

P-82: Optical-Strain Characteristics of Ordered Reactive Mesogen Birefringent Films for Viewing-Angle Compensation

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Abstract

We have fabricated birefringent films from a photo-polymerizable liquid crystal polymer. In-situ transmission measurements of these ordered films under tensile strain were performed to examine the optical properties of a variety of director configurations. The optical response with increasing strain was modeled and a dual wavelength technique for measuring birefringence was developed.

1. Introduction

Polymer films are now clearly integral to the performance of most liquid crystal displays well beyond their original roles as absorbing polarizing films. Birefringent films have long served as optical compensators and retarders, but reflective polarizers, brightness enhancement films, color filters, and scattering films have also become prominent. Many of these devices can be embossed or created by stretching, but several new approaches require the photo-polymerization of reactive liquid crystals (LCs). For instance, Fuji Photo Film Co. developed compensation films^{1,2} based on reactive discotic LC molecules³ with an improved viewing-angle for the TN-mode LCD. Over the last few years, Philips has developed several products using liquid crystalline polymers for the LCD, camera, and projection markets including a cholesteric reflective polarizer, scattering shutters, and compensation films.⁴ With the increasing use and understanding of these materials, information on the mechanical properties is even more essential to device design, manufacturing, and durability.

Liquid crystal polymers, otherwise known as reactive mesogens⁵⁻⁷ (RMs), are low molecular weight liquid crystals that can be polymerized to form high-molecular weight structures. All the standard alignment techniques used to align conventional low molecular weight liquid crystals, such as surfaces, electric and magnetic fields, shear, etc., can be applied to RM materials prior to photo-polymerization. This allows one to tailor sophisticated molecular architectures that can be permanently captured as a polymer film. The application potential for these materials is enormous, particularly in the area of passive optical elements.

Our experiments were conducted with the reactive mesogen LC242 (nematic range: [70°C, 120°C], BASF). The measured birefringence of a 5 μ m film in surface-induced homogeneous alignment is shown in Figure 1. Samples polymerized at 80°C typically exhibit a birefringence of about 0.125. The aligned prepolymer showed the common behavior of a nematic approaching its clearing temperature where the drop in the order parameter leads to a dramatic drop in the birefringence. It is interesting to note that all of these films maintained their nematic order (supercooled) for several hours when brought below the crystallization temperature, a potentially useful characteristic.

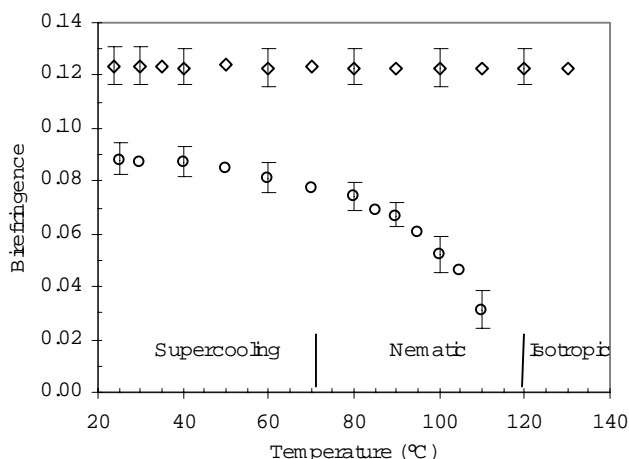


Figure 1: Measured birefringence of LC242 reactive liquid crystal before (O) and after (◇) polymerization of a 5 μ m cell uniformly aligned with buffed polyimide.

It is our objective in this work to understand the strain-dependent birefringence characteristics of simple ordered films fabricated from a RM.

2. Experimental Setup

Our samples were simultaneously probed *in-situ* using a dual wavelength method in order to find both the birefringence and the sample thickness under strain. The prepolymer mixture was composed of 98% reactive liquid crystalline monomer LC242 and 2% photo-initiator (Darocur-1173, Ciba). A dogbone template was constructed using a poly(ethylene terephthalate) (PET) template (125 μ m thick) placed between two glass substrates. The template was capillary-filled with this mixture while a hotplate was used to maintain an elevated temperature of 80°C, well within the nematic phase. Uniform alignment of the nematic was induced by a buffed polyimide layer (SE-2170, Nissan Chemical) on both substrates. Polymerization in all films was induced using a metal-halide UV lamp, and were subsequently delaminated by separating the substrates and carefully detaching the RM dogbone from the PET template.

Three ordered nematic configurations were examined: parallel (0°), perpendicular (90°), and diagonal (45°) alignment of the nematic director with respect to the tensile axis. As shown in Figure 2(a) and (c), the tensile axis was directed along the long axis of the dogbone in all experiments. The optical-strain characteristics of the material were therefore observed with the applied strain at three angles to the mesogenic units.

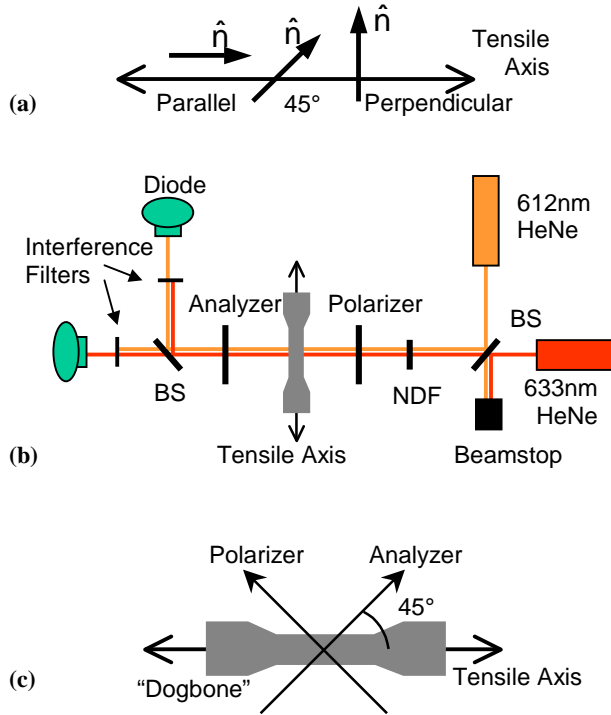


Figure 2: Opto-mechanical setup: (a) nematic director orientations; (b) experimental setup; (c) polarizing axes.

The prepared films were deformed in a tensile loading configuration using a miniature tensile testing machine (Rheometrics Minimat 2000). The samples were loaded at a strain-rate [based on nominal strain] of 10^{-4} s^{-1} in uniaxial tension while both load and displacement were recorded. Since the miniature tensile testing machine maintains an unobstructed optical path through the sample, it is well suited for incorporation into optical experiments.

Our experimental setup is shown in Figure 2(b) and (c). Two HeNe lasers operating at 633nm and 612nm were superimposed and normally incident on a RM dogbone placed between crossed polarizers. The tensile axis was placed 45° to the polarizer axis. The output from the analyzer was then split and passed through narrowband interference filters in order to separate the two wavelengths to enable independent monitoring. In addition to the three ordered nematic configurations (parallel, perpendicular, and 45°), an isotropic film was also tested, but revealed no change in the optical transmission before failure.

3. Strained α -Plate Model

We modeled the transmission using the standard expression for a planar uniaxial birefringent film (α -plate) between two crossed polarizers:⁸

$$T = \frac{1}{2} T_0 \sin^2(2\theta) \sin^2\left(\frac{\pi \Delta n d}{\lambda}\right) \quad (1)$$

where T_0 is the power incident on the polarizer, λ is the wavelength, d is the film thickness, and θ is the angle between the effective optical axis of the RM ordering and the transmission axis of the polarizer. The optic axis, film thickness, and birefringence could all potentially vary as functions of the applied strain.

However, since we are working with a main-chain polymer, we do not expect θ to vary since the net torque on most of the chains should be zero. However, as a strain is applied, the film thickness d will decrease approximately linearly, which we expect to cause a substantial modulation of the transmission. Since the period of this oscillation will be proportional to $\lambda/\Delta n d$, the instantaneous birefringence and thickness appear as a product. Although we are unable to have access to $d(\epsilon)$ directly, we instead infer it using Poisson's Ratio (ν):

$$\frac{d(\epsilon) - d_0}{d_0} \equiv -\nu \epsilon = -\nu \frac{L(\epsilon) - L_0}{L_0} \quad (2)$$

where L_0 is the original length of the dogbone, d_0 is the original thickness, and ϵ is the percent strain. This leads to an expression for the instantaneous thickness where the only unknown parameter is Poisson's Ratio for the film:

$$d(\epsilon) = d_0 [1 - \nu \epsilon] \quad (3)$$

Therefore, the period of the strain-induced oscillation in the transmission is fully described by 2 unknown parameters, the birefringence $\Delta n(\epsilon)$ and Poisson's Ratio ν . The general equation governing the strain dependent transmission can be derived by combining Equations 1-3:

$$T = \frac{1}{2} T_0 \sin^2(2\theta) \sin^2\left(\frac{\pi d_0}{\lambda} \Delta n(\epsilon) [1 - \nu \epsilon]\right) \quad (4)$$

If the birefringence does not vary substantially with strain, as will be shown for the parallel alignment configuration, Equation 4 can be simplified somewhat, while no simplification is available for the perpendicular configuration:

$$T_{PAR} = \frac{1}{2} T_0 \sin^2\left(\frac{\pi \Delta n d_0}{\lambda} [1 - \nu \epsilon]\right) \quad \parallel \text{ case } (5)$$

$$T_{PERP} = \frac{1}{2} T_0 \sin^2\left(\frac{\pi d_0}{\lambda} \Delta n(\epsilon) [1 - \nu \epsilon]\right) \quad \perp \text{ case } (6)$$

The transmission characteristic of our strained polymer film is dependent on the product of two unknown parameters: $\Delta n \cdot \nu$, the birefringence and Poisson's Ratio. Therefore it is necessary to use at least two different wavelengths to uniquely determine these values. For increased accuracy in this experimental method, many wavelengths or even a continual spectrum could be used, but a more sophisticated detector (such as a spectroradiometer) would be necessary.

4. Results

4.1 Mechanical Properties

After pulling films of each configuration, we found that the stress-strain behavior of the films was similar to many liquid crystalline polymeric materials. The initial slopes lead to Young's modulus and are tabulated in Table 1. The modulus is greatest for the parallel and least for the perpendicular alignment samples. This is consistent with Broer's findings where he measured the dynamic tensile modulus.⁵ The mechanical properties resemble that of many oriented polymer structures, with a higher modulus parallel to the direction of the chains, rather than perpendicular. The moduli of both the 45° and the isotropic films are essentially the average moduli from the other two orientations. It is interesting to

note that the relaxation process following failure includes an initial rapid change followed by an exponential decay in transmission. This is first due to the elastic, then viscoelastic, recovery of the polymer after the catastrophic failure. Light transmission measurements could be an excellent way of probing this recovery mechanism.

4.2 Nematic Axis Parallel to Tensile Axis

The normalized optical response of a 195 μm thick parallel-aligned sample is shown in Figure 3. The period of oscillation remains substantially constant throughout the pull, indicating that there is little or no change in the birefringence in this alignment. This follows since the polymer chains are already aligned with the tensile axis due to the rubbed polyimide surfaces, and that no substantial molecular realignment occurs. Most of the films in this configuration failed in the 6-8% range.

The strained *a*-plate model (Equation 5) was fit using a least-squares method. Typical values fit over several samples resulted in a fixed birefringence of $\Delta n = 0.116 \pm 0.01$ and Poisson's Ratio $\nu = 0.47 \pm 0.015$ (shown as a solid curve in Figure 3). We find that there is little change in the birefringence before catastrophic failure when the film is strained parallel to the polymer chains (the optic axis). Furthermore, since the bonding is strongest along the tensile axis and weakest in the transverse directions, it is reasonable that Poisson's Ratio is near 0.5 for this configuration, meaning that there is a high lateral compressibility. We suspect that if films could survive higher strains in this configuration the birefringence could only get stronger due to the better alignment of the polymer chains, and we are pursuing further experiments to confirm this behavior.

4.3 Nematic Axis Perpendicular to Tensile Axis

Far more interesting behavior was revealed in the optical response for the perpendicular-alignment, as shown in Figure 4 for a 233 μm thick sample. Most prominently, the amplitude of the modulation was no longer constant, but rather, increased with strain. Additionally, the period of oscillation decreases with increasing strain, and the strain at break was substantially higher (~10-12%) for most samples.

The only aspect of our model that could capture the behavior of the increasing amplitude is a reorientation of the optical axis within the plane of the substrate *toward* 45°. Perhaps this could be due to a bulk realignment of the polymer chains or a local reordering of particular links. However, the optical axis for this configuration was *already* nominally aligned at 45°, and since the required reorientation would need to be substantial (exceeding 20°), this explanation is in our opinion unphysical. While we are currently pursuing further experiments to explain this effect, we speculate that the change of the order parameter due to the applied strain is affecting the out of plane alignment of the polymer chains here in a more pronounced manner than the previous configuration.

If we ignore the increasing amplitude effect, we can again fit the data with the strained *a*-plate model (Equation 6). In this case, we find that Poisson's Ratio is slightly lower $\nu = 0.44 \pm 0.015$ and the birefringence decreases by about ~1% ($\Delta n = 0.124 \rightarrow 0.123$) before catastrophic failure occurs. This seems reasonable, since the tensile force is now perpendicular to the polymer chains and is almost certainly causing local disordering of the chain links. In effect, since the order parameter is decreased, the birefringence

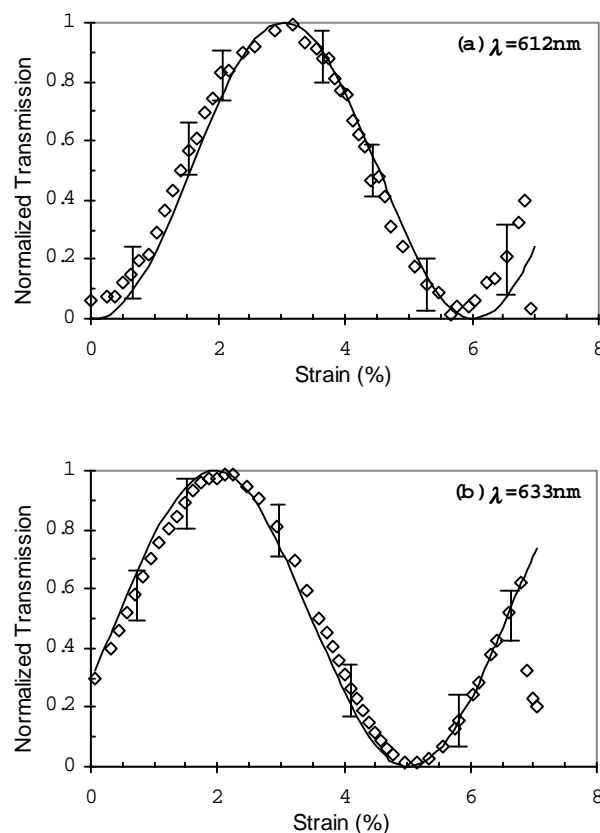


Figure 3: Transmission of a parallel-aligned reactive mesogen film at (a) 612nm and (b) 633nm. (\diamond – experimental data, black curve – strained *a*-plate simulation)

must follow. The rate of this decrease is approximately -0.0008 change in birefringence per 1% strain.

It follows that the film is more compressible due to the weaker bonding when the tensile strain is perpendicular to the alignment. In our films, both the modulus and Poisson's Ratio (a measure of lateral compressibility) were highest when the tensile direction was parallel to the aligned axis.

Finally, a sample with an optical axis at 45° to the tensile axis was also examined. In this case the optical axis is parallel to the axis of the polarizer such that $\theta = 0^\circ$ and no transmission is possible unless the optical axis realigns (see Equation 1). The opto-mechanical curve remained constant, indicating no bulk realignment of the polymer chains up to 10% strain. A summary is shown in Table 1, where all fitting was performed using a least-squares algorithm.

5. Conclusion

Birefringent films fabricated from liquid crystalline polymers are of great interest because of their many uses as optical compensation films, reflective polarizers, and switchable polymer-network devices. The strain-optical characteristics of these materials are important when considering roll-to-roll manufacturing processes and in-service deformation caused by bending or mechanical shock. We have shown that strain along the axis of the polymer chains does not substantially affect the birefringence, and that perpendicular strain changes the birefringence only nominally ($\sim 1\%$ decrease for 10% strain).

There are several interesting directions we are pursuing: Studies of the physical and optical recovery from moderate strain levels and failure modes for repeated wear are necessary. Non-uniform configurations such as the homeotropic, TN, cholesteric, and tumbled are also intriguing modes to investigate.

Table 1: Summary of mechanical and optical properties.

	Nematic Alignment to Tensile Axis		
	0°	90°	45°
Modulus (GPa)	0.81	0.55	0.68
Poisson's Ratio	0.47 ± 0.015	0.45 ± 0.015	--
Birefringence	0.116 ± 0.01	0.124 ± 0.01	--

6. Acknowledgements

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7. References

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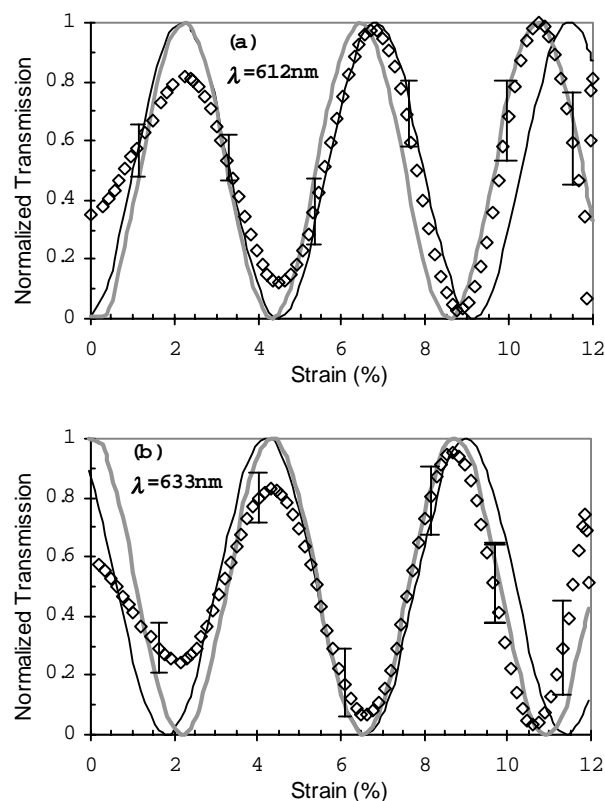


Figure 4: Transmission of a perpendicular-aligned reactive mesogen film at (a) 612nm and (b) 633nm. (\diamond – experimental data, black curve – fixed birefringence model, gray curve – varied birefringence model)