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Responsive Liquid Crystal Polymer Rods

Matthew S. Shafran

**Thesis submitted to the
College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Mechanical Engineering**

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Department of Mechanical and Aerospace Engineering

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Abstract

Responsive Liquid Crystal Polymer Rods

Matthew S. Shafran

In this dissertation I report on the successful fabrication of anisotropic liquid crystal polymer rods. These polymer rods demonstrated re-orientation by an applied external field. The polymer rods, 200 nm in diameter and a maximum of 60 μm in length, were produced by a template synthesis technique. A reactive liquid crystal monomer was filled into porous Anopore membranes which were used as a confining media. The liquid crystal monomer was polymerized by UV light while the liquid crystal remained in the nematic temperature range. The polymerization process permanently “freezes” the orientational order of the confined liquid crystal molecules, producing rods that are temperature independent after curing. The curing is kept in the nematic range to ensure proper orientational alignment in the pore of the membrane, where the responsive nature of the rods can be tailored by temperature, external fields, and/or surface treatments. The rods were suspended in low viscosity silicone oil and injected into indium tin oxide coated glass cells.

Both DC and AC electric fields were applied to the electro-optical glass cells, resulting in different types of rod movement. Switching times (time to change orientation from horizontal to vertical) has been observed to be as fast as 0.1 seconds and the threshold voltage has been as low as 5 volts. The switching times of the rods are mainly driven by the strength of the applied field and the molecular orientation of the rods. A model was used to describe the best case scenario of the rod structures and outlines that faster switching times are possible. Translational movement (moving vertical with the rod staying in the horizontal position) was also noted with the DC applied field. AC fields give different types of movement including rotational, vibrating, and swimming motions. The average rotational speed was found to vary linearly with the applied field strength, where the fastest speeds were at the highest field strength. Also, responsive rods were noted to move and push unresponsive rods in and out of the viewing area. The responsive rods are technologically important for possible electro-rheological fluids, magneto-rheological fluids, and components in microfluidic devices.

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Nomenclature

AC	Alternating Current
DC	Direct Current
ITO	Indium tin oxide glass
T	Electric torque
ϵ_0	Permittivity of Free Space, $8.85 \times 10^{-12} \text{ C}^2/\text{Nm}^2$
$\Delta\epsilon$	Dielectric Anisotropy
ρ	Density
I	Moment of Inertia
M	Mass
ω	Angular velocity
E	Electric field strength v/m, N/C
V	Volume
V	volt
m	meter
N	Newton
C	Coulomb

Chapter 1: Introduction

The fabrication of anisotropic particles and structures is an increasingly popular area of research, where anisotropy refers to different or varying properties when measured on different axes. These properties can include but are not limited to: electrical^[1], optical^[2, 3, 4], surface chemistry^[5], mechanical,^[6] or shape^[2, 7, 8, 9].

This work specifically expands in an area of responsive microstructures that was introduced by Cairns *et al.*^[10] Cairns and coworkers were able to make solid anisotropic polymer spheres from liquid crystal monomers. Upon application of an electric field the spheres would rotate which was observed with optical polarizing microscopy. A second work published by Cairns *et al.*^[11] demonstrated a means to produce rod-like structures through the use of Anopore membranes as the confining media. But there has been no further progress in the successful manipulation of liquid crystal polymer rods fabricated by this template technique. Therefore, the work of this research was initiated with the thought that the anisotropic liquid crystal polymer rods should demonstrate rotation or manipulation with an applied electric field.

The main objectives of the research include:

- Fabrication of liquid crystal polymer rods
- Application of electric fields to cause movement of the rods
- Observation of the rods with various field strengths
- Classification of movement
- Fabrication parameters vs. rod behavior
- Quantification of switching times

It will be shown that the rods are responsive with applied electric fields. More importantly a variety of movements have been documented with different types of external fields. The rods have shown simple movements such as, up and down, and translational movement with a DC applied field and have also demonstrated very complex movements like swimming with an AC applied field.

This work is the first to report on the successful rotation of anisotropic liquid crystal polymer rods with an applied electric field. These rods might show promise as microfluidic components, micro-mixers, optical switches, electro-rheological fluids and/or display type devices.

Chapter 2: Essential Theory

2.1 States of Matter

Solid, liquid, and gas are the three states of matter most often used to classify objects. The various states, which are temperature dependent, differ by the amount of kinetic energy and also the molecular structure. A solid is defined as “a magnitude that has the three dimensions length, breadth, and thickness: a part of space (as a cube, a sphere) bounded on all sides.”^[12] Therefore, the molecules of a solid will have 3 dimensional long ranged order.^[13]

However, liquids are different than solids because they have a “definite volume without having a definite shape except such as is temporarily given by a container and such as is readily lost.”^[12] This change in state is driven by temperature and leads to the liquid having no position or orientational order. In other words, the molecules are free to tumble and move around the container. The liquid is therefore in an isotropic state because the molecules are randomly positioned in any direction.

Finally, the third state of matter is the gas state. Gases are described as “a fluid that has neither independent shape nor volume but tends to expand indefinitely: a substance at a temperature above its critical temperature.”^[12] Gases are formed at higher temperatures than liquids, for constant pressure, and therefore will possess even more kinetic energy leading to the gas trying to expand to fill its container entirely.

Liquid crystals can be introduced as a mesophase that is observed between the solid and liquid state.^[14] This mesophase will retain properties from both the solid state and the liquid state. From the solid state the liquid crystal will retain some of the original

orientational order, but the liquid crystal will lose positional order.^[15] Without positional order the molecules are free to move around the container like a liquid.

2.2 Characteristics of Liquid Crystals

2.2.1 Shape Anisotropy

The shape of the liquid crystal molecules is an important factor that gives liquid crystals their unique properties.^[14] Liquid crystals have shape anisotropy, which means that their shape differs with respect to different directions. The shapes that liquid crystal molecules can adopt are rod-shaped molecules with a ratio of length to width about 3-8, disk like molecule (discotic liquid crystals) and bow-tie molecules (bent).^[16] Rod shaped molecules are formed mostly in organic substances; the chemical structure will have a rigid backbone with small ends leading to the rod shaped structure.^[13, 16]

Figure 2.2-1: Shape Anisotropy

2.2.2 Temperature and Orientation

Temperature is the main contributing factor for the liquid crystal state. Figure 2.2-2 demonstrates the change in molecular orientation with an increase in temperature. Also shown in figure 2.2-2, is the liquid crystal molecules ability and tendency to align with neighboring molecules in the liquid crystal phase.

Figure 2.2-2: Molecular orientation with increasing temperature

The solid state will first melt into the liquid crystal phase at the melting point. The liquid crystal phase can usually be noted by a milky white appearance. ^[15] The degree of orientational order of the liquid crystal molecules will subside as heating is continued. At a certain temperature a clearing point will be reached where the milky white appearance of the liquid crystal phase will transform to a transparent isotropic

liquid, this is the liquid state. ^[15] The physical appearance of RM257 liquid crystal which was used in this research is shown in figure 2.2-3.

Figure 2.2-3: Appearance of RM257: Solid, liquid crystal, and liquid state

2.2.3 Order Parameter

As stated in the last section, the liquid crystals will on average align with their neighbors; they will not have a strict parallel arrangement but rather will have group-favored orientation. ^[17] This alignment will happen because of two reasons; attractive forces from Van der Waals forces, and also because packing of the molecules is easier when they are aligned. ^[13] The order parameter is a means to describe the amount of orientational order that a liquid crystal possesses. ^[15] The order parameter can range from

0 to 1, but will often range from 0.3 to 0.9; 0 refers to no order (complete disorder, like an isotropic liquid), and 1 refers to complete order (like a solid).^[13, 15] The order parameter versus temperature can be seen in figure 2.2-4; one can see that the order parameter falls sharply at the clearing point of the liquid crystal or the start of the isotropic liquid phase.

Figure 2.2-4: Order parameter vs. Temperature^[15]

The order parameter is defined by averaging the function $\frac{1}{2}(3\cos^2 \theta - 1)$ for all the liquid crystal molecules, where θ is the angle between the director (n) and the molecule axis.^[15] The director and the angle can be seen in figure 2.2-5.

Figure 2.2-5: Director

2.2.4 Electric and Magnetic Fields

The anisotropy of liquid crystal molecules has a pronounced effect on their behavior in electric or magnetic fields.^[13] It is this principle of manipulation by electric fields that is exploited in liquid crystal displays (LCDs).^[15]

The majority of molecules in the nematic phase will have a permanent or induced electric dipole.^[13, 15] With no application of an electric field the permanent dipole liquid crystal molecules will have an equal chance of pointing in one of two possible directions (ie. North or South).^[13] Once an electric field is present the molecules will rotate until their long axis is aligned with the applied field.^[15] The success at rotating the molecules and the amount of polarization depends on the electric field application parallel or perpendicular to the director.^[13] This leads to a different dielectric constant with respect to the director.^[13] If many molecules are contained and the director is “locked in place” then the dipoles of each molecule can add together to form one large electric dipole.^[15] Magnetic fields can also produce very similar effects in liquid crystals that are

diamagnetic.^[13] The only difference is that the molecules are affected by magnetic fields instead of electric fields.

This manipulation by electric and magnetic fields only applies during the liquid crystal phase. During the isotropic liquid phase the molecules possess too much energy and movement to ever align themselves with the field direction.^[15] On the other hand, during the solid phase the bond energy is too strong to allow movement of the molecules.^[15]

2.3 Confining Liquid Crystals

Liquid crystals are able to flow like a liquid; therefore for most applications they need to be confined. Most of the time, the liquid crystals are sandwiched between two flat substrates, for example an LCD display.^[18] Along with confinement, the director of the liquid crystal can be controlled by rubbing the surface (creates microscopic grooves), coating the surface with surfactants, or externally applied fields.^[13, 14] Controlling the alignment of the liquid crystals is essential for most optical devices to work correctly, for example in LCD applications the liquid crystals must lay parallel (homogeneous) to the surface of the substrate.^[15, 19] Other various alignments are possible including perpendicular (hometropic) and tilted which can be achieved with surface treatments and applied fields.^[19]

2.3.1 Confinement to Spherical Geometries

The curved geometry of a spherical cavity has a pronounced effect on the alignment of the liquid crystals. ^[18] Confining liquid crystals in spherical droplets has been researched since the early 1900s, and properties are different from their bulk counterpart because of a high surface to volume ratio. ^[20] During the late 1950s, it became apparent how an electric field could change the director configuration, which is shown by the top two pictures in figure 2-3.1. ^[20] A major breakthrough happened in the 1980s with the invention of the PDLCs (Polymer Dispersed Liquid Crystals), a new device which was the first major application for polymer liquid crystal spheres. ^[20] PDLCs are constructed from liquid crystals bound in a polymer film. ^[20] PDLCs most popular application is electro-optical devices; one example is the privacy window, which can switch between transparent and opaque depending on an applied electric field. ^[18, 20]

There are many director configurations possible in spheres, which include radial, axial, bipolar, concentric, and escaped concentric. ^[21] The various configurations can be influenced by anchoring characteristics of the bounding matrix, electric and magnetic fields, shape and size. ^[18] Bipolar, radial, and axial are graphically shown in figure 2.3-1.

Figure 2.3-1: a-b) Bipolar with applied field c) radial d) concentric ^[20, 21]

2.3.2 Confinement to Cylindrical Geometries

Liquid crystals confined to spherical geometries have been studied as far back as the early 1900s, but it took until the early 1970s for interest to build in cylindrical cavities. ^[20] Multiple different types of cylindrical cavities have been used in the past to confine liquid crystals including: Anopore membranes, ^[20, 22, 23] Nucleopore membranes, ^[20] Vycor glass, ^[20] Aerogels, ^[20] and carbon nanotubes ^[24] but the focus of this research is on Anopore membranes. An Anopore membrane is constructed by the anodic oxidation of aluminum and has a porosity of 40%. ^[25] The membranes are available in multiple sizes, which range from 0.02 to 0.2 μm in diameter with a thickness of 60 μm . ^[25] An SEM picture of a 0.2 μm Anopore membrane is shown in figure 2.3-2. Once again like spheres, the director configuration can be distorted by the curvature of the cylinder, size of the cylinder, surface treatments, and applied fields. ^[20] A few examples of possible director fields are shown in figure 2.3-3. The director configurations that are of interest in this thesis have a parallel alignment to the cylinder axis, which is achieved by an untreated Anopore membrane. ^[26]

Figure 2.3-2: SEM image of Anopore membrane (200nm dia.)

Figure 2.3-3: Possible director fields in cylindrical cavities ^[20]

2.4 Reactive Mesogen

Liquid crystal monomers, known as reactive mesogens, are photo-polymerizable liquid crystals which will form densely cross-linked polymer networks when irradiated with UV light, shown in figure 2.5-1. ^[27, 28, 29] Reactive mesogens can give the necessary bridging material between liquid crystals, polymers, and responsive microstructures. Reactive mesogens are the type of liquid crystal used throughout this work.

Figure 2.4-1: Cross-linking of Reactive Mesogen ^[27]

The cross-linking process permanently “freezes” the molecular orientation of the liquid crystal forming a rigid polymer structure, which is independent of temperature after curing. ^[27, 28, 29] Therefore, before polymerization, the use of externally applied fields, surface treatments and photo-masks can be used to modify the molecular order which can lead to structures and films that are optimized to meet specific mechanical and optical needs. Reactive monomers can open a path to a range of applications including: responsive microstructures for electro-optical switches, ^[10] geometrical and optical anisotropic colloids, ^[2, 3] thermally reactive polymer films, ^[30-32] polymer structures, ^[11, 33] and optical filters/films. ^[34-36]

2.5 Capturing Anisotropy

Photo-polymerization is used to capture anisotropy and can lead to structures which have unique properties. Fernandez-Nieves *et al.* ^[3] have produced anisotropic colloids by mechanically deforming reactive monomer bipolar droplets. The droplets were suspended in a polyvinyl alcohol (PVA) film and were uniaxially stretched to lengths 12 times their original diameter and then photo-polymerized. After dissolving the PVA matrix, the resulting structures formed an ellipsoidal shape.

Stretched PVA - PDLC films were characterized by, Amimori *et al.* ^[37] to determine the relationship between polarization and stress-strain properties. It was found that the liquid crystal alignment was dependent on both shape anisotropy within the PVA matrix and the polymer orientation while stretching. In a second work by Amimori *et al.* ^[38] the stretched bipolar droplets were observed with deuterium nuclear magnetic resonance. The resulting NMR spectra confirmed that the ellipsoidal shapes had a bipolar director field and the liquid crystals aligned with the stretched axis.

Other highly ordered microstructures including rods, toroids and yarn balls have been produced by Cairns *et al.* ^[11] The fabrication process used Anopore membranes as the confining template. The microstructures were self-assembled by varying the concentration of reactive monomer and/or chloroform and the addition of surface treatments.

Steinhart *et al.* ^[39] fabricated polymer/liquid crystal nanotubes, using alumina templates with a pore diameter of 400 nm and reported on the influence of confinement with respect to different pore diameters. The outside of the nanotubes were constructed from PMMA which had a layer thickness 30 nm. The inner layer of the tubes was a discotic liquid crystal with a layer thickness of 5-10 nm.

2.6 Responsive microstructures

There is currently interest as a whole in externally activated responsive systems. For example magnetically-activated rod arrays were produced by Evans and coworkers ^[40] that may be useful in microfluidics and sensing applications. The nano and micro rods were fabricated from poly(dimethylsiloxane) (PDMS) and iron oxide particles. One end of each rod was attached to a substrate and the opposite end was free to move, resulting in various movements of the rod arrays including; back-and-forth and rotational.

Optoelectronic devices were fabricated by Wu *et al.* ^[41] from CdS semiconductor nanorods and nematic liquid crystals. The liquid crystals in this example were used to induce alignment on the CdS nanorods. The cells were created by rubbing ITO glass, which induced parallel alignment of the liquid crystal. Upon application of an electric field the liquid crystal realigned to perpendicular alignment with respect to the ITO glass, which caused the CdS rods to follow suit.

Dierking *et al.* ^[42] produced a magnetically operated switch with nematic liquid crystals and carbon nanotubes. The single wall nanotubes rely on the liquid crystal to stimulate movement. When the switch is off the nanotubes and the liquid crystals are parallel to the ITO substrate. With application of a magnetic field the liquid crystals and the carbon nanotubes rotate to perpendicular alignment with respect to the ITO layer. This causes the conductive nanotubes to complete the connection between two ITO substrates, which was verified by conduction measurements.

Van der Zande *et al.* ^[43] were able to demonstrate alignment of rod shaped gold particles with an applied electric field. The orientational order of the rods was determined by the absorbance spectra. Saturation occurred at high electric field strengths but a linear dependence was noted at low electric field strengths.

Liquid crystal droplets have been shown to have sub-millisecond switching times in an optical switch application. ^[44] In this example the droplets of liquid crystal were rotated optically by “optical tweezers.” Wood *et al.* ^[45] experimentally characterized which properties of liquid crystal droplets had the largest effect on the transfer of optical torque. The strength of the light intensity was proportional to the amount of torque induced on the liquid crystal droplet, where the highest intensities gave the largest torque values. It was also determined that size and birefringence of the liquid crystal droplets plays a role in the transfer of torque to the droplet. High birefringence materials allow more torque to be transferred and 2.5 μm and 8.0 μm diameter droplets gave the highest drag torque values which were attributed to wave plate-like behavior.

Reactive mesogens, as stated before, can be used to produce responsive microstructures. Cairns *et al.* ^[10] were able to produce responsive spheres by dispersing

reactive mesogen in glycerol and then exposing the solution to UV light. Curing while in the nematic range captures the bipolar director field, which allows the rotation of the spheres to be observed by optical microscopy, on application of an electric field. Figure 2.5-2 shown below demonstrates the rotating spheres in a patterned set of electrodes which was highlighted by Cairns *et al.* ^[10] The rotation speed of the spheres was found to be dependant on field strength, viscosity, and director field alignment.

Figure 2.6-1: Pictures of rotating spheres ^[10]

The dispersion of solid polymer rotating spheres, Cairns *et al.*, ^[10] is a PDLC film in reverse. A PDLC uses the polymer film as a rigid bounding matrix where the liquid crystal is bound in spherical cavities in this film. With application of an electric field the bipolar director field of the droplets will align with the electric field which allows the light to pass through the film. The spheres produced by Cairns *et al.* are rigid polymers with a “locked in” director field. The solid polymer spheres are dispersed in glycerol and the solid spheres rotate with the electric field.

Vennes *et al.* ^[46] synthesized 10 different liquid crystal monomers that could be dispersion polymerized into spheres. Some of these solid spheres were able to be rotated with polarized light which could lead to the ability to rotate unresponsive structures. Also various dilutions and mixtures of their liquid crystal monomers were characterized to find the typical diameter of the resulting spheres. Garces-Chavez *et al.* ^[47] also fabricated spheres from a UV photo-polymerizable liquid crystal. They characterized spin direction and found the spheres rotation increased linearly with intensifying light beam power.

2.7 Thermally Responsive Structures

Thermally responsive films have been made by Sousa *et al.* ^[31] through the use of reactive monomers and photo-masks. Pre-selected strips in the film were first polymerized while in the chiral nematic phase; and then the uncured sections were polymerized while in the isotropic phase. The chiral nematic region expands more than the isotropic regions, because of its different thermal expansion attributes, leading to a film with adjustable topography. Mol *et al.* ^[32] also fabricated thermally responsive films from reactive mesogens. The films were cured between glass plates and two different molecular orientations were achieved: twisted and splayed depending on surface treatments. With the application of heat the twisted orientation film tended to bend in two directions and formed a saddle shape. The drawback of the twisted orientation was the difficulty in terms of precise film control. On the other hand, the splayed orientation demonstrated more control over deformation. Once again the film was heated but the film bent in a curling fashion from a larger expansion on one surface of the film.

Chapter 3: Supplies and Fabrication

3.1 Supplies

Reactive Mesogen:

The liquid crystal used in this work is RM257 (manufactured by Merck). RM257 is a diacrylate reactive liquid crystal, which is polymerizable by UV curing. The nematic phase and clearing point is 67 °C and 127 °C respectively. In the bulk state RM257 is a white powder.

Photo-initiator:

The photo-initiator mixed with the RM257 is Daracur 1173 (manufactured by Ciba Specialty Chemicals Inc.). A photo-initiator is the catalyst that starts the chain reactions during the UV curing.

Spacers:

The spacers used to separate the ITO glass substrates are polymethacrylate spheres. The spheres are 60 μm in size with a standard deviation of $<2 \mu\text{m}$ (coefficient of variance $<2\%$). As packaged the particles are dispersed in water with a concentration of 10% solid.

Figure 3.1-1: Spacers as packaged

Figure 3.1-2: SEM image of spacers

Anopore Membrane:

An Anopore membrane which is constructed by the anodic oxidation of aluminum is used as the confining media. The Anopore membrane (manufactured by Whatman, Anodisc 13), is 200 nm in diameter, 60 μm in thickness, and has a porosity of 40%. ^[25] Below in figure 3.1-3 is an Anopore membrane, shown on the left, with a reference for size comparison.

Figure 3.1-3: Anopore membrane with size comparison

Indium tin oxide glass (ITO):

Indium tin oxide glass (ITO) is transparent glass with indium tin oxide sputtered onto one surface of the glass. This will make one surface of the glass conductive and the other surface non-conductive. ITO glass is used to make the glass cells.

3.2 Equipment

Hot Stage:

Two hot plates are used during the preparation of the samples which is shown in figure 3.2-1. The first hot plate (Corning) has been modified to fit in the curing chamber and also to keep the sample away from the heat of the mercury lamp inside the curing chamber. The top is constructed from steel with a white enamel finish and has a temperature range of 25 – 355 °C.

Figure 3.2-1: Corning modified hot plate (left). Digital Fischer scientific hot plate (right)

The second hot plate (Fisher Scientific) is used on the outside of the curing chamber for the sole purpose of keeping the liquid crystal in the liquid crystal phase. This hot plate has a ceramic top and has a temperature range of 25 – 540 °C.

Sonicator:

Below in figure 3.2-2 is the Sonicator (Branson 1510 R, 42 kHz) used to sonicate the rods.

Figure 3.2-2: Branson Sonicator (42 kHz)

Curing Chamber:

The small area curing chamber and lamp house (manufactured by UVEXS, California) is shown in figure 3.2-3. The lamp housing contains a mercury vapor lamp which is able to supply UV light in the 200-400 nm spectrum. The lamp housing is also fitted with a reflector that filters out up to 95% of IR spectrum light. This helps to ensure that excess temperature from the lamps is kept to a minimum.

Figure 3.2-3: Sample Chamber (bottom), Lamp Housing (top)

The power supply is a separate unit, figure 3.2-4. The power supply is able to adjust the intensity of the lamp (150-200-300 watts per inch). Also the power supply will automatically time the shutter speed so curing time can be made uniform for the samples.

Figure 3.2-4: Power Supply

3.3 Procedure (Polymer Rods)

The entire procedure can be outlined in figure 3.3-1.

Figure 3.3-1: Fabrication Outline

Mixing:

The first step in fabrication of the liquid crystal rods is mixing the photo-initiator (Daracur 1173 (Ciba)) at a weight percentage of 95% RM257 and 5% photo-initiator. The photo-initiator is used to start the polymerization process during UV curing.

Both RM257 and photo-initiator are combined in a glass vial and placed on a hot stage. The hot stage is used to bring the RM257 into the liquid crystal phase. Once the RM257 has liquefied the mixture is agitated by a tip of a pipette; this ensures that the

RM257 and photo-initiator are thoroughly mixed. Once this is done the mixture will cure with the application of UV light.

Filling:

The Anopore membranes are broken into smaller pieces roughly the size of a 2.0 mm square, care should be taken because the filters are extremely brittle. The filters are broken to limit waste and also to make fabrication more manageable. A droplet of RM257/photo-initiator mixture is taken from the vial and placed on a glass slide which is heated on top the hot stage. The Anopore membrane is now placed on the edge of the RM257/photo-initiator droplet, the membrane will fill by capillary action. Some RM257/photo-initiator will pool on the top of the filter which will lead to a thick polymer top after curing. The thick polymer top will lead to problems during sonication. To prevent this the filled Anopore membrane is pressed between two filter papers which will remove excess RM257, but will usually not entirely remove the polymer film. ^[25] The film can be seen in figure 3.3-2. The cracks, which are most likely from shrinkage during polymerization, reveal the rods hidden beneath. ^[48]

Figure 3.3-2: Excessive polymer top

After removing the excess material the filled membrane is placed back on the heated glass slide. Part of the membrane can be hung over the side of the glass slide to provide a leverage point for removal after curing. The glass slide should now be placed on a hot stage inside the curing chamber. This is done to keep the liquid crystal at the correct temperature and subsequently at the correct molecular order during curing.

The temperature of the hot plate is monitored by a thermocouple (k-type), figure 3.3-3. The thermocouple is held in place by a weighted glass slide. This allows the monitoring of the temperature rise during curing. A temperature rise of 1 – 4 °C is normal on the low power setting of 150 watts per inch. The hot plate inside the curing chamber with the thermocouple monitoring temperature is shown below.

Figure 3.3-3: Thermocouple on the inside hot plate

Curing:

The curing chamber is able to be set to provide proper curing time and curing intensity. Most curing is done on low power setting, 150 Watts per inch, for 30 seconds. Curing is achieved by placing the filled membrane on the hot plate inside the curing chamber and then turning the curing chamber on for the prescribed time. After curing for 30 seconds the liquid crystal will polymerize into a solid polymer rods as a result of the Anopore membrane confinement.

Etching:

Now the RM257 is completely cured inside the Anopore membrane. Separating the rods from the membrane is achieved by etching away the membrane leaving only the polymerized liquid crystal cylinders. A 0.4 -0.6 M solution of NaOH is prepared. The membrane is placed in a vial with the solution of NaOH. The NaOH base solution reacts only with the Anopore membrane. Etching only takes a few hours to complete and is noted by the film becoming flexible.

Sonication:

Sonication is needed to separate the rods after curing and etching. The NaOH solution is removed and the film is washed with distilled water. Once this is complete ethanol is added to the vial. This is then placed in a sonicator (Branson 1510 R, 42 kHz) for approximately 15 minutes. This leaves a dispersion of polymer rods in ethanol. Finally, the ethanol is allowed to evaporate at room temperature leaving only rods.

Figure 3.3-4 demonstrates individual rods with a cluster of rods that never fully separated.

Figure 3.3-4: Sonicated Rods

After the ethanol has fully evaporated silicone oil (Brookfield 4.7 cP) is added to the vial and rods. Sonication is used once more to completely disperse the rods in the silicone oil. At this point the rods are ready to be added to the glass cells.

3.4 Procedure (Glass Cells)

The electro-optical glass cells provide a means to apply an electric field to the rods and also allow observation with an optical microscope. A typical graphical representation of the glass cells with rods is shown in figure 3.4-1.

Figure 3.4-1: Typical glass cell

Construction:

The cells are fabricated from 1.0 inch by 1.0 inch squares of ITO glass. The ITO side is thoroughly cleaned with acetone and a lint free cloth to remove any residue or dust particles. Next tacky adhesive putty is used to remove any remaining particles that are left behind from the cloth. It is very import to remove any foreign particles from the ITO surfaces to ensure that the bottom and top ITO surface do not short circuit, which would render the glass cell inoperative.

The polymethacrylate spheres are used as spacers to separate the top and bottom ITO glass. The spheres will create a 60 μm gap (sphere diameter: 60 μm) between the two ITO surfaces. This size of gap was chosen because the maximum rod length is 60

μm and will allow for full rotation of the rod. The polymethacrylate spheres and water solution is diluted in ethanol to allow fast evaporation during construction. The solution is mixed with a weight percentage of 5% sphere/water mixture and 95% ethanol.

The first step in fabrication of the glass cell is to place a clean 1.0 inch piece of glass, ITO side up (note the ITO side can be found with an ohm meter), step a in figure 3.4-2.

Figure 3.4-2: Procedure outline for glass cells

A droplet of the sphere/ethanol mixture is next placed on the ITO with a pipette, step b. It will take 5-10 minutes for the ethanol to completely evaporate leaving only spheres in the ITO surface. Once this is complete another 1 inch piece of ITO glass, ITO side down, is placed on top of the first ITO glass, step c. The two ITO pieces of glass should be staggered to allow the attachment of a lead for later use. Epoxy glue is now used to glue two sides of the glass cell, step c.

Once the glue has dried the rod/silicone oil mixture can be added to the glass cell. The glass cell easily fills from capillary action, step d. Once the cell is completely filled the remaining sides of the glass cell are glued with epoxy glue, step e. This now completely seals the glass cell. The last step is to attach two leads to the glass cell with conductive silver paint. Step f in figure 3.4-2 demonstrates a complete glass cell with rods and silicone oil ready for observation.

Chapter 4: Results

4.1 Fabrication of Rods

The first step in this research was the successful repeatable fabrication of the liquid crystal rods. The initial samples of just liquid crystal monomer had a tendency to cure improperly and some samples exhibited a burnt appearance. The poor curing and burnt appearance was attributed to excessive heat from the lamps in the curing chamber. Modifying the hot plate which lowers it from the lamps rectified this problem.

Once curing was achieved it was possible to fill the Anopore filters with the liquid crystal monomer, cure, and then etch. Rods were observed first by Scanning Electron Microscopy (SEM) imaging; figure 4.1-1 demonstrates a 200 nm diameter sample captured using SEM.

Figure 4.1-1: SEM imaging of 200 nm rods

An efficient way of removing the excessive polymer top is still to be explored as shown in chapter 3. However, a few techniques were tried including; the use of less

liquid crystal monomer, wiping the top surface with solvent, and sealing the top with adhesive tape. The only way to limit the polymer top thickness was by squeezing the filter between filter papers, but it still does not entirely remove the excessive monomer. Therefore all samples were made by this technique, of removing the excess monomer with filter papers, which helps tremendously with sonication of the rods. If the thickness of the polymer film is too great the rods will not separate.

4.2 Sonicated Rods

Once the rods were confirmed by optical and SEM microscopy the sample was sonicated. Sonication is a process used to separate the rod clusters. Figure 4.2-1 demonstrates separated rods, 200 nm in diameter, by optical imaging at various magnifications.

Figure 4.2-1: Optical image of separated rods

4.3 Dispersion Fluid

The first glass cell created used alcohol as the dispersion fluid. Alcohol was chosen because it is transparent and has a low viscosity. With the application of an electric field the rods demonstrate no movement. It is unclear why the alcohol did not allow movement of the rods. In the second attempt the dispersion fluid was changed to petroleum based oil. This oil was chosen because it has a low viscosity and also a low volatility. The petroleum oil had a red dye added which made optical observation impossible. Movement might have occurred in the petroleum oil sample, but the red tint ultimately prevented the optical microscope from capturing the image. The third attempt changed the dispersion fluid to clear silicone oil. The silicone oil was chosen because it has a low volatility, is completely transparent, and also was available in a wide range of viscosities. The specific silicone oil used had a viscosity of 4.7 cP. With the addition of silicone oil the rods demonstrated movement with an applied electric field. Therefore, silicone oil was used for the rest of the samples.

4.4 Responsive to Applied Fields

The rods were observed to re-orientate with an externally applied direct current (DC) and alternating current (AC) electric fields. The power supply was connected to the glass cells and a pictorial representation of ideal rods moving with an applied DC field is shown in figure 4.4-1.

Figure 4.4-1: Responding to a DC voltage

4.4.1 DC applied field

With an applied DC field the rods demonstrated two different types of movement; switching up and down or translational. Switching up and down movement can be achieved by turning the DC power supply off and on. Translational movement is accomplished by changing the polarity of the DC power supply. Both types of movement can be seen in figure 4-4.2.

Figure 4.4-2: Side View with DC field

Figure 4.4-3 demonstrates a rod switching with an applied voltage of 10 V. These rods were fabricated with the temperature being constant in the range of 71-74 °C. The rods were observed using an optical microscope (Leitz LaborLux 12 Me, Mag. 20x). The re-orientation time for the highlighted rod shown in figure 4.4-3 is approximately 0.385 seconds. During analysis, optical images were captured every 0.055 seconds with a frame grabber (Guppy, Allied Visions Technology).

Figure 4.4-3: Reorientation with 10 volts DC

The apparent length of the rod was measured during switching and relaxation with a program written in Matlab (Evans, Appendix 1). Switching is defined as the process when the rod rotates from parallel with the ITO glass plane to perpendicular with the ITO glass plane. Relaxation time was also calculated and initiates when the electric field is turned off and the rod moves back to the original parallel orientation with the ITO glass plane. The angle of the rod with respect to the glass plate plane is calculated using equations 1 and 2.

Where θ is the angle defined between the rod long axis and the glass plate plane, l_o is the initial rod length when $\theta = 0$, and l is the apparent rod length measured.

$$\theta = \cos^{-1}\left(\frac{l_o - x}{l_o}\right) \quad (1)$$

$$x = l_o - l \quad (2)$$

The switching and relaxation times were measured for the rod shown in figure 4.4-3 at increasing field strengths. From these times, switching and relaxation curves were constructed for various field strengths shown in figure 4.4-4. Figure 4.4-5a highlights various portions of the curve; switching, fully on, and relaxation; while figure 4.4-5b, graphical demonstrates the rod position through the switching and relaxation curve of 10 volts.

Figure 4.4-4: Switching and Relaxation Curve

Figure 4.4-5: a) Switching, fully on, and relaxation b) Rod during switching curves

The switching time is driven by the electric field which is the positive slope at the beginning of the graph, figure 4.4-4 and 4.4-5. The responsive nature of the rod during switching is shown to reduce with a decrease of electric field strength. The fastest switching time recorded, 0.11 seconds, is achieved with a field strength of 60 V ($1 \text{ V}/\mu\text{m}$). The polymer rod is still active at a relatively low voltage of 5 V ($0.08 \text{ V}/\mu\text{m}$); however this is the threshold voltage. At this low voltage the field strength is not strong enough to cause rotation of the rod completely; the rod only rotates approximately 75° with respect to the x-axis.

On the other hand, the relaxation time is when the electric field is turned off and the rod goes back the original position before the applied field. The relaxation time is the second portion of the plot which is of negative slope, figure 4.4-4 and 4.4-5. Relaxation time is not affected by field strength and is relatively constant for the different field strengths. Finally, the portion of the graph between the end of the switching curve and

the beginning of the relaxation curve is when the rod is held in position by the electric field and is positioned vertically with respect to the ITO plane.

4.4.2 AC applied field

An AC power supply demonstrated different movements as compared to DC field because of the frequent change in polarity. The movements include vibrating, rotational and swimming motions in the cell. Many rods did not exhibit pure rotation but rather translation and rotation. The vibrating rods have also been shown to move randomly through the glass cell. An ideal representation is shown in figure 4.4-6.

Figure 4.4-6: a) Vibrating rod b) Rotation (top view)

Quantifying responsiveness in the AC sample proved complex due to activeness of the sample. The lowest threshold voltage found for the sample in figure 4.4-7 was 42 volts AC. Three rods were observed to be inactive during observation, but the area was constantly changing do to rods moving drastically. Figure 4.4-7 shows a rod moving through the area and overtaking an inactive rod and pushing it out of the viewing area. These disturbances by very active rods caused problems which were not seen in the DC field samples.

Figure 4.4-7: Active rod overtaking an unresponsive rod

A rotating rod was observed at decreasing AC field strengths, figure 4.4-8a. The minimum voltage to cause rotation of the rod was found to be 40 volts. These rods were also observed using the same optical microscope and frame grabber as the DC switching. The pictures were analyzed using a Matlab program (Evans, Appendix 2) which measured the angle of rotation from a given setpoint. The angular velocity was then calculated at various voltages. The highest voltage possible with our power supply was 110 volts AC, which gave the fastest rotation, approximately 1.0 second. Decreasing the voltage gave a linear relationship between voltage and average degree of rotation per second. Data were not obtainable for 60 and 50 volts due to the rod becoming “stuck”. The slower rotation of the rod at lower voltages allowed the rod to become wedged on the unresponsive rod shown in figure 4.4-8a.

Figure 4.4-8: a) Rotating rod. b) Graph of Voltage vs. Angular Velocity

Another sample with an applied AC field demonstrated the rods pushing a spacer. The spacer highlighted in figure 4.4-9 has a diameter less than 60 μm . In the first picture

the rods are very close to the spacer. With an application of an AC field the rods begin to vibrate. In the second picture after approximately 1.0 seconds the spacer has moved from the rod's vibration. The spacer continues to move until it becomes stuck in a large cluster of rods.

Figure 4.4-9: Rods causing spacer to move

4.5 Magnetic field during cure

Changing variables during curing was attempted once the rods were shown to be responsive to DC and AC fields. The main goal was to control the type and speed of movement. The first attempt of control used magnetic fields to control molecular order. The filled Anopore membranes, 200 nm in diameter, were cured while placed on top of a magnet. The temperature of the hotplate was once again kept between 70-75 °C. The resulting rods demonstrated a few unique phenomena. The first notable difference was the dense clustering of the rods, where there were very few non-clustered rods. Clustering was common in other cured samples, but the magnetically cured sample was

the most pronounced. DC voltage had little effect on the rods due to the tightly packed rods. Small movements were noticed but full rotation was limited. The second phenomenon happened during the application of AC voltage. Figure 4.5-1 shown below demonstrates a cluster at the start of a 110 volt AC field. No movement is noted until 2.75 seconds of field application. At this time one rod starts to vibrate up and down. From this point on more rods become active and start to vibrate uncontrollably. This can be seen at 6.88 and 11.0 seconds. At 12.93 seconds the entire cluster starts to move as a whole, any rods that are not active are dragged by the active rods. The amount of movement can be seen at 18.37 seconds.

Figure 4.5-1: Cluster moving together

4.6 Electric field during cure

A sample consisting of 200 nm diameter rods was fabricated with an applied electric field during curing. This type of curing is much like curing on a magnet, in which the electric field causes more control of molecular ordering. The temperature was still kept at the lower end of the nematic region 70-75 °C. There was clustering in this sample but it was not as extensive as the magnetically cured sample. Figure 4.6-1 demonstrates some of the clustering.

Figure 4.6-1: Clustering 200 nm diameter rods

Most singular rods were unresponsive to an applied DC field; for example only one singular rod showed responsiveness. The clusters on the other hand were very responsive. Ten different clusters were observed and all demonstrated a form of responsiveness. Eight out of the ten clusters were responsive to an on/off 60 volt DC field; the degree of responsiveness varied from very slight flinching back and forth to major displacement. The last two clusters demonstrated responsiveness to a change in polarity which caused translational movement in the glass cell. Ten random locations in the glass cell were then chosen to test the translational responsiveness in the clusters. 22

clusters were counted in these 10 locations and 18 demonstrated translational movement with a 60 volt change in polarity. The figure below demonstrates a cluster undergoing a change in polarity. The lowest threshold voltage of translational movement was 20 volts. Picture a, is in focus at the start of the experiment. Next the field strength was kept constant, but the leads were reversed which changed the polarity. This step can be seen in picture b, which is out of focus. The cluster is out of focus due to the cluster translating up or down in the glass cell with the polarity change. The cluster will stay in this new position until the polarity is reversed again. Picture c, demonstrates this by making the polarity the same as picture a, where picture c has now back to in focus.

Figure 4.6-2: Translational movement

4.7 Curing Time

The responsiveness was observed in different samples cured at 5, 10, 20, 30, and 40 seconds to determine the most efficient cure time. All 5 cure times properly produced rods which were observed using an optical microscope. Figure 4.7-1 depicts rods cured at 5 and 40 seconds. Note that both samples look identical.

After observation with DC and AC fields it was determined that curing time has no major effect on the responsiveness of the rods. All clusters in each of the samples demonstrated some type of movement with an applied DC field excluding the 30 second cure time. The two most responsive samples (5 and 40 seconds) demonstrated the most compact and tightest packing, shown below in figure 4.7-1.

Figure 4.7-1: a) 5 second cure b) 40 second cure

The above clusters proved to be exceptionally responsive. Clusters from both of these samples broke apart after a strong application of 110 volts AC. Figure 4.7-2 below highlights a cluster from the 5 second sample that was broken apart after an applied AC field.

Figure 4.7-2: Cluster after strong application of AC field

The least responsive was determined to be the 30 second sample. Experimentally this does not fall within the trends of the other samples. It is concluded that this sample is poorly active because of fabrication issues. During fabrication of this particular sample problems arose with hot plate temperature adjustments and other factors. Figure 4.7-3 below demonstrates a small cluster from this sample. It can be noted that the sample did not form large densely packed clusters like the 5 & 40 second samples.

Figure 4.7-3: Small cluster from 30 second cure sample

Chapter 5: Discussion

The polymer rods demonstrated behavior which was not predicted at the beginning of this work. The general initial thoughts of the rods moving were those shown in figure 4.4-1, switching up and down. The actual results demonstrated a wide variety of movements and behaviors that were found difficult to control.

5.1 Director

The director configure plays a tremendous role in the type of behavior that the rods will demonstrate. As mentioned in Chapter 2, if the director of many liquid crystal molecules is “locked in place” then the dipoles of the individual molecules will add and form one large dipole.^[15] Once again, the director field possible in a cylindrical cavity depends on surface treatments, cavity size, and applied fields, figure 5.5-1.^[20] In an untreated Anopore membrane the liquid crystal will align with the pore axis as shown in the “red circle” in figure 5.5-1.^[20]

Figure 5.1-1: Director fields possible in cylindrical cavities^[20]

It should be noted that liquid crystals can have either a positive or negative dielectric anisotropy value. A positive dielectric anisotropy value will align the long axis of the molecule with the electric field. While a negative dielectric anisotropy value will align perpendicular with the applied field, figure 5.1-2.

Figure 5.1-2: Rotation in a Field

RM257 has a negative dielectric anisotropy value which causes perpendicular alignment with an applied field. This caused the bipolar droplets of Cairns *et al.* ^[10] to align perpendicular to the field direction, graphically shown below in figure 5.1-3.

Figure 5.1-3: Rotation of Bipolar Droplet

Therefore it is thought that the up and down movement of the polymer rods are from a director configuration similar to figure 5.1-4a and the translation movement is from the parallel axial alignment, figure 5.1-4b. These director fields shown in figure 5.1-4 are the best case scenarios for the polymer rods. Some rods have shown hybrid movements of both up and down and also translational and could be attributed to a combination of director fields. The majority of the observed rods demonstrated translational movement which is attributed to the parallel-axial alignment with a negative dielectric liquid crystal. The spheres fabricated by Cairns *et al.* ^[10] were confirmed to have a bipolar director field by the optical patterning between crossed polarizers. This is difficult in the rods due to the small diameter.

Figure 5.1-4: Possible director fields.

The rotation in the AC sample is a special case because the rotation is not perpendicular with the ITO plane but rather is parallel with it. Figure 5.1-5 demonstrates another rod that is rotating similar to the one shown previously in figure 4.4-8. This rod is slightly different because it starts out by rotating about the center of the rod and by the

end of the video clip it is rotating about the end of the rod. Also, this rod is not staying in one spot but rather moving slightly in all directions.

Figure 5.1-5: Rotating rod

Currently there is no explanation for the rotation. A different video clip of the example described in Chapter 4 demonstrated just vibration when close to 40 volts. Possibly the rods that rotate are vibrating but have one end that is slightly heavier, larger, or attached to another rod which slows one end down which causes rotation.

Another area which is unclear is the relaxation of the up and down moving rods with the DC applied field, mentioned in chapter 4.4.1. With this type of movement it was noticed that some rods returned to the original position and other rods stayed in the vertical position when the electric was turned off. The relaxation is thought to be attributed from residual charging on the ITO surface, but at this time the relaxation cannot be fully explained.

5.2 Model

Following the same derivation for Cairns *et al.* ^[10] spheres a model was used to calculate the theoretical switching times. Electric torque, Equation 1, and torque as defined by mechanics, Equation 2, were combined and then integrated twice resulting in an equation relating time and angle (Equation 4).

$$T = |\Delta\epsilon|\epsilon_o E^2 V \cos\theta \sin\theta \quad (1)$$

$$\omega \frac{d\omega}{d\theta} = \frac{T}{I} \quad (2)$$

The moment of inertia for a slender rod taken about the end of the rod is shown below in Equation 3.

$$I = \frac{1}{3} ML^2 \quad (3)$$

$$\Delta t = \sqrt{\frac{\rho L^2}{3|\Delta\epsilon|\epsilon_o E^2}} \left[\ln\left(\tan\left(\frac{\theta_2}{2}\right)\right) - \ln\left(\tan\left(\frac{\theta_1}{2}\right)\right) \right] \quad (4)$$

where ρ is the density (1000 kg/m³), L is the length (30 μ m), $|\Delta\epsilon|$ is the dielectric anisotropy of a perfectly aligned nematic (2), ϵ_o is the permittivity of free space, E is the field strength, θ_2 is the final angle (90°), and θ_1 is the initial angle.

Equation 4 models the time for the rod to align parallel with the applied field from various initial angles. This model assumes perfect alignment of the liquid crystal, no viscosity and uniform electric field strength. The switching times predicted, Figure 5.2-1a, are considerably faster as compared to measured values; for example at 60 V and 5 V the rod is switching at approximately 700 μ s and 8500 μ s, respectively. There is considerable discrepancy between the theoretical and experimental values. This may be

caused by improperly aligned domains in the rods which would influence the uniformity of the field director. Also, the up and down movement is attributed to a director field similar to figure 5.1-4 which would be the best case scenario or the far right director field (twisted-bipolar) shown in figure 5.1-1. The twisted-bipolar director has a varying symmetry axis which would decrease the total net anisotropy. This decrease in the total net anisotropy would explain the large difference between theoretical and experimental values.

The model, equation 4, calculating switching times assumes a dielectric anisotropy value, $\Delta\epsilon$, equal to -2 which is for perfect alignment of the director field. The effective dielectric anisotropy value was calculated by using the actual switching time data and equation 4. This leads to a $|\Delta\epsilon|$ value of 2.43×10^{-4} for a field strength of 10 V; comparing the corrected $|\Delta\epsilon|$ value to the perfect alignment value of 2 demonstrates that perfect alignment has not been achieved, which further demonstrates why there is a large amount of discrepancy between the theoretical and experimental switching times. Now, using this “corrected” anisotropy value the theoretical switching times can be plotted again. Figure 5.2-1b compares the actual data for a field strength of 10 V and the corrected theoretical switching times, which give similar curves.

Figure 5.2-1: a) Theoretical switching times for various voltages. b) Comparison of actual and theoretical with corrected anisotropy value.

5.3 Clustering

Clustering has been found in all the samples made and is defined when the rods have a tendency to group or clump together. Large amounts of clustering were not fully noticed until the sample of rods was cured on a magnet. This sample demonstrated large scale clustering with only a handful of stray rods. The degree of clustering was so great that the 60 volt DC power supply could hardly cause any movement in the clusters. The strong 110 volt AC field was able to break apart the clusters, but this even took a large amount of time, 2.75 seconds until any movement was noted. The sample cured with an applied electric field should have also demonstrated similar clustering and responsiveness as the magnetically cured sample. This of course did not happen and is attributed to a weak DC field applied (60 volts) and also a large gap between the electrodes (approximately 1.0 mm). The gap was large due to the filled Anopore membrane placed on a glass slide which was sandwiched between two ITO pieces of glass. Therefore, this experiment using an electric field during curing should be repeated with a more powerful power supply and then compared to the magnetically cured sample.

One of the unique attributes noticed during observation was the majority of stray rods not moving. This statement does not apply to all stray rods because a limited amount of strays were noted to move and this also does not take in account a cluster that has been broken apart with an AC field to produce more separated rods. This simple fact that active rods like to cluster is a unique trait. One explanation for this could be because of charge distribution. This goes back to the idea of permanent and induced dipoles. Therefore the rods might have a positive and negative pole which likes to attract the opposite of another rod. Leading to large networks of rods all attracted to each other.

The magnetically cured sample could be causing more ordering which is leading to a more pronounced dipole.

A sample was observed while filling a cell with the silicone oil/rod dispersions, figure 5.3-1. The main goal was to find either: the rods clustered while in the cell, clustered during the filling process, or introduced to the cell all ready clustered. The dispersion used to fill the cell was the sample cured for 5 second which was used to justify curing time. Prior to filling the cell the dispersion was well agitated with a pipette.

Figure 5.3-1: Observation during filling cell

Figure 5.3-1a shows the cell completely dry before filling. The next picture, b, is in the process of filling and the angled line is the oil/rod dispersions entering the viewing area. The left most spacer has all ready “captured” the first rod. Picture c, depicts more rods becoming clustered around the spacers as their movement is halted by the obstruction. Also highlighted in “red” in picture c is a large cluster moving together. Picture d, follows this cluster as it is moving through the viewing area. In picture e, the

cluster is gone as it has moved to a different area in the cell. Picture f depicts the cell at the end of filling. Highlighted in picture f is smaller cluster that has become trapped on the spacers.

As shown in figure 5.3-1 clustering can happen from becoming trapped in any irregularities in the cell, which most likely will be the spacers used for gaping. Also clustering happens before the sample is ever introduced to the cell. This is most likely from the dipole interaction mentioned before. To further this study samples should be sonicated immediately before being introduced to the cell. Possibly the agitation by the pipette was not sufficient enough to cause separation.

Chapter 6: Applications

6.1 Microfluidics

Some potential applications of the responsive rods include components in microfluidic devices highlighted in figure 6.1-1. Microfluidics are characterized by channel dimensions which are less than 1.0 mm.^[49] Within this small scale the fluid will have laminar flow and small amounts of mixing.^[49] Therefore the first application is a micro-mixer in microfluidic devices. The micro-mixer would be made from rods that demonstrate propeller type movement with an applied AC field. The second application would be to stop fluid flow in these small channels. This would be accomplished by rotating the rods to block the flow through a channel.

Figure 6.1-1: Components in Microfluidic Devices

6.2 Displays

Another potential application is in a display, which utilizes black-pigmented liquid crystal polymer rods shown in figure 6.2-1. This type of display does not need polarizers and the rods act as light modulators. Traditional liquid crystal displays (LCDs) use polarizers to allow the transmittance of properly oriented light.^[50] Drawbacks of

polarizers are their poor efficiency (maximum of 50%), their high cost to manufacture and their degradation over the life span of the device. ^[15] Therefore the absence of a polarizer would reduce the power consumption and total cost of the device. The off state can be seen in figure 6.2-1a; in this mode the rods will block the light from traveling through the device. Grayscale will be achieved using voltages between the minimum and maximum operational value. An intermediate voltage will not cause full rotation of the rods. The black-pigmented rods will modulate the amount of light allowed through the display; this is demonstrated in figure 6.2-1b. Finally, at the full on voltage figure 6.2-1c, the cell will transmit maximum light to the observer.

Figure 6.2-1: a) Display off. b) Display on medium voltage. c) Display full voltage

A second potential display device would be based on the electrophoresis effect shown in figure 6.2-2. A traditional electrophoretic display uses charged particle dispersions and is often referred to as E-ink or electronic paper. ^[51] In this application rods with translational movement would move horizontally between the bottom and top

ITO layer. When the pixel is activated the black-pigmented rod, dispersed in a white liquid, would move horizontal to the top ITO layer and will reflect the incoming light back to the observer. In the off state the rods will stay on the bottom ITO layer and the light would be absorbed by the white liquid.

Figure 6.2-2: Electrophoresis Display

6.3 Electro-Rheological and Magneto-Rheological fluids

Finally, another possible application would be as an electro-rheological or magneto-rheological fluid (smart fluid). These fluids are able to change viscosities with an application of either an electric or magnetic field. ^[52] With no applied field the liquid has a low viscosity, but with an application of a field the liquid can have a viscosity like a gel. With the responsive nature of the polymer rods it is possible that they might show “smart fluid” capabilities.

Chapter 7: Conclusions

This research has shown a means to fabricate a fascinating responsive structure. The polymer rods produced have been manipulated with both DC and AC fields, where the field type has been shown to greatly affect the rod behavior. Switching times have been measured for a singular rod at a maximum of 60 volts. The threshold voltage of the rod studied was 5 volts and this low voltage was not strong enough to cause full rotation. The field strength is the main driving force for the switching speed and a more powerful power supply should result in faster times. A model was used to describe the rod and find the theoretical fastest switching speed. The modeled speed is considerably faster than the actual speed but the model does not factor: viscosity of the oil, misalignment of the liquid crystal molecules, defects in the director field, resistance of the ITO glass, and excessive polymer on the ends of the rod. The modeled speed does give a lower bound that might be approachable through more experience in rod fabrication and more importantly, better control of alignment in the rods.

The rods behavior has been shown to be influenced on the type of field applied. A few examples that have been shown include: up and down, translational, rotation, vibrating and sporadic swimming. The rotation of the rod with AC voltage was shown to also be influenced by the field strength where higher strength gave faster times. Also it was shown that the AC field can lead to very chaotic movement which makes observation and experiments very difficult. AC fields gave the most interesting movement especially with rods moving in and out of the viewing area. Rod behavior around the spacers was also peculiar when rods were shown to “push” the spacer.

A few alignment techniques were employed including: temperature, magnetic fields, and electric fields. It was shown that the magnetic field led to very responsive rods that had a tendency to cluster in very tight packing. This tight packing restricted movement at first but a high strength AC field was able to ultimately overcome the clustering forces. Clustering was speculated to be caused by a permanent dipole in the rod structures which causes attractions between. The electric field should have also given very tight clustering similar to the magnetically cured sample. But this was not seen, which was attributed to low electric field strength and a large gap between the electrodes during curing. Using only temperature to control alignment is the crudest technique but also gives adequate results. The rotational rod and switching rod were both fabricated with only temperature control. Therefore the use of fields while curing should give faster times but measurement was impossible due to the clustering.

Future efforts should focus on the use of external fields and surface treatments to control the alignment which would lead to faster switching times. Another important area should be on the fabrication of rods for one specific type of movement. Therefore the cells created would have rods that all move up and down or translationally. This would greatly help in observation but more importantly could pave the way toward devices like electro-optical switches. Another research area should be clustering. Clustering can be beneficial because large clumps can move together like a moving structure. Clustering can also make viewing difficult due to limitations in rod movement. It would also be interesting to look at different diameter and length rods. Switching times and possibly movement could be altered through these two parameters. Finally, one last idea would be on a positive dielectric liquid crystal. The positive dielectric liquid crystal should result

in up and down movement of the rod structures. It would then be interesting to see if these rods structures were closer to the theoretical switching times. Also, a positive anisotropy value could lead to more movements and reactions to externally applied fields.

This area of research is something new and exciting especially if device fabrication is the foreseeable future. This could only be achieved through more predictable rods and faster switching times. Therefore, the key for future research in this area will benefit from alterations to the rods to ultimately end in fast, reliable, and predictable movements.

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Appendix 1

```
% Script file: Dist_Mea.m
%
%Purpose:
% This program measures distances in a picture once given a reference value.
%
% Record of revisions:
%   Date       Programmer   Description of Change
%   =====
%   06/14/07    Phil Evans   Original Code
%   10/04/07    Phil Evans   Added Repeatability
%
% Define Variables:
% I - Image being worked with
% x - horizontal temporary coordinates of lines
% y - vertical temporary coordinates of lines
% deter - menu choice determinate
% refdis - pixel length of the ref line
% refmea - distance of the ref line
% meadis - pixel length of line to be measured
% ratio - ratio of the reference in pixels per length
% run - checks to see if a reference ratio exists
% newmea - calculated distance of new line
% scrsz - gets the size of the window for the figure

%Set Variables
I = (0);
x = [0 0];
y = [0 0];
deter = 1;
refdis = (0);
refmea = (0);
meadis = (0);
ratio = (1);
run(2) = 0;
newmea = (0);
scrsz = get(0,'ScreenSize');

%Check to see if ran before
if (run(1)>0)
    ratio = run(1);
end

%Set Starting Picture
I = input('What picture do you wish to load?\n');
```

```

%Menu to decide what to do
while deter<4
    deter = menu('What would you like to do?','Load New Picture','Set New Reference
Value','Measure Distance','Exit');

    %Loads Picture to use
    if (deter == 1)
        I = input('What picture do you wish to load?\n');
    end

    %Gains Reference Value
    if (deter == 2)
        imshow(I);
        [x, y] = getline;
        refdis = sqrt(((x(2)-x(1))^2+(y(2)-y(1))^2));
        refmea = input('What is the distance for the reference value?\n');
        ratio = refdis/refmea;
    end

    run(1) = ratio;

    %Marks length of line
    if (deter == 3)
        imshow(I);
        [x, y] = getline;
        meadis = sqrt(((x(2)-x(1))^2+(y(2)-y(1))^2));
        newmea = meadis/ratio;
        disp('The measured distance is: ');
        disp(newmea);
    end

    %Exits the program
    if ((deter == 4)|| (deter<1))
        close all;
        break;
    end
end
end

```

Appendix 2

```
% Script file: Ang.m
%
%Purpose:
% This program uses the counting of pixels to correctly ascertain the % angle between
three points over multiple pictures.
%
% Record of revisions:
%   Date       Programmer   Description of Change
%   =====
%   02/05/08    Phil Evans   Original Code
%   03/13/08      ---        Documentation
%
% Define Variables:
% deter        = value used in determining menu selection
% I            = holding array for picture to be scanned
% angini       = initial angle set at base point creation
% angmea       = angle found during measure section
% angout       = angle outputted by system, = angina - angmea
% x            = x-coordinate location for point collection
% xbase        = first x-coordinate used in angini calculation
% xini         = initial length in x direction for reference angle
% xline        = length in y direction of measured angle
% xmea         = difference between measured length and reference in x
% xref         = second x-coordinate used in angini calculation
% y            = x-coordinate location for point collection
% ybase        = first x-coordinate used in angini calculation
% yini         = initial length in x direction for reference angle
% yline        = length in y direction of measured angle
% ymea         = difference between measured length and reference in x
% yref         = second x-coordinate used in angini calculation

deter = 0;

%Set Starting Picture
I = input('What picture do you wish to load?\n');

%Menu to decide what to do
while deter<4
    deter = menu('What would you like to do?','Load New Picture',...
        'Create New Base Point','Measure Angle','Exit');

    %Loads Picture to use
    if (deter == 1)
        I = input('What picture do you wish to load?\n');
    end
```

```

%Determine Initial Angle
if (deter == 2)
    disp('Select Base Point');
    figure(2),imshow (I);
    [x, y] = getpts;
    xbase = x(1);
    ybase = y(1);
    disp('Select End of Reference Line');
    [x, y] = getpts;
    xref = x(1);
    yref = y(1);
    xini = xbase - xref;
    yini = ybase - yref;
    if (yini == 0)
        angini = 0;
    else
        angini = atand(xini/yini);
    end
end

%Measure New Angle
if (deter == 3)
    figure(2),imshow (I);
    disp('Select End of Measuring Line');
    [x, y] = getpts;
    xline = x(1);
    yline = y(1);
    xmea = xbase - xline;
    ymea = ybase - yline;
    angmea = atand(xmea/ymea);
    angout = angini-angmea;
    if (angout < 0)
        angout = 180 + angout;
    end
    disp('Measured angle is:');
    disp (angout);
end

%Exits the program
if ((deter == 4)||(deter<1))
    close all;
    break;
end
end

```