Observation of Polymer Birefringence in Near-Field Optical Microscopy

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Birefringence, arising from locally preferred orientation of molecules or functional groups in polymeric and related materials has been observed in a near-field scanning optical microscope (NSOM) at suboptical spatial resolution. Our observations were successfully correlated to existing structural models of the samples, demonstrating the utility of birefringence observations in NSOM. We present data acquired from thin sections of a partially ordered polymer fiber (Kevlar) and a polymer dispersed small-molecule-liquid-crystal composite.

Observation of birefringence in conventional, or far-field, polarization light microscopy is an enormously useful and widespread form of characterization. It is routinely utilized in materials and polymer research and many other fields of science, including geology, pharmacology, and biology. Birefringence provides a unique contrast mechanism, as well as information regarding sample anisotropy, for a multitude of materials. Dynamical changes in birefringence as a function of temperature, pressure, or concentration are utilized, for instance, to discern phase boundaries in liquid crystalline systems. Such observations in far-field polarization microscopy are, however, limited in spatial resolution by diffraction, which is a shortcoming shared with other forms of far-field visible light microscopy. The diffraction limit to resolution can be overcome by resorting to near-field scanning optical microscopy (NSOM),12 utilizing a variety of contrast mechanisms based on fluorescence and luminescence,3–6 interference,7 and polarization,8 including the observation of Faraday rotation in magneto-optical bits.9

In this paper we exploit an aspect of polarization different from Faraday rotation. We demonstrate that the utility of birefringence observation can be preserved in a near-field microscope, and that it can be utilized for the investigation of surfaces and thin films of polymeric and related materials. Two classes of material have been studied. One is poly(p-phenyleneeterephthalamide) (PPTA) fibers (Kevlar). The other system consisted of a polymer-dispersed small-molecule-liquid-crystal (PDLC) composite. The apparatus utilized for this work is a force-regulated, near-field linear polarizing optical microscope10.
(see below). We believe this system is ideally suited to the investigation of polymeric samples, due to three significant attributes, namely, its (i) capability to provide high resolution and sensitivity in images of birefringence effects, independent of the variation of other optical characteristics such as transmissivity or reflectivity, (ii) ability to preserve the sign of the birefringence signal, so as to determine the relative orientation of the optical anisotropy parameters of the structures under study, and (iii) ability to correlate optical information with the simultaneously generated topographic map of the sample, to distinguish inherent birefringence from topographically induced and correlated birefringence, as well as to determine the origin of the observed birefringence (surface or subsurface).

To appreciate the significance of the attributes other than high resolution and sensitivity, we note that the normal mode of performing polarizing microscopy (viewing the sample between crossed polarizers) results in a square-law dependence of the signal on the birefringence. In this process, besides reducing sensitivity, one loses the sign of the birefringence. Thus, no direct conclusions can be drawn about the relative structural values of the system under examination. In addition, complementary high-resolution techniques for investigating such polymeric structures, such as linear dichroic X-ray microscopy, do not offer a simultaneous topographic imaging capability, an issue which can be of great significance in image interpretation. We also note here that the polarization of light as it emerges from the aperture in an NSOM has been shown to be maintained to a very high degree.

On the basis of theoretical considerations, however, one would expect the output light to include a certain amount of other orthogonal polarizations, which increases as the aperture diameter becomes very small. In our experiments, we did not observe any significant anomalies associated with this effect.

The system design is shown in Figure 1. At the heart of the system is a pulsed length of polarization preserving fiber, whose curved surface has been covered with a layer of aluminum, a process that leaves a small aperture at the very tip, and renders the rest of the structure opaque. The aperture size depends on the exact fabrication parameters and can be as small as about 20 nm. The system uses a He–Ne laser (at 633 nm), and pre-postmodulation via an electro-optical modulator (Pockels cell) that is driven at a frequency \( f_m \) to acquire two complementary images simultaneously.

![Figure 1](image)

**Figure 1.** Schematic of NSOM setup. In addition to the now common near-field microscopy components, the NSOM utilized here employs pre-postmodulation via an electro-optical modulator (Pockels cell) that is driven at a frequency \( f_m \) to acquire two complementary images simultaneously.

by lock-in detection of the signal from the detector at frequency \( f_m \), (first harmonic) and \( 2f_m \) (second harmonic). The polarizer and analyzer are at 90° with respect to each other. In the simplest case, the first harmonic image is proportional to \( \sin(\Delta \phi) \), whereas the second harmonic image is proportional to \( \cos(\Delta \phi) \). Both images contain intensity changes which depend on the sample transmission or reflectivity. Judicious adjustment of the Pockels cell allows these variations to be matched in intensity. Consequently, a pure, linear representation of the sample birefringence can be obtained in the limit of small phase changes, by dividing the first harmonic image by the second harmonic image. The resulting “tangent” image is therefore independent of the sample transmissivity or reflectivity (only scanning microscopes can be modified and operated in this fashion). The system has the inherent capability of performing simultaneous force microscopy of the sample and has been described elsewhere in detail.

Of the various commercial grades of Kevlar fibers available, we investigated Kevlar-29 which has the smallest degree of crystallinity and thus shows the least orientational order along the fiber axis. All Kevlar fibers exhibit a radially symmetric structure, in which the degree of radial order varies with different fiber grades. A model of a radially symmetric structure imaged with our microscope predicts that the first harmonic signal is proportional to \([\sin(\Delta \phi) \sin(2\gamma)]\), whereas the second harmonic signal is proportional to \([\cos(\Delta \phi) \sin^2(2\gamma) + \cos^2(2\gamma)]\), where \( \gamma \) is the angle between the instantaneous


\[\text{(15) Ade, H.; Smith, A. P.; Subramoney, S.; Hsiao, B. In preparation.}\]
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lies parallel to the polymer walls, and two point disclinations at opposite ends of the droplet define an axis of cylindrical symmetry.\textsuperscript{19} As a result of this geometry, and in contrast to the cross-sectioned Kevlar fibers, the intensity and definition of the patterns could be altered, in linear polarization imaging, by rotating the sample with respect to the polarizer/analyzer axes. Since these droplets are below the surface, they are not fully in the near-field. As a result, the resolution of most features in this sample is not as high as the system is capable of for features closer to the surface (within about 40 nm). Conversely, our imaging method allows differentiation of surface and subsurface features as correlated to topography. Of particular interest in these images are the halos around all of the LC domains or previous domains, such as the crater. This apparent feature suggests that the initially random poly(vinyl alcohol) matrix has undergone conformational ordering in the vicinity of the polymer/LC interface, which is consistent with a variety of bulk property measurements.\textsuperscript{20}

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\textsuperscript{19} Drzaic, P. S. J. Appl. Phys. 1986, 80, 2142.

\textsuperscript{20} Roy, S. C.; Spontak, R. J. In preparation.