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SWITCHABLE WHITENESS IN HUMIDITY-SENSITIVE LIQUID CRYSTAL NETWORKS

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ABSTRACT

Hilma Panula: Switchable whiteness in humidity-sensitive liquid crystal networks

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White coloration is a result of material's ability to scatter light evenly at all visible light wavelengths. In natural systems, whiteness is typically achieved through highly scattering particles with a high refractive index. Conversely, synthetic systems that exhibit a highly white appearance but possess a low refractive index are under investigation due to their promising applications in paints, plastics and optics.

Stimuli-responsive systems have been studied due to their significant potential for applications in, *e.g.* optical switching, biosensing and smart windows. These materials respond to environmental changes, such as pH, temperature, or humidity, by altering their shape, color or chemical properties. Liquid crystal networks (LCN) are crosslinked polymers composed of liquid crystal molecules. LCNs have been utilized in numerous stimuli-responsive systems such as soft actuators and color-changing devices.

Switchable whiteness represents a form of stimuli-responsive behavior. Previous studies have examined macro-crosslinked hydrogels that exhibit switchable whiteness around their lower critical solution temperature. The objective of this thesis is to characterize an LCN that exhibits switchable whiteness in response to wetting and drying with different solvents. How do LCNs respond to solvents with different polarity in terms of their whiteness properties? Which kind of structure allows LCNs to show appearance changes when exposed to humidity? Investigating switchable whiteness in LCNs presents a compelling area of research, as this phenomenon is novel within LCN materials. Prior studies have primarily focused on hydrogels, making the exploration of switchable whiteness in LCNs an exciting advancement in the field.

This thesis includes the synthesis and characterization of six different LCNs. The LCNs were prepared using UV-initiated photopolymerization. Sample thickness was chosen to be 100 μm , which is relatively thin compared to hydrogels studied for the same purpose. Switchable whiteness was characterized with scattering measurements, that were performed with UV-Vis spectroscopy using integrating sphere configuration.

Four of the studied samples showed switchable whiteness upon exposing to humid environment, most commonly water. At dry state, their appearance is transparent and at wet state they become white (opaque). The best composition showed a white state scattering of 80-85 % in the visible range. The phenomenon is driven by hydrophilic and hydrophobic moieties in the LCN structure create pores that enable phase separation while LCN is exposed to water, resulting in white coloration. The LCNs synthesized in this thesis have great ability to change appearance from transparent to opaque white when exposed to polar solvents. This opens new aspect for LCN studies as only hydrogels have shown similar results before.

Keywords: switchable whiteness, stimuli-responsive, liquid crystal network, scattering, phase separation

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TIIVISTELMÄ

Hilma Panula: Kosteusherätteinen valkoisuus nestekideverkostoissa

Switchable whiteness in humidity-sensitive liquid crystal networks

Kandidaatintyö

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Tekniikan ja luonnontieteiden TkK-tutkinto-ohjelma, ympäristö- ja energiatekniikka

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Valkoinen väri on seurausta materiaalin kyvystä sirottaa valoa tasaisesti kaikilla näkyvän valon aallonpituuksilla. Luonnonmateriaaleissa valkoisuus saavutetaan tyypillisesti voimakkaasti valoa sirottavien hiukkasten avulla, joilla on korkea taitekerroin. Matalan taitekertoimen omaavia synteettisiä valkoisia materiaaleja tutkitaan, koska niitä voidaan soveltaa esimerkiksi maaleissa, muoveissa ja optisissa laitteissa.

Ympäristön ärsykkeisiin reagoivia materiaaleja on tutkittu esimerkiksi optisissa kytkimissä, biosensoreissa ja älykkunoissa. Nämä materiaalit reagoivat ympäristössä tapahtuviin muutoksiin, kuten pH-arvoon, lämpötilaan tai kosteuteen, muuttamalla muotoaan, väriään tai kemiallisia ominaisuuksiaan. Nestekideverkostot ovat ristosilloitettuja polymeerejä, jotka koostuvat nestekiteisistä molekyyleistä. Nestekideverkostoja on käytetty lukuisissa materiaaleissa, jotka reagoivat ulkoihin ärsykkeisiin esimerkiksi muuttamalla muotoaan tai vaihtamalla väriään.

Vaihteleva valkoisuus on ympäristön ärsykkeisiin vastaavaa käyttäytymistä. Aiemmat tutkimukset ovat keskittyneet makroristosilloitettuihin hydrogeeleihin, joiden sirontaominaisuudet vaihtelevat alhaisen kriittisen liuoslämpötilan ympärillä. Tämän kandidaatintyön tavoitteena on karakterisoida nestekideverkostoja, joiden valkoisuus vaihtelee ympäristön kosteuden muutosten seurauksena. Miten nestekideverkostot reagoivat vaihteleviin kosteustasoihin valkoisuusominaisuuksiensa suhteen? Millainen rakenne tarvitaan, jotta valkoisuuden muutos on mahdollista? Tutkimusaihe on mielenkiintoinen, sillä vaihtelevaa valkoisuutta nestekideverkostoissa ei ole aiemmin tutkittu. Aiemmat tutkimukset ovat keskittyneet pääasiassa hydrogeeleihin.

Tämä työ sisältää kuuden eri nestekideverkoston synteessin ja karakterisoinnin. Materiaalit valmistettiin UV-valopolymeroinnin avulla. Näytteiden paksuudeksi valittiin 100 µm, mikä on ohuempi kuin useimmat aiemmin tutkitut hydrogeelinäytteet. Vaihtelevaa valkoisuutta tutkittiin sirontamittauksilla, jotka suoritettiin UV-Vis spektrofotometrillä käyttäen integroivaa palloa.

Neljän näytteen valkoisuus vaihteli ympäristön kosteuden muutosten seurauksena. Kuivana ne olivat läpinäkyviä ja kosteudelle altistettuna ne muuttuivat valkoisiksi. Paras näyte sirotti 80–85 %:n näkyvästä valosta. Ilmiö johtuu nestekideverkostojen rakenteessa olevista hydrofiilisistä ja hydrofobisista osista, jotka faasierottuvat voimakkaasti sirottaviksi, valkoisiksi ja huokosiksi rakenteiksi kosteuden seurauksena. Tässä työssä tutkitut näytteet pystyvät muuttamaan ulkonäköään erittäin läpinäkyvistä kirkkaan valkoisiksi altistuessaan polaarille liuottimille. Työ avaa uuden näkökulman nestekideverkostojen tutkimukseen, koska ilmiö on aikaisemmin havaittu vain hydrogeeleissä..

Avainsanat: valkoisuus, ärsykeherkkyys, nestekideverkosto, sironta, faasierottuminen

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ABBREVIATIONS AND SYMBOLS

1,4-I	1,4-diiodotetrafluorobenzene
5CB	pentyl cyanobiphenyl
A	acrylic acid
IRG-651	1,2-Diphenyl-2,2-dimethoxyethanone
LC	liquid crystal
LCD	liquid crystal display
LCE	liquid crystal elastomer
LCN	liquid crystal network
LCST	lower critical solution temperature
N	2-(Dimethylamino)ethyl methacrylate
PVA	polyvinyl alcohol
RM-105	4-methoxyphenyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate
RM-82	1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene
RT	room temperature
UV	ultraviolet, electromagnetic radiation with a wavelength of 300 – 400 nm
wt. %	weight percentage

1. INTRODUCTION

Stimuli-responsive materials respond to environmental cues, such as temperature, humidity, pH or pressure [1]. In response to the external stimuli, these materials can transform their appearance, structure or other characteristics by changing their chemical or physical properties. Switchable whiteness is one form of such stimuli-responsiveness. Switchable whiteness in materials is defined as a characteristic, which allows material to change its appearance from a white (opaque) state to transparent or vice versa through external stimuli. Switchable whiteness can be harnessed in smart-windows [2], responsive displays and optical switches [3].

Liquid crystal networks (LCNs) are polymers consisting of liquid crystal (LC) monomers. LCNs are crosslinked, meaning that their structure incorporates some diacrylates or other bifunctional units that can form crosslinked networks. Liquid crystals have features of both liquids and solids, and their properties are both anisotropic and fluid-like [4]. Liquid crystal networks can be prepared by polymerizing LCs and crosslinking monomers, typically with ultraviolet (UV) -light [4]. LCNs' characteristics can be modified with various methods. For example to impart humidity sensitivity to LCNs, one can incorporate hydrophilic molecules into their structure [5].

Whiteness is achieved when material has ability to scatter light over the whole visible wavelength range [6,7]. In nature, whiteness is often a result of high refractive index contrast between the external medium such as air or water and the material [6]. Polymeric systems typically have low refractive index, which challenges them to achieve a highly white appearance while maintaining low thickness [7]. Nevertheless, synthetic porous poly(methyl methacrylate) (PMMA) films, which can evenly scatter light even at minimal thicknesses, have been previously studied. These thin films were inspired by the naturally white beetles exhibiting highly white chitin-networks on their shells [8]. Hydrogels can exhibit switchable whiteness, but some limitations related to their characteristics should be considered. Hydrogels are soft polymer networks, that can absorb high amount of water. The high water content of hydrogels imparts them with softness and flexibility, characteristics that are similar to living tissues. Previously studied stimuli-responsive hydrogels, showing switchable whiteness around their LCST, exhibited high

whiteness at a sample thickness of 500 μm [3]. Since many applications utilizing switchable whiteness need the material to be at film-like layer, it is desirable to aim for low thickness [9].

The aim of this thesis is to study and characterize humidity-responsive LCNs, that show switch from transparent (dry) to white (wet) state with exposure to polar solvent, most commonly water. Switchable whiteness is approached through incorporating hydrophilic molecules into LCNs. How do LCNs respond to solvent polarity in terms of their whiteness properties? Which kind of structure allows LCNs to show whiteness changes when exposed to humidity? Interestingly, switchable whiteness is typically found in natural systems in the opposite manner, where in dry conditions the material is white, but upon exposure to water it becomes transparent [6]. Discovery and characterization of humidity-sensitive LCN with an ability to perform reversible white appearance in wet conditions opens new aspects of stimuli-responsive LCN research.

In the beginning of this thesis, the basics of white coloration in nature and in synthetic systems and the properties of LCs and LCNs are presented to provide general understanding on switchable whiteness in synthetic materials. The following chapter presents the research methodology used. Results and discussion containing analysis of the results as well as comparison with previous studies are presented before concluding and summarizing the most important results of this study.

2. BACKGROUND

To understand the research conducted in this thesis, it is important to know the fundamentals of white coloration in materials and of the properties of liquid crystals and liquid crystal networks. Stimuli-responsive switchable whiteness is introduced through previous studies, conducted in hydrogels.

2.1 Whiteness as a phenomenon

White coloration occurs when a material evenly scatters all visible light wavelengths [6]. This scattering property is usually achievable if the material has an inhomogeneous molecular orientation or a high refractive index relative to the surrounding medium [6]. Inhomogeneous structure in this case means that the orientation of scattering particles is random, making the material porous. Inhomogeneous and porous nanocellulose films can exhibit high whiteness, whereas uniformly structured nanocellulose appears transparent [6]. Achieving opaque whiteness requires a large number of scatterers, which typically results in a relatively thick structure [10]. Both natural and synthetic systems have different mechanisms to appear white, as will be discussed in the following sub-chapters.

2.1.1 Bright whiteness in nature

Bright whiteness in nature is found in multiple forms. In nature, white appearance is possible to achieve without pigmented particles that have high refractive index. Number of different species have white appearance due to their disordered nanostructures, and they use whiteness as a camouflage and signaling mechanism [8]. White beetles of the genus *Cyphochilus* have chitinous networks on their shells, which are recognized as some of the most scattering materials in nature [10]. Despite chitin's relatively low refractive index of $n \approx 1.55$, these beetles scatter light effectively [8]. Their chitinous networks are oriented randomly and are arranged in thin layers. This natural phenomenon suggests that achieving white coloration with thin layers of materials with low refractive index contrast is possible.

Switchable whiteness can be found in a flower, *Diphylleia grayi*. In dry conditions, its petals are white, but they become transparent when exposed to humid environment [6].

This transformation is due to micropores in the flower's petals. When dry, the loose structure of the petals scatters light, giving them a white appearance. Upon wetting, water penetrates into the petals, making the refractive index contrast between the petal material and the voids lower and transparent appearance dominant [6].

2.1.2 Whiteness in synthetic materials

Synthetic materials, like titanium dioxide TiO_2 , have brightly white appearance. TiO_2 is added to paints, white pigments and plastics to make them white. TiO_2 has a high refractive index of $n \approx 2.6$, which reinforces white coloration. White appearance is achieved by TiO_2 's high refractive index contrast between the material and the surrounding medium [8].

Switchable whiteness has been previously studied in hydrogels [3,11]. Hydrogels are polymeric networks, that contain hydrophilic polymer chains and significant amount of water [1]. Their structure is three dimensional and they are oftentimes crosslinked with external stimulus, such as UV-light. Hydrogels are widely used in biomedical applications, since their ability for water absorption mimics behavior of tissues [1]. Stimuli-responsiveness in hydrogels is typically linked to their water uptake. External triggers such as pH, light irradiation or chemicals can influence the hydrogel's ability to absorb water [12], providing means for switching their visual appearance and functionality.

Eklund *et al.* [3,11] and Ding *et al.* [13] have studied switchable whiteness in hydrogel-based polymer networks, which respond to temperature changes. Eklund *et al.* have synthesized channeled and macro-crosslinked hydrogel networks, that possess switchable whiteness around their lower critical solution temperature (LCST) [3]. LCST can be observed in polymers that undergo phase separation from a solvent in a certain temperature range [14]. White appearance is achieved above LCST ($\sim 31^\circ\text{C}$ in the case of Eklund *et al.*) and transparent appearance at room temperature (RT). This phenomenon can be seen in **Fig. 1**, which illustrates how differently fabricated poly(N-isopropylacrylamide) (PNIPAm) hydrogel samples change their white coloration above and below LCST [3,11].

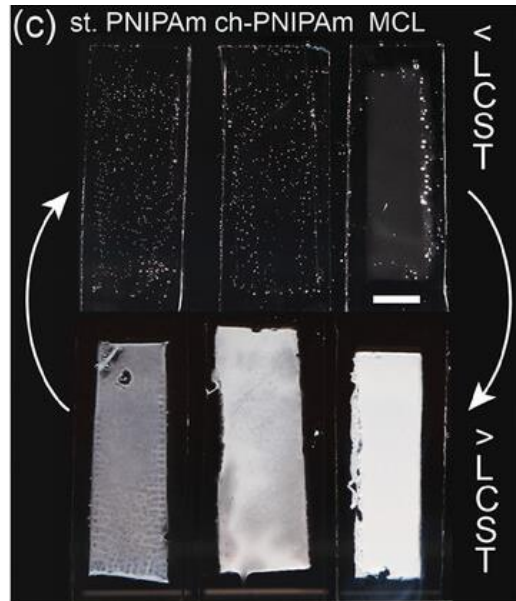


Figure 1. PNIPAm hydrogel samples at 200 μm sample thickness showing switchable whiteness above and below their LCST. [3]

The whiteness can be characterized using reflectance measurements within the visible light wavelength range (400 – 700 nm), an indication of bright whiteness being uniform and high reflectance across all visible light wavelengths. The hydrogels shown in **Fig. 1** achieved a maximum reflectance of 76 % above their LCST at a sample thickness of 500 μm [3]. Thickness is a critical factor in achieving opaque whiteness. However, when the hydrogels are made thinner, their reflectance drops to 45 % [3], as illustrated in **Fig 2**.

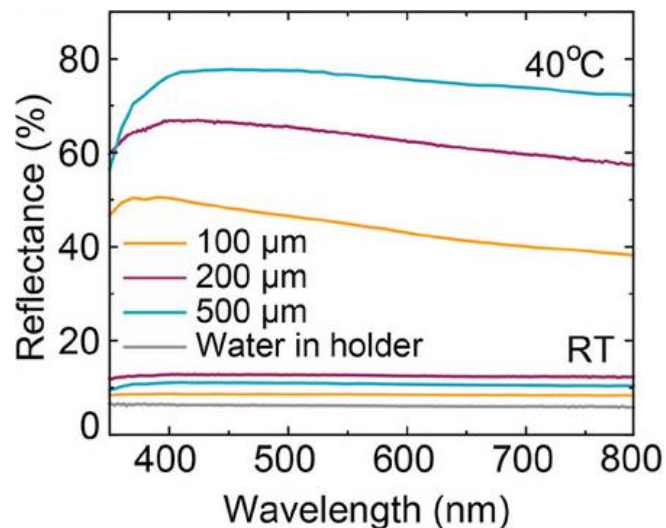


Figure 2. Reflectance spectra of different thickness hydrogel samples above their LCST and at room temperature. [3]

The hydrogels that Eklund *et al.* have studied obtain transparent appearance below LCST. At RT, the studied hydrogels are transparent, and they exhibit low reflectance of

around 10 %. If high switchable whiteness is desired, achieving a highly transparent appearance is just as important as having highly white coloration.

Achieving low thickness while maintaining whiteness in synthetic materials is challenging due to the reduction in the number of scattering centers. In thin materials, the decreased number of scattering centers results in diminished whiteness compared to thicker materials. For applications requiring switchable whiteness, thin layers are typically preferred as they conserve resources and minimize additional weight or stress on the applied surface.

2.1.3 Characterizing whiteness in materials

Whiteness in materials can be characterized through various methods. One way to determine whether material is white is to observe its reflectance spectrum, like previously discussed. Another way to characterize whiteness in a material is to measure its total scattering. Scattering refers to a material's ability to redirect radiation [15]. Scattering involves redirection of light in all directions. If a material is highly scattering, it redirects the radiation effectively and prevents it from being absorbed [15]. White coloration results from high scattering, as white surfaces scatter all visible light wavelengths. Therefore, scattering values for white materials should be high. For thin samples, measuring total scattering is more effective than just measuring total reflectance, as thin samples have the ability to scatter to both front and back side of the sample.

Total scattering can be calculated if material's ability to reflect and transmit light is known [15]. The reflectance and transmittance can be measured for different materials using UV-Vis spectroscopy. This can be done using an integrating sphere, a hollow spherical device with a highly scattering inner surface from the UV to the near-infrared (NIR) region [16]. To calculate scattering, diffuse reflectance and transmittance data is needed.

Diffuse reflectance refers to the portion of incident light that is scattered from a material's surface to a random direction. Diffuse reflectance ignores collimated light passing through the material, and only describes the amount of reflected or back scattered light [16]. When light interacts with a medium, some of it scatters back in the same direction, while some is absorbed by the material. This occurs if the material is opaque. If the material is partially transparent, some of the radiation also passes through the material, and this portion of light radiation is called diffuse transmittance [16].

The integrating sphere is a useful device for scattering measurements. The integrating sphere allows fast measurements of the total luminous flux and the reflectance/transmittance of materials. Because the total scattering describes the material's ability to redirect light, it can be calculated by summing diffuse reflectance and transmittance.

$$S = R_{Diff} + T_{Diff}, \quad (1)$$

where S is scattering, R_{Diff} is diffuse reflectance and T_{Diff} is diffuse transmittance.

2.2 Applications of switchable whiteness

Brightly white materials, most commonly TiO_2 derivatives, provide brightly white appearance for pigments, coatings, paper, cosmetics and plastics [17]. Concentrating solely on the whiteness properties, TiO_2 is the best white pigment available since it has high refractive index, it is chemically inert, has low manufacturing costs and good availability. However, alternatives to TiO_2 are actively being investigated due to concerns related to possible impacts on human health and ecosystems [18]. Nanomaterials inspired by *Cyclophilus* beetle's chitin-networks, e.g. porous fluoropolymers [7] and thin-PMMA films [8] have shown potential for use in applications of bright whiteness.

There are multiple ways to utilize switchable whiteness in real-life applications. The most known application harnessing switchable whiteness is smart windows. Smart windows are designed to tune their opaqueness due to environmental triggers such as temperature or humidity [2]. Energy efficiency in buildings is a critical area of development due to the rapid increase in electricity, heating and cooling costs as well as the need to reduce fossil fuel usage for environmental reasons [2]. Windows are among the least energy-efficient components of buildings. Therefore, it is logical to focus on the development of more energy-efficient windows.

By regulating opaqueness, smart materials can control the transmitting radiation of sunlight through windows. If the goal is to keep building cool, smart windows can block radiation and by that way prevent the insides from getting too warm. Smart windows can be stimulated with various environmental factors. Hydrogel based materials which respond to thermotropic changes have been studied for further utilization in smart windows [2]. Some humidity-sensitive approaches with hydrogel-networks [19] have also been studied, but LCNs have not showed switching from transparent to white before.

Temperature- or humidity -sensitive materials could also be used in privacy windows. At night, when air -humidity increases and outside temperature drops, these responsive materials could adjust to become transparent and opaque. This would provide the desired privacy when it gets dark outside.

Switchable whiteness has also been utilized in optical switches [11]. Optical switches are used in data communication, replacing traditional electronic switches. Optical switches possess lower costs and better energy-efficiency compared to electronic ones. They can

be utilized in modern-day computers, where routing optical signals rather than electronic ones is possible. Optical switches reduce power consumption in integrated optical circuits and therefore make them more energy efficient. Optical switches also enable high-speed communication in long-distance internet communications with higher bandwidth in optical fibers [20].

2.3 Liquid Crystals

Liquid crystals (LC) exhibit unique features that combine characteristics of both liquid and solid phases. They represent a distinct state of matter; the liquid crystal phase. LCs can flow like liquids while maintaining some structural order at the same time. They are typically large aromatic molecules, mostly shaped rod-like [21]. Liquid crystals have multidomain microstructure, that can be aligned with various techniques such as electric or magnetic fields [4]. They are widely used in liquid crystal displays (LCDs), which are found in devices such as smartphones and TVs. The most studied LC molecule is 4-cyano-4'-pentylbiphenyl (5CB), which is illustrated in **Fig. 3**. It was first synthesized in 1972 by Gray et al. at the University of Hull [22]. High-resolution LCDs use 5CB still to this day since its characteristics are easily extendable with doping [21].



Figure 3. Structure of 4-cyano-4'-pentylbiphenyl, better known as 5CB.

Temperature affects molecular movement in all states of matter. Liquid crystals can exist in multiple phases depending on the temperature [21]. Melting point is a phase transition temperature below which the LC is in a completely solid state, arranged in a crystalline form [21]. Above melting point, LCs exhibit thermotropic phases [21]. Thermotropic phases provide LCs their unique ability to possess some of the properties typically associated to solid and liquid states at the same time. These phases appear in designated temperature ranges which are characteristic for each LC. Examples of thermotropic phases include nematic, smectic and chiral nematic phase [21], illustrated in **Fig. 4**.

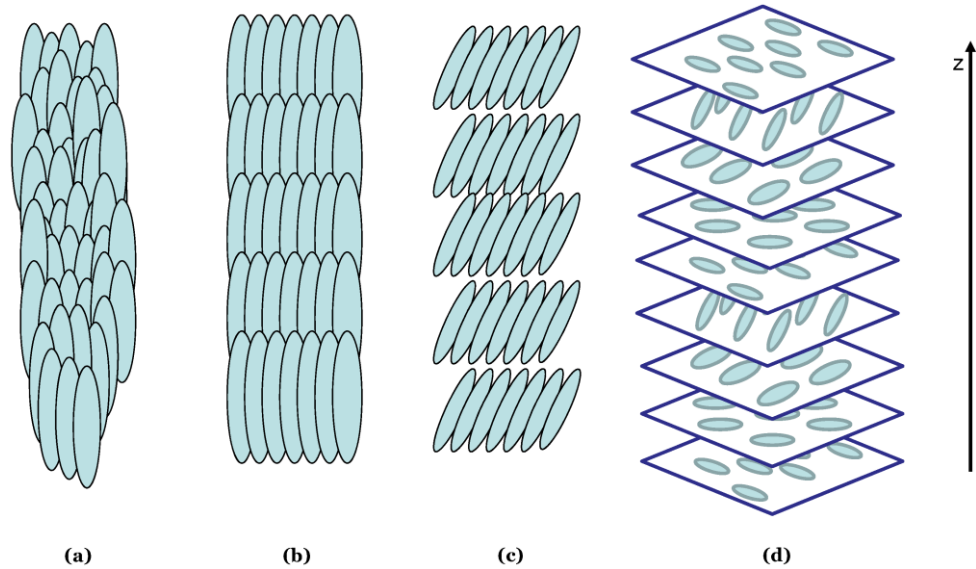


Figure 4. Illustrations of different liquid crystal phases. a) Nematic phase, b) Smectic A phase, c) Smectic C phase, d) Chiral nematic phase. Adapted from [23].

Clearing point is the temperature above which the LC becomes isotropic. In the isotropic state, molecules are randomly arranged in all directions. Liquids are isotropic, since molecules in a liquid don't have any directional order [24]. Within the temperature range between crystalline solid and isotropic liquid states, different thermotropic phases can be detected depending on the LC. 5CB's melting point is at 22.5 °C and clearing point at 35 °C [22]. 5CB has only nematic mesophase unlike some LCs, that can have multiple mesophases between the crystalline and liquid states.

The liquid crystal phase in LC-molecules gave material science new characteristics and applications to study. LCs have had an important role in the development of mobile information technologies. The properties of various mesophases combined with the ability to form films or fibers is useful for many applications [25]. Multiple mesophases of LC-molecules can give materials temperature-dependent characteristics.

2.4 Liquid Crystal Networks

Liquid crystal networks combine the properties of liquid crystals and polymer networks. Liquid crystal properties make LCNs adaptive and stimuli-responsive materials and promising for numerous applications [26]. LCNs anisotropic structure and possibility to incorporate functional groups allow them to interfere with external stimuli. LCNs can be polymerized in aligned or randomly oriented states. Alignment is achieved through polymerizing the system in aligned state.

LCNs are crosslinked polymer networks, characterized by a three-dimensional configuration [12]. Crosslinking involves combining polymer chains predominantly through covalent bonds, although some networks also utilize ionic, hydrogen and halogen bonds. This process is often achieved through photoinitiated radical polymerization, a reaction triggered by UV light that causes multifunctional monomers to form crosslinked polymers [27]. The presence of a photoinitiator is essential for successful UV-crosslinking. Liquid crystal monomers have reactive tails that facilitate bond formation, resulting in densely polymerized, “glassy” networks. This crosslinking process preserves the liquid crystal properties even after polymerization [28].

The density of crosslinking divides the resulting polymer networks into two categories: liquid crystal elastomers (LCEs) and glassy liquid crystal networks. LCEs are lightly crosslinked, exhibiting macroscopic properties that resemble properties of conventional rubbers [28]. Light crosslinking density allows LCEs to undergo spontaneous shape changes, making them ideal material for applications such as artificial muscles and sensors [28]. This thesis focuses on glassy networks, which are highly crosslinked and incorporate both covalent and non-covalent crosslinks. Humidity-sensitivity can be added to LCNs by incorporation of hydrophilic groups such as carboxylic acids into the composition. Humidity-sensitive LCEs that have hydrogen bonds in their network have been studied previously [5]. In this thesis humidity-sensitivity is approached by incorporating acrylic acid into LCN composition. **Fig. 5** highlights the structural difference between glassy networks and LCEs.

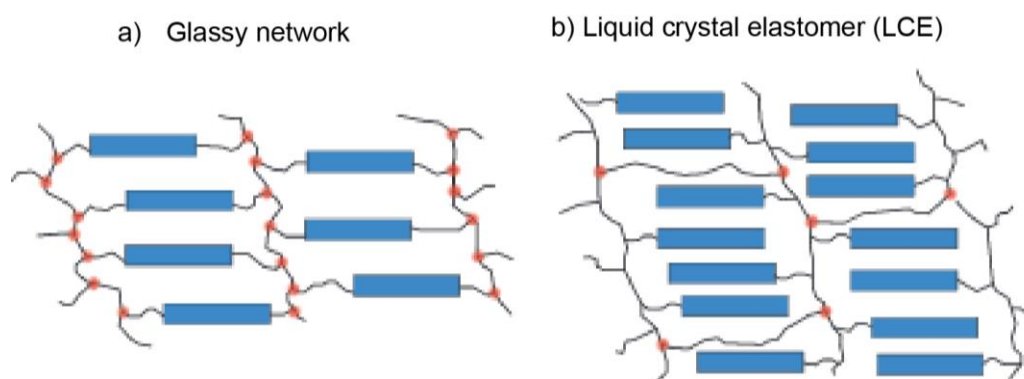


Figure 5. Structures of a) glassy network and b) liquid crystal elastomer. Adapted from [28].

Glassy networks, referred to as LCNs in this thesis, typically result from the copolymerization of some monoacrylate and diacrylate mesogens. In **Fig. 6**, diacrylate RM82 and monoacrylate RM105 are illustrated. RM82 was first used in polymeric networks in 1988, when it was successfully added to a stable liquid crystal network [29].

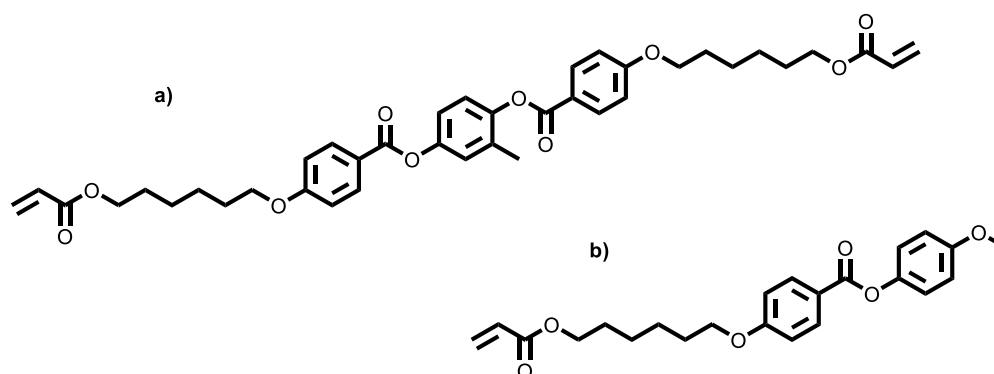


Figure 6. Structures of a) 1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene, better known as RM-82 and b) 4-methoxyphenyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate, better known as RM-105.

The UV-initiated crosslinking of acrylates follows a free-radical polymerization mechanism, in which the diacrylate is acting as a crosslinker [27]. In this process, a photoinitiator is required to initiate the polymerization reaction. A photoinitiator is often an aromatic carbonyl compound that produces reactive molecules, such as free radicals, upon absorbing UV-light [27]. After initiation, the formed free radicals react with monomers, creating polymer-chains and finally resulting to crosslinked networks [27].

Temperature is an important aspect in photopolymerization of LCNs. RM82 exhibits a smectic phase below 88 °C and a nematic phase between 108 to 155 °C [29]. During polymerization, the mesogens' phases can be "frozen" with adapting the polymerization temperature to match the desired liquid crystalline phase [29]. With RM82, the smectic phase is achieved when polymerization temperature is below 88 °C and nematic phase above 108 °C.

Dynamic bonding is one way to shape material properties and functionalities in LCNs. Halogen and hydrogen bonds are considered as dynamic bonds, since they can form reversible connections in specific conditions [30]. Hydrogen bonds are generally added to LCNs through carboxylic acids or phenols. Carboxylic acids are hydrophilic moieties that can additionally be used to enhance humidity-sensitivity in LCNs. Earlier studies have used halogen bonding in LCNs for temperature-dependent shape memory characteristics [31]. Halogen bonds offer another non-covalent interaction into LCN system, enhancing durability and different functionalities. Halogen bonds are considered hydrophobic.

Stimuli-responsive materials undergo chemical or physical changes in response to external stimulus, such as variations in temperature, pH or humidity. The high crosslinking

density exhibits LCNs to have considerable resistance to chemicals, heat and radiation [27].

3. MATERIALS AND METHODS

The experimental part of this thesis consists of LCN preparation and scattering measurements. In the following subsections description of materials and different compositions used are presented. Also, the methods used for sample preparation, photopolymerization and scattering measurements are described.

3.1 Starting materials and compositions

Two reactive mesogens were chosen for the LCN: 1,4-Bis[4-(6-acryloyloxyhexyloxy)benzoyloxy]-2-methylbenzene (**RM-82**) (99 %, Synthon Chemicals GmbH & Co) and 4-Methoxyphenyl 4-((6-(acryloyloxy)hexyl)oxy)benzoate (**RM-105**) (99 %, Synthon Chemicals GmbH & Co). **RM-82** acts as a crosslinker in the system, since it has acrylate tails in both ends.

Halogen bonding was added for dynamic bonding with 1,4-Diiodotetrafluorobenzene (**1,4-I**) (99 %, BLDpharm) and 2-(Dimethylamino)ethyl methacrylate (**N**) (>98.5 +%, TCI). It is known that halogen bonding is hydrophobic in nature [30]. Halogen bonds also facilitate dynamic stimuli-responsiveness, since they are able to break and reform due to temperature changes unlike covalent bonds [30]. Halogen bond forms between electron-deficient halogen atom and a Lewis base [31]. Iodine is the strongest halogen-bond donor and with tertiary amine **N** it can form strong noncovalent interactions. Earlier studies have used halogen bonding in LCNs for temperature-dependent shape memory characteristics [31]. In this thesis, halogen bonding is used to make LCNs porous and maximize the inhomogeneous structure that can create high refractive index contrast between polymer and medium.

Acrylic acid (**A**) (99 %, Sigma-Aldrich) was added to form hydrogen bonding and as a hydrophilic entity. **A** can form supramolecular non-covalent crosslinks into the network. These bonds facilitate hydrophilic nature, that causes swelling and relatively high absorption of water. Depending on water content, these bonds can break and reform. Through hydrogen bonds, **A** can also stabilize the LCN structure. The prepared LCN structure is illustrated in **Fig. 7**.

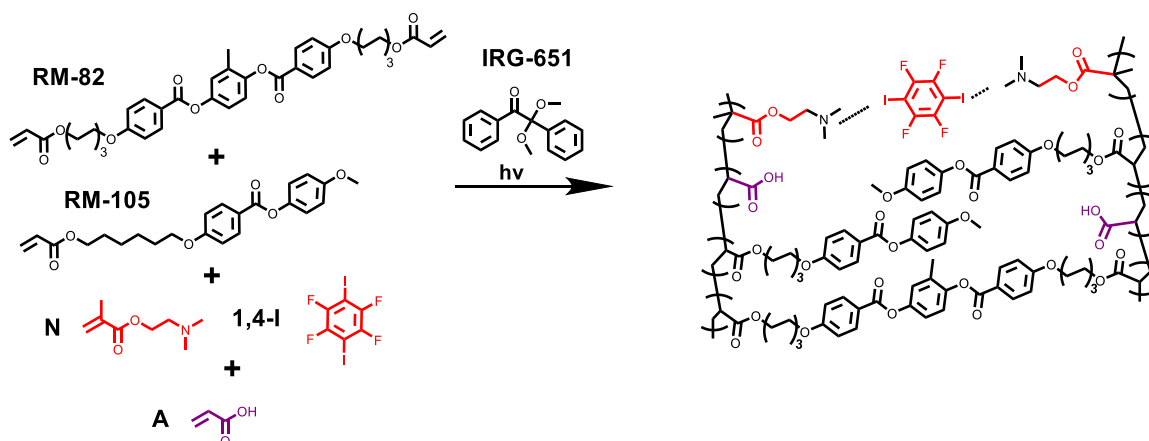


Figure 7. Chemical structures of starting materials and a scheme of the formed LCN.

Six different compositions were prepared using identical starting materials, with variations in the proportions of acrylic acid and halogen-bond forming molecules in each composition. The goal for the preparation of different composition LCNs was to find out which LCN composition shows switchable whiteness the best. The details of these compositions are presented in **Table 1**.

Table 1. Six different LCN-compositions presented in mole fractions (mmol).

Composition name	RM-82	RM-105	A	N	1,4-I
LCN-1	3	15	150	-	-
LCN-2	3	15	120	30	15
LCN-3	3	15	100	50	25
LCN-4	3	15	80	70	35
LCN-5	3	15	-	150	75
LCN-6	3	15	100	50	-

In addition, each LCN composition incorporated 1,2-Diphenyl-2,2-dimethoxyethanone (IRG-651) (99 %, Sigma-Aldrich) as a photoinitiator. The concentration of the IRG-651 in each formulation was maintained at 2 wt.%.

3.2 Sample preparation

Sample preparation has two main steps: Substrate preparation and photopolymerization. Before preparing the actual LCN samples, the glass cells in which the photopolymerization was conducted were prepared. The cells were made from microscope slides (3x1 inch), which were cut to two identical pieces with a glass cutter. The cut pieces were

cleaned with an Elmasonic P sonicator in isopropanol at frequency of 80 kHz for 5 minutes. After sonication, they were wiped with clean paper towels and dried with compressed nitrogen gas.

The cleaned glass slides were spin coated with 5 wt.% polyvinyl alcohol (PVA) solution. Spin coating is a technique used to apply uniform thin films to flat substrates. A small amount of liquid coating is placed on the substrate, after which the substrate is rotated at high speeds and the centrifugal force spreads the coating liquid evenly across the surface [32]. The PVA-solution was prepared by dissolving 5 wt.% of PVA in distilled water. The solution was heated and magnetically stirred until all PVA was dissolved. Spin-coating was carried out with WS-650-23NPPB Spin Coater (Laurell Technologies Corporation). Each glass slide was spin-coated from one side with 600-700 μl of PVA-solution at 4000 rpm for 1 minute. The spin-coated glass slides were placed on a 100 °C hot plate for 5 minutes, with PVA-coated side facing upwards. The PVA-coating prevents the LCN to adhere to the glass.

Glass cells were prepared with PVA-coated glass substrates by glueing them together with UVS 91 (Norland Products Inc.) UV-glue. Desired 100 μm space between two glass substrates was achieved by mixing UV-glue with Dry Soda Lime Glass Microspheres with 100 μm diameter (Duke Standards) spacers. The coated glass substrates were glued together from the corners of the substrate, PVA-coated sides facing inwards. The glued cells were radiated with a 365 nm LED for 1-2 minutes for curing the glue and solidifying the cell.

All LCN monomers were mixed in 5 ml glass vial and heated above the melting point of the mixture (115 °C). The glass cells were heated to 115 °C and filled with the LCN mixture using 200 μl micropipette via capillary action. The filled cells were cooled down to 60 °C, which is the chosen polymerization temperature. At 60 °C, the polymer mixture exhibits an isotropic state which results in the mesogens to be randomly arranged.

UV -polymerization was carried out with CoolLED pE-4000 light-source using 385 nm light wavelength. The 60 °C temperature was maintained during polymerization using Linkam Scientific LTS120 temperature controller. UV -light with an intensity of 35 mW cm^{-2} was used for 1 minute for each sample. The polymerized samples have a shape of a film and they are transparent after polymerization. The LCN films were removed from the glass cells with razor blades. The glass cells were first heated at 60 °C to make the polymer softer and avoid it breaking while cutting.

3.3 Scattering measurements

Scattering measurements were performed with Shimadzu UV-3600 UV-VIS-NIR Spectrophotometer with an integrating sphere configuration ISR-3100. The device consists of a light source, a monochromator, and a sphere with at least three ports and a detector. Both diffuse reflectance and diffuse transmittance were measured for all samples. Total reflectance was measured for LCN-3 to compare total reflectance values with previous studies [3]. Total reflectance refers to the complete reflection of light from a surface. This includes both specular and diffuse reflectance [33]. The diffuse reflectance, diffuse transmittance and total reflectance measurement configurations of integrating sphere are illustrated in **Fig. 8**.

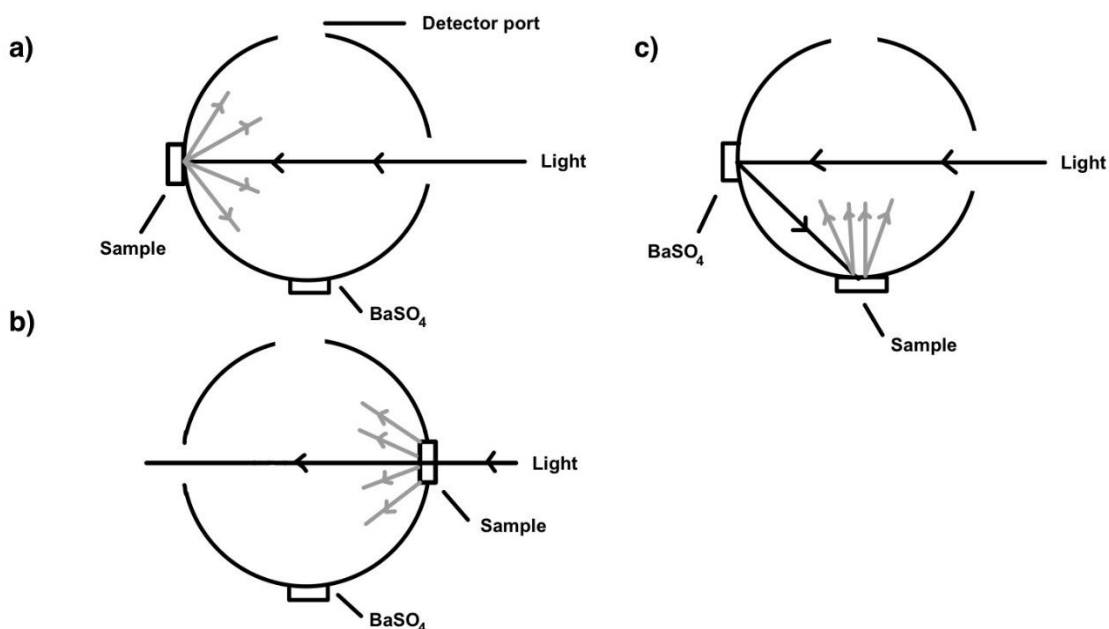


Figure 8. a) Diffuse reflectance, b) diffuse transmittance and c) total reflectance measurement configurations in ISR-3100 integrating sphere.

Integrating sphere is an optical device that measures the total luminous flux. It involves a barium sulfate (BaSO₄) coated sphere, drawing all scattered light to the detector. Before actual measurements, baseline was measured with a clean BaSO₄ plate. Each measurement was made at a wavelength range of 300-900 nm. Used slit width was 5 nm and sampling interval 2 nm.

Before measurements, sample was heated on a 100 °C heating pad to remove any moisture and make the sample as dry as possible. All samples were measured free standing, except for LCN-5 which was impossible to remove from the glass cell. Diffuse transmittance and reflectance at dry state was measured first. After measurement, the samples

were put in water bath for 1-2 minutes at RT to wet their structure. The samples were removed from the water bath and extra water was wiped from the surface with a clean paper towel. Diffuse reflectance and transmittance were then measured for wet samples. Total scattering was calculated from the diffuse reflectance and transmittance data using equation (1).

4. RESULTS AND DISCUSSION

A total of six different LCN compositions were prepared. The ability to change appearance from transparent to white (opaque) was tested and observed first with naked eye. Subsequently, scattering values were quantified with integrating sphere. Total reflectance measurements were also conducted for comparison with previous studies. The data and results are presented in this chapter and compared to prior studies.

4.1 Switching whiteness observations

The switchable whiteness phenomenon was first observed with the naked eye to see if samples show reversible whiteness change. Each sample was dipped in RT water. LCN-2, LCN-3, LCN-4 and LCN-6 showed white coloration when dipped in water. LCN-1 and LCN-5 didn't change their appearance when wet. **Fig. 9** shows each LCN sample and its appearance at dry and wet states.

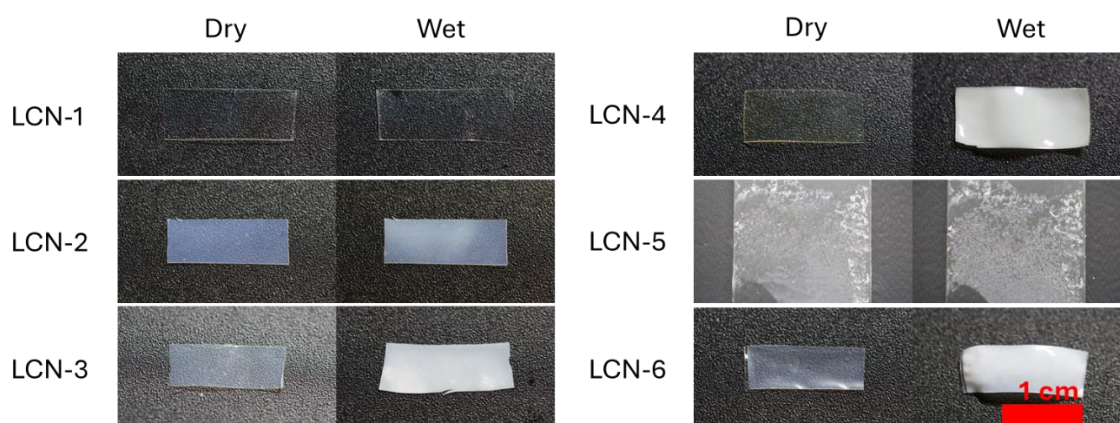


Figure 9. Images of all samples from LCN-1 to LCN-6 at dry and wet states with 100 μm thickness.

Each sample that showed whiteness in water was also capable of reversibly becoming transparent upon drying when heated. Wet samples were placed on a heating pad at approximately 100 $^{\circ}\text{C}$ to remove all water from the material. Additionally, some wet samples were left to air-dry at RT to determine if they would become transparent spontaneously. It was observed that the LCNs couldn't achieve transparency through air-drying alone and required high temperatures to remove the water and regain transparency.

Air humidity tests were conducted for LCN-3. The sample was placed inside a sectioned Petri-dish. One side of the dish was filled with water and the other side was kept dry while the LCN placed to the dry side. The lid was closed and this way humid environment

was achieved. LCN-3 was kept at a humid environment for 24 hours and it became white during that time. The air-humidity level wasn't monitored since it was not possible in the circumstances of the experiment. This experiment just gave the general idea that it is also possible for LCNs to achieve white coloration in humid environments and not only in direct contact with water. **Fig. 10a** illustrates the whiteness of LCN-3 in humid environment.

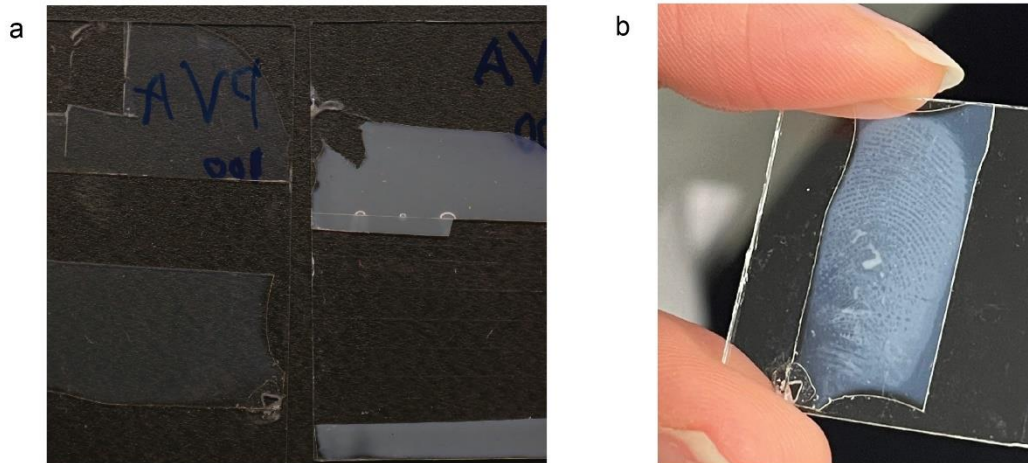


Figure 10. a) Humidity test for LCN-3. Left sample is at dry state and right sample has been exposed to humid environment for 24 hours. b) Fingerprint on LCN-3. Wet finger was pressed on a dry sample.

The circumstances in the lab during experimental parts of this research have varied depending on the day and season. If air humidity is high in the lab, it could affect the results since it's now proven that LCNs can also change appearance due to high air humidity. That is why samples are always heated on top of 100 °C heating pad to remove any excess moisture before experiments.

Fig. 10b shows a fingerprint that has been successfully printed on top of LCN-3. Wet finger was placed on a dry LCN-3 sample for 2-3 seconds and then removed. Fingerprint stayed in LCN-3, and it was quickly captured. The fingerprinting could be erased by re-heating the sample, but some grease from the finger was left.

4.2 Scattering data

Diffuse reflectance and transmittance were measured for all six samples. From this data, scattering was calculated with equation (1) and plotted. **Fig. 11** shows the scattering of each sample at dry and wet states.

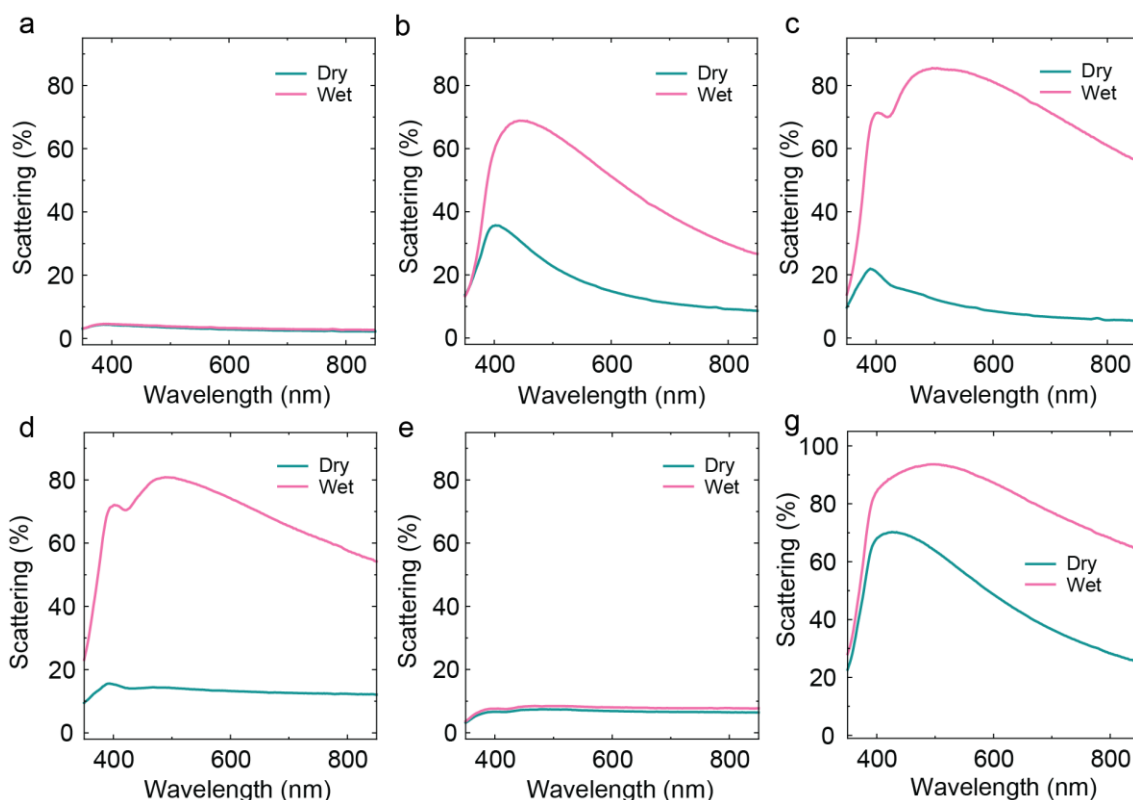


Figure 11. Total scattering of a) LCN-1, b) LCN-2, c) LCN-3, d) LCN-4, e) LCN-5 and g) LCN-6 at dry and wet states.

Fig. 11 confirms the observations made with naked eye: LCN-1 and LCN-5 do not become opaque in water, as there is no change in scattering between dry and wet states. LCN-2, LCN-3, LCN-4 and LCN-6 exhibit significant changes in scattering between dry and wet states.

When evaluating the best composition for switchable whiteness, multiple factors must be considered. The highest scattering value in the wet state does not automatically indicate the best composition, as the scattering values in the dry state are also important. The sample that has greatest change in scattering, demonstrates the best ability to transition between transparency and opaque whiteness, which is the desired characteristic for a material that can adjust its whiteness. In **Fig. 12a**, the change in scattering is compared between different samples.

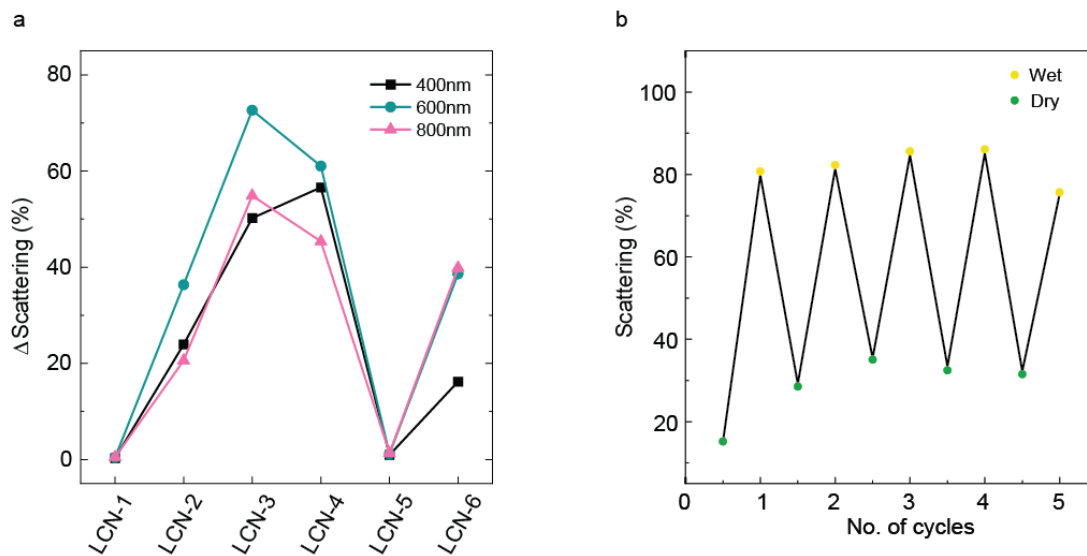


Figure 12. a) Change in scattering for different samples at 400, 600 and 800 nm wavelengths. b) Multiple-cycle scattering for LCN-3 at a wavelength of 450 nm.

LCN-3 exhibits the most significant change in scattering at wavelengths of 600 and 800 nm. Overall, LCN-3 shows the greatest white state scattering among LCN-1 to LCN-5 throughout visible range. Although LCN-6 has the highest white state scattering, it also exhibits high scattering in dry state (**Fig. 11**). With a maximum dry state scattering of 65 %, LCN-6 cannot be considered transparent. Therefore, despite LCN-6's higher scattering compared to LCN-3, its dry state scattering does not contribute to transparent appearance. As samples were polymerized at an isotropic state, the mesogens were randomly arranged, and scattering values were not exactly the same when measured at different spots or different samples, and some change of $\pm 3\%$ was observed on every measurement.

All samples that showed whiteness changes were able to change their opaqueness reversibly. To prove this with scattering data, multiple-cycle scattering measurement was conducted for the LCN-3, which exhibited the highest scattering contrast. Wetting and drying was done over 5 cycles, and scattering data was recorded. **Fig. 12b** illustrates this multiple-cycle experiment. The similarity in dry and wet state scattering over the cycles confirms that LCNs can be used for multiple switching cycles.

Previously studied hydrogels by Eklund *et al.*, that exhibited switchable whiteness exhibited 40-50 % reflectance at 400-800 nm at the white state with a film thickness of 100 μm [3]. For comparison, the total reflectance was measured for LCN-3 as shown on **Fig. 13**.

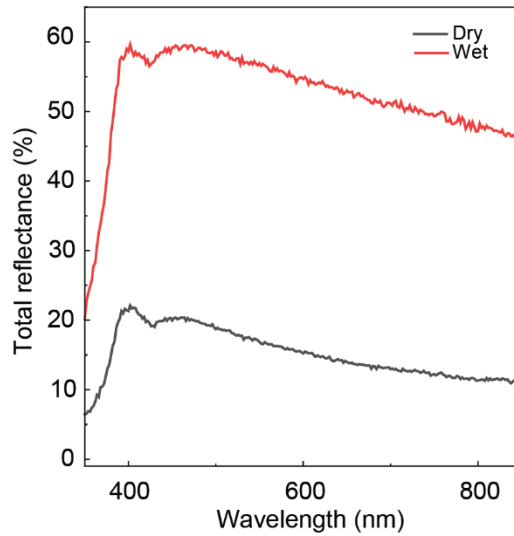


Figure 13. Total reflectance of LCN-3 at dry and wet states.

LCN-3 exhibits higher total reflectance values with a sample thickness of 100 μm than the previously studied hydrogels [3] within the whole visible light wavelength range. This can be seen when comparing **Fig. 13** and **Fig. 2**. Both dry and wet state reflectance values are higher for LCN-3. This means that LCN-3 appears whiter but not as transparent as the hydrogels that Eklund *et al.* have studied [3]. LCN-3 exhibits 60 % reflectance at 400 nm wavelength, while the hydrogels show reflectance of 50 % with the same film thickness and wavelength [3]. Ding *et al.* synthesized hydrogels with 500 μm thickness, which showed total reflectance of ~ 67 % at white state [13]. These samples are 5 times thicker compared to LCN-3 but exhibit only 7 % higher reflectance values.

The integrating sphere configuration is a possible error source for scattering measurement. As illustrated on **Fig. 8**, the integrating sphere has a total of four ports. The measured sample was placed at one of the ports depending on the configuration **a)**, **b)** or **c)** (**Fig. 8**) used. If sample was not placed correctly covering the whole port, it could “leak” some light out of the sphere unintentionally and by that way affect the results in a negative way. Also, if sample is not completely planar, it can affect the results. If some wrinkles appear while wetting the sample, the thickness might change and affect scattering values, since thicker structure usually indicates higher scattering ability.

Thickness and reflectance values are good for comparing the ability to show whiteness. However, LCNs and hydrogels differ from each other fundamentally. LCNs are highly crosslinked polymer networks, that have more dense and durable structure compared to hydrogels. Hydrogels have water incorporated to their structure and their mechanical properties are not as strong as LCNs'. Previously studied hydrogels responded to environmental temperature changes [3], while LCNs in this study respond to humidity

changes. Based on required conditions, and environmental factors, both hydrogels and LCNs can serve as switchable white material.

LCN-2, LCN-3 and LCN-4 contain both halogen and hydrogen bond forming groups, with varying molar fractions. As the amount of **A** decreases from LCN-2 to LCN-4, the molar ratios of **N** and **1,4-I** increase. These samples exhibit changes in whiteness when exposed to humidity, with LCN-3 showing the best results in scattering measurements. This suggests that both halogen and hydrogen bonds are necessary for switchable whiteness. However, LCN-6, which includes hydrogen bonds, amine and no halogen donor shows significant changes in scattering measurements between dry and wet states. Comparing LCN-3 and LCN-6, the absence of halogen containing group **1,4-I** in LCN-6 means it lacks halogen bonds yet still demonstrates switchable whiteness. In contrast, comparing LCN-1 and LCN-6 reveals that LCN-6 includes **N**, indicating that both **A** and **N** are required for switchable whiteness and halogen bonding is not strictly essential for switchable whiteness but rather enhancing the phenomenon. Achieving whiteness is all about finding a balance between hydrophilic and hydrophobic domains in the LCN.

Phase separation is a process where different components of the LCN separate into different domains or phases. Chemical differences in components, such as hydrophobicity or hydrophilicity can cause phase separation due to changing environmental circumstances such as changes in humidity-level. Phase separation may lead to varying optical or mechanical properties within different domains [34].

Halogen bonding is enhancing the whiteness of samples, even though it possesses a hydrophobic nature. In a transparent state, all the samples are smooth and consistent. The hypothesis is that when LCN-2, LCN-3, LCN-4 and LCN-6 are wet, pores are formed in their structure through phase separation. Hydrophilic and hydrophobic moieties in LCN composition enable pore formation due to phase separation when LCN is exposed to water. For maximal whiteness, both hydrophilic and hydrophobic parts are required. While pores are filled with water, refractive index contrast increases and material appears white. Upon heating and removal of water from the system, the pores disappear, and samples become smooth again regaining their transparent appearance while refractive index contrast decreases.

To further study the impact of solvent polarity, LCN-3 was dipped in eight different solvents with varying polarity levels. Whiteness with different solvents can be seen in **Fig. 14**.

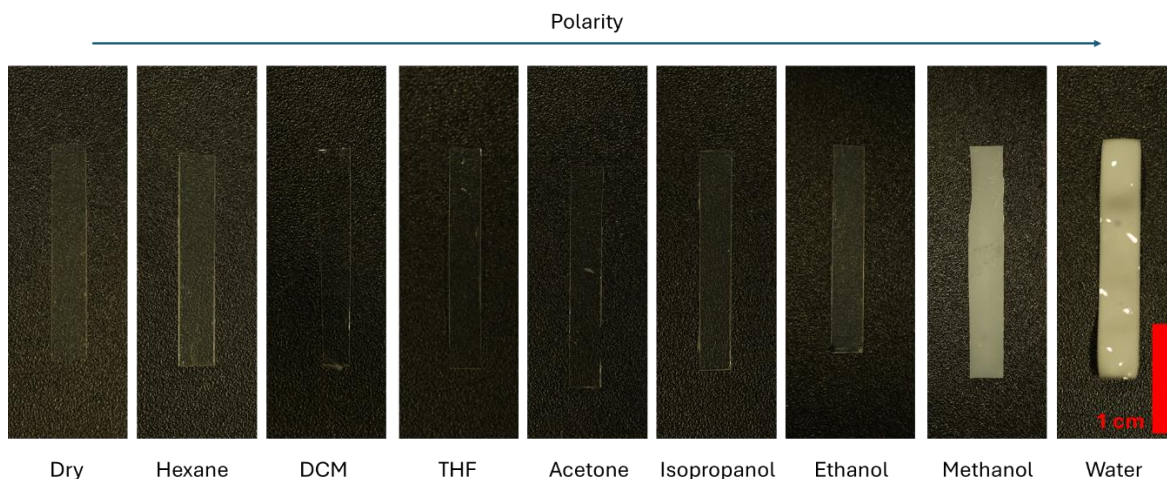


Figure 14. LCN-3 dipped in different polarity solvents. Polarity increases from left to right.

Whiteness can be achieved only with highly polar solvents, as seen on **Fig. 14**. Water and methanol induce LCN-3 white appearance, but non-polar or low-polar solvents hexane, dichloromethane (DCM), tetrahydrofuran (THF), acetone, isopropanol and ethanol do not trigger the same result.

Polar solvent interacts with polar components **A** and **N**, creating pores in the LCN structure. Pores are filled with water and opaque appearance is achieved. In polar solvent, LCN sample swells, as it incorporates the solvent to its structure. Analysis with scanning electron microscope (SEM) would provide detailed pictures of LCN structure, to further study pore formation in dry and wet states. Since LCN structure consists of hydrophobic components and the structure is cross linked, the samples don't dissolve in water. Hydrophilic components penetrate water into the system while hydrophobic components maintain film like shape and clear phase-separated structure between film and polar medium. Since no SEM analysis is performed within this thesis, these conclusions are only drawn from other observations. Liquid crystalline hydrogels [35] consist of hydrophilic and hydrophobic moieties similarly to LCNs in this study. Non-polar solvents don't react with hydrophilic components, resulting that no pores are formed. The structure of LCN stays consistent when dipped in non-polar solvents. Thus, no phase separation occurs with non-polar solvents.

5. CONCLUSIONS

The aim of this thesis was to characterize LCNs responding to polarity changes in the surrounding medium through change in whiteness. Liquid crystal networks have possibilities to show stimuli-responsive behavior with different environmental triggers. Humidity-sensitive approaches of stimuli-responsive LC materials [5] have been previously studied, but synthesized systems have not been concentrated around whiteness change. Macro-crosslinked hydrogels have shown switching whiteness with temperature-triggers.

The experimental part of this thesis included LCN preparation and scattering measurements. A total of six different compositions were prepared to characterize and better understand the reasons for whiteness change. Whiteness change was observed with dipping the samples in room temperature water. Scattering measurements were conducted for all samples. The aim of scattering measurements was to determine the best composition for switchable whiteness.

Samples containing only hydrogen bonding, or halogen bonding did not show changes in whiteness nor in scattering when exposed to polar solvents. All other samples exhibited significant changes in scattering upon exposure to water, achieving white coloration. When comparing the change in scattering at different wavelengths, LCN-3 was determined to have the best composition for switchable whiteness. It incorporates a good balance of both hydrogen- and halogen bonds, which enable pore formation while sample is exposed to highly polar solvent. Hydrophilic molecules cause LCN to swell by incorporating water into its structure. Water molecules increase the refractive index contrast of the LCN resulting in white coloration. Halogen bonding is hydrophobic yet enhances switchable whiteness by maintaining clear phase separated structure between film and a polar medium. Achieving whiteness is all about finding a balance between hydrophilic and hydrophobic moieties.

LCN-3 achieved a maximum wet state scattering of 84 % at 500 nm wavelength. The biggest change in scattering was found to be 77 % at 600 nm wavelength. Multiple cycle scattering experiment was also conducted for LCN-3 to better study the multiple cycle behavior of whiteness change. Wet state scattering of approximately 80 % remained almost the same during the experiment. The similarity in dry and wet state scattering over the cycles confirmed that LCNs can show switching between transparent and white states multiple times in a row.

Total reflectance values were measured for LCN-3 at dry and wet states to compare the results with previously studied hydrogels. The maximum white state total reflectance value of LCN-3 was found to be 60 % at 400 nm wavelength. Previously studied hydrogels have shown a 50 % reflectance with 100 μm sample thickness at 400 nm wavelength. With this comparison, LCN-3 has better ability to exhibit white coloration.

In addition to scattering measurements, one LCN-3 sample was exposed to air-humidity for 24 hours and it showed white coloration. No scattering data was measured from this experiment, as it was only conducted to have the general idea of air-humidity affecting LCN-3 appearance. Different polarity solvents were also used in terms of testing the switchable whiteness with varying polarity-levels. Only highly polar solvents showed whiteness change in LCN-3.

LCNs synthesized in this thesis have great ability to change appearance from transparent to opaque white when exposed to polar solvents. This opens new aspect for LCN studies as only hydrogels have shown similar results before. Smart windows and biosensing have utilized switchable whiteness in temperature dependent hydrogels, but the possibilities for humidity sensitive LCNs still lie undiscovered. Further work with SEM is needed for investigating pore formation and phase separation in detail. Research of mechanical properties would also be beneficial in terms of material use in possible applications in the future. This thesis introduced the phenomenon of switchable whiteness in LCNs and it can be refined further with more research in the future.

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