

Near-Field Optical Imaging of Microphase Separated and Semi-Crystalline Polymer Systems

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Polymer self-assembly presents an attractive means of creating the micro- and nano-patterned spatial arrays required for many opto-electronic and coatings technologies. Two of these ordering processes are microphase separation (MS), exhibited by block copolymers, and crystallization, common in many polymer species. In this work, we present optical micrographs of block copolymer MS morphology and thin-film polymer crystallites having sub-diffraction-limit resolution ($\approx 100\text{nm}$) as afforded by Near-Field Scanning Optical Microscopy (NSOM). Images obtained via transmission aperture NSOM and polarization-modulated (PM) NSOM, which yields the local dichroism and birefringence, will be discussed. These images provide insights into the structure and local optical properties of these specimens, resolved at the level of single microphase domains and defects.

A detailed review of aperture transmission NSOM can be found in reference [1]. Our PM-NSOM uses Al-coated aperture probes, fabricated from drawn optical fibers, and a 488nm light source. Measurements of polarimetric quantities were made via the PM technique [2], adapted for NSOM in a manner similar to McDaniel and Hsu [3], but improved upon here by employing Fourier analysis. Modulated (50kHz) source-light polarization is created via a photoelastic modulator and complimentary optics. Fourier analysis of the transmitted signal yields the sample dichroism and birefringence (if a post-sample analyzer is in place) at each point. Our measurement techniques and analysis rectify probe-fiber birefringence and any inherent dichroism of the probe-aperture.

Microphase separation is driven by the immiscibility of the end-linked polymer chains, or blocks, constituent to a block copolymer (BC). A variety of pattern motifs and equilibrium periodicities (L_0) are achieved by controlling the BC composition and molecular weight (MW), respectively [4]. Recent synthetic efforts have created ultrahigh MW BCs, with L_0 of 150-300nm, that exhibit tunable photonic band gaps in the visible range [5,6]. Figs. 1-3 shows NSOM and PM-NSOM data collected from a 100nm-thick polystyrene-b-polyisoprene (PS-b-PI) photonic BC specimen. OsO_4 was used to impart a light stain to PI domains. Z-ranges are supplied in brackets, [], in each figure caption. Transmission NSOM (Fig. 1) illuminates single lamellar domains, and defects exhibiting enhanced optical contrast. PM-NSOM data gives the local dichroism (Fig. 2), which marks domain interfaces, and birefringence (Fig. 3), which reflects the local domain/chain orientation.

Polymer crystallites consist of layers (lamella) of folded chains and intermediate amorphous domains. While the structure of bulk polymer crystallites (spherulites) is well established [7], a variety of less-understood forms are found in ultra-thin ($<100\text{nm}$) films [8]. The sensitivity and resolution of PM-NSOM can illuminate the structure of these "2D" crystallites, where traditional techniques may fail due to low resolution and the sparse signal inherent to thin samples. This capability is demonstrated in Figure 4, which shows PM NSOM micrographs of a 100nm-thick isotactic PS spherulite. These images show the radial arrangement of crystallite lamella, defect

structures located near the crystal nucleus, and possible chain alignment in the “depletion zone” at the spherulite periphery.

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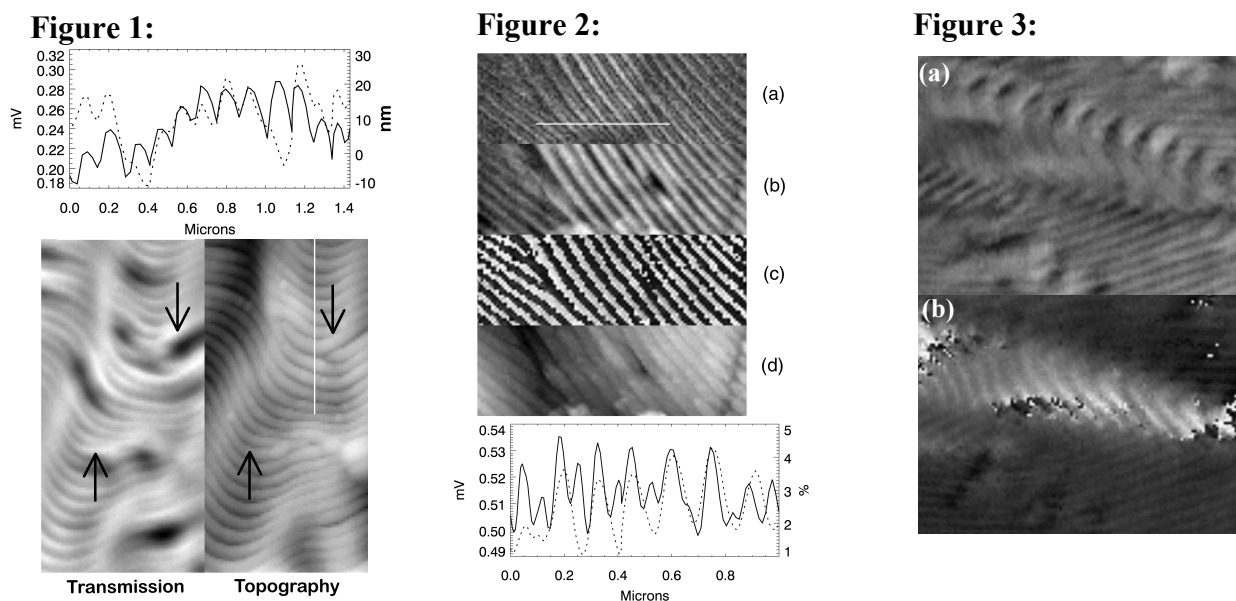


Fig. 1. NSOM micrograph of PS-b-PI. The top plot shows topography (dotted) and transmission (solid) along the white line (1.4 μm) in the topography image. Arrows indicate edge defects.

Fig. 2. PM-NSOM of PS-b-PI. (a) Dichroism [5%], (b) Transmission [0.2-0.5mV (a.u.)], (c) Dichroism angle [180°], (d) Topography [25nm]. The bottom plot shows transmission (dotted) and dichroism (solid) along white line (1 μm) (a).

Fig. 3. PM-NSOM of PS-b-PI twin boundary. (a) Transmission [0.2-0.25mV (a.u)] (b) Birefringence angle (fast axis) [180°] reflecting lamellar orientation. Images are 4 μm wide.

Figure 4:

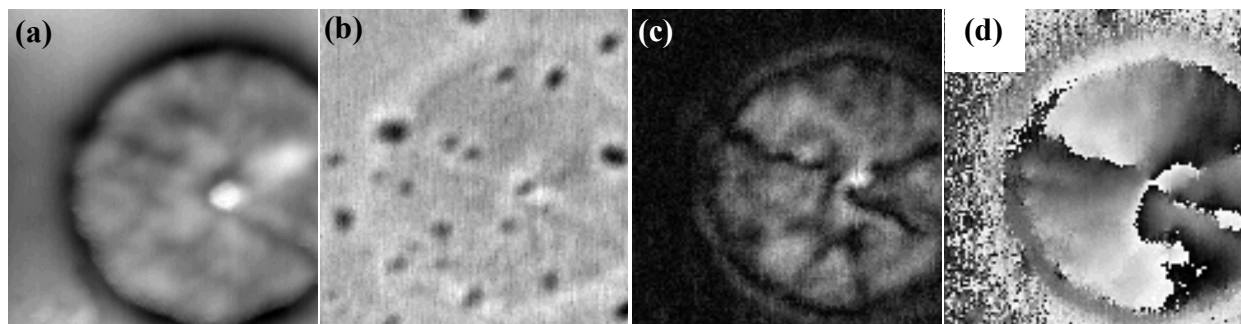


Fig. 4. PM NSOM of PS spherulite. Images are 6x6 μm . (a) topography [43nm], (b) transmission [0.2-0.25mV (a.u.)], (c) Birefringence (retardance) [6°], (d) Birefringence angle (fast axis) [180°].