Improvements in the Strength of Visible Selective Reflection in Lyotropic Liquid Crystals Made from Cellulose Urethanes

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Abstract:

Lyotropic liquid crystals based on mixtures of cellulose tricarbanilates (urethanes) generated stronger selective reflection in the visible range after an increase in concentration of approximately 9 wt.-% above the concentrations described by Müller, Zentel, and Keller in "Solid Opalescent Films Originating from Urethanes of Cellulose".[2] The cellulose urethanes used were of a lower molecular weight (less than 30,000 g mol^{-1}) than the material used in [2], which had a molecular weight of approximately 50,000 g mol^{-1}. In preparing the liquid crystal samples, the cellulose urethane was dissolved in a volatile solvent before mixing with the acrylate host. The solvent dramatically reduced sample preparation time and, as a result of its volatile nature, could be removed from the sample during film casting. Additionally, physically blending two urethane homopolymers, rather than using a copolymer, has the potential to allow for greater control over the concentrations and reproduction of lyotropic liquid crystal samples. The physical blend of homopolymers still incorporates multiple R-groups into a sample as with a copolymer. However, unlike a copolymer, new compounds do not need to be synthesized each time a new concentration of these R-groups is required to produce a different selective reflection color. This method of creating a homopolymer blend, rather than synthesizing numerous

copolymers, would simplify the procedure for reproducing such samples and would allow for the concentrations of the samples to be more easily adjusted.

Introduction:

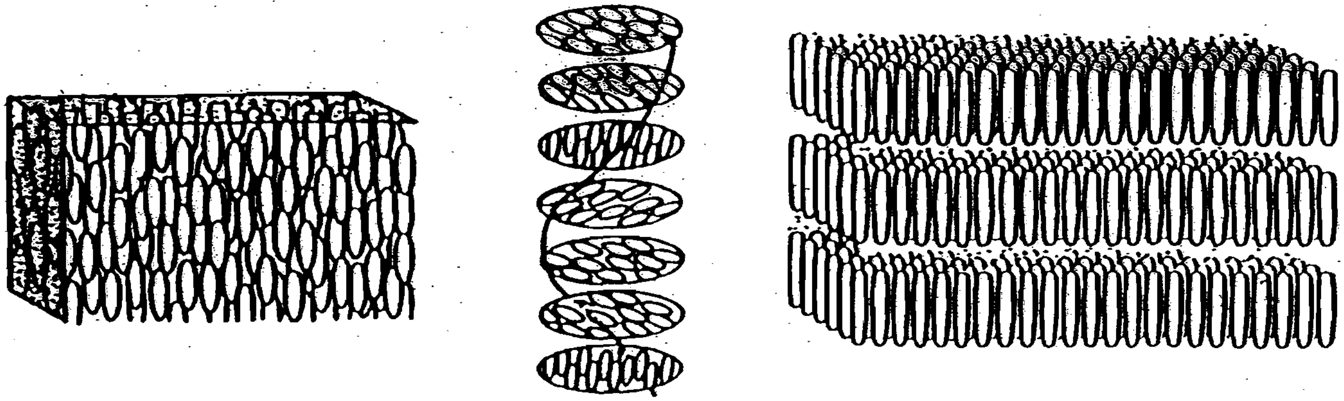
As their name might suggest, liquid crystals fall between the liquid and the crystalline phases of matter. Unable to be classified as strictly a liquid or a crystal, the liquid crystal mesophase exhibits properties of both its neighboring phases. Mechanically, liquid crystals behave like liquids, as exemplified by their viscosities. Optically, on the other hand, liquid crystals seem more similar to crystals. Some of their crystalline qualities include the optical properties of birefringence and selective reflection. Liquid crystals are also anisotropic, meaning their properties, such as selective reflection, vary depending on the angle of observation. In addition, liquid crystal material is uniquely sensitive to fluctuations in temperature, as in thermotropic liquid crystals, and some are even affected by changes in temperature and solute concentration, called lyotropic liquid crystals. [1]

Cholesteric liquid crystals respond to these minute alterations with a change in color, giving rise to their multitude of practical applications. Thermotropic liquid crystals can be used in special thermometers and other temperature-dependent devices. They are also often used as filters because their selective reflection properties allow them to block-out a certain band of light, while transmitting all other wavelengths. This ability becomes useful in products such as notch filters and safety glasses. Cholesteric liquid crystals are also essential to the OMEGA laser system as perfect circular polarizers.

The liquid crystal mesophase is divided into classes based on the arrangement of their cigar-shaped molecules (Fig. 1). The class having the most molecular order is the *smectic.*

Figure 1:

Structures of Liquid Crystal Phases



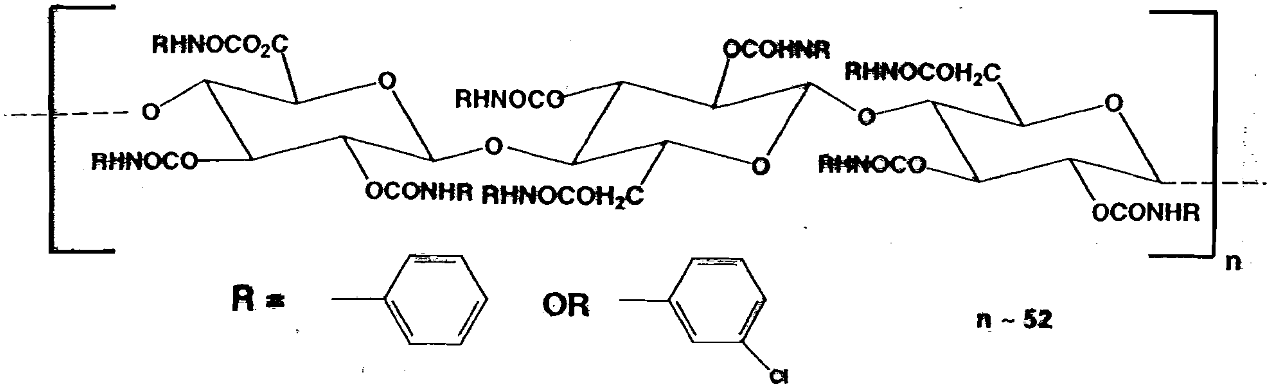
Nematic **Cholesteric** **Smectic**

Goals:

The goal of this experiment was to strengthen the selective reflection produced by lyotropic liquid crystals based on cellulose tricarbanilates (urethanes) as presented in the work of [2] by Müller, Zentel, and Keller in Advanced Materials. The molecular structure of these urethanes is shown in Figure 2. Upon attempting to reproduce such experiments it became apparent that the method of preparation and analysis of the liquid crystal mixtures was in need of improvement. Specifically, reducing the sample preparation time and developing a means of casting smoother films of more uniform thickness became an additional goal of the project. Because of a lack of a supply of the 3-chlorophenyl isocyanate urethane used in [2] to create courethanes with the phenyl isocyanate urethane, the synthesis of the 3-chlorophenyl isocyanate cellulose urethane was also undertaken.

Members of this group show molecules arranged into ordered layers, each layer being one molecule thick. Within the layers, the molecules can be organized randomly or into rows with their long axes positioned parallel to each other. Van der Waals' forces keep the molecules within a layer from shifting out of position, but do not prevent the layers themselves from sliding over one another. The *nematic* class has the least molecular order. While its molecules are positioned parallel to each other, they are not separated into layers. The molecules are also free to slide past each other, similar to a box of toothpicks. *Cholesteric* liquid crystals comprise the third class of the mesophase. These liquid crystals are composed of very thin layers in which the molecules reside parallel to each other as well as to the plane of the layer. The direction of the long axes of the molecules rotates slightly among adjacent layers, eventually developing into a helical structure. This molecular arrangement is quite delicate, which explains why slight disturbances in the chemical environment can have a noticeable effect on the material's optical behavior. The cholesteric form also exhibits circular dichroism, or selective reflection. Thus, the findings presented in this paper, primarily the generation of strong selective reflection colors, are based strictly on experiments with cholesteric liquid crystals. [1]

Figure 2:

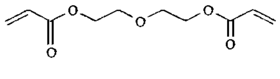
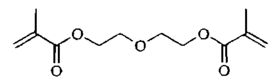
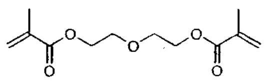


CELLULOSE TRICARBANILATE

Experimental:

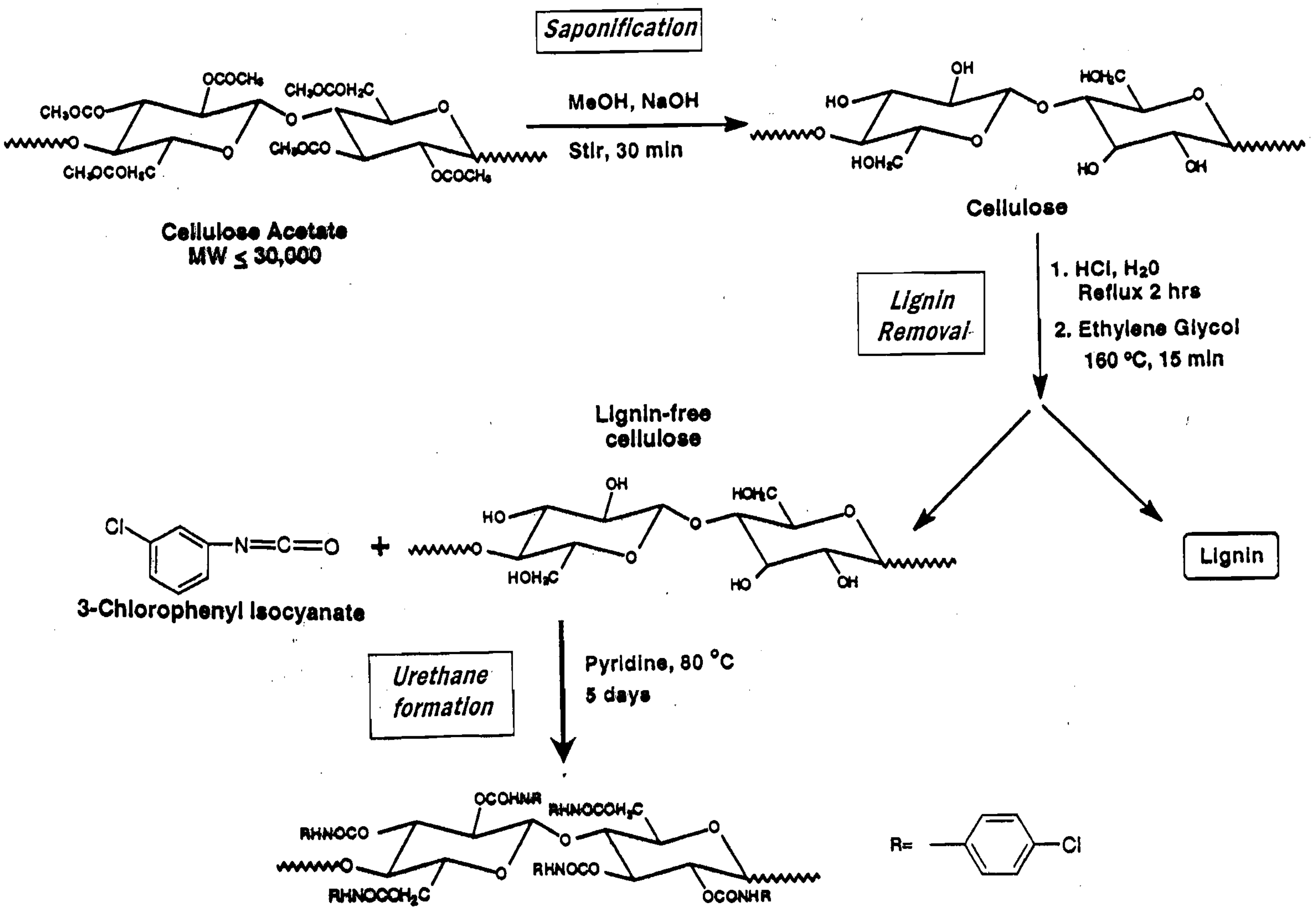
Cellulose tricarbanilate, (less than 30,000 g mol^{-1}), made with phenyl isocyanate, as prepared by Sarah Mitchell in [3], was mixed with an acrylate host before being cast into a film on a microscope slide and analyzed under the polarizing microscope. The cellulose urethane was measured out in a variety of concentration ratios with the acrylate host, differing by increments of 5 wt.-%. Three different hosts, 2-ethoxyethyl acrylate, di(ethylene glycol) diacrylate, and di(ethylene glycol) dimethacrylate, were used in the experiment. The solid cellulose urethane was dissolved in a volatile solvent, such as tetrahydrofuran, before being mixed with the acrylate host. After mixing with a magnetic stir bar in the dark for at least one hour, the solution was transferred and spread dropwise onto a microscope slide using a Pasteur pipette until a thin film covered the top surface on one end of the slide. A cover slip was used to shear the sample and generate proper cholesteric liquid crystal alignment. Any excess solvent that would dilute the concentration and prevent the liquid crystal phase from forming was removed from the sample using a hot stage. Each sample was observed under the polarizing microscope in search of strong selective reflection color, as well as liquid crystal texture and birefringence. All samples made from the phenyl isocyanate cellulose urethane were stored for days to weeks in a dark, closed drawer before any selective reflection color in the visible range appeared. These colors, and the concentration ratios that produced them, are listed in Table 1.

Table 1:

Wt.-% of Purified Phenyl Isocyanate Cellulose Urethane	**Host Name**	**Visible Selective Reflection Color**
70	 di(ethylene glycol) diacrylate	red
50	 di(ethylene glycol) dimethacrylate	green, red
55	 di(ethylene glycol) dimethacrylate	red

The synthesis of the 3-chlorophenyl isocyanate urethane for use in a blend of homopolymers with the phenyl isocyanate urethane was performed at half-scale using the procedure described in reference [3] and shown in Figure 3. The synthesis was not executed under a blanket of nitrogen and began at the urethane formation step by adding 5.0g of purified cellulose acetate to a reaction vessel, followed by the addition of 100ml of pyridine. After proceeding with the addition of 25ml of 3-chlorophenyl isocyanate, the solution exhibited a yellow color and an exothermic reaction occurred. The reaction was brought to 80°C using a heating mantle before being refluxed at this temperature for five days. Upon the conclusion of the reflux, the solution appeared dark brown in color and was allowed to cool for approximately

Figure 3:



The synthesis of 3-chlorophenyl isocyanate cellulose urethane is a multi-step procedure.

References:

[1] Fergason, James L. "Liquid Crystals", *Scientific American*, Vol. 211--No. 2, pp. 72-82, 85 (1964).

[2] Müller, Manfred and Zentel, Rudolf and Keller, Harold. "Solid Opalescent Films Originating from Urethanes of Cellulose", Advanced Materials, Vol. 9—No. 2, pp. 159-162 (1997).

[3] Mitchell, Sarah. "Self-Organizing Lyotropic Liquid Crystals Based on Cellulose Derivatives", *1997 Summer Research Program for High School Juniors at the University of Rochester's Laboratory for Laser Energetics: Student Research Reports*, (1997).

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three hours. The solution was then transferred to a beaker and the product was precipitated with methanol. Because a large quantity of methanol was required to produce any crystals and these crystals were too fine to be collected by suction filtration, an improved method for isolation of the 3-chlorophenyl isocyanate product was desired. After attempting to dissolve and re-crystallize the material with a variety of solvent combinations, ethyl acetate and methanol were found to work most effectively in comparison to the other methods. Before purification with these solvents, the product was heated under vacuum using a rotovapor in order to remove the excess methanol and pyridine. The concentrated product was taken up in ethyl acetate, and the material went completely into solution after heating briefly. The solution was then placed in an ice bath while adding methanol in order to reach a cloud point. The solution was removed from the ice bath and suction filtered. The crystals were immediately collected off the filter paper to prevent the product from adhering to the paper. The product, although still not completely purified, was incorporated into a few samples containing a blend of homopolymers in varying concentrations with the 2-ethoxyethyl acrylate and the di(ethylene glycol) dimethacrylate hosts by following the same sample preparation and analysis procedures used with the phenyl isocyanate urethane samples. The blend of homopolymers contained 49 mol-% of the 3-chlorophenyl isocyanate urethane and was made by physically blending the 3-chlorophenyl isocyanate urethane with the phenyl isocyanate urethane.

Conclusions:

Dissolving the solid cellulose urethanes in a volatile solvent significantly shortened sample preparation time, which according to the procedure presented in [2], required three to five days of mixing in a closed vessel before films could be cast and cured. In addition, using tetrahydrofuran in the mixtures made the solutions easier to cast by lowering the viscosity of the gel formed by the urethane-acrylate combination. The fact that the solvent could then be eliminated from the films using a hot stage was also a desirable result. However, it was found that tetrahydrofuran was too volatile for the purpose of casting smooth films because it caused ridges and bubbles in the film as it rapidly evaporated. Fortunately, ethyl acetate—a slightly higher boiling, yet volatile liquid—proved to be a more effective solvent for the work with liquid crystal castings. Ethyl acetate thoroughly dissolved the solid urethane material and also facilitated the smooth casting of films with uniform thickness. Another advantage of using this volatile solvent is that it has the ability to produce larger aperture films through knife or spin coating. Additionally, using a solvent allows the mixtures to be microfiltered, thus producing particle-free films that can be used for critical applications.

It should also be noted that samples made from the phenyl isocyanate cellulose urethane have proven to be capable of generating strong selective reflection in the visible range. These results came after adding approximately 9 wt.-% more of the urethane to each sample than was used in [2].

Results from physically blending the 3-chlorophenyl isocyanate urethane with the phenyl isocyanate urethane have yet to be determined. Further experimentation is needed to perfect the proportion of the two homopolymers, and the concentration of the homopolymer blend, being put into the samples.