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# Surface segregation and self-stratification in blends of spin-cast polyfluorene derivatives

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## Abstract

We have used helium-3 nuclear reaction analysis to study the morphology of spin-cast blends of poly(9,9'-dioctylfluorene) (F8) and poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) as a function of composition, casting solvent, and initial solvent concentration. In blends cast from toluene, a surface segregated layer is observed for a broad range of F8 compositions. The surface excess has a maximum of  $\sim 4$  nm at an F8 volume fraction  $\phi = 0.5$ , dropping down to  $\sim 1$ – $2$  nm for  $\phi = 0.2$  and  $0.8$ . The existence of such surface segregated layers could play an important role in charge transport in optoelectronic devices made from blends of conjugated polymers. Films cast from chloroform show negligible surface segregation. Scanning probe microscopy experiments show that films cast from toluene exhibit significant in-plane structure, in contrast to those cast from chloroform, which show minimal lateral structure.

## 1. Introduction

Conjugated polymers are an interesting class of material, due to their semiconducting properties, and applications in electronic and optoelectronic devices. Polymer light-emitting diodes (LEDs), photovoltaic devices (e.g. solar cells), and field-effect transistors are examples of the kind of devices made using conjugated polymers. Blending conjugated polymers [1] has been shown to have the potential to improve the performance of LEDs and photovoltaics, and it is this latter category, photovoltaic devices, that may truly benefit from the blending of different conjugated polymers. The usual method is to blend a material with a high hole mobility with a material optimized for electron mobility, because this facilitates charge transport to the electrodes. In a photovoltaic cell a photon is absorbed by one of the polymers in the blend,

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exciting an electron to the lowest unoccupied molecular orbital, and leaving a hole behind. This excited electron–hole pair (exciton) can transfer from one polymer chain to another, and this exciton diffusion will continue until either the exciton is non-radiatively quenched, recombines to emit a photon, or undergoes dissociation at an interface between the two different types of polymer. Photovoltaic cells need to maximize the latter process. Efficient charge separation at the interface is achieved when the differences in the electron affinities and ionization potentials of the two polymers are large (and of the same sign) compared to the coulombic binding energy of the exciton. The bicontinuous morphology typical of polymer blends in the early stages of phase separation is beneficial for charge separation due to the large interfacial area between the different phases. However, phase-separated films do not necessarily consist of a continuous phase of each component leading to the electrodes. The optimal morphology of phase-separated conjugated polymers will depend on the competition between efficient charge separation and efficient charge transport. Characterization of blend morphology is therefore crucial if we are to fully understand photovoltaic device performance.

Work on studying the correlation between morphology and device performance is still in its infancy, but it is still possible to identify some desirable features. For instance, significant increases in the efficiency of photovoltaic cells can be achieved by controlling the phase separation process to produce a predominantly vertically phase-separated morphology [2]. Phase separation proceeds in bulk materials by the nucleation and growth of one phase in a surrounding phase, or by the spontaneous (spinodal) route. In polymer blend films, the surface breaks the symmetry of an inherently unstable system and can impose a direction on phase separation [3]. The bulk phase separation will remain and the final structure will be a competition between both wetting and phase separation [4]. Vertical phase separation occurs when the growth of wetting layers dominates over bulk phase separation, and indeed dramatic structures have been studied in spin-coated films of polymer blends [5, 6]. Although the original focus of this early work was on model (insulating) polymers, recent studies have looked at mixtures of conjugated polymers, with the aim of controlling blend morphology to improve the performance of optoelectronic and electronic devices [1, 7]. In these thin-film devices (thicknesses of order 100 nm), the surface (or substrate) may significantly perturb the entire film morphology compared to the bulk. Blends of polyfluorene-based polymers have been shown to form either predominantly self-stratified (vertically phase-separated) or predominantly laterally phase-separated structures, depending on processing conditions. The first reported vertical segregation in a semiconductor blend was that of poly(9,9'-dioctylfluorene-*alt*-benzothiadiazole) (F8BT) and poly(9,9'-dioctylfluorene-*alt*-bis-*N,N'*-(4-butylphenyl)-bis-*N,N'*-phenyl-1,4-phenylenediamine) (PFB) in which the phase separation perpendicular to the substrate was inferred from scanning probe microscopy and external quantum efficiency measurements [2]. More recently, evidence of preferential wetting of both surface and substrate by one component of a polyfluorene-based blend was found using x-ray photoelectron spectroscopy [8]. The main advantage of vertical segregation for semiconducting blends is the increased efficiency of taking electrons and holes to their respective electrodes. The ability to create self-stratifying blends (i.e. only one processing step, that of casting the film) further increases the desirability of such mixtures.

Blending polymers to create LEDs is also a useful method for efficient device performance, but in this case it is less likely that a coarse scale phase-separated morphology with a large interfacial area provides any benefit to the device. LEDs require electrons and holes to combine to create an exciton, which then decays to give a photon. It seems likely that the wetting of anode and cathode by the relevant charge carrying polymer, without strong lateral phase separation and with a well defined interface, would be the best morphology for an LED, as this would aid in charge injection and transport, whilst facilitating the opportunities for exciton generation. It

has indeed been shown that predominantly vertically phase-separated morphologies do result in greater efficiency than laterally phase-separated LEDs [9].

Blends of poly(9,9'-dioctylfluorene) (F8) and F8BT are particularly well-suited as model light-emitting devices. F8 is a blue-emitting polymer with a high mobility for hole transport, whilst the alternating copolymer, F8BT, is a green-emitting polymer with a high electron mobility. Blends of F8 and F8BT have also been used to some effect as a polymer LED [10–12]. Optimal LED performance has been observed for blends containing 95% by mass F8. Because F8 and F8BT have similar ionization potentials, energy transfer rather than charge separation is likely to occur at the F8/F8BT interface. For this reason, the F8/F8BT blend is not expected to be appropriate for a photovoltaic device.

While blend morphologies can be usefully categorized as exhibiting either predominantly vertically or laterally segregated morphologies, in general a film may contain elements of both structures. One particularly interesting question is whether films showing clear laterally phase-separated domains also have surface or substrate wetting layers. This can be anticipated, given the likely inequality of the surface energies of the phase-separated phases, with the proviso that the kinetics may be quenched before such a layer can develop. In a recent publication we used nuclear reaction analysis to directly measure the composition of a blend as a function of depth within the film [13]. This work clearly demonstrated the existence of such a wetting layer in one particular blend of F8BT and F8, which also showed lateral phase separation. In this paper we extend previous work [13, 14] to study the structure of spin-coated films of F8/F8BT blends, as a function of composition, initial polymer concentration, and casting solvent.

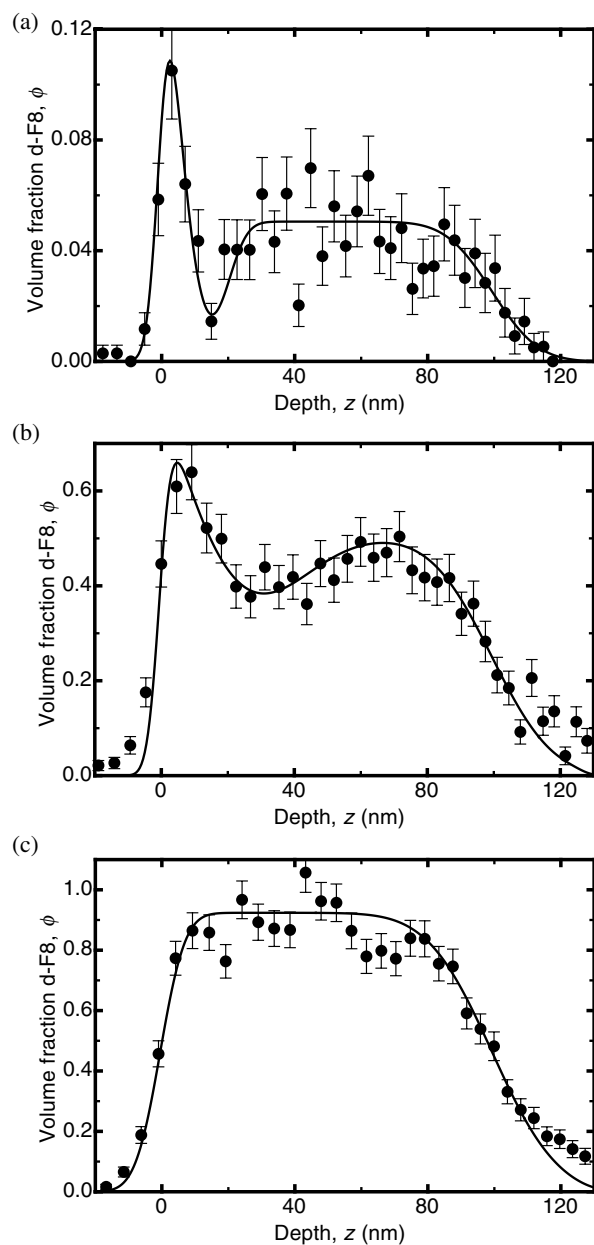
## 2. Experimental details

F8BT of (number average) molecular weight ( $M_n$ ) 101 kDa and deuterated F8 ( $M_n = 145$  kDa) were supplied by Cambridge Display Technology. The monomer units have molecular weights of 388 Da (F8) and 522 Da (F8BT). The polymers have polydispersity indices of 1.95 and 3.76, respectively. Blend films of  $\sim 90$  nm thickness were made by dissolving the components in toluene or chloroform and spin-coating at  $\sim 2000$  rpm to evaporate the solvent. Notwithstanding the large polydispersity indices, and taking the densities of the polymers to be identical, the blend is symmetric with a critical volume fraction of 0.50.

In order to determine the composition of the film as a function of depth, the ion beam method of  $^3\text{He}$  nuclear reaction analysis [15, 16] was performed on the films. With this technique, a mono-energetic (700 keV) beam of  $^3\text{He}^+$  ions is incident on the sample. On impact with the film, the remaining electron is stripped from the ion, and the nucleus propagates through the sample, losing energy through electronic collisions. In the presence of deuterium, the nucleus may undergo a nuclear reaction, producing protons and alpha particles, either of which may be detected. In these experiments we detect the protons. The energy of such particles is dependent upon the energy of the  $^3\text{He}^{2+}$  ion, which in turn is dependent on its depth in the sample. The efficiency of retardation of  $^3\text{He}^{2+}$  ions in a variety of matrix materials is tabulated, and so it is a routine procedure to calculate the depth at which the reaction took place. In this way a volume fraction–depth profile for any deuterated material in a given matrix may be obtained.

## 3. Results and discussion

In figure 1 we present sample NRA data for F8/F8BT blends; the quality of the fits is good, with a wetting layer clearly visible. The wetting layer may be characterized by a surface excess,

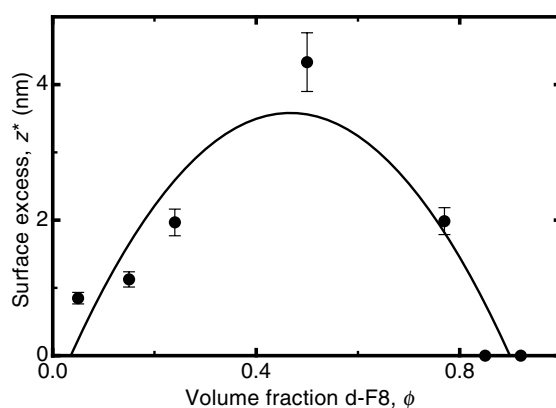


**Figure 1.** NRA data are presented here for toluene cast films containing (a) 5% d-F8, (b) 50% d-F8, and (c) 92% d-F8 by volume.

which may be defined by

$$z^* = \int_0^{\infty} (\phi(z) - \phi_{\infty}) dz, \quad (1)$$

where  $\phi(z)$  is the volume fraction at a depth  $z$  away from the surface (which is at  $z = 0$ ), and  $\phi_{\infty}$  is the bulk volume fraction. As the surface layer forms, a depletion layer necessarily

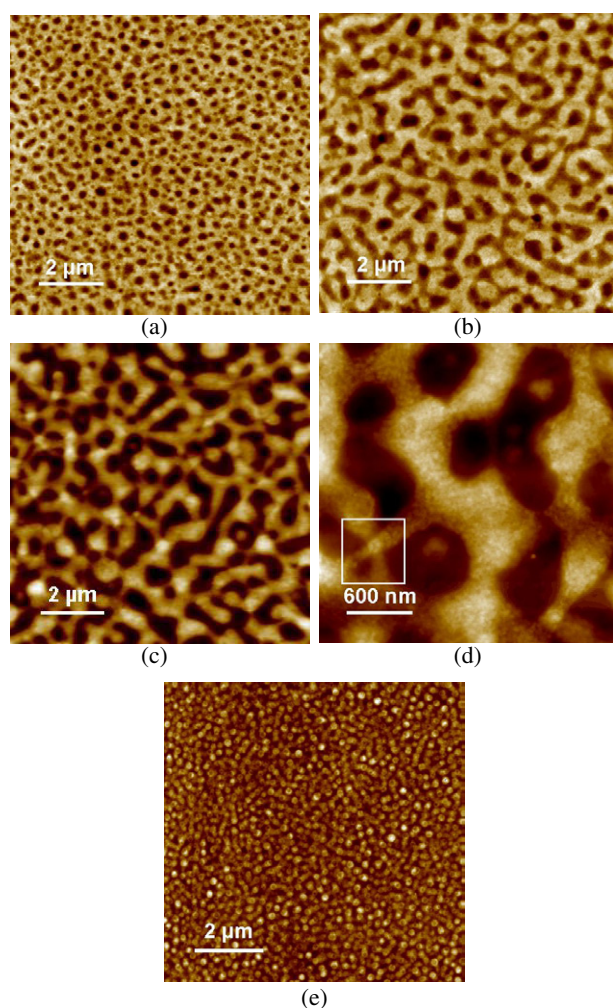


**Figure 2.** Surface excess for 85 nm thick blends cast from toluene. The solid curve is a fit to the data to a quadratic as described in the text. (The fit does not account for the error bars, which are 10% of  $z^*$ , because of the effect of the unknown errors on the  $\phi = 0.85$  and  $0.92$  data for which  $z^* \approx 0$ .)

forms behind it, and this is observed in figures 1(a) and (b). Where a depletion layer exists, one cannot assume that the surface excess is in equilibrium with the bulk but rather the surface layer is in equilibrium with the depletion layer [17]. For this reason,  $\phi_\infty$  in equation (1) above should be replaced with the volume fraction of the depletion layer, which we obtain from the simulation of our data. The upper limit of integration is therefore replaced by the value of  $z$  corresponding to the volume fraction of the depletion layer. In such thin films with large surface interactions there is rarely a ‘bulk’, since much of the material present in the film is affected by the surface. Even if the film were thick enough to support a ‘bulk’ layer, it would be phase-separated.

The surface excess is plotted as a function of volume fraction for these samples in figure 2. The 50% F8 sample clearly has the largest surface excess, and the data are reasonably symmetric about this volume fraction. Such a result supports the suggestion that there is a very strong (dominant) contribution to the final structure from the enthalpic pairwise interaction between the F8 and F8BT.

To investigate these results further, we measured the surface topography of these blends using scanning force microscopy (SFM). The SFM images in figure 3 show very similar morphologies to the previously reported measurements for greater than 50% F8 blends spin-coated from either toluene [14] or xylene [10, 18]. We find isolated circular features for the  $\phi = 0.77$  sample [10, 14, 18] and a bicontinuous structure for  $\phi = 0.50$  [14], both characterized by a single dominant length-scale. In the 50% blend we also note the existence of a more complex three-dimensional topology in which different strands of the same phase appear to loop under or over one another (see figure 3(d)). This looks very much like the flattened remnant of a structure that formed when the film was much thicker than the final thickness (i.e. at a relatively high solvent concentration during spin coating) when it first crossed into the two-phase region. The existence of such three-dimensional topologies could have important implications for charge transport. Few SFM studies have been published on blends with less than  $\phi = 0.50$  [10, 14] (for the reason that low concentrations of F8 result in poor devices). In contrast to the higher F8 fractions, these films exhibit quite different morphologies. Rather than the isolated raised regions visible in the  $\phi = 0.77$  sample, the structure in the  $\phi = 0.24$  sample shows a near-bicontinuous structure. At  $\phi = 0.15$ , the

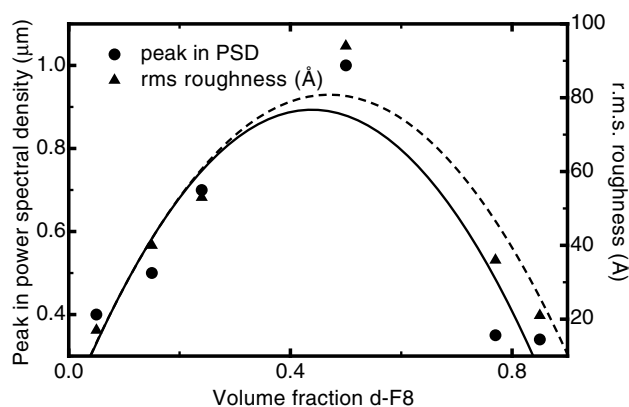


**Figure 3.** SFM images of 85 nm films cast from toluene with  $\phi = 0.15$  (a), 0.24 (b), 0.50 (c) and (d), and 0.77 (e). The structure in (d) is a smaller-size scan, which reveals a region where a three-dimensional topology exists, with a strand of one phase apparently looping over another strand of the same phase (see the boxed region).

(This figure is in colour only in the electronic version)

morphology still has a characteristic length scale, but now consists of more or less isolated depressions. This difference in morphology at high or low concentrations of F8 reflects the fact that the surface layer must perturb the final morphology of the film. However, in both the  $\phi = 0.15$  and 0.24 blends there is no evidence of the three-dimensional structure seen in the 50/50 blend, further corroborating the idea that the 50/50 blend represents a critical composition where the system crosses into the two-phase region while still a relatively thick, high solvent content film, thus allowing a three-dimensional network to be formed.

A film with a critical volume fraction for phase separation of  $\sim 0.5$  may well be expected to have similar morphologies either side of this critical concentration. Likely explanations for the observed asymmetry are that either the two polymers have different solubilities in the casting



**Figure 4.** The lateral length scale of phase separation in the films measured by the peak in the power spectral density (PSD) function in the SFM data is plotted, along with the rms roughness of the toluene case films. The solid curve is a fit to the PSD data using a quadratic function as described in the text, and the dashed curve is a quadratic fit to the roughness data.

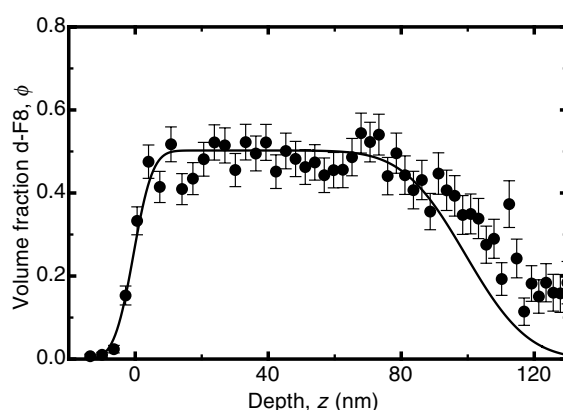
solvent, and/or the perturbation of the film by the symmetry-breaking preferential segregation of F8 to the surface has a significant effect on the final structure.

Previous SNOM experiments have shown that the protruding regions in blends with  $\phi = 0.75$  sample are rich in F8 compared to the more depressed regions [18]. Given the segregation of F8 to the surface throughout these films, our NRA results suggest that these regions have close to 100% F8.

In figure 4, we show the peak in the power spectral density plot, which is a measure of dominant length scales in the films. The root-mean-square (rms) roughness is also obtained from the SFM data and is also shown in figure 4. We note from these data that the largest in-plane structure and roughness corresponds to the 50% film, with a similar form to that of the surface excess measured from the NRA data.

The physics of wetting in phase-separating systems is a rather complicated process, and it has only been studied analytically on a few model systems [3–5, 19–25], where sample annealing can be used as a tool to control structure formation. Unannealed samples represent more practical situations, because annealing is a further processing step, which may well have only a limited effect on highly immiscible films. There have been a few studies of the structure of spin-cast polymer blends [6, 13, 26–30], but these have been largely qualitative, although more quantitative studies are now appearing [31, 32]. A simple approach to understanding the mechanism of spin-casting is to consider it in several stages, the first of which is the removal of excess material (polymer and solvent) during spinning. Afterwards the film thins as the solvent evaporates. At a given solvent concentration, assumed to be the cloud point, the polymer chains start to interact significantly enough for phase separation to occur. Phase separation stops when the polymer passes through its glass transition, which does not have to be the same for the two phases [6]. Phase separation results from competition between enthalpy and entropy, but in spin-cast blends there are kinetic effects that should also be considered. For example, a fast quench may result in far-from-equilibrium states frozen in by a glass transition. It is difficult to identify how entropic, enthalpic, and kinetic effects contribute to the final morphology, especially since there is the additional complication of the two polymers both having crystalline phases. However, the ternary phase rich in F8 can be expected to have the lower surface energy, because this is the component that remains at the surface.





**Figure 5.** NRA data for a chloroform-cast blend (50% d-F8 by volume). Here we see no clear surface structure. Given that the resolution (Gaussian width) of the experiment is  $\sim 4.7$  nm, this would imply that any surface layer in this film must be  $< 1$  nm. The volatility of chloroform is such that spin-cast films are generally inhomogeneous, with thickness varying across the film, resulting in poorly-resolved structure near the substrate.

The increased roughness and segregation for 50% blends is representative of the shape of the ternary phase diagram. Because the polymer blend is symmetric, it would be expected to cross the cloud point at an earlier stage in spin coating than for other F8 volume fractions. The reason that the 50% F8 films have larger domain sizes and greater roughness reflects this greater time available for the phase separation; the earlier in the spin coating process that domains form, the more time they have to grow. The observation of roughness, domain size, and surface excess reaching a maximum in the 50% F8 films is as would be expected without complicating effects such as liquid crystallinity or the glass transition freezing in structure at different times in the different phases.

Polymer blend structures are very dependent on the solubilities of the different polymers with the casting solvent, and so changing the solvent can have a remarkable effect on final film structure [33]. To this end, we replaced toluene by chloroform. NRA data on such films show no noticeable surface segregation (figure 5), and SFM measurements reveal a very small in-plane structure [14]. The explanation for the smaller in-plane structure in the chloroform-cast blends could be because chloroform is a much better solvent than toluene for these two polymers. Because chloroform is a better solvent than toluene, the polymers stay in solution longer, and the film vitrifies before significant structure has had time to form. Such a result reinforces conclusions from a comparison between experiments on F8BT and PFB, where xylene-cast blends exhibited a strong lateral structure whereas those cast from chloroform had a very fine structure [30]. An alternative explanation relies on the volatility of chloroform with respect to toluene. A more volatile solvent could evaporate faster than the polymer phases separate, leading to a faster quench.

#### 4. Summary and conclusions

We have used scanning probe and ion beam techniques to obtain information on the structure of a symmetric blend of polyfluorene derivative polymers. NRA data show that there is significant surface segregation in the samples cast from toluene with less than 80% d-F8. We cannot exclude surface segregation in the other toluene-cast samples on account of the small

surface segregated peak that would be present in a sample containing so much deuterated material (experiments with deuterated F8BT would be useful in this situation). NRA data on samples cast from chloroform showed no measurable segregation. An analysis of SFM measurements on the surface topography of these samples shows that there is much larger scale phase separation in the 50% sample cast from toluene than in any of the other samples.

The results can be explained by considering the behaviour of the polymers in the context of a ternary (polymer/polymer/solvent) phase diagram. In the better solvent, the higher solubility impedes wetting layer formation, which might suggest different device performances, which is certainly observed in photoemission in our experiments [14]. We do have the possibility to tune the domain and segregated layer size by varying the volume fraction of each component, as well as the casting solvent, which certainly does affect the efficiency of organic LEDs [14].

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