Case Study 2: Depth Profiling Polymer Thin Films

Summary

Ion beam analysis (IBA) methods have been crucial in understanding the mixing and demixing behaviours of polymers. Using this understanding, many novel and highly useful types of devices and materials can be made. Plastic electronics is now a huge market, as also is plastic packaging and coating. The Figure shows a photovoltaic (PV) panel after some rain: we rely on plastic coatings for durability under very testing conditions, and it is the polymer chemists who have to deliver this performance.

As an example, we concentrate on an application of demixing incompatible polymers in a model PS:F/amPET system [1] to obtain hydrophobic and lipophobic (“water and fat hating”) surfaces extremely efficiently. The polystyrene (PS) is fluorinated, making it very surface-active and the “amPET” is an amorphous co-polymer analogous to the (semi-crystalline) polyetheleneterephthalate (PET). Understandings obtained on this model system immediately apply to commercial systems.

The polymer chemists regularly use neutron reflection (NR) to obtain very high resolution depth profiles in intermixing experiments. However NR is insensitive to slow concentration changes, so using NR/IBA synergistically is very powerful. In this case the NR demonstrates that segregation of the two polymers is complete in the first 5 nm of the film after annealing, with a sharp interface of no more than 1 nm thickness. But nuclear reaction analysis (NRA: a form of IBA) allows the PS/PET diffusion constants before annealing to be obtained very precisely.

This application is aimed at doing cheaply what is quite easy to do if expense is of no concern. Plastics are produced in very high volumes, and cheap feedstock materials (or limited quantities of more expensive ones) are of the essence for commercial production. Using the methods investigated here a small quantity of pricey polymer can be added to the bulk and it will segregate to the surface to give the required barrier properties.
Polymers are cheap and ubiquitous materials which can very easily be deposited as thin films for an astonishing variety of purposes. Polymer chemists have investigated the interdiffusion structures of miscible and immiscible polymers and as well as coatings have now made (for example) organic light-emitting diodes (OLEDs), organic PV cells, polymer field-effect transistors (FETs) and materials with high potential for photonic applications.

In all these cases, to understand the complex thermodynamics driving the development of structure, a materials science approach following and accounting for this structure is required. Many methods are used, as usual in this multi-disciplinary field, but “nuclear reaction analysis” (NRA) using the $^3\text{H}(^3\text{He}, ^1\text{H})^4\text{He}$ [2] reaction together with deuteration of one of the mixing components has been found extraordinarily powerful in combination with neutron reflectivity. The NRA method is useful precisely because the isotopic effect due to deuteration is well understood (see Jones et al, PRL 1989 [3]). Straightforward Rutherford backscattering spectrometry (RBS) [4] is also powerful where one of the polymers is distinguished by a heavy component (sulfur, for example).

In the example (James et al, Reactive & Functional Polymers 2015 [1]), diffusion coefficients for the molecules used are obtained directly from a parameterised fit of multiple NRA spectra collected for different glancing beam incident angles, with an absolute (model-free) depth resolution comparable to about 10 nm and an information depth extending more than a quarter of a micron. Bayesian techniques give reliable estimates of the uncertainty of these (parameterised) coefficients: in this case the thickness of the surface enriched layer is obtained with a precision of about 1 nm, where the interface width between the surface enriched layer and the depleted layer immediately beneath it is obtained with a precision of about 3 Å. Of course neutron reflectivity has a much higher absolute depth resolution than this but a much lower sensitivity to slow changes in concentration.
The NRA used in James et al, 2015, is essentially the same as that used by Chappell et al (2003) [5] (see Figure). In this work, a blend of the conjugated polymers poly(9,9′-dioctylfluorene) (PFO) and poly(9,9′-dioctylfluorene-altbenzothiadiazole) (F8BT) is used. This blend is successfully used in experimental light emitting diodes (LEDs) but in this sort of material the exciton diffusion distance is very small (<10 nm) so that nanostructuring is essential to obtain electronic performance. As for James et al, the NRA enabled the understanding of the real nanostructuring behaviour due to phase separation in this polymer blend.

Phase separation or miscibility in polymer blends is central to polymer thin film technology, and characterising it is essential. Another interesting example in material being evaluated for electronic device purposes is given by Goffri et al (Nature Materials 2006) [6]. They explore the electronic performance in field-effect transistors (FETs) of bicomponent films of crystalline poly(3-hexylthiophene) (P3HT) with amorphous polystyrene (a-PS) or (crystalline) high density polyethylene (HDPE), and demonstrate the mechanism for the advantage in electronic performance that crystalline materials have over amorphous (see Figure, left). Similar segregation behaviour in a completely different context can be seen by RBS in (for example) Malléol et al, Langmuir 2002 [7] and in Aramandia et al, Langmuir 2003 [8].

An interesting example of self-assembly of a photonic crystal was demonstrated very recently by Utgenannt et al (ACS Nano, 2016) [9]. The Figure (right) shows an RBS spectrum from the process that worked: this was very helpful to the polymer scientists to identify it from all the variants that did not work! A 3D ordered structure is self-assembled from Au nanoparticles using as the drying of a suspension of spherical polymer particles in a volatile liquid to create a soluble “former”. The process is clearly understood from the polymer chemistry and can be completely modelled (see the video: Movie-Utgenannt_ACSnano2016.pptx).
Keywords
Polymers, thin films, OLED, FET, photonic, deuteration, diffusion coefficient, Bayes, PFO, F8BT, nanostructuring, phase separation, self-assembly, nanoparticles

Complementary Techniques
IBA: ion beam analysis (including RBS and NRA)
RBS: Rutherford backscattering
NRA: nuclear reaction analysis
NR: neutron reflectivity

Cited Literature