Characterization of medium-range order in organic-inorganic hybrid nanomaterials by fluctuation x-ray microscopy

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Introduction

Medium-range order (MRO) is crucial for understanding the nature of defects, mechanical behaviors, rheology in polymers, order-disorder processes and nucleation, etc. Measuring MRO is a challenging problem. Recently, we have developed fluctuation x-ray microscopy (FXM), which offers quantitative insight into MRO in materials at the micrometer scale [1-4]. In this paper, we have applied our further-developed technique for characterization of MRO in nanomaterials.

The study of mesostructured polymer-inorganic hybrid materials is an exciting, emerging research area offering enormous scientific and technological promise. The ability to control the shape, size and order of hybrid materials is a key requirement for their future development. By choice of the appropriate block copolymer system and inorganic precursors, the shape and size of the hybrid materials can be controlled at the nanometer scale. However, the control of formation and ordering of the nanostructures with medium to long range order remains a challenge that limits advances in many fields of nanotechnology. By using FXM here we examine the influence of sol-gel process variables on medium range order.

Methods and Materials

The FXM method is described elsewhere [1-4]. Two hybrids of PI-b-PEO/aluminosilicates with ~20nm phase separation length scale were prepared using known procedures [5]. The PI-b-PEO amphiphilic block copolymer was synthesized via anionic polymerization techniques. Hybrids were fabricated by dissolving 0.05 g of PI-b-PEO in tetrahydrofuran (THF) (sample A) or a THF/chloroform mixture (28/72 v/v) (sample B) and adding 0.3 g of pre-hydrolyzed sol-gel inorganic precursors (3-glycidyloxypropyl-trimethoxysilane and aluminum-tri-sec-butoxide). Samples were spin coated onto Si_3N_4 windows on Si substrate [6]. Both samples were UV/ozone treated for degrading the isoprene components in order to increase contrast for x-ray scattering experiments. The sample A was further cacinated at 350°C to remove all organic components (PEO and PI).

Results and Discussions

The experiments were performed at the 2-ID-B beamline at the Advanced Photon Source. The coherent x-ray beam is required for examining variance of speckle patterns. A nanofocusing technique using a zone plate and varying illumination size through using a pinhole set as a zone-plate mask was developed to study the order correlations at the scales from 50 nm to 500 nm. By scanning the sample and exchanging zone-plate masks, we obtained speckle patterns over a range of sample positions for three illumination sizes: 120 nm, 200 nm and 400 nm. As an example, Fig .1 shows the mean and normalized variance calculated from ~1000 speckle patterns for sample A. The characteristic length scale of MRO can be quantitatively obtained by plotting R^2/V vs R^2 as shown in Fig. 2, where R is the illumination size and V is the normalized variance [4, 7].

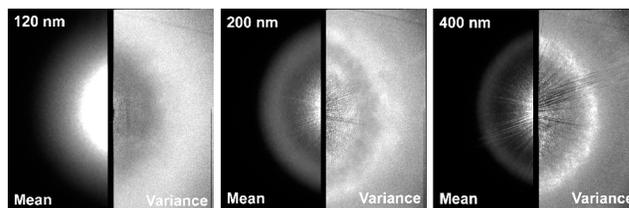*Fig.1: Mean (left) and variance (right) from A sample with thickness ~1 µm at the three illumination sizes indicated and at x-ray energy of 1.83 keV.*

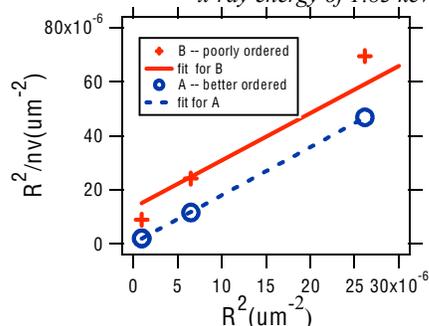

Fig.2: The plots of R^2/V vs R^2 for two samples.

The correlation lengths are 380nm±57nm and 57nm±2nm for samples A and B, respectively. Mainly because of higher THF/chloroform ratio sample A is better ordered than B. The THF acts as a good solvent for all three components. A solution with THF as the sole solvent thus generates well-ordered samples upon evaporation. On the other hand, chloroform evaporates much faster than THF and is a less good solvent for the inorganic precursors. During spin coating the transition from the solution to the solid film is thus shorter leaving the polymer/inorganic mixture less time to co-assemble and rearrange, resulting in poorly-ordered samples. The calcination step can significantly sharpen the interface between the inorganic matrix and voids which may add a little bit to the better order. The higher order of sample A revealed by FXM is consistant with our AFM measuments. While AFM sees only surface ordering phenomena, FXM shows that the order extends ~1 µm into the film of the hybrids.

Reference

1. L. Fan et al. *Nucl. Inst. and Meth. B,* 238, 196-199 (2005).
2. L. Fan et al. *Mater. Res. Soc. Symp. Proc.* 840, Q6.7.1-Q.6.7.6 (2005).
3. M. M. J. Treacy, et al. *Rep. Prog. Phys*. 68, 2899-2944 (2005)
4. L. Fan et al. J. of Microscopy in process
5. M. Templin et al. *Science* 278, 1795-1798 (1997).
6. P. Du et al., Adv. Mater. 16, 953-957 (2004).
7. J.M. Gibson et al. Ultramicroscopy, 83, 169 (2000).

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