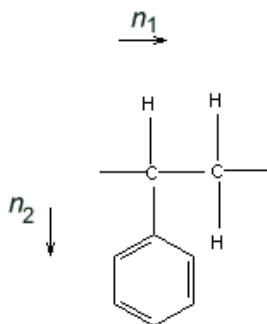


## The Theory of Birefringence

Birefringence spectroscopy is the optical technique of measuring orientation in an optically anisotropic sample by measuring the retardation of polarized light passing through the sample. Birefringence makes use of the refractive index,  $n$ , of a material, as defined below.

$$n = \frac{c}{v} = \frac{\text{speed of light in vacuo}}{\text{speed of light in sample}}$$

The refractive index varies linearly with the polarizability of the bonds in the sample. The refractive index of a material can be broken down into 3 orthogonal refractive indices. For polymers, two of the indices are usually relevant. An example is shown in Figure 1. For the polystyrene example shown here, the refractive index parallel to the main chain encounters primarily C-C bonds, which do not have significant polarizability. Consequently, the refractive index  $n_1$  is closer to 1. Light traveling perpendicular to the main chain will encounter the double bonds in the phenyl group, which will retard the light more, leading to a larger refractive index  $n_2$ .



**Figure 1: Polystyrene repeat unit, showing two principle refractive indices. The refractive index parallel to the molecules' backbone,  $n_1$ , is smaller than the refractive index perpendicular to the backbone,  $n_2$ .**

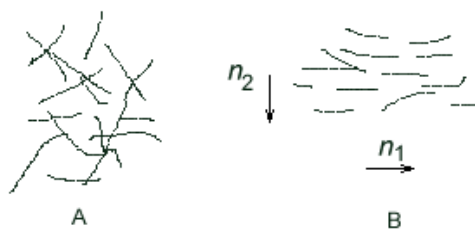
Birefringence  $\Delta n'$  is defined as the difference between the refractive indices in two planes, or

$$\Delta n' = n_1 - n_2 \quad (1)$$

When molecules are lying in with no specific orientation, the backbone of the molecules will be pointing in all directions, and no net refractive index can be observed, as shown in Figure 2.

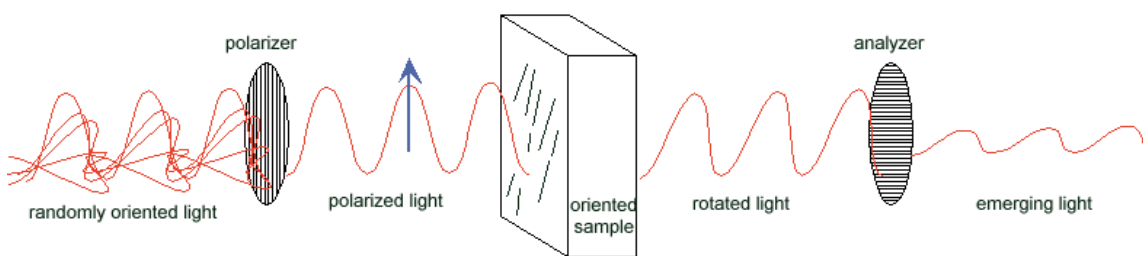
In order for a sample to exhibit birefringence, three criteria must be met:

1. There must be a non-zero difference in two of the refractive indices of the sample (equation 1)
2. There must be a net orientation in the sample to yield a primary refractive index in the sample.
3. The optics used to view the sample must be oriented correctly (see below).



**Figure 2: Two samples with different degrees of orientation. A: random orientation, exhibiting no birefringence. B: orientation, exhibiting birefringence.**

In order to view the birefringence in an aligned sample, polarized light must be used. A typical optical setup is shown in Figure 3. It is important that the polarizer is oriented so that it is neither parallel nor perpendicular to the principle axis of the sample, as will be discussed further.



**Figure 3: Randomly oriented light passes through a polarizer, which yields plane-polarized light with a principle axis shown with the blue arrow. The polarized light passes through the oriented sample, which partially rotates the light. The light then enters the analyzer, which is oriented 90° to the polarizer. Only the portion of the light that is parallel to the analyzer axis emerges on the other side of the analyzer.**

To understand how the light is rotated by the sample in the schematic diagram in Figure 3, it is necessary to decouple the light beam into orthogonal vectors based on the axis of the refractive index of the sample. An example of this decoupling is shown in Figure 4.

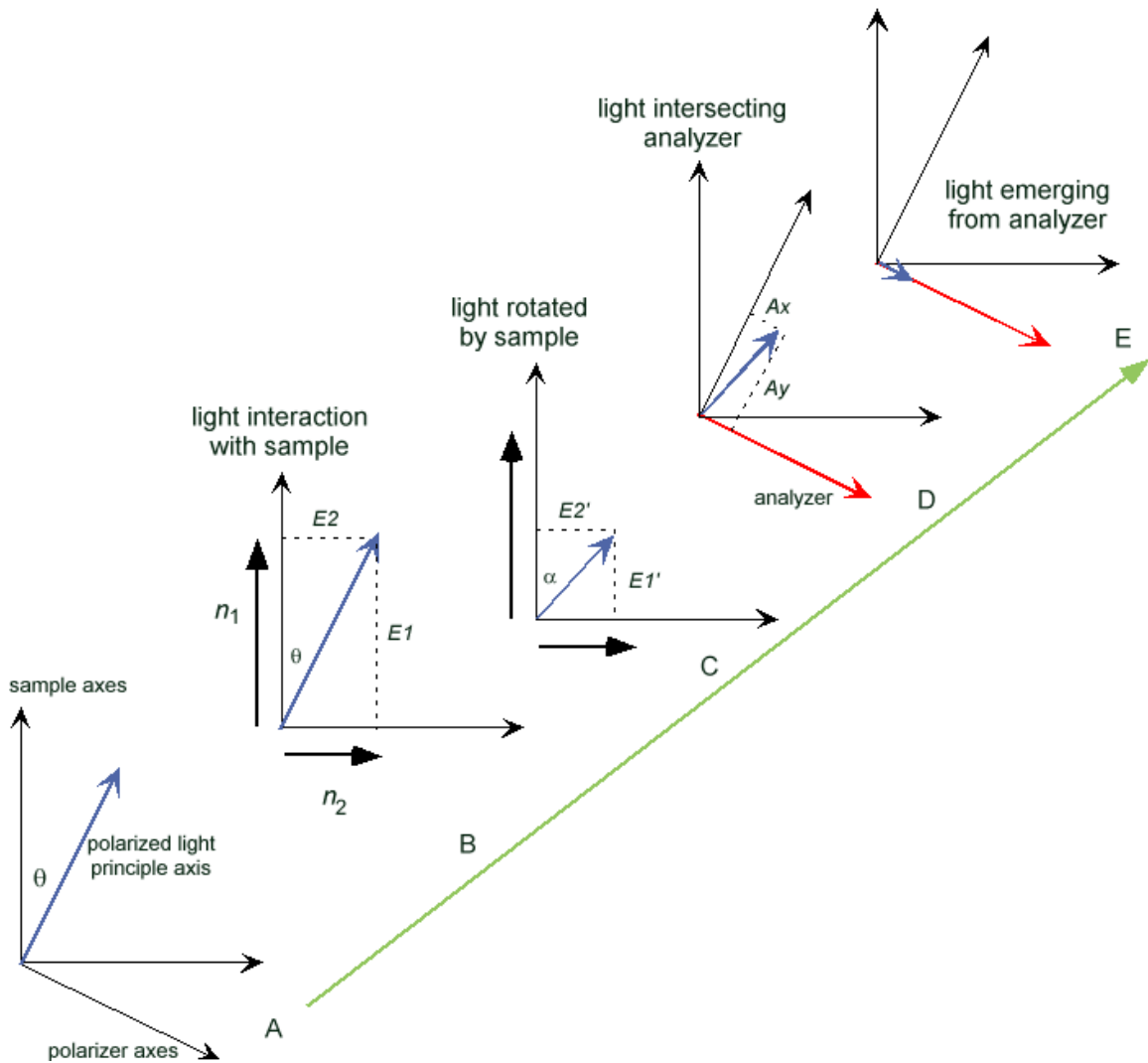
The amplitude of the emerging  $A_x$  is measured as a light intensity with an optical detector. The results for a specific sample are usually reported in terms of the retardation  $\delta$ . A graphical representation of the retardation is shown in Figure 5. Retardation is usually reported in degree ranging from 0-360°. As shown in Figure 5, the amount of retardation is dependent on the thickness of the sample,  $L$ , as well as the birefringence  $\Delta n'$  of the sample and the wavelength of the light,  $\lambda$ . The retardation is defined in terms of these parameters as:

$$\delta = \frac{2\pi L \Delta n'}{\lambda} \quad (2)$$

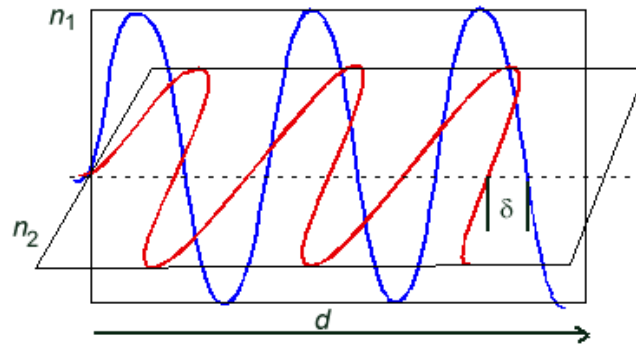
The measured light intensity  $I$  for a birefringence measurement is computed from the following equation:

$$I = I_0 \sin^2(2\theta) \sin^2(\delta/2) \quad (3)$$

where  $I_0$  is the intensity of light emerging from the polarizer. As equation 3 indicates, the measured intensity is zero for  $\theta = n\pi$  ( $n=0, 1, 2, \dots$ ) and for  $\delta = 2n\pi$  ( $n=0, 1, 2, \dots$ ).



**Figure 4: Rotation path of light interacting with sample. The principle axes are aligned with the refractive indices of the sample ( $n_1$  and  $n_2$ ). The initial polarizer is oriented at an angle  $\theta$  relative to the principle axes (A), so that the light (blue arrow) enters the sample at an angle  $\theta$ (B). The light beam can be decoupled into two orthogonal vectors  $E1$  and  $E2$  based on the principle axes of the sample. The vector  $E1$  is retarded by the refractive index  $n_1$ , and vector  $E2$  is retarded by the refractive index  $n_2$ . In this example, the light is retarded more in  $n_1$  than in  $n_2$ , so resulting in the new vectors  $E1'$  and  $E2'$ , and the new light angle  $\alpha$ . The rotated polarized light beam now meets the analyzer, which is rotated  $90^\circ$  to the polarizer, and again is decoupled into two orthogonal vectors  $Ax$  and  $Ay$  on the analyzer axes. Only the light vector  $Ax$  will pass through the analyzer;  $Ay$  is blocked. The amplitude of  $Ax$  is a function of the angle  $\theta$  and the birefringence in the sample.**



**Figure 5: Decoupled light waves entering sample. The wave component parallel to  $n_2$  is slowed down, or retarded, more than the wave component parallel to  $n_1$  by the amount  $\delta$ , which is the retardation. The greater the thickness of the sample  $d$ , the greater the retardation.**

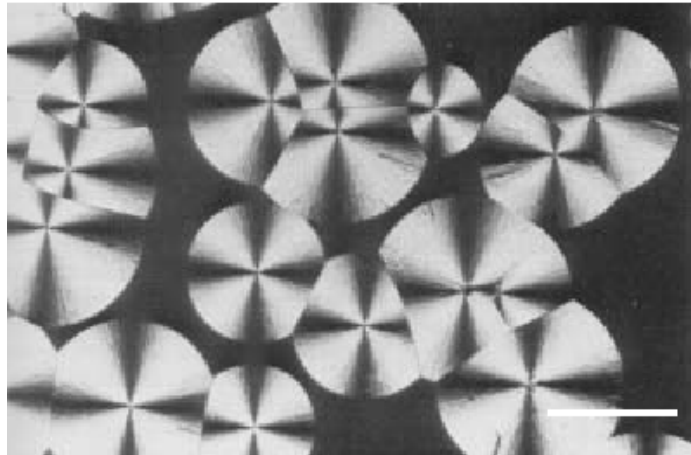
### Growing Crystallites

Crystalline material is usually highly birefringent due to the large degree of ordering, and hence anisotropy, in their structure. Birefringence measurements can be used to assess if crystallinity is present in a material, and to monitor the growth of crystals from either a melt or a solution. All that is necessary to perform such an experiment is a set of polarizers, an optical microscope, and a crystallizing material. For melts work, a hot stage is also needed.

A common undergraduate birefringence experiment is measuring the kinetics of crystallization in polypropylene, which is a semi-crystalline polymer. Polypropylene crystals form by chain folding, as shown in Figure 6. The folded chains grow in radially from a nucleation point, creating a 3 dimensional spherulite. When observed under crossed polarizers (i.e. oriented  $90^\circ$  to each other), a classic ‘Maltese Cross’ pattern emerges, as shown in Figure 7. The dark regions correspond to where either the axis of the polarizer or analyzer is oriented parallel to the principle axis of a chain fold.



**Figure 6: Schematic diagram of a spherulite of polypropylene, showing the large scale structure (left), the chain folding (middle), and the molecular level polymer structure in the folds (right).**



**Figure 7: Maltese cross pattern formed in polypropylene crystallized from the melt.**