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Evolution of elliptical SAXS patterns from aligned objects and lamellar arrays during deformation

N. Sanjeeva Murthy[1] and David T. Grubb[2]

[1]*Rutgers University, Piscataway, New Jersey U.S.A.* [2]*Cornell University, Ithaca, New York U.S.A.*
murthy@chem.rutgers.edu

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Two distinct features of small-angle X-ray scattering (SAXS) patterns are the central diffuse scattering (CDS) from uncorrelated structures and the discrete reflections from long-range order. Upon deformation, the CDS from voids, particles and interfaces present in polymers becomes an equatorial streak. Polymers with lamellar structures aligned by stretching or by a magnetic field produce four distinct SAXS patterns: 2-point 'banana', 4-point pattern, 4- point 'eyebrow', and 4-point 'butterfly' (Fig. 1) [1, 2]. Simulations show that when stack orientation (interlamellar shear), angle α, and chain slip, angle φ, act to rotate the lamellae in the same sense, the result is an eye brow pattern; opposite sense give a 'butterfly pattern [3]. When the lamellae are not tilted, then the result is a 2-point pattern. Changes in these two features in semicrystalline polymers during deformation were monitored to understand the changes in the structure at microstructural length scales and their implications on polymer properties.

In semicrystalline polymers, structures that gives rise to 4-point patterns reversibly transform under strain into structures that gives rise to 2-point patterns [1]; these patterns arise from lamellae with oblique and normal lamellar surfaces, respectively. These two structures represent bistable states of the lamellae that coexist until fiber breakage. The structures that give rise to the 2-point pattern is probably the load carrying lamellar entity in these fibers, and determine the ultimate strength of the fiber.
In magnetically aligned liquid crystalline (LC) phases of bent-core mesogens (BCMs), evolution from smectic C (SmC) to cybotactic nematic (Ncyb) and finally to isotropic phase can be understood by following the changes in their 4-point pattern [2]. As the temperature is increased, the increase in the orientational disorder is accompanied by a decrease in the tilt angle of the lamellae and in the ellipticity of the lamellar intensity distributions.

Detailed analyses show that the peak intensities of the reflections lie not on a layer line, or on the arc of a circle but are distributed in an elliptical trajectory (Figure 1). A moderate amount of disorder can make the peak positions trace out the ellipse.
Elliptical shape of the scattering pattern is a natural consequence of the scattering objects being elongated along the flow or the draw direction. Thus, in addition to the 2 - and 4-point reflections, even equatorial streaks (CDS) with shapes of an oval, diamond or 2-bladed propeller also have elliptical characteristics [4]. These equatorial streaks are commonly present in Poiseuille and extension flows [4], and in fibrous materials embedded with elongated voids or solid particles [5].

Elliptical features of the SAXS patterns, including the equatorial streak, suggests that the entire SAXS pattern can be optimally fitted in elliptical coordinates with least number of parameters. In contrast to this functional fitting, structural models generated using known principles of lamellar assembly and evolution can be validated by simulating scattering to agree with the observed diffraction patterns. Currently available computational tools allow these microstructures to be rapidly refined [3].

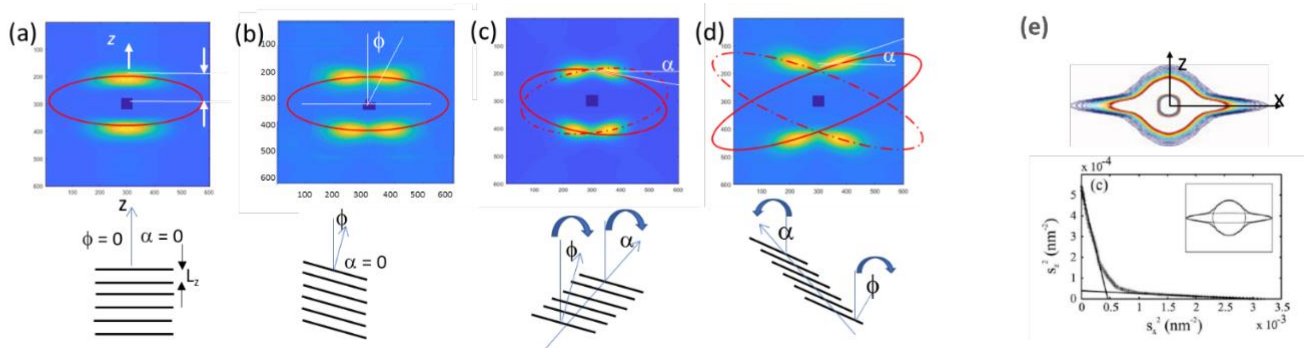

FIGURE 1. (a-d) Four classes of SAXS patterns and corresponding lamellar arrangements. Overlaid are the proposed elliptical tracks. (a) two-point banana pattern; (b) four-point pattern; (c) four-point eyebrow; (d) four-point butterfly. (e) Central diffuse scattering interpreted as composite of isotropic and an elliptical shaped equatorial streak.

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