



Depth Profiling Polymer Thin Films

In [Chappell et al \(2003\)](#) [5], a blend of the conjugated polymers poly(9,9'-dioctylfluorene) (PFO) and poly(9,9'-dioctylfluorene-alt-benzothiadiazole) (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.

This is one example where IBA has provided critical information. There are many such, and this Case Study aims to give an idea of the breadth of usefulness of IBA (with complementary techniques) to surface and interface science for polymer functional materials.

The polymer chemists regularly use [neutron reflectivity](#) (NR), a technique which needs one of the big "neutron spallation sources" (like [ISIS](#) in the UK), to obtain very high resolution depth profiles in intermixing experiments. However, because NR is insensitive to slow concentration changes, using NR/IBA synergistically has been found extraordinarily powerful.

A recent example of this is an application ([James et al, 2015](#) [1]) of demixing incompatible polymers in a model ("PS:F/amPET") system 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) poly-ethelene-terephthalate (PET). The PS is deuterated, to allow both NRA and NR. Understandings obtained on this model system immediately apply to commercial systems (such as surface coatings on solar panels).

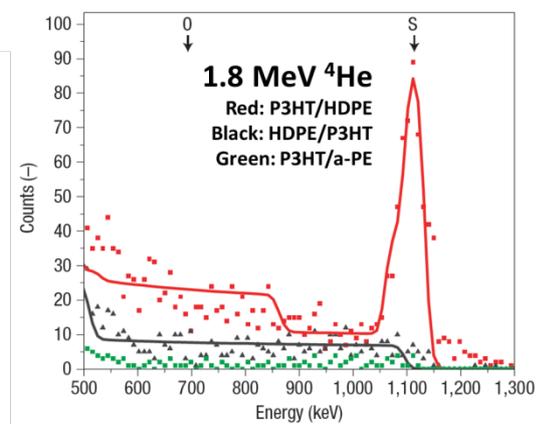
In this example, diffusion coefficients for the molecules used are obtained directly from a parameterised fit of multiple NRA spectra collected for different glancing beam incident angles, with an absolute (model-free) depth resolution comparable to about 10 nm and an information depth extending more 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.

For the PS:F/amPET model system, neutron reflectivity has a much higher absolute depth resolution than NRA but a much lower sensitivity to slow changes in concentration. Given the (relatively low resolution) depth profile from NRA, the NR data can be interpreted unambiguously to yield high resolution depth profiles showing the detailed interface behaviour of the system. In particular in this case, the NR shows entire surface phase separation of the two polymers, that is, there is a complete wetting layer of PS at the surface.

The NRA method has long been known (see [Payne et al, 1989](#) [2]) and 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) is also powerful where one of the polymers is distinguished by a heavy component (sulfur, for example). Phase separation or



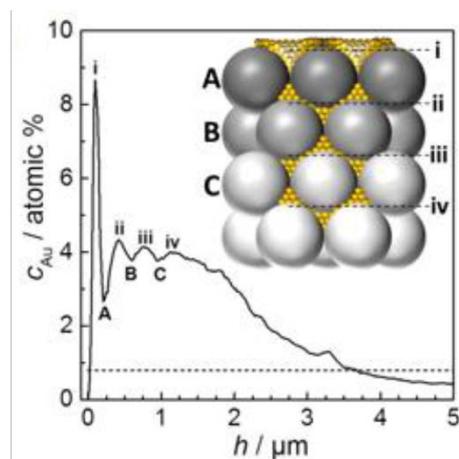
Fitted RBS spectra from blends of polyethylene (PE) with a hexylthiophene (P3HT: $C_{10}H_{16}S$). Where the P3HT crystallises first (red) a thin layer of P3HT segregates to the surface. Where the HDPE crystallises first (black) there is no segregation, as for the amorphous PE (green). The surface signals of S and O are marked.

Reproduced from Figure 3b of Goffri *et al*, *Nature Materials* 2006

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) Mallégoil *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 depth profile 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 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 published with the paper, which is open access).



Self-assembly of a photonic crystal from Au nanoparticles in a suspension of polymer spheres (soluble in toluene) in water. A Au depth profile from the dried film is shown, obtained with 5.45 MeV $^7Li^{++}$ RBS.

Figure 1e of Utgenannt *et al* (*ACS Nano*, 2016)



Cited Literature

- [1] Christopher D James, Christopher Jeynes, Nuno P. Barradas, Luke Clifton, Robert M Dalgliesh, Rebecca F Smith, Stephen W. Sankey, Lian R. Hutchings, Richard L. Thompson, [Modifying polyester surfaces with incompatible polymer additives](#), *Reactive and functional polymers*, **89** (2015) 40–48; DOI: 10.1016/j.reactfunctpolym.2015.03.002.
- [2] R.S. Payne, A.S. Clough, P. Murphy, P.J. Mills, [Use of the \$D\(^3\text{He,P}\)^4\text{He}\$ reaction to study polymer diffusion in polymer melts](#), *Nuclear Instruments & Methods B*, **42** (1989) 130-134; DOI: 10.1016/0168-583X(89)90018-9.
- [3] Richard A.L. Jones, Edward J. Kramer, Miriam H. Rafailovich, Jonathon Sokolov, Steven A. Schwarz, [Surface enrichment in an isotopic polymer blend](#), *Physical Review Letters*, **62** (1989) 280; DOI: 10.1103/PhysRevLett.62.280.
- [5] John Chappell, David G. Lidzey, Paul C. Jukes, Anthony M. Higgins, Richard L. Thompson, Stephen O'Connor, Ilaria Grizzi, Robert Fletcher, Jim O'Brien, Mark Geoghegan, Richard A.L. Jones, [Correlating structure with fluorescence emission in phase-separated conjugated-polymer blends](#), *Nature Materials*, **2** (2003) 616-621; DOI: 10.1038/nmat959.
- [6] Shalom Goffri, Christian Müller, Natalie Stingelin-Stutzmann, Dag W. Breiby, Christopher P. Radano, Jens W. Andreasen, Richard Thompson, René A.J. Janssen, Martin M. Nielsen, Paul Smith, Henning Sirringhaus, [Multicomponent semiconducting polymer systems with low crystallization-induced percolation threshold](#), *Nature Materials*, **5** (2006) 950-956; DOI: 10.1038/nmat1779.
- [7] J. Mallécol, J.-P. Gorce, O. Dupont, C. Jeynes, P.J. McDonald, J.L. Keddie, [Origins and effects of a surfactant excess near the surface of waterborne acrylic pressure-sensitive adhesives](#), *Langmuir*, **18** (2002) 4478-4487; DOI: 10.1021/la0117698.
- [8] Esteban Aramendia, Jacky Mallécol, Chris Jeynes, María J. Barandiaran, Joseph L. Keddie, José M. Asua, [Distribution of surfactants near acrylic latex film surfaces: A comparison of conventional and reactive surfactants \(surfmers\)](#), *Langmuir*, **19** (2003) 3212–3221; DOI: 10.1021/la0267950.
- [9] Andre Utgennant, Ross Maspero, Andrea Fortini, Rebecca Turner, Marian Florescu, Christopher Jeynes, Antonios G. Kanaras, Otto L. Muskens, Richard P. Sear, Joseph L. Keddie, [Fast assembly of gold nanoparticles in large-area 2-D nanogrids using a one-step, near-infrared radiation-assisted evaporation process](#), *ACS Nano* (2016); DOI: 10.1021/acsnano.5b06886.