

Time-Resolved Light Scattering Studies of Phase Separation in Thin Film Semiconducting Polymer Blends during Spin-Coating

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Thin films of blends of incompatible semiconducting polymers find technological applications in organic electronic devices, such as LEDs and photovoltaics, where a more efficient device can be produced by blending two or more polymers to combine favorable electronic properties.¹ These films are usually formed by spin-coating and exhibit complex lateral structures formed by phase separation during the rapid removal of solvent. This produces a distribution of interfaces throughout the film, which can be beneficial for devices since charge association and dissociation occur primarily at the interfaces.^{2,3} The morphology and size of the phase-separated structures can have a profound effect on the properties of the device,⁴ so a better understanding of mechanisms of phase separation should permit the rational design of processing routes for optimum device performance.

In spin-coating a substrate is flooded with a solution of the two immiscible polymers in a common solvent and spun round at a rate of a few thousand revolutions per minute. Most of the solution is cast off during the early stages of this process, leaving a thin fluid layer on the substrate. This layer subsequently thins, first due to fluid flow and later by solvent evaporation.⁵ As the solvent evaporates, the system will cross from a one-phase region of the ternary (polymer/polymer/solvent) phase diagram to a two-phase region. The final result of spin-casting such a mixture is usually a thin film with a well-defined topographical structure of lateral domains, which can be imaged using techniques such as atomic force microscopy (AFM).

Several studies have investigated the phase separation morphology induced by removal of solvent from binary and ternary polymer blends. Dalnoki-Veress et al.⁶ investigated the average domain area as a function of composition and spin speed for blends of polystyrene/polyisoprene and polystyrene/poly(methyl methacrylate) (PS/PMMA). Walheim et al.⁷ proposed that the height difference between phases in PS/PMMA blends can be accounted for by the relative solubilities of the two polymers in the common solvent. Several different models have also been proposed in attempts to explain the observed structure formation in spin-cast polymer blends. Tanaka et al.⁸ proposed that incomplete wetting of the surface by the lower surface energy component will force the higher surface energy component to protrude from the film surface. Ton-That et al.⁹ argued

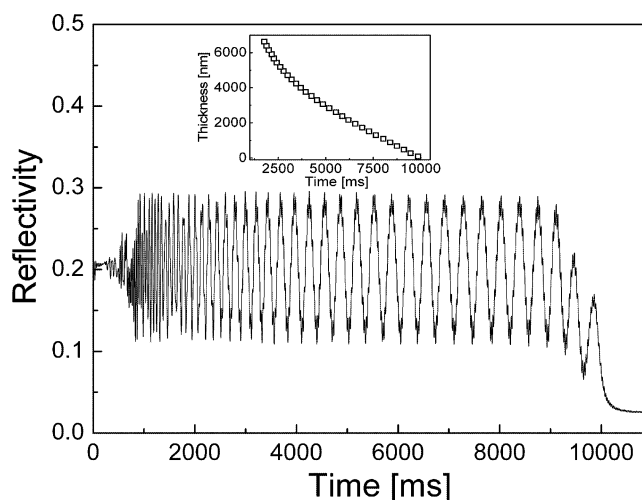


Figure 1. Specular reflectivity for a 44/56 F8BT/PFB blend spin-cast at 2000 rpm from a 2% solution in xylene. The inset shows the thickness–time curve extracted from these data.

that two polymers undergoing a solvent quench will first form a stratified bilayer structure driven by surface energy differences, the top layer of which will then partially dewet (due to an interfacial instability) to leave the familiar morphology of lateral domains. This idea was further explored recently by Sprenger et al.,¹⁰ who attribute multiple length scales in the phase separation morphology of binary and ternary polymer blends to separate instabilities, of different wavelengths, at both the polymer–polymer interface and the free surface. In systems where the stratified structure is retained until the end of the spin-coating process, the resulting lamellar structures can be directly observed,¹¹ this situation has recently been seen in a blend of an insulating and conducting polymer.¹² Up to now, conclusive tests of these ideas have not been possible due to a lack of direct information on the kinetics of morphology development.

In this paper we describe an instrument that provides this information, allowing both the evolution of film thickness and the development of phase-separated structure to be monitored as a function of time during the spin-coating process. A light scattering apparatus with integrated spin-coater measures both specular reflectivity and off-specular scattering. The specular reflectivity is used to monitor changes in the film thickness during spinning, while off-specular scattering is used to observe the onset of phase separation and then to monitor the evolution of length scales in the phase-separating blend. In-situ specular reflectivity measurements have been used previously to study the thinning behavior of fluids on a spinning disk,^{13–15} but this work represents the first attempt to monitor demixing in a blend system under such conditions.

A spin-coater, capable of reaching spin speeds in the range 0–10 000 rpm within 200 ms, is mounted at the center of rotation of two large aluminum disks, to which the laser and the detector arms are fixed. Light from the laser (633 nm, HeNe) is reflected from the spinning substrate; specularly reflected light is detected by a Si photodiode with a time resolution of 1 ms. The scattered light is collected on a screen and recorded using a progressive scan CCD camera with a time resolution of 30 ms.

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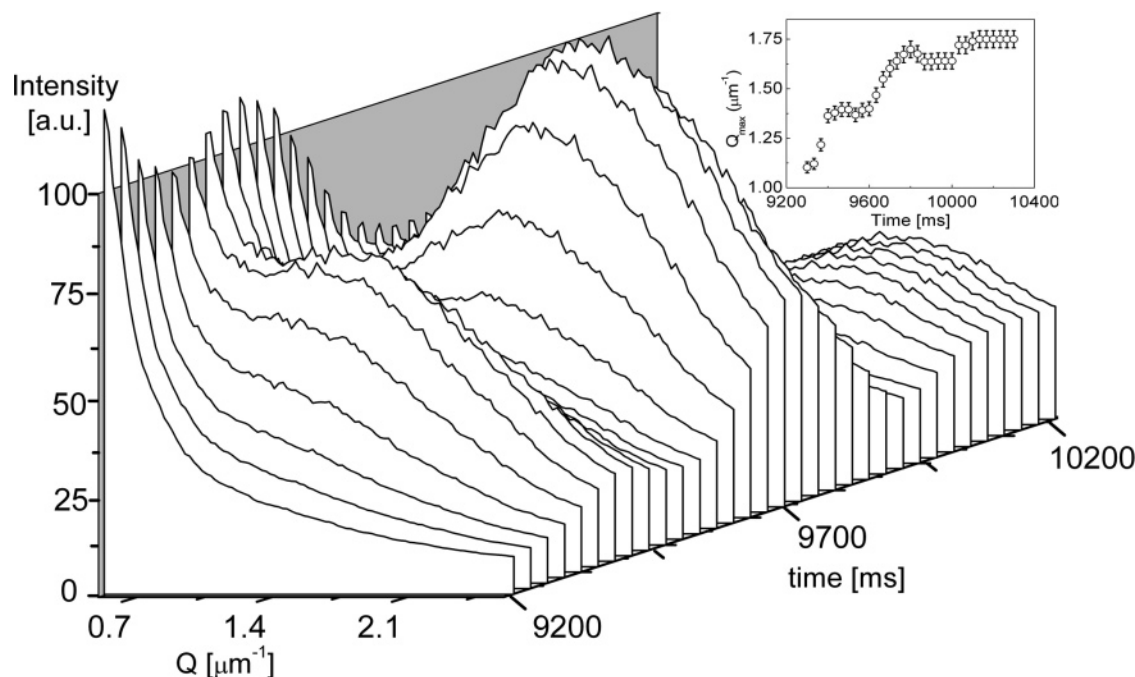


Figure 2. In-situ light scattering taken during the spin-coating of a 44/56 BT/PFB blend from a 2% solution in xylene at 2000 rpm. The data shown are for a portion of the spinning event from the “cloudpoint” to the point where the length scale stops evolving. The inset shows the time dependence of the peak wavevector Q_{\max} .

Figure 1 shows the time dependence of the specular reflectivity for a blend of the polyfluorene derivatives, poly(9,9'-dioctylfluorene-*co*-benzothiadiazole) (F8BT) and poly(9,9'-dioctylfluorene-*co*-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine) (PFB) (all data shown are for a 44/56 BT/PFB blend, 2% solution in xylene). This is a blend of two conjugated polymers (PFB is a hole acceptor and F8BT an electron acceptor) which is of interest for applications in blend-based photodiodes; further details of the polymers can be found elsewhere.^{16–19} The variation of electronic properties with processing conditions for this system have been studied extensively; for example, it has been found that a finer scale phase separation produces a more efficient device^{4,16} and that spinning from a highly viscous and volatile solvent can lead to a vertically segregated structure.^{18,19} During spin-coating the reflectivity exhibits a series of peaks and troughs that correspond to constructive and destructive interference conditions of the reflected light as the film thickness decreases. With knowledge of the final thickness (88 nm in this case, as determined by measuring the depth of a scratch in the film using AFM), we can count back the positions of the maxima and use the standard condition for constructive interference to deduce the time dependence of the film thickness. We need to assume a linear change in refractive index with time from the mixed polymer/solvent state to the final solid polymer film in order to correct for the changing refractive index.

Typical data are shown in the inset of Figure 1. This shows rapid initial thinning followed by a regime characterized by a constant evaporation rate. The final peak marks the end of rapid thinning by evaporation and the solid film drying onto the substrate. However, a small amount of residual solvent will remain in the system, and the film will continue to thin slowly as the remaining solvent evaporates.

The scattering out of the specular direction should tell us about the development of lateral structure in the film. Radially averaged scattering data are shown as a

function of time in Figure 2. The scattering patterns obtained are radially symmetric and remain so throughout the phase separation process. These plots show radially averaged data taken from around the first frame that exhibits scattering at 9200 ± 30 ms to the point where the scattering pattern ceases to evolve at approximately 10 000 ms, presumably because the polymer solution has become concentrated enough to form a glass.

The point where scattering is first detected corresponds to the cloudpoint of a bulk phase separation experiment—the onset of lateral phase separation in the system. It is worth noting that when comparing the scattering data to the reflectivity, there is no obvious loss in specular intensity at the point where the film starts scattering; this shows both that phase separation cannot be detected using specular reflectivity alone and that multiple scattering is not likely to be a significant complication.

The scattering data show two prominent features. The first is that the scattering exhibits pulsations in intensity with a periodicity that mirrors that seen in the specular reflectivity. These changes in scattering intensity arise because what is scattered is not a simple plane wave; interference effects lead to a time-dependent variation of electric field intensity inside the film. After having accounted for this periodic modulation of overall scattering intensity, the scattering curves initially show a strong similarity with the scattering from bulk phase separation systems. A scattering peak, characterized by a well-defined intensity maximum, grows smoothly out of the background, in a way that is strongly reminiscent of spinodal decomposition.

However, as phase separation proceeds, the behavior becomes very different to conventional bulk phase separation. It is clear from Figure 2 that the Q value of maximum scattering as a function of time Q_{\max} moves to a higher value as phase separation proceeds, implying that the overall length scale is decreasing as phase separation proceeds. A more detailed analysis shows

that the average size of the phase-separated domains, as deduced from Q_{\max} , is initially $5.7 \mu\text{m}$ and then rapidly shrinks to a final size of $\sim 3.6 \mu\text{m}$. (This value is in agreement with the length scale extracted from the FFT analysis of a micrograph of the final morphology.) The size of the domains follows a roughly $t^{-1/2}$ dependence on the spinning time, t . This result is somewhat surprising, and the fact that domains appear to shrink contradicts a previous model,⁷ where domains nucleate from the initially homogeneous mixture below a critical solvent concentration and then grow until their size reaches the thickness of the film.

One possible explanation of these results is that the initial lateral structure might form, not from bulk-like phase separation within the film, but as a result of an instability in transient wetting layers at the surface and substrate. The spinning fluid may initially form a layered structure, with the driving force for this being the difference in surface energy between the two polymer solutions; evidence from contact angle measurements implies that there is a considerable surface energy difference between F8BT and PFB14. As the solvent evaporates, the surface and interfacial tensions that stabilize this configuration are changing continuously, and interfacial instabilities may develop. The origin of these instabilities is not yet clear; the thickness of the film at the time at which significant scattering begins is too large for dispersion forces to drive such an instability, so it may that hydrodynamic instabilities originating from transient solvent concentration gradients may be operative.²⁰ Whatever their origin, these instabilities would lead to dewetting and breakup of the layered arrangement and the development of the lateral domain structure with an exact morphology dependent on the initial composition of the blend. Lateral structure would be detected as soon as the layers begin to break up. Some evidence in support of such a mechanism comes from reports that spin-coating the same polymer blend from isodurene, a highly viscous and volatile solvent, forms a bilayer with the lower surface energy F8BT on top.^{18,19} In effect, the structural evolution is frozen at the layered stage before lateral domains can form. More direct evidence of layering during the spin-coating process has been found in another system by a detailed analysis of the time dependence of the specular reflectivity.²⁰ The apparent decrease in size of the average domain size could correspond to the appearance of secondary phase separation on a smaller length scale within the larger domains formed by the interfacial instability. We have some preliminary evidence of secondary phase separation in micrographs of the films after spinning, and further work will test this hypothesis in detail.

In summary, we have shown that it is possible to measure the kinetics of film formation and phase separation in a spin-cast polymer blend using in-situ reflectivity and light scattering techniques. We have

discussed the results of these experiments in the light of two possible mechanisms: one in which morphology arises by the unstable growth of either a composition fluctuation and another in which it results from an interfacial instability initiated by the loss of solvent. A single length scale of fluctuation is initially selected, but contrary to the normal situation in bulk spinodal decomposition following a temperature quench, this length scale subsequently appears to shrink rather than grow.

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