Improvement of Self-Organization and Selective Reflection Quality in Lyotropic Crystalline Polysaccharide Films

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1. Introduction

3-Chloro and phenyl cellulose tricarbanilates (CTCs) have been used in combination with phototopolymerizable acrylate hosts to create lyotropic cholesteric liquid crystal gels that are then polymerized using UV light into permanently aligned films that exhibit selective reflection of certain wavelengths of light. These liquid crystal films present an inexpensive and easily producible product that can be used as circular polarizers, in color filters, laser protection glasses, and document security devices. Improvement of the films in these experiments has resulted in the reduction of viscosity and the enhanced quality of selective reflection in the liquid crystal films. Lower viscosity allows for easier formation of liquid crystal phases, thus stronger selective reflection. Lower MW CTCs have been found to lower the viscosity of samples and allow phases to align more rapidly to demonstrate selective reflection. Also, using a non-reactive diluent with an acetate group or functionality has been demonstrated to reduce the viscosity of samples, lower the temperature at which selective reflection occurs, and lengthen the pitch of the liquid crystals causing a wider color range of selective reflection to be obtained. Finally, it was found that the wavelength of selective reflection can be adjusted with the variance of the sample temperature before polymerization.

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Summary

Liquid crystal films have many potential uses from color filters to laser protection glasses. They have the ability to reflect (selective reflection) and polarize certain wavelengths of light. Previously, solid films were costly and time consuming to produce. In my research, inexpensive cellulose and solvent host materials were used to synthesize films produced in hours rather than days. These films had improved selective reflection in which the wavelengths of light can be adjusted.

a. Liquid Crystals and Selective Reflection

Liquid crystals exist as a mesophase between the crystalline and isotropic states of matter, possessing characteristics of both. Liquid crystals are semisolids, showing characteristics of liquids, but also exhibiting optical properties that are characteristic of crystals, such as birefringence, double refraction, and scattering.

Three examples of liquid crystal structures are nematic, smectic, and cholesteric (see Figure 1). Nematic liquid crystals possess the least amount of order out of the three classes. They are ordered in one dimension with the molecules lined up parallel to each other, but with the ability to slide past one another. Smectic liquid crystals on the other hand are the most highly ordered with the molecules arranged parallel to one another and in layers one molecule thick. The molecules of cholesteric liquid crystals are arranged in a helical fashion and are the type of liquid crystal most commonly used to create films with selective reflection.

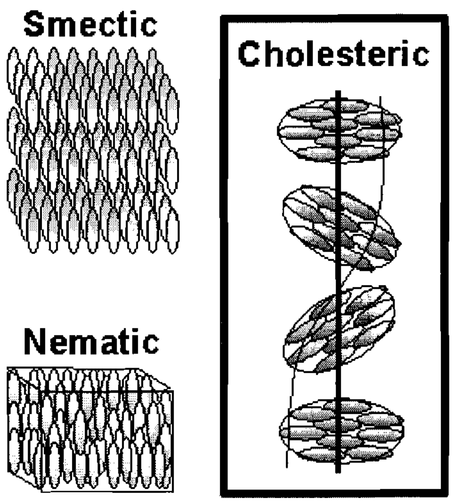

Figure 1: Three types of liquid crystal structures

Selective reflection is an optical property unique to liquid crystal systems. Specifically, selective reflection is obtained from the helical structure of cholesteric liquid crystals. The wavelength of light that is reflected depends upon the pitch length of the helical liquid crystal molecules and their average refractive index. The pitch length is the distance it takes for the helix to rotate 360°. Wavelengths of light, λ, that satisfy the relationship $\lambda = \bar{n}\,p$, where $\bar{n}$ is the average refractive index and p is the pitch length, are reflected by the sample (see Figure 2). Thus shorter pitch lengths of the helix are required to reflect shorter wavelengths of light (violet and blue).

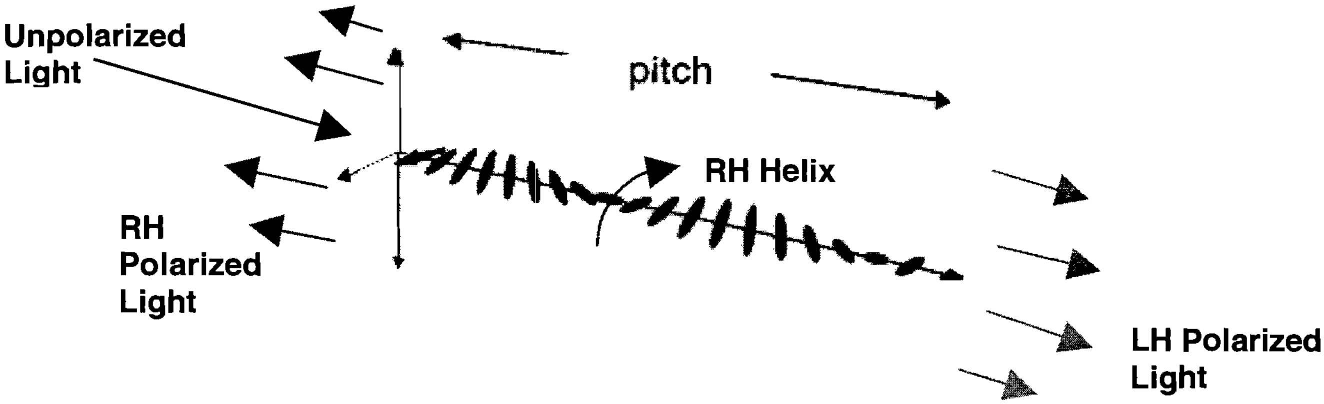

Figure 2: The helix structure of the cholesteric liquid crystals used in this work allows samples to polarize light into right-handed and left-handed light, depending upon the handedness of the helix. In this example, unpolarized light strikes a right-handed helix, which transmits left-handed light and reflects right-handed light.

One application of cholesteric liquid crystals is perfect circular polarizers, since unpolarized light passing through cholesteric liquid crystal samples is polarized into a single-handedness of light depending upon the helicity of the sample. For example, cholesteric liquid crystals are used as circular polarizers for laser systems such as OMEGA during laser shots. OMEGA is currently the world's largest laser, housed in the Laboratory for Laser Energetics, used for various types of research including achieving the goal of fusion. Current monomer liquid crystal polarizers are fluid-filled glass cells that are time consuming to produce and use. These polarizers could one day be replaced with low-cost films that are easy to produce and that are either free-standing or that require only a single substrate for support. Liquid crystal mixtures can be adjusted to reflect certain wavelengths of light and then made into photopolymerized films in which the molecules of the film become linked creating a solid selectively reflective film, rather than using the fluid-filled cells.

Lyotropic liquid crystals can be used to try to create strong selectively reflective films that exhibit many advantages over their thermotropic liquid crystal counterparts. Lyotropic liquid crystals experience phase changes with changes in both the solute concentration and temperature of the sample, unlike thermotropic liquid crystals that only exhibit such changes with variations in temperature. This gives more control and opportunity to adjust the selective reflection in lyotropic liquid crystal films. Lyotropic liquid crystals can also be dissolved into various solvent hosts that are photochemically reactive, commonly available, and very inexpensive. Whereas, the available thermotropic liquid crystal films are already mixed in solvent hosts and pre-polymerized, which limits the opportunities to adjust the selective reflection and causes them to be expensive.

Cholesteric liquid crystals are created from cellulose tricarbanilates (also called urethanes) that are dissolved in suitable photopolymerizable hosts (i.e., an acrylate) and crosslinked to obtain temperature-insensitive, robust films that show selective reflection. Cellulose tricarbanilates (CTCs) are polysaccharides with either benzene or cyclohexane subsituents that contain a halogen (F, Cl, Br) or other aliphatic or aromatic groups (see Figure 3). Cellulose is a desirable starting material because it is derived from plants and thus extremely low-cost and plentiful. Cellulose must first go through several processes before it can be used to synthesize liquid crystals. The process of degradation lowers the MW of cellulose acetate from more than one million to optimally 100,000 or less, saponification removes the acetate group from cellulose molecules, and urethane formation attaches a urethane R group to cellulose molecules forming both phenyl and 3-chloro phenyl CTCs.[3]

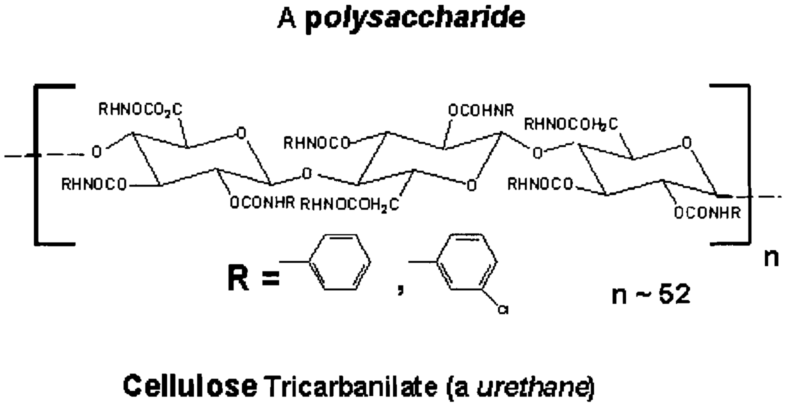

Figure 3: The structure of one segment of a CTC molecule used to create liquid crystals.

The following experiments worked toward the goal of producing strong selective reflection in polymerized films by improving high quality spontaneous molecular alignment at room temperature. To achieve this, lower molecular weight distributions of CTCs and host materials with lower viscosities were used. It is also desirable to be able to tune the selective reflection maximum over a broad range of wavelengths by adjusting the host chemistry and composition and the temperature of the sample prior to crosslinking. Previously, lyotropic cholesteric liquid crystal formulations took from 48 hours to several weeks at elevated temperatures before demonstrating any molecular alignment and selective reflection, as described by Muller, Zentel, and Keller[1]. More recent research[2] with phenyl and 3-Chloro phenyl CTCs reduced the time requirement to 15 minutes at 50°C. However, this process is still not practical or efficient.

With further development of liquid crystals with selective reflection, polymerized films have much potential for optical applications. These films have the capacity to be used for liquid crystal displays (i.e., computer screens and watches), modulators, document security, polarization rotators, and polarizing pigments. Films made using CTC-based liquid crystals can also be used in color filters, notch filters, and laser protection glasses since their selective reflection properties allow them to stop certain wavelengths of light and transmit all others.

2. Experimental

Nearly all lyotropic cholesteric liquid crystal films in this project were made using one basic process. Both phenyl and 3-Chloro phenyl CTCs were used as the starting material. CTCs were first added to a liquid host of acrylate and diacrylate reactive monomers, usually 2-ethoxyethyl acrylate and di(ethylene glycol) dimethacrylate. The starting formulation for liquid crystal samples consisted of 45 wt-% CTCs combined with 45 wt-% 2-ethoxyethyl acrylate and 10 wt-% di(ethylene glycol) dimethacrylate. The sample was then heated at 50°C for one hour to allow the CTCs to dissolve into the host and form a homogenous liquid crystal gel. Next, the sample was knife-cast onto a glass microscope slide and polymerized with UV light at a wavelength of 365 nm in combination with Lucirin TPO photoinitiator in a process called crosslinking to achieve a selectively reflective CTC liquid crystal film with an average thickness of 25 μm.

a. Molecular Weight

1) High MW

Initially, research[2] using CTCs with molecular weights of 244K and above was repeated. In many cases, the CTCs simply did not dissolve into the acrylate hosts; samples that were created in the original formulation and heated to 50°C on a hot plate for one hour were grainy with a milky appearance. Adding a non-reactive diluent with an acetate group (i.e. ethyl acetate or amyl acetate), heating at a higher temperature (60°C), and heating for upwards of 24 hours yielded no improvement in dissolving the cellulose CTCs. Previous research[2] and samples of CTCs (MW 244K) in the original formulation were heated until dissolved (about five days), knife cast onto a glass slide, and then heated for a minimum additional 15 minutes at 50°C to show selective reflection with an optical density of only about 0.14 at about 400 nm (see Figure 4). Such high MW caused samples to become extremely viscous, which prevents the liquid crystal phases from aligning easily and showing selective reflection. Extremely high MW also caused the difficulty in initially dissolving the CTC molecules because they were so large. Such high viscosity, difficulty in creating samples, long time for selective reflection to occur, and low optical density levels make these previous samples undesirable.

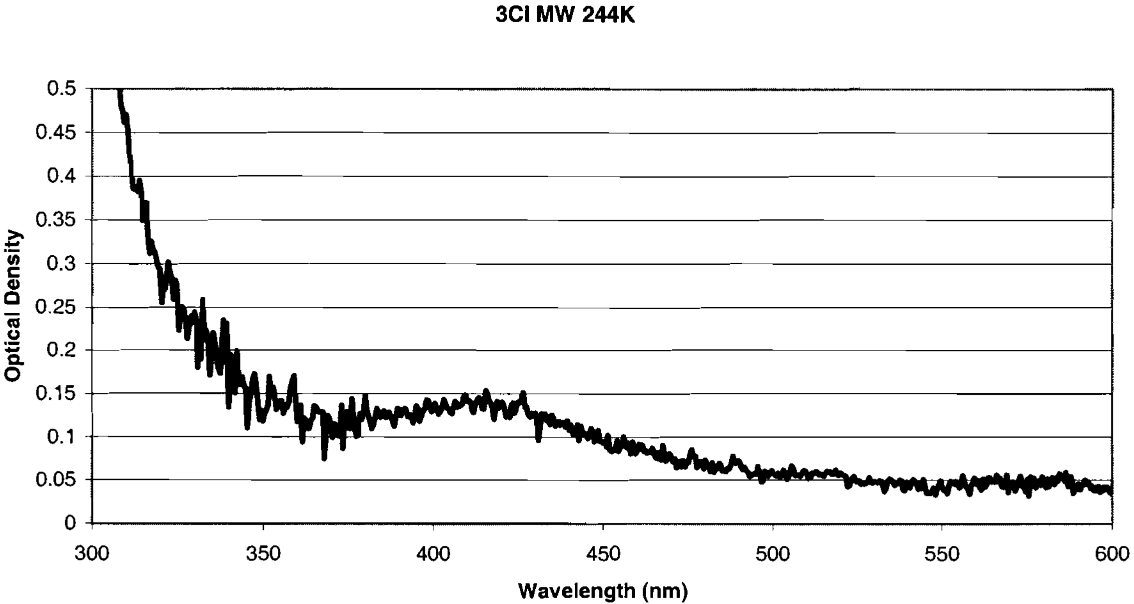

Figure 4: Optical density of a polymerized 3-Chloro phenyl CTC (MW 244K) film viewed in absorption mode in a spectrophotometer

2) Low MW

Lower molecular weight CTCs were therefore used. Longer degradations were performed on the original cellulose materials, ranging from 6 to 36 hours, yielding cellulose CTCs with MWs that were measured to range from 37,080 to 129,000. First, lower MW cellulose CTCs were observed to have greatly reduced sample viscosity by a factor of about 50 compared with that of high MW cellulose CTC samples. Reduced system viscosity alone provided numerous advantages. It made the samples easier to knife cast onto glass slides. It also made it easier to shear samples by moving the glass slide and coverslip against one another to align samples in the liquid crystal phase.

Lower molecular weight cellulose CTCs were also found to have the advantage of dissolving into the host material much more rapidly than higher MW material. CTC samples with molecular weights of 129K and 85K were prepared in the starting formulation and were fully dissolved into a homogeneous mixture after being heated for only one hour at 50°C compared with five days.

Slides of 3-Chloro phenyl cellulose CTC MW 129K produced selective reflection instantaneously upon knife casting at room temperature. The samples of cellulose CTC MW 129K also had an optical density of 0.32 (see Figure 5), more than double that of the cellulose CTC MW 244K. The rapid alignment is due to reduced viscosity and because the smaller molecules move more readily in the sample to align properly than do larger, bulkier molecules of higher molecular weights.

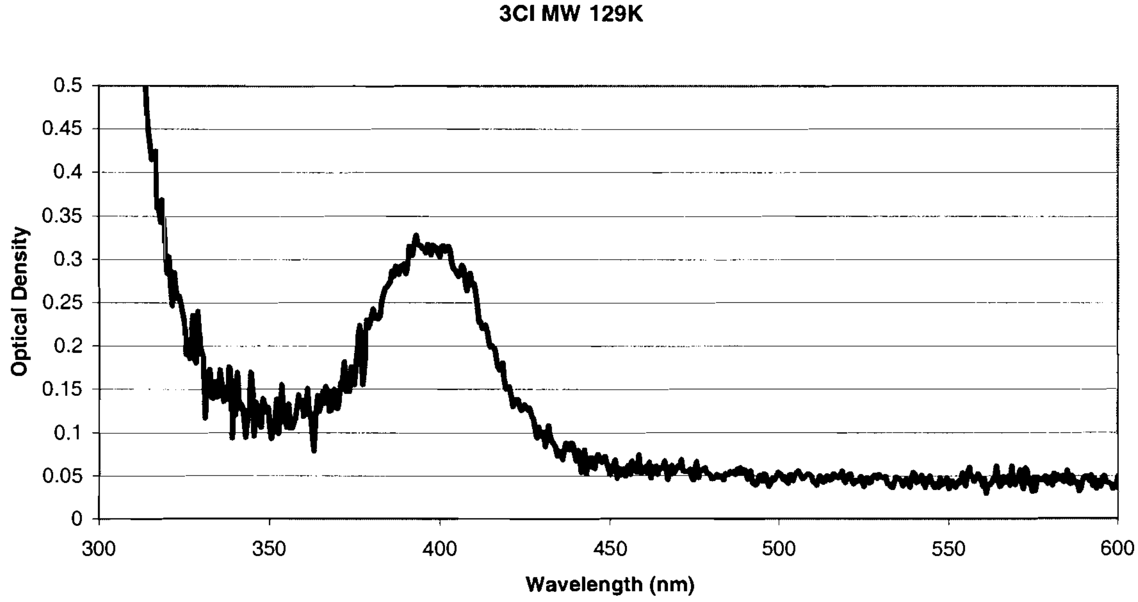

Figure 5: Optical density of a polymerized 3-Chloro phenyl CTC (MW 129K) film viewed in absorption mode in a spectrophotometer

b. Addition of non-reactive diluents

Additional improvements were found when acetate-containing, non-reactive diluents are added to low MW CTC and host mixtures. Amyl acetate and ethyl acetate were the two non-reactive diluents used. Both are isotropic materials and do not chemically react with the hosts or the CTCs of the liquid crystal mixtures. Rather, the diluents affect the physical characteristics of the samples.

First, the acetate-containing non-reactive diluents were found to greatly reduce the viscosity of CTC samples. The structures of the molecules of amyl and ethyl acetate are not very rod-like and thus have a very low ordering capability when added to mixtures, contributing to the disorder of the liquid crystal molecules within the samples. With greater molecular disorder, the viscosity is reduced and the casting of films is made easier. Lowering the viscosity of extremely viscous samples also allows the liquid crystal phases to align more easily, thus producing selective reflection.

Secondly, when a non-reactive diluent was added to a sample, I observed that the onset color temperature of the sample was reduced to room temperature and that the spectrum of reflected colors was widened. Without the acetate-containing non-reactive diluents, I found samples to be colorless at room temperature (samples exhibit selective reflection only at elevated temperatures from about 52 – 70°C with color reflection only ranging from violet to green). However, upon adding a diluent, violet selective reflection is observed at room temperature. For example, a sample was created consisting of 60 wt-% 3-Chloro phenyl CTC (MW 53K), 35 wt-% 2-ethoxyethyl acrylate, and 5 wt-% di(ethylene glycol) dimethacrylate. This sample showed no color at room temperature, only blue selective reflection from 66 – 74°C. When 59.25μl of amyl acetate was added to the 0.1g sample, the color onset temperature was lowered and violet selective reflection was observed at room temperature. With continued addition of an acetate-containing non-reactive diluent, the initial onset color at room temperature is shifted from violet, across the visible spectrum, to red. For example, a 0.1g sample of 3-

Chloro phenyl CTC (MW 129K) was prepared in the starting formulation with 26µl of additional amyl acetate and exhibited red selective reflection at room temperature. (Refer to Figure 6 and Figure 7).

Comparison of selective reflection temperatures in 3Cl polymerized films with and without amyl acetate

Film composition → Selective reflection color↓	*3Cl MW 129K*	*3Cl MW 129K with ~10 wt-% amyl acetate*	*3Cl MW 85K*	*3Cl MW 85K with ~10 wt-% amyl acetate*
violet	50°C	38°C	40°C	-°C
blue	60	40	-	-
teal	60	45	-	-
green	65	50	50	25
red	65	50	-	-
clears	70	60	60	30

Figure 6: 3Cl polymerized films were created in the original formulation, using molecular weights of 129K and 85K. Four films were created, two without amyl acetate and two with ~10 wt-% amyl acetate. The addition of ~10 wt-% amyl acetate reduced the color onset temperature in each case.

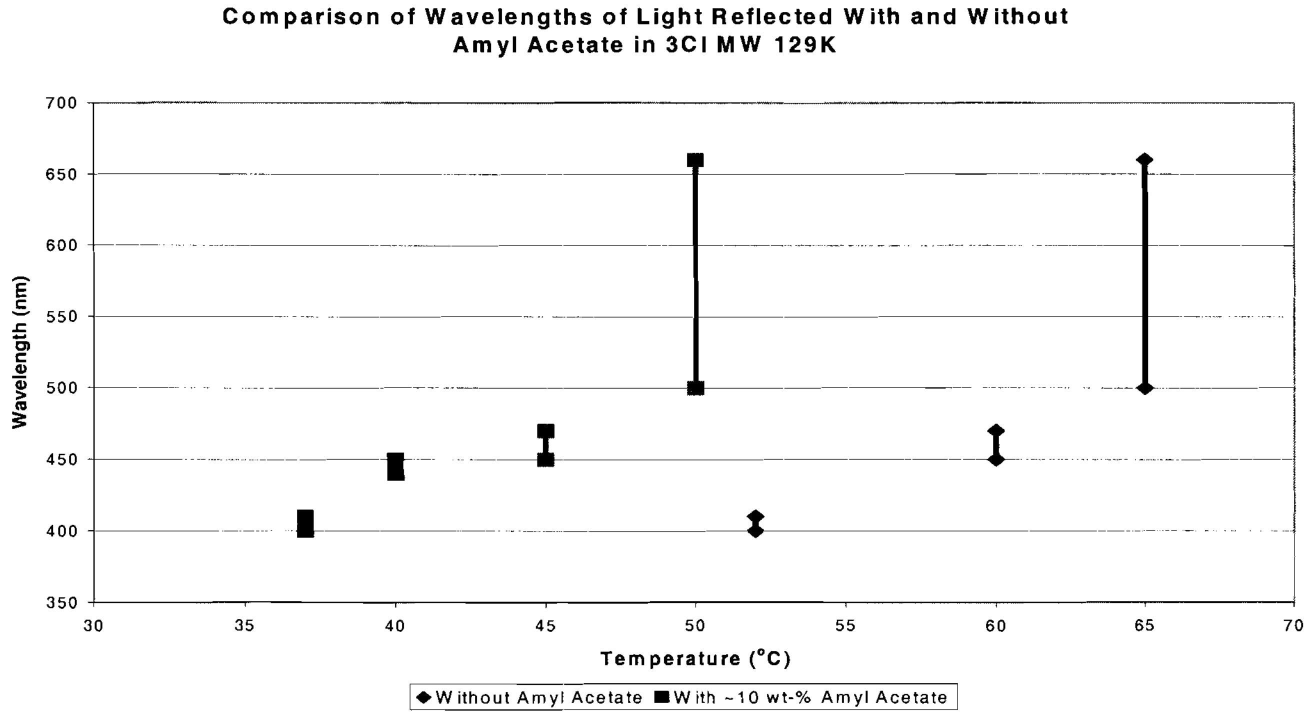

Figure 7: The observed wavelength ranges of reflected light are shown at their respective measured temperatures. As shown by the graph, with the addition of ~10 wt-% amyl acetate the onset temperature for selective reflection is reduced by about 25°C.

These changes in the selective reflection of 3-Chloro phenyl CTC samples are understood to be a result of the low ordering capability of the isotropic diluents. The diluents add to the disorder of mixtures, depressing the liquid crystal phase transition temperature of the whole mixture, thus lowering the color onset temperature to room temperature. Secondly, amyl and ethyl acetate are slightly more polar than the acrylate hosts of liquid crystal samples are, which broadens the selective reflection color range by elongating the helix.

3. Conclusion

I found that the selective reflection of lyotropic cholesteric liquid crystal films could be greatly improved by using low MW CTCs. The lower MW CTCs dissolve much more readily than high MW CTCs that were previously used and resulted in samples with a much lower viscosity. These results allow films to be created easier and in a matter of hours rather than days. The low MW CTC samples also showed stronger selective reflection than the higher MW samples. Selective reflection was found to occur instantaneously rather than over a period of up to several weeks. Lower viscosity in host systems also allows liquid crystals to align more rapidly and enhance the quality of selective reflection.

In addition, adding non-reactive diluents to low molecular weight cellulose CTC mixtures, the selective reflection obtained in liquid crystal films was greatly increased and it was possible to adjust its wavelength of reflection. Non-reactive diluents added to liquid crystal mixtures lowered the selective reflection onset temperature, broadened the color temperature range, and further reduced the overall system viscosity. These effects are thought to be caused by the lengthening of the helical pitch of the liquid crystal molecules by the diluents.

By adjusting CTC MW, the host composition, and the amount of acetate-containing non-reactive diluents in the liquid crystals it is possible to adjust the selective reflection properties. Liquid crystal films can be photopolymerized to create solid films. These films have numerous applications in laser systems as inexpensive circular polarizers, as document security devices, polarizing pigments, modulators, polarization rotators, liquid crystal displays, color filters, notch filters, and laser protection glasses.

<u>References:</u>

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2. K. L. Marshall and D. Mott, unpublished results
3. Oliver, Gloria. Improvements in the Strength of Visible Selective Reflection in Lyotropic Liquid Crystals Made from Cellulose Urethanes. LLE High School Summer Research Program, summer, 2000.