represent the intensity as determined by the key to the right of the plot. The intense peak $<0.1 \mu\text{m}^{-1}$ corresponds to the specular spot. Up to around 2.5 s, only specular reflection occurs and it modulates in intensity. This matches the period for the specular reflectivity in Fig. 1. After 2.5 s there is lateral phase separation of the polymers and light is scattered out of the q direction. Scattering is observed as a ring around the specular spot, and therefore as a peak when it is radially averaged. The inset shows some selected snapshots of the profiles. A movie included on the online Supplementary Information shows the real-time light scattering of the PS:PMMA film during spin-coating.

shown in Fig. 1. For pure PMMA, there is little variation throughout the spin-coating process. Only a slow decrease in the fringe visibility followed by a sharper increase is observed, and this is attributed to some roughening of the film. However, for the PS:PMMA film at early stages of the spinning process, the blend film shows a systematic modulation of the fringe visibility with time that is not observed for the pure polymer. This can be interpreted to indicate that the film has split into two layers, one rich in PS and one rich in PMMA. A qualitative understanding of this result can be obtained by thinking of this situation as a one-dimensional scattering problem. For a uniform film, diffraction arises from interference from two scattering objects, the film surface and its image in the substrate.

If each of these layers has a thickness roughly half of the total film thickness, then the period of the modulation should be twice that of the main fringe frequency. Later in the spinning process, at a time that corresponds exactly to the onset of off-specular scattering, the fringe visibility decreases whereas the average reflectivity remains constant. This can be accounted for by assuming that the average roughness of the free surface increases, leading to a reduction in the reflectance of that interface. We model this effect semiquantitatively by assuming that the effect of small-length-scale roughness on the reflectance of the top surface can be accounted for by a Debye–Waller-like factor as derived for X-rays²⁷. This analysis indicates that, during this initial phase of the instability, the r.m.s. roughness increases to a value of 120 nm, attaining this at a time when the total film thickness is 3,442 nm. The end of this phase is marked by an abrupt shift in the position of the peak in off-specular scattering intensity; this shift corresponds to a decrease in the characteristic length scale from a value of 53–25 μm .

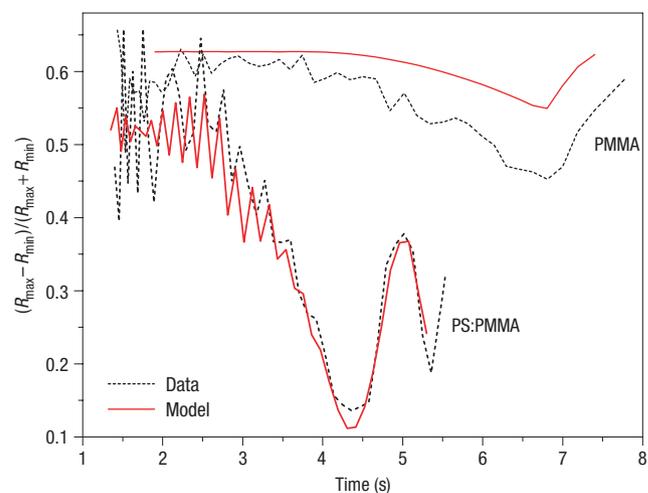


Figure 4 Fringe visibility for PMMA and PS:PMMA with corresponding models.

Fringe visibility is defined as $(R_{\text{max}} - R_{\text{min}})/(R_{\text{max}} + R_{\text{min}})$ from the data shown in Fig. 1. A decrease in the fringe visibility is indicative of roughening of the film and modulation of the visibility for PS:PMMA is attributed to polymers separating into two layers.

Using the classical expression for the reflectivity of a dielectric film on a substrate, it is possible to model the reflectivity as a film thins. The model is further explained in the Supplementary Information. Figure 5 shows the models of a pure PMMA and a 50:50 blend of PS:PMMA (initially as a layer of PS on top of a layer of PMMA, then a single layer containing equal amounts of PS and PMMA). In these models, the solvent concentration is assumed to be uniform throughout the film, and interfacial roughness is included as described above. For the pure PMMA layer, the model accounts for the data well, except that the data show a systematically lower visibility than the model. This may be accounted for by the presence of gradients in solvent concentration through the film, which are not included in the model. Agreement for the mixed film is less good, but the model does capture the most striking feature of the data—the periodic modulation of fringe visibility. Of course, many factors that are certainly present in reality are not included in the model.

We summarize our conclusions in Fig. 6a. Phase separation initially takes place by the formation of wetting layers at the surface and substrate (i)–(iii). When the thickness decreases to a critical value, the interface becomes unstable; thermally excited capillary waves are amplified with a mechanism to select a length scale, resulting in the observed off-specular scattering (iv). One candidate mechanism can be ruled out; the dispersion force-driven interfacial instability considered in ref. 28 would require an unphysically large value for the Hamaker constant to account for the observed length scale, given that the onset of the instability occurs at a total film thickness of 6,410 nm.

Instead, we speculate that the instability at the polymer–polymer interface arises because of a solvent-concentration gradient through the film. The solvent at the film surface evaporates at a faster rate than the solvent in the bulk can diffuse through the film. This results in a significantly lower solvent concentration at the surface compared with that at the substrate²⁹. The interfacial tension at a polymer–polymer interface is a strong function of the solvent concentration³⁰, so if an interface is in the plane of the film, it is very probable that it will be subject to a Marangoni-like instability.

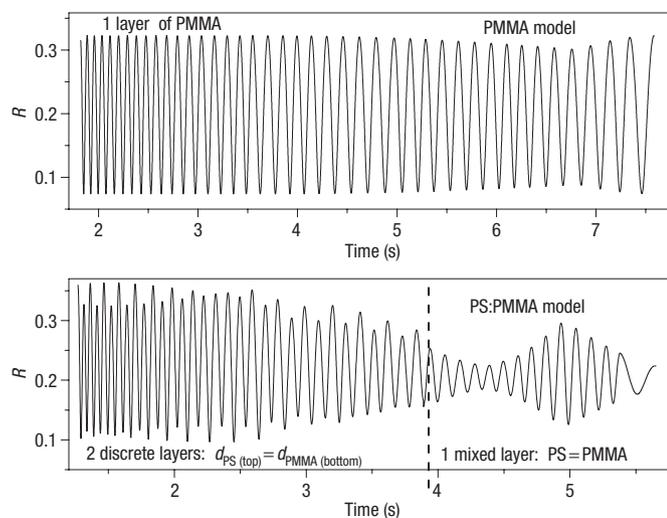


Figure 5 Models of PMMA and PS:PMMA. For PMMA (top), the calculation assumed a single layer of pure PMMA, thinning at the same rate as deduced from the thickness–time curve. For PS:PMMA (bottom), up to 3.9 s we modelled two layers of equal thickness with PS on top of PMMA. After 3.9 s the model was changed to a single layer containing equal amounts of PS and PMMA. Again the film is thinning at the same rate as the data. For both PS and PS:PMMA, some roughening was introduced in an attempt to mimic the data.

As the film thins further we expect the instability to grow, whatever its origin; this leads to an increase in the off-specular scattered intensity and also an increase in the roughness of the top surface of the film. At some point, the amplitude of the instability becomes such that the liquid–liquid interface meets the surface. At this point there is a rapid movement of the contact lines to yield the laterally phase-separated structure shown in step (v) of Fig. 6a. This stage is marked by a decrease in surface roughness and an abrupt change in the peak in the scattering pattern. Simultaneously, or subsequently, as the total polymer concentration is increasing and the equilibrium phase boundaries change, phase separation may be initiated in one or both phases, leading to a hierarchical, secondary phase-separation step (vi). The final film morphology shows these features, as displayed in Fig. 6b.

In thin films in which a pair of immiscible polymer blends are cast from a common solvent, our experiments demonstrate that phase separation can proceed, at least for the materials and parameters we studied, in a multistage process that is summed up in Fig. 6a. First, the thinning film splits into two layers, leading to a characteristic modulation in the visibility of interference fringes measured during the scattering process. Second, the interface between these two layers develops an instability with a well defined wavevector; this is made manifest both in a continuous decrease in fringe visibility and in the onset of off-specular scattering. When the instabilities grow to such an extent that the highest interfacial protrusions touch the top surface of the film, the film breaks up rapidly into lateral domains. At some point during this process, secondary phase separation takes place in the domains. This process is not detected in the *in situ* light-scattering experiment, but is obvious from the morphology of the final film, which is shown in Fig. 6b as determined by an atomic force microscope image.

One issue that remains is how general this mechanism for phase separation in thin films is. Certainly, self-stratification has been observed in a number of other spin-cast polymer blend systems, for example, polybutadiene and PS cast from toluene¹, polyfluorene blends for some spinning conditions²⁰, and blends

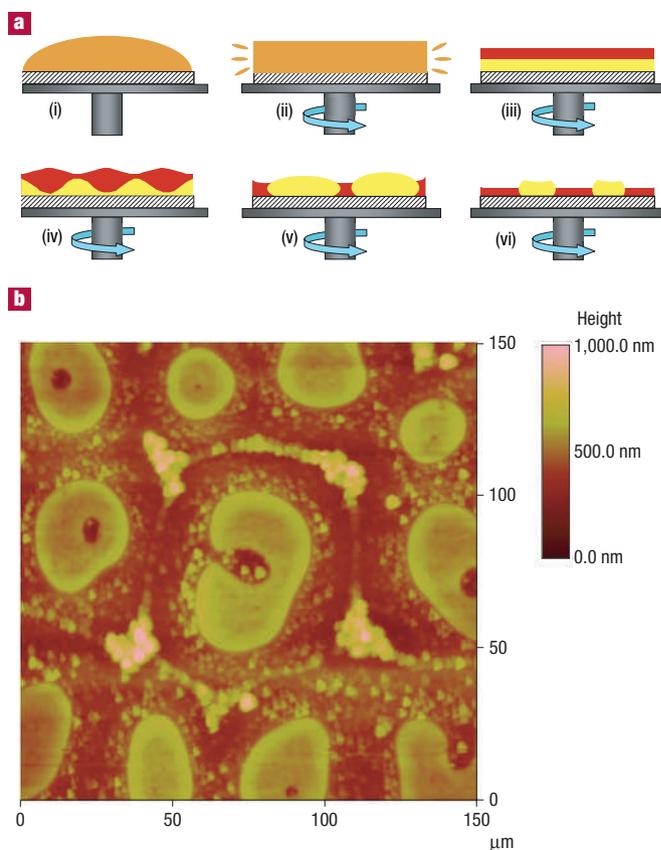


Figure 6 A schematic model describing the film formation during the spin-coating process, and the final film morphology. **a**, After the initial spin-off stage where both polymer and solvent are removed (i), (ii), the film separates into two layers (iii) and the film thins owing to solvent evaporation only. The interface between the polymers destabilizes (iv) and the film phase-separates laterally (v), (vi). **b**, An atomic force microscope image of the final morphology, imaged with a MultiMode SPM with a Nanoscope IIIa controller.

of PS and polyaniline cast from chloroform³¹. If our speculation about the importance of solvent-concentration gradients through the film is correct, we would expect that the dominant factor controlling whether the interface in an initially self-stratified film becomes unstable is the solvent evaporation rate or, to be more precise, a Peclet number that expresses in dimensionless form the relative rates of evaporation and solvent diffusion³². For a relatively low evaporation rate, solvent diffusion will be able to maintain a spatially uniform solvent concentration, removing the driving force for interfacial instability. Intriguingly, in the polyfluorene system studied in ref. 20, control of the solvent evaporation rate made it possible to obtain final morphologies that were either self-stratified or laterally phase separated. One question that this hypothesis leaves open is the mechanism by which film–substrate interactions influence the final morphology of polymer blend films (see ref. 21 for an example).

This work has provided an insight into the process of spin-coating and phase separation. In the past it was assumed that phase separation was simply attributed the processes that are observed in the bulk. However, these data provide strong evidence that suggests that the process is much more complex, being the formation of a layered structure followed potentially by its break-up into lateral domains. These results have strong implications for future development for polymer technologies, especially for

electrical devices, and with this understanding it will eventually be possible to control these film-formation processes in order to achieve the desired structure by both quick and simple routes.

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Competing financial interests

The authors declare that they have no competing financial interests.

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