NEXAFS microscopy of polymeric materials: Successes and challenges encountered when characterizing organic devices

H. Ade¹, B. Watts¹, S. Swaraj¹, C. McNeill², L. Thomsen¹, W. Belcher³, and P. C. Dastoor³

¹Dept. of Physics, North Carolina State University, Raleigh, NC27685-8202, USA
²Cavendish Lab., Dept. of Physics, Univ. of Cambridge, Cambridge, CB3 0HE, UK
³Centre for Organic Electronics, Univ. of Newcastle, Callaghan, NSW 2308, AU

E-mail: harald_ade@ncsu.edu

Abstract. We summarize recent developments in x-ray microscopy of polymers by focusing on the characterization of organic electronic devices. The quantitative compositions of model polymer blends have been mapped at a resolution of ~35 nm. Since it could be inferred that these devices have structures smaller than 35 nm, quantitative compositional mapping at length scales below the present resolution limit of x-ray microscopy is required. Organic devices thus serve to both highlight the success of NEXAFS microscopy to date, but to also outline the very real need for higher spatial resolution. New approaches to create improved optics or different acquisition modalities are required if x-ray microscopy is to make sustained contributions to such an important area of research as organic devices.

1. Introduction

Over the past decade, x-ray microscopy characterization of organic and polymeric materials [1-3] has been very successful due to the high compositional sensitivity of Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy and the minor damage of soft X-rays [4]. We summarize recent efforts by focusing on NEXAFS microscopy of organic electronic devices. Organic photovoltaics based on solution processed conjugated polymers have the potential to meet the need for efficient and cheap solar cell technology [5]. In organic solar cells, the exciton created by the absorbed photon needs to be split at a donor-acceptor interface and the most common “bulk heterojunction” devices have these interfaces distributed throughout the active layer. Since solution processed films of donor and acceptor materials result in complex nonequilibrium morphologies with phase separation at multiple length scales, a quantitative compositional characterization tool is required to investigate the relationship between local composition and device performance. McNeill et al. have thus used NEXAFS microscopy to investigate a number of organic PV devices [6-9]. Here, we review the influence of annealing on the morphology of initially intimately mixed blends of the conjugated polymers poly(9,9’-dioctylfluorene-co-bis-N,N’-(4, butylphenyl)-bis-N,N’-phenyl-1,4-phenylene-diamine) (PFB) and poly(9,9’-dioctylfluorene-co-benzothiadiazole) (F8BT) and provide a context for higher resolution requirements in x-ray microscopy.

4 To whom any correspondence should be addressed.
2. Experimental

~150 nm thick PFB/F8BT blends cast from chloroform onto poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid coated glass slides were annealed for 10 min on a hotplate, quenched to room temperature, and floated off onto TEM grids [9]. Measurements were performed with the 5.3.2 STXM at the Advanced Light Source [10]. Full details of the experiment and analysis can be found in a previous publication [6].

3. Results

Quantitative composition maps of an as-spun PFB/F8BT blend film and films annealed at 140, 160, 180 and 200 °C are displayed in Fig. 1, along with the photoluminescence quantum efficiency (PLQE) of these films and a F8BT reference film. Some compositional variations can be observed even for the as-cast films. For the 140 and 160 °C films, there is little difference compared to the as-spun film. In contrast, there is a pronounced coarsening of the morphology and corresponding increase in compositional variation for the 180 and 200 °C films. They also exhibit a bicontinuous morphology that evolves in a way reminiscent of spinodal decomposition. The quantitative analysis of feature size and compositional variation is summarized in Fig. 2, along with the domain size inferred from the PL data through the use of a model that takes the exciton diffusion length into account.

![Figure 1. Composition maps of PFB/F8BT blend films: as-spun (a) and annealed at T=140 °C (b), 160 °C (c), 180 °C (d), and 200 °C (e). (f) Photoluminescence quantum efficiency (PLQE) of annealed blend films and a pure F8BT film.](image)

![Figure 2. Compositional variation, measured feature size and calculated domain size from PLQE measurements versus annealing temperature.](image)

4. Discussion

For the as-spun films, some structure is observed with dimension of ~ 85 nm. These structures are not pure phases and there must be significant intermixing with a hierarchy of phase separation existing on the length scale of less than 85 nm. With annealing, this finer scale of phase separation should evolve as pure (or very nearly pure) domains within these 85 nm structures. This hypothesis is supported by the fact that the length scales derived from PLQE data imply morphological evolution at annealing temperatures for which little variation can yet be observed with NEXAFS microscopy. At 160 °C, the size of the internal domains approaches that of the enclosing structures. Above 160 °C, the evolution...
of the morphology is directly recorded with x-ray microscopy and is characterized by a bicontinuous morphology favourable for charge transport. A Monte Carlo model of exciton diffusion and dissociation was able to achieve good agreement for T>140 ºC between the domain size measured by STXM and those calculated by the model using an exciton diffusion length of 12 nm [9].

Clearly, real space characterization of these samples would greatly benefit from improved spatial resolution and tomography. Given that the exciton diffusion length in these organic materials is ~10 nm, the optimum devices will have to have phases ~10 nm in size. Consequently, characterization at that length scale is required for optimal understanding and significant improvements in spatial resolution are required to do. Unfortunately, advances in spatial resolution have become increasingly more difficult. Extrapolation of the best spatial resolution over the last two decades implies (see Fig. 3) that the 10 nm resolution limit might only be achieved in about a decade from now.

Organic devices thus serve to highlight the success of NEXAFS microscopy to date, but these devices also emphasize the very real need for higher spatial resolution. Clearly new approaches to zone plate fabrication or new methods are necessary to achieve faster progress. Recent zone plate developments [11,12] or x-ray ptychography [13] might be excellent ways forward.

Acknowledgments
The authors thank D. Kilcoyne and T. Tyliszczak for assistance and support. The work was supported by the EPSRC, U.K. (Advanced Research Fellowship EP/E051804/1), the Australian Research Council’s Discovery funding scheme (DP0559417), and the U.S. Department of Energy under contracts DE-AC02-05CH11231 and DE-FG02-98ER45737.

References:
[1] Ade, H, Zhang, X, Cameron, S et al., 1992 Science 258 972.
[2] Ade, H and Hsiao, B, 1993 Science 262 1427.
[3] Ade, H and Hitchcock, A P, 2008 Polymer 49 643.
[4] Rightor, E G, Hitchcock, A P, Ade, H et al., 1997 J. Phys. Chem. B 101 1950.
[5] Mayer, A C, Scully, S R, Hardin, B E et al., 2007 Mater Today 10 28.
[6] McNeill, C R, Watts, B, Thomsen, L et al., 2006 Small 2 1432.
[7] McNeill, C R, Watts, B, Thomsen, L et al., 2007 Macromol. 40 3263.
[8] McNeill, C R, Watts, B, Thomsen, L et al., 2008 Nanotechnology 19 424015.
[9] McNeill, C R, Watts, B, Thomsen, L et al., 2008 Macromol. (submitted).
[10] Kilcoyne, A L D, Tyliszczak, T, Steele, W F et al., 2003 J Synchrotron Radiat 10 125.
[11] Chao, W L, Harteneck, B D, Liddle, J A et al., 2005 Nature 435 1210.
[12] Jefimovs, K, Vila-Comamala, J, Pilvi, T et al., 2007 Phys. Rev. Lett. 99 264801.
[13] Thibault, P, Dierolf, M, Menzel, A et al., 2008 Science 321 379.