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Abstract

The purpose of this project was to test different variables that would affect the amount of rotation that would take place in a nematic liquid crystal (E7) sample. The variables were different azo dyes (Disperse Orange 3 and Methyl Red), sample thickness (7.5, 12, and 25 μm spacers), and pump intensity. Once the rotation was measured, samples with optimal rotation were used to try to make holograms. Even though holograms were never made, interesting effects involving the different azo dyes and pump intensity were found.

Background

Liquid crystals are a fourth state of matter that have properties of both solids and liquids. They have the ability to flow, like a liquid. Unlike a liquid, they maintain different degrees of orientational and positional order, but not as much as a solid. The average direction of all the molecules is called the director $\hat{n}$, shown in Figure 1. To measure how well the molecules align with the director, the order parameter *S* is used,

$$S = \langle P_2(\cos\theta) \rangle = \left\langle \frac{3}{2}\cos^2\theta - \frac{1}{2} \right\rangle \quad (1)$$

where P_2 is the second Legendre polynomial and θ (Figure 1) is the angle of one molecule with the director. Samples that are perfectly aligned have order parameter of one and samples with no order have order parameters of zero [1]. Most liquid crystals have an order parameter between 0.3-0.7.

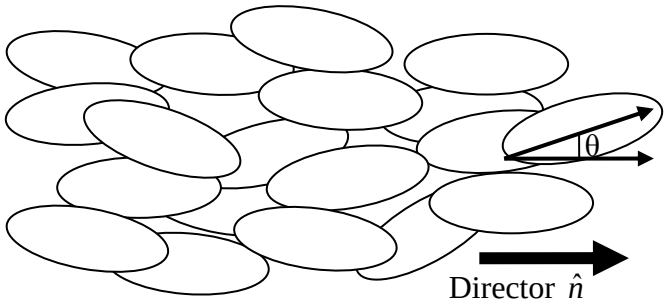


Figure 1: Diagram to show director of liquid crystal sample and how the order parameter changes for each molecule.

The most common type of liquid crystals are calamitic. In this kind of liquid crystal the molecules are rod shaped, with one end significantly longer than the other two. This characteristic makes them anisotropic, meaning that when properties, such as index of refraction or viscosity, are measured that different values will be measured

depending on the orientation of the molecules. One phase of calimatic liquid crystals is the nematic phase, which has orientational order and no positional order [1]. The liquid crystal that was used for this experiment was E7 (Merck), E7 is a mixture of four different nematic liquid crystals, the chemical structures of each liquid crystal, names and percentages is shown in Figure 2 [2].

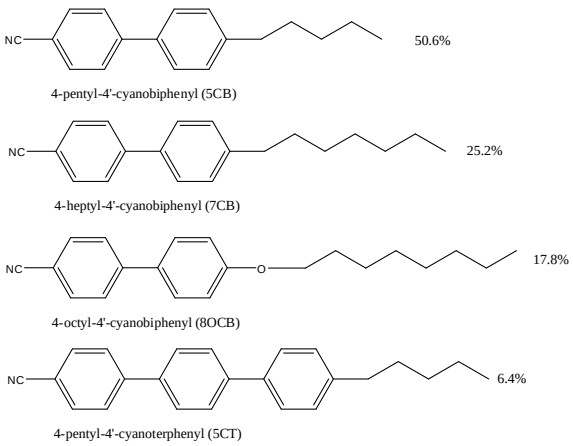


Figure 2: Chemical structure and percentages of liquid crystals that make up E7.

When an electric field is applied to a liquid crystal molecule, it becomes polarized (Figure 3). A dipole moment per unit volume is induced within the molecule, given by

$$\vec{P} = \varepsilon_0 \chi_e \left(\hat{n} \cdot \vec{E}\right)\hat{n} \tag{2}$$

where ε_0 is the permittivity of free space, χ_e is the electric susceptibility and $\vec{E}$ is the applied electric field [1].

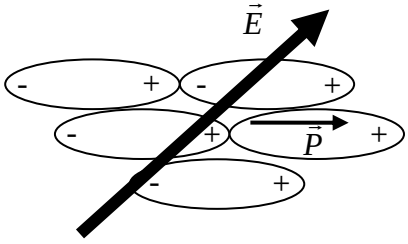


Figure 3: Polarization of liquid crystals when an Electric Field is applied.

The interaction between the dipole moment and electric field creates a torque per unit volume on the molecule

$$\vec{\Gamma} = \vec{P} \times \vec{E} \tag{3}$$

This torque causes a reorientation in the molecule. When the liquid crystal molecules are aligned with the electric field the free energy is minimized, so this is the preferred orientation. The amount of energy needed to induce rotation is called the Freédericksz Transition. If the electric field is less than the Freédericksz Transition the molecules will not move [1].

The free energy density is used to describe the molecules of the liquid crystal will appose distortion to their orientation, the equation is

$$F_v = \frac{1}{2} K_1 \left[\nabla \cdot \hat{n}\right]^2 + \frac{1}{2} K_2 \left[\hat{n} \cdot \left(\nabla \times \hat{n}\right)\right]^2 + \frac{1}{2} K_3 \left|\hat{n} \times \left(\nabla \times \hat{n}\right)\right|^2 \tag{4}$$

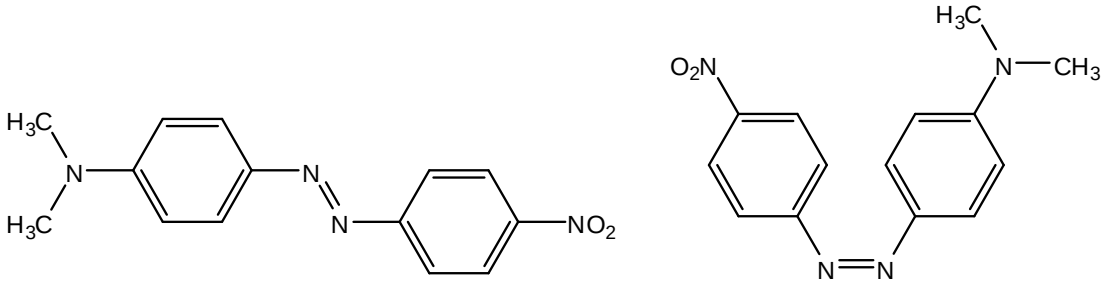
where $\hat{n}$ is the director, K_1 is the splay distortion constant, K_2 is the twist distortion constant, and K_3 is the bend distortion constant. These three distortion constants are analogous to the spring constant and describe how attached the liquid crystal are to the distortions of the director. The free energy density measures how much energy per area is needed to cause these different distortions [1] to take place. For a nematic liquid crystal, only the twist distortion constant matters [1], so the free energy is

$$F_v = \frac{1}{2} K_2 \left(\frac{\partial \varphi}{\partial z}\right)^2, \tag{5}$$

where φ is the change in angle along the z-axis.

The speed of rotation for the liquid crystal molecules depends on how well they are anchored. In the bulk of a sample, rotation is very fast because they are not anchored to anything. This rotation is spring like, so the molecules return to their initial position. For molecules that are on the surface, the anchoring strength depends on the polymer that is coating the slides. Rotation of the molecules on the surface has come to be known as gliding. Gliding is very slow and results in a semi-permanent change of the easy axis of the sample. The easy axis is where the energy between the liquid crystal molecules and polymer is minimized. The amount of gliding depends on the polymer that is attaching the liquid crystals to the surface [3]. This effect has been studied with different variables, such as pump intensity [3] and anchoring polymer [4]. The two polymers that were used are polymide (PI) and polyethyl-methacrylate (PEMA). PI is considered a hard polymer because it has a higher anchoring strength and PEMA is a soft polymer because it hgas weaker anchoring.

To decrease the Freédericksz Transition, small amounts of azo dyes can be used. At certain wavelengths of light, azo dyes absorb the light and changes from a trans structure to a cis structure. This process is called photoisomerization. In the trans state the liquid crystal molecule and dye molecule are both rod shaped and align very well with each other, Figure 4 [5].



Disperse Orange 3- Trans Isomer Disperse Orange 3- Cis Isomer

Figure 4: Chemical of structure of DO3 in the Trans and Cis Isomer.

When the dye molecule isomerizes to the cis structure, it is no longer rod shaped and disrupts the alignment of the liquid crystal molecules resulting in a lowered Freédericksz Transition energy.

One description of gliding and the bulk reorientation is the adsorption and/or desorption of the dye by the polymer. This means that the liquid crystal molecules are either adsorbed or desorbed by the polymer on the surface of the cells. When an azo dye is added to the liquid crystals, adsorption and/or desorption produces an easy orientation axis on the surface [3]. The first layer of adsorbed liquid crystals molecules align along the initial direction of the easy axis, which is an interaction between a physically anisotropic surface and liquid crystal molecules [4]. The mismatching between the director and the easy axis is due to the finite anchoring, that leads to adsorption of molecules along a new direction. The molecules further away from the surface continue the adsorption process and cause the bulk reorientation.

The two azo dyes that were studied are methyl red (MR) and disperse orange 3 (DO3), shown in Figure 5 [5,7].

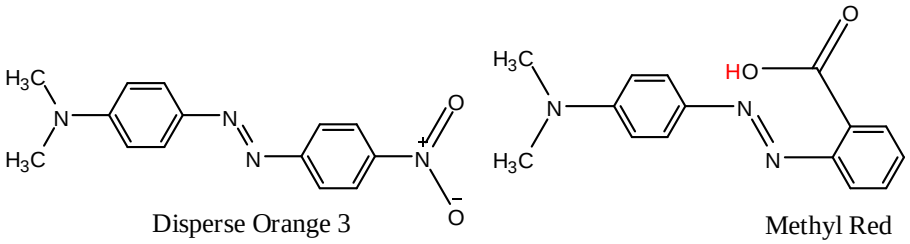


Figure 5: Chemical structure of DO3 and MR with active hydrogen marked in red on MR structure.

These two dyes have very similar structures and absorb light at similar wavelengths, which are 530 nm for MR [6] and 440 nm for DO3 [8]. The difference is that MR has

an active hydrogen atom. This particular hydrogen atom is able to bond with another compound and leave the MR molecule. This is why it is used at a pH indicator [9]. DO3 has been used in past experiments at Allegheny College [3] and MR has been used in other current experiments [4,6].

Recently, liquid crystals have been used to make holograms [10, 11]. Holograms are three-dimensional recordings of the entire signal of a wave. Unlike a photograph, that only records the amplitude of the wave, a hologram also records information about the phase information of the wave [12]. The purpose of this project was to find the combination of liquid crystal, polymer, azo dye and sample thickness that will allow the most amount of rotation for the liquid crystal molecules.

Experimental Setup

The cell preparation procedure is included in Appendix A. Samples were made with 7.5, 12, and 25 micrometer (μm) spacers (Chemplex and Grafix wrap). The liquid crystal that was used was E7 (Merck) mixed with 1.0%, by weight, MR (Sargent-Welch) or DO3. The samples were filled via capillarity action and glued with epoxy.

To test the amount of rotation by the liquid crystal molecules, a pump-probe set up was used, Figure 6 [3].

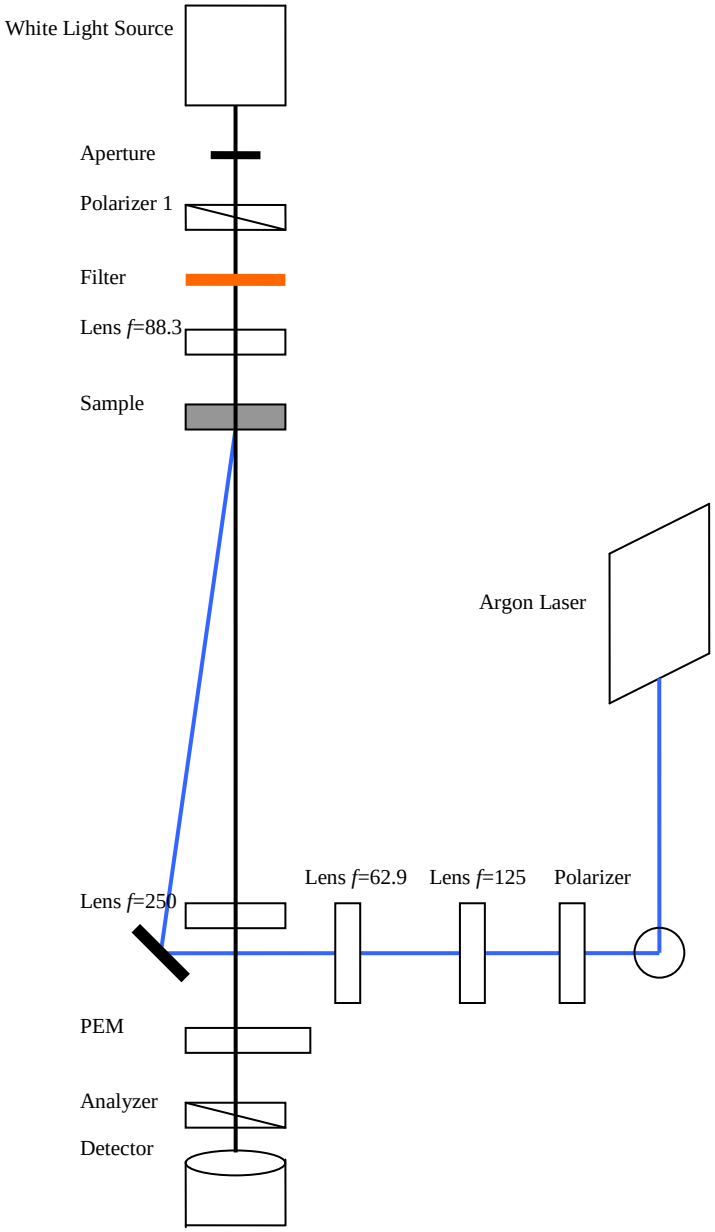


Figure 6: Diagram of setup used to measure rotation.

The pump beam creates an electric field that causes the photoisomerization of the azo dye allowing the liquid crystal molecules to rotate. The probe beam measures this reorientation by recording how the intensity of the polarization changes. Each optical device in the experimental setup has a different purpose. In the probe arm, a white light source was used instead of a Helium Neon (HeNe) Laser, because of the possibilities that the HeNe laser will interfere with itself. This interference pattern would change the Stokes Parameters and the ellipticity of the light, changing the entire measurement. Polarizer 1 is used to polarize the white light source so that it is aligned parallel with the director of the liquid crystals in the sample. The first filter filters out wavelengths from the room that might excite the dye in the sample. The two lenses are used as a beam expander to focus the light on to the sample and then on to the detector. The Photo-Elastic Modulator (PEM) is needed because the linearly polarized light that enters the sample leaves the sample as elliptically polarized light, because the liquid crystals are anisotropic so the indexes of refraction are different for the horizontal and vertical component of light. The PEM is used as an analyzer to find the state of the polarized beam by measuring the Stokes Parameters. The Stokes Parameters correspond to the intensity and ellipticities of different components of the beam. The second harmonic was measured, which corresponds to the second Stokes Parameter. The analyzer is always at an angle of 45º from Polarizer 1, because of the workings of the PEM. This is done by removing the sample and PEM, crossing the two polarizers so no light can go through and rotating the analyzer 45 º. The detector at the end of the pump beam directly measures the intensity of the white light source. As the liquid crystals in the sample

rotate, they change the polarization of the white light source which also changes the intensity of the light, which is why the intensity can be converted into degrees rotated. To do this, Polarizer 1 is moved to be behind the sample but in front of the PEM and then rotated one degree. This is how much the intensity will change for one degree of rotation, which is used to calibrate all other measurements.

A CHOERENT Innova7 Argon laser was used as the pump beam with wavelength of 488 nanometers. The wavelength is important because it is close to the maximum absorption wavelength for the two dyes, which are 530 nm for MR and 440 nm for DO3. The polarization of the beam is set to 45 º by the polarizer. The lenses are arranged to create a beam expander so that the pump beam size is greater than the probe beam when they cross in the liquid crystal sample.

The two beams enter the sample in different directions to be able to probe the same surface that is being excited by the pump. It is assumed that the polarization of the probe light follows the director of the sample, because it is within the Mauguin limit. The reason that this assumption is valid, is because the pitch, the distance it would take the liquid crystal molecules to rotate 360 º, is larger that the wavelength. From the data, the pitch is 3.6×10^{-4}* meters and the wavelength is on the order of 5.0×10^{-7} meters. Since the difference in lengths is three orders of magnitude different, the system is within the Mauguian limit.

Once the amount of rotation of a sample was measured, a second set up was used to create a hologram, Figure 7.

* From Figure 11, molecules rotated 25º for a thickness of 25µm, so to rotate 360º the thickness can be solved for by $\frac{25^\circ}{25\mu m} = \frac{360^\circ}{x}$, x= 360 µm

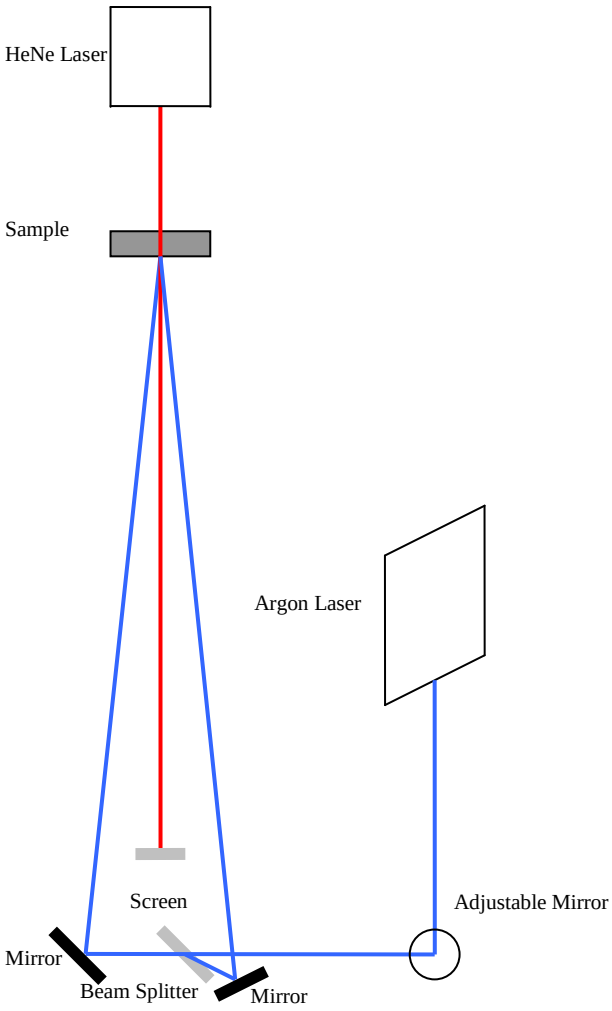


Figure 7: Diagram of setup used to make holograms.

In this setup, the beam from an Argon laser was split and interfered with itself within the sample. A HeNe Laser was used to see if a hologram was being made. To check if the beams were interfering, a barium titanate crystal was used to couple the beams. The reason for using the barium titanate crystal is that the spacing between the fringes was calculated to be 7,320 nm[†] when using an Argon Laser at 488 nm, which is not visible by the naked eye. The distance between the fringes was calculated by using the scattering wavevector q from the X-ray diffraction conditions [1]. When the

[†] $q = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} = \frac{2\pi}{L}$ from setup theta was measured to be 0.10/3 $L = 15\lambda = 7320nm$

beams were coupled, one of the input beams could be blocked but there still remained two beams on the other side of the crystal. When the beams were coupled, the barium titanate crystal was replaced with a liquid crystal sample. The reasoning behind this set up was that the interfering Argon beam would create a diffraction pattern inside the sample. The dye molecules that were exposed to the bright fringes would undergo photoisomerization and the liquid crystal molecules would rotate. Areas that were exposed to the dark fringes would not undergo photoisomerization and therefore not rotate, in turn creating a diffraction grating. To create the actual hologram the sample was exposed to the Argon laser for thirty minutes, with the HeNe laser probing the sample. If a hologram was created, an interference pattern should appear on the screen [13].

Experimental Results

For these tests, samples were exposed to the Argon Laser for 30 minutes, then the laser was turned off and LabView recorded data for an additional 30 minutes. This way both the rotation and relaxation of the liquid crystal samples was measured. In these samples the liquid crystal E7 is doped with 1.0% by weight of the azo dye. The glass slides were coated with PI and PEMA polymer and were probed on the PEMA side. Several different variables were measured, which were azo dye, cell thickness, polymer, and pump intensity.

Azo Dye Comparison

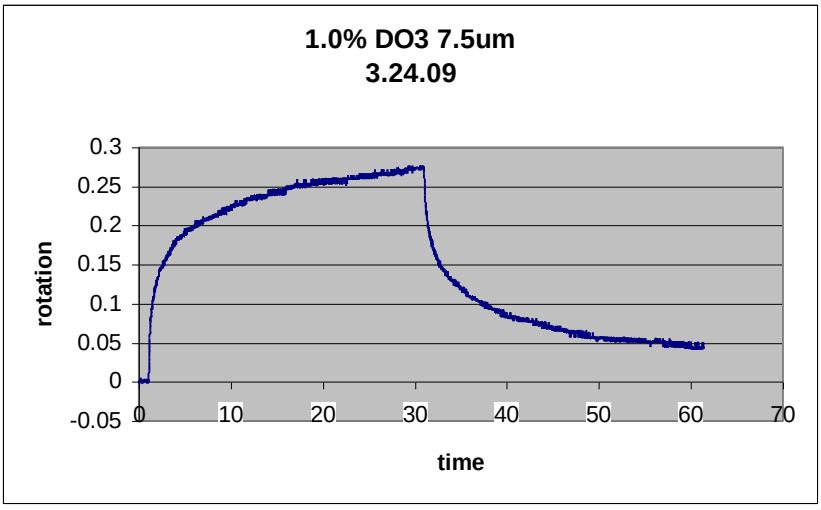


Figure 8: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% DO3.

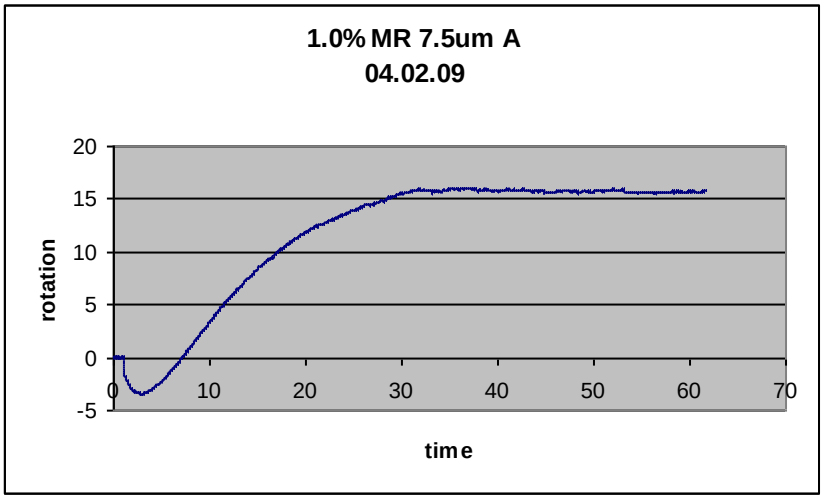


Figure 9: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% MR.

Thickness Comparison

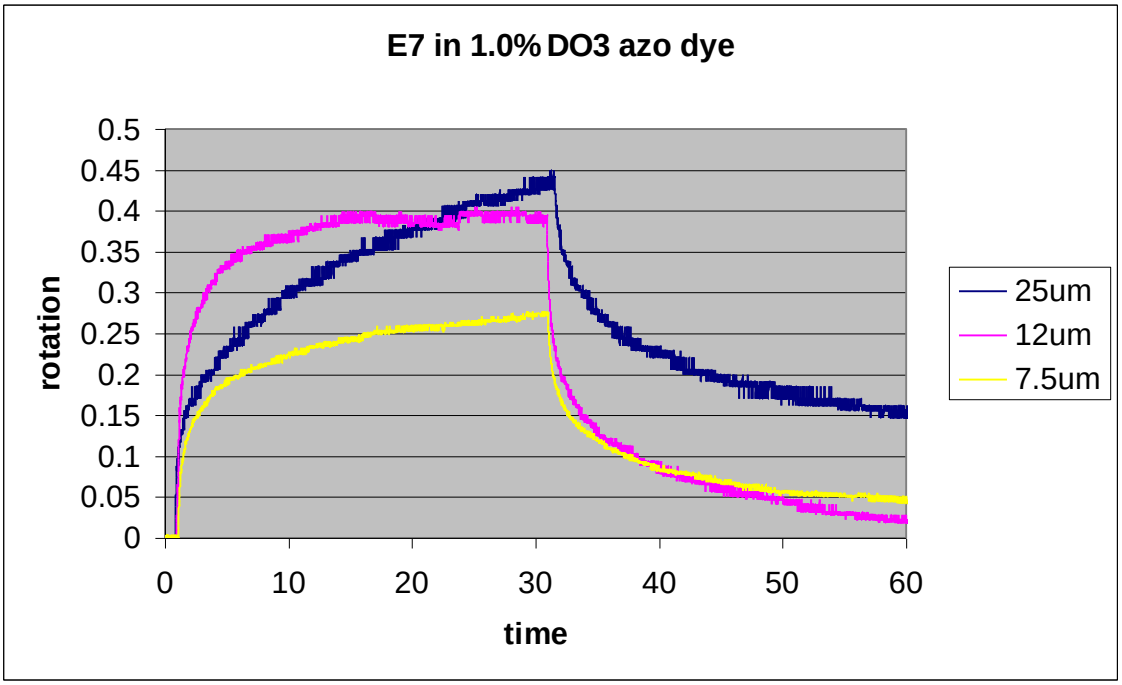


Figure 10: Rotation of 3 samples filled with E7 liquid crystal doped with 1.0% DO3 with different spacer thickness.

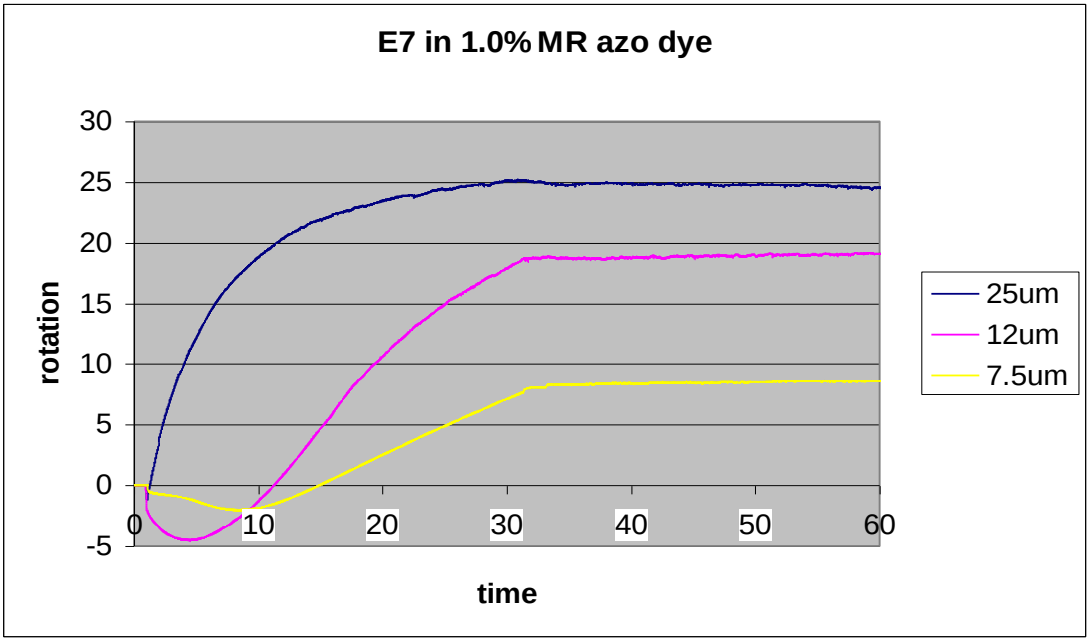


Figure 11: Rotation of 3 samples filled with E7 liquid crystal doped with 1.0% DO3 with different spacer thickness.

Intensity Comparison

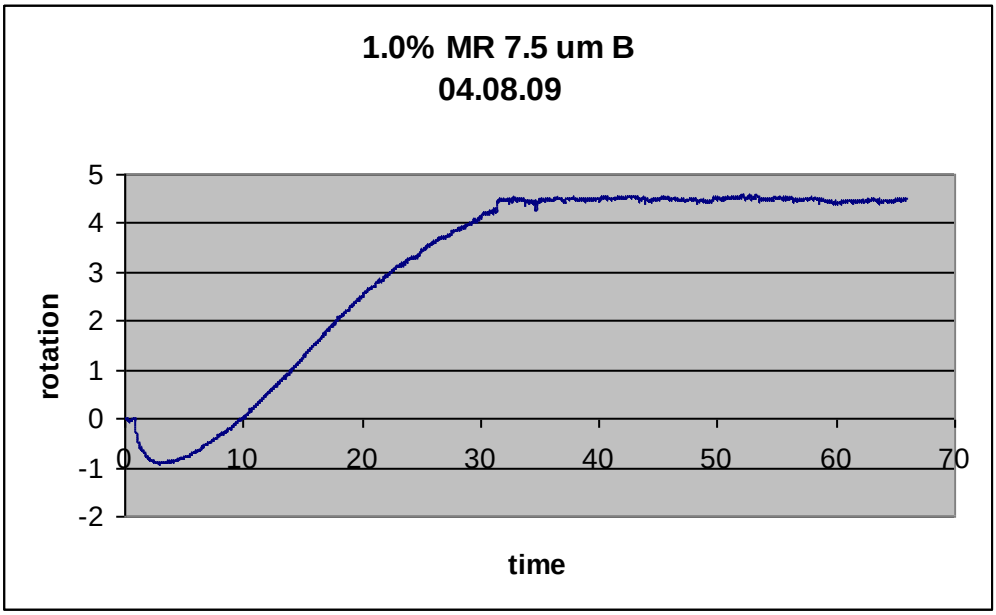


Figure 12: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% MR at full pump intensity.

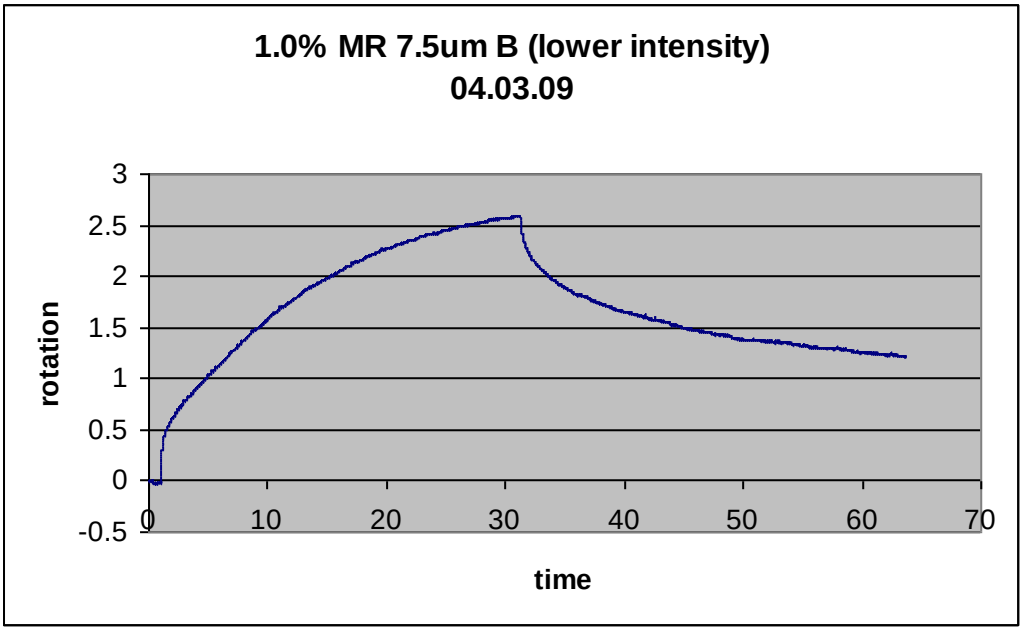


Figure 13: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% MR at lowered pump intensity.

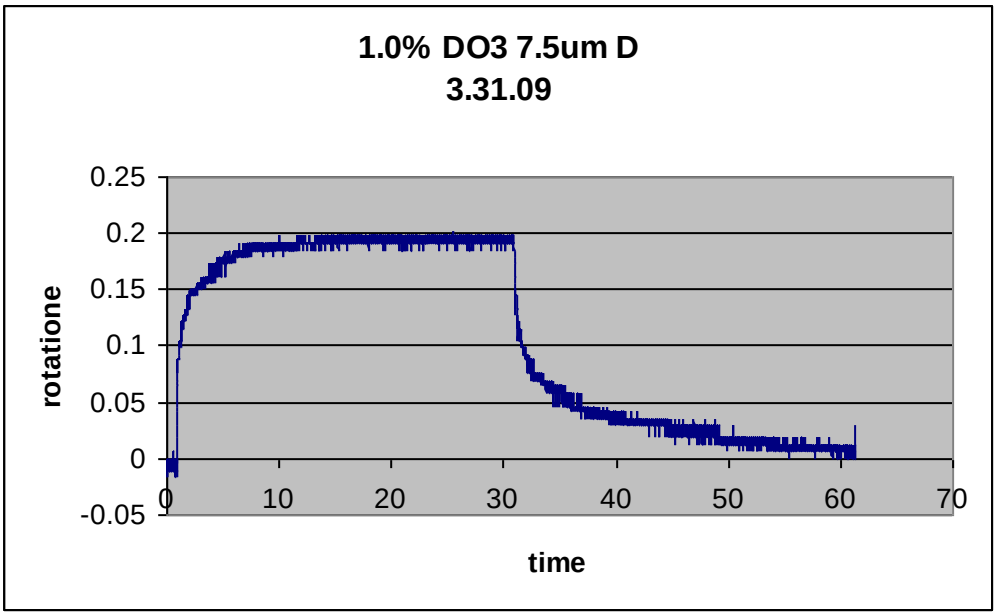


Figure 14: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% DO3 at full pump intensity.

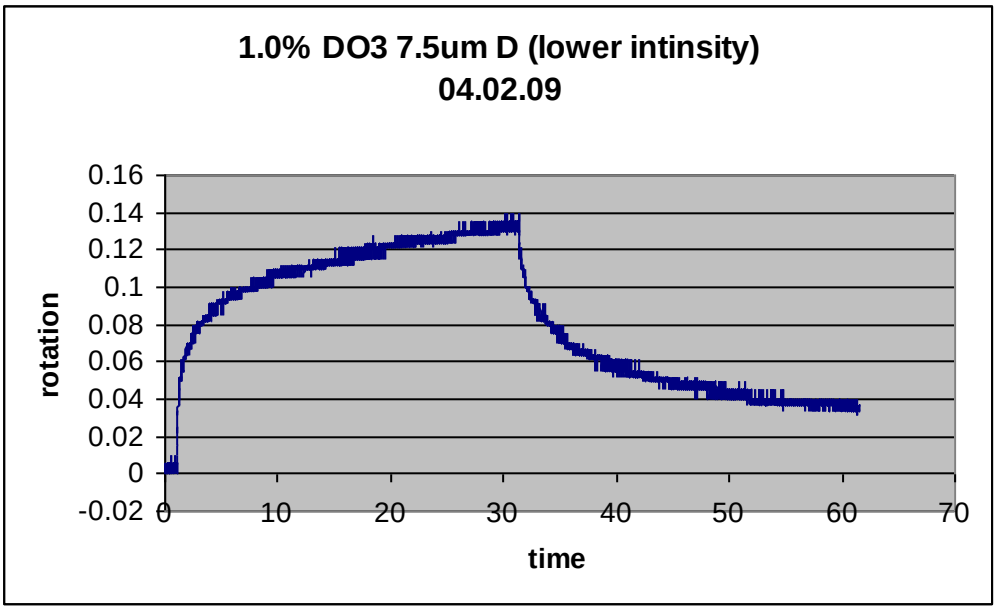


Figure 15: Rotation of a sample with 7.5µm spacers filled with E7 liquid crystal doped with 1.0% DO3 at lowered pump intensity.

Discussion

In the first comparison of the azo dyes, there are three major differences between the DO3 (Figure 8) and MR (Figure 9) dye, which were the amount of rotation, the negative rotation, and the permanence of the rotation. The adsorption/desorption applies to both azo dyes but clearly there is something else happening in the MR azo dye. Since the only difference between the two dyes is the active hydrogen spot on the MR (Figure 5), the difference in rotation must come from this. One theory is that the MR dye creates an dark adsorbed layer of MR molecules. This layer of dark absorption is created by the MR dye molecules being adsorbed by the polymer [6]. Experiments in previous years, have measured rotation angles between 0.3 and 1.2 degrees for samples with 1.0% DO3 dye in E63 liquid crystal. These tests have similar shapes as these DO3 tests. In these test there is a difference between the bulk and surface rotation. The bulk rotation happens very fast and immediately when the laser is turned on and off. The slower rotation is that of the surface, or gliding. This effect is slower because of the anchoring of the liquid crystals to the polymers. Unlike the bulk rotation, the surface rotation does not spring back immediately to its initial position. This is evident by the fact that the rotation does not go back to zero in the test. Even after equal amount of excitation and relaxation, the liquid crystal is still rotated 0.04 degrees. This effect is know as the memory effect and shows a "permanent" change in the easy axis.

For the sample with MR dye, the rotation is very different. The initial negative rotation, again, is the rotation of the bulk of the liquid crystal sample. Then the slower positive rotation is a result of gliding. When the laser is turned off at 30 minutes, there is no rotation back. This shows that the surface rotation has become

permanent, for at least 30 minutes. The amount of rotation is much greater than any other measurement that has been done at Allegheny College, but not as great as other reports.

The second comparison is between the thickness of the cells, as seen in Figures 10 and 11, DO3 and MR, respectively. Three different thicknesses were tested, which were 7.5, 12, and 25 μm. As expected, when the thickness increased the amount of rotation increased. This is expected because the molecules in the bulk have more freedom to rotate and less resistance. With a thicker sample, there are more molecules in the bulk, compared to the molecules that are anchored to the polymers, which leads to more rotation.

The third comparison between the intensity of the pump beam was found by accident. When the samples filled with 1.0% MR with 12 μm were measured for rotation, the intensity of the probe became too large for the detector to handle and the Lock-In Amplifier overloaded. To fix this problem, the intensity of the probe and pump beam were decreased. Figures 12 and 13 were done with the probe laser at 55% intensity, and only the intensity of the pump laser was changed. Figure 13 at full intensity and Figure 12 at lower intensity. The exact intensities were not measured. This resulted in significantly different graphs for the rotation, which were not seen in samples that had liquid crystals doped with the DO3 azo dye. With these samples the rotation looked the same but the amount of rotation decreased from 0.2º (Figure 14) to 0.12º (Figure 15).

All tests have been calibrated so that the majority of the rotation is positive. The reason that some cells had rotation in the opposite direction is that no matter how

well aligned the order parameter will never be one. There will always be molecules at some angle to the director. If a majority of molecules rotated in the same direction, this will influence the rotation to take place in the same direction. Another contribution to the direction of rotation is the azo dyes. The pump is used to induce photoisomerization in the azo dye. Depending on which direction the azo dye rotates when it goes from tran isomer to cis isomer will also effect the direction of rotation of the liquid crystal molecules. In the end what is more important is how much the liquid crystals rotate, which means the absolute magnitude of rotation.

Conclusions

The original purpose of the project to make novel holograms using liquid crystal samples was not accomplished. Multiple attempts were made to create holograms, but none were successful. The reason for there failure is still unknown. Instead a comparison of two different azo dyes was preformed. The reason that these two dyes were compared is because of the similar chemical structure. What was found is that there is a significant difference between the amount of rotation and how the rotation takes place. This research also supports theories about what is taking place inside the samples to cause the rotation and why sample doped with MR azo dye are able to rotate so many degrees.

Future Work

There are many different directions that this project can go in. The first would be to successfully create holograms using liquid crystal samples. To further investigate the difference between the azo dyes, DO3 and MR, samples should be tested that have PI polymer on both sides of the sample. When the hard polymer is tested in samples that are coated with PEMA and PI the results are different from samples where both sides are coated with PI. Additional, more tests need to be done to understand why the intensity of the pump beams changes the rotation in samples doped with MR dye. Tests need to be run where the intensity of the pump beam is recorded and tested at multiple intervals. Also, different polymers should be tried. The amount of gilding in samples tested here has increased but there are reports of even high angles of rotation.

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Appendix A

Sample Preparation

Cleaning

1. Per-cleaned glass slides were measured and cut to proper sizes. Slides that were to be coated with the PI polymer were 3.7 cm and slides that were to be coated with the PEMA polymer were 2.6 cm.
2. Slides were washed with Alconox and put into a 50 mL beaker using magnetic spacers to separate the slides. Four slides were put into each beaker.
3. Beakers were filled with deionized (DI) water and placed in a Branson 2510 sonicator for 15 minutes.
4. Beakers were filled with DI water and empty three times.
5. Step 3 was repeated with 1M NaOH solution, followed by step 4.
6. Step 3 was repeated with Isopropyl Alcohol (IPA), followed by step 4.
7. Step 3 was repeated with DI water.
8. The slides were dried by using compress Nitrogen gas.

Polyimide (PI) polymer

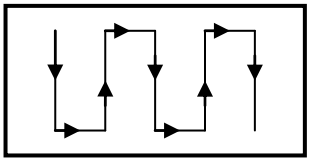
1. 2 mL of toluene (Sigma-Aldrich) and 8 mL of 1-mthyl-2-pyrrolidone (Sigma-Aldrich) were combined.
2. 9 mL of the toluene and 1-mthyl-2-pyrrolidone were mixed with 3 mL of polyimide (PI2555)(HD MicroSystems).

Polyethyl-methacrylate(PEMA) polymer

1. 0.1 g of PEMA (Aldrich) was mixed with 1.8 g of toluene to make a 5% mixture by weight.

Spin coating

1. The glass slides were placed in a home made spin-coating device, consisting of a pie tin attached to a motor with a variac controlling the speed of spinning.
2. Slides were spun on the 140 V at 40% for 1 minute to get rid of any dust that accumulated on slides.
3. A pipette was used to spread either polymer on to the slides. This was done in a "S" shaped motion.



4. The sides were again spun on the 140V at 40% for four minutes to ensure even coating.
5. Slides were removed and the underside was wiped with IPA to remove any excess polymer.

Mirror

Curing PI

1. After spin coating, slides were placed in a Black and Decker toaster oven at 95º for 5 minutes.
2. The temperature was increased to 130 ºC for 5 minutes.
3. The temperature was increased to 150 ºC for 60 minutes
4. The temperature was decreased to 130 ºC for 5 minutes
5. The temperature was increased to 150 ºC for 5 minutes

Curing PEMA

1. After spin coating, slides were placed in a Black and Decker toaster oven at 90 ºC for 60 minutes.

Rubbing PI coated slides

1. Once the slides were allowed to cool, only the slides coated and cured with the PI polymer were rubbed to provide alignment.
2. Slides were rubbed 5 times in the same direction with a home made rubbing device.

Gluing samples

1. Depending on the desired thickness different sized spacers were used.
2. Two spacers were cut and glued with epoxy to the edge of one of the glass slides.
3. Epoxy was then placed on top of the spacers, very sparingly.
4. The top glass slide was place on top, with the polymer coated side facing inward.
5. The slides were aligned so that one end was match and the other had an overhang.
6. Cells were allowed to dry for 24 hours.

Mixing liquid crystals

1. Samples were filled with liquid crystals that had been doped with azo dyes by weight.
2. The desired amount of liquid crystal was pipetted into a vile and weighed.
3. The amount of azo dye used was Figured out from the weight of liquid crystal and the desired concentration.

Filling Samples

1. Cells were filled by dropping approximately 0.1mL of doped liquid crystal on the ledge and allowing it to fill the cell via capillary action.
2. Excess liquid crystal was wiped from edged.
3. Epoxy was used to seal cell.
4. Cells were allowed to dry for 24 hours.