2004-03-01

Investigation of Novel Liquid Crystal Materials for their Possible Applications

Minseok Chang
Technological University Dublin

Recommended Citation

Chang, M. (2004). *Investigation of novel liquid crystal materials for their possible applications*. Masters dissertation. Technological University Dublin. doi:10.21427/D7GD0P

Investigation of novel liquid crystal materials for their possible applications

(Dendrimers and De Vries Smectic A phases)

Name of the candidate: Minseok Chang

Award in pursuit: MPhil

Name of the institute: Dublin Institute of Technology

Name of supervisor: Dr. Yuri Panarin

School of Electronic and Communications Engineering

Submission date: Mar 2004

Declaration

I certify that this thesis which I now submit for examination for the award of MPhil, is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

This thesis was prepared according to the regulations for postgraduate study by research of the Dublin Institute of Technology and has not been submitted in whole or in part for an award in any other Institute or University.

Acknowledgement

I am deeply indebted to my supervisor Dr. Yuri Panarin for his advice on my research and his careful attention. He is the first and only person who has introduced me to the world of liquid crystals and, has made my research possible.

I would like to thank my family in Korea, whom having been apart for more than one year, has been cheering me on during my study in Ireland.

I also want to thank Dr. Sanseong Soemun, a Postdoctoral research fellow in University of Dublin, Trinity College for giving me some helpful advice.

Abstract

In this thesis I present four main topics. One is an introduction to liquid crystals and the second is an opto-electronic experimental setup. The third is an investigation of the dynamic properties of dendrimers, which show ferroelectric features. The last one is a research focused on understanding of the structures of two different types of De Vries smectic A liquid crystal phases. All research activities are performed by the hand-made but automatically controlled opto-electronic experimental setup.

First, an introduction to liquid crystals is presented in easy language. Mainly there are two kinds of liquid crystals, thermotropic and lyotropic, but I focus only on the thermotropic LCs (liquid crystals) because they are the very materials being used in display industry nowadays and this goes well with my research aim.

Second, I present the experimental setup/techniques and the process of making a liquid crystal cell. This part deals with detailed practical laboratory skills concerned with doing investigation of liquid crystals.

Third, dendrimers, a new type of liquid crystal, have been receiving a great amount of attention from scientists from many different disciplines. Dendrimers can be utilized in various industries, such as, medicine, display materials, catalysis, inks, nanoelectronics, etc. I specifically focus on the ferroelectric properties of dendrimers, the main feature of LCD industry. As a result I found that optical switching depends on the generation number of the dendrimers.

Finally, I propose two possible structures for a new type of LC phase, De Vries smectic A phase. Several materials were found to possess such a phase; however, it was extremely hard to tell which structure those De Vries smectic A liquid crystals have, because of the size of the matters. But I have very satisfying evidence to support two possible molecular arrangements for those De Vries phases using our opto-electronic setup.

Table of Contents

Chapters

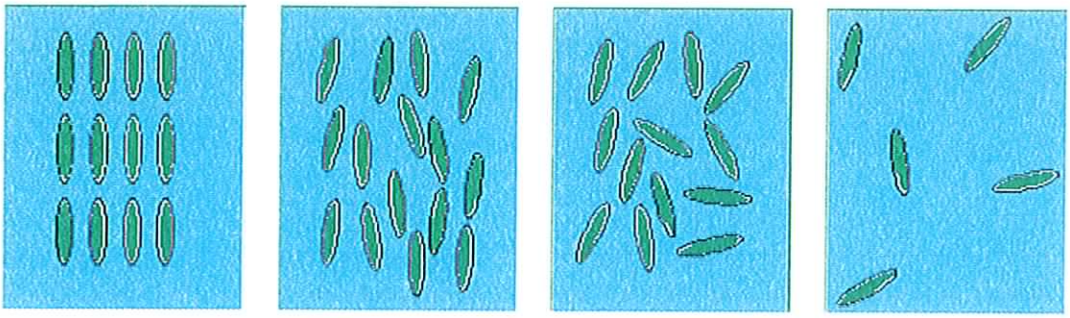
Chapter 1

Introduction to Liquid Crystals

People are taught from the beginning of their education that there are three kinds of matter in the universe, and most people believe that. Those three types of matter are solid, liquid, and gas. However, interestingly enough, there is another novel state of matter which I did not know about until I started my research on that issue. It is called liquid crystal. In the 21st century, we are often confronted by the word, liquid crystals, because of the rapidly growing display industry. Despite the ubiquity of that word, people do not have a well-defined idea about liquid crystals. In this chapter, I present the basic and essential idea behind liquid crystals. The recommended text for the beginner is *Liquid Crystals* by Peter J. Collings [1]. Study of liquid crystals is one of the most interdisciplinary subjects, so a lot of research activities have been done and are being done by many scientists from departments of physics, chemical engineering, electrical & electronic engineering and chemistry, etc.

1.1 What Are Liquid Crystals?

In 1888 an Australian botanist found very interesting results on a material named cholesteryl benzoate, which was strongly believed to possess crystal properties. He heated the material and finally found that it had two melting points which can be easily distinguished by the naked eye. First it changed into an opaque state and then into a clear state. Before it changed into a very clear transparent state, it existed as a liquid crystal. People grew to call that kind of hazy state of matter liquid crystal.



[Fig 1] Schematic presentation of solid, liquid crystal, liquid and gas

As **[Fig 1]** suggests, liquid crystals lie between solid (crystal) and liquid. Since they are thermodynamically stable, they can form a distinctive state of matter. Each green oval represents a molecule in a material and such ovals are arranged in four different styles, respectively. In the solid state all molecules are highly ordered in space, and they occupy a specific area and hardly change their positions. However, in the liquid state, molecules are free to move from place to place though they still have enough attractive force to bond to one another. In the gas state molecules are free to move. They do not have enough attractive force to bond to one another and they do not have any order. Interestingly enough in the liquid crystal phase molecules are aligned in some sense. They have both a short-range order as well as a long range order because they attract one another. They are bound together, however, their movements are not restricted. This is the very reason why they are called liquid crystals. They seem to exist in a phase between a liquid and a crystal state.

From **[Fig 1]** we find that the liquid crystal phase is more ordered than the liquid phase, but less ordered than the solid phase. When we compare these four states of matter, it is necessary to take two things into our consideration. They are positional and orientational orders.

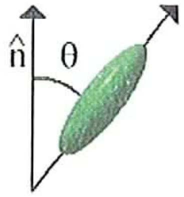
First we have to consider positional order. In both liquid and gas phases molecules do not have any positional order, which means all the molecules can travel in a random way from place to place. On the contrary in the solid (crystal) state molecules have a positional order, that is, each molecule occupies one specific position. None of the molecules in the solid state wanders around. They are strictly bound to each other, and they form either a crystalline structure or an amorphous structure. In the liquid crystal phase molecules may or may not posses a positional order. It depends on the types of liquid crystals, which will be discussed later.

The second point that we have to consider is orientational order. Orientational order is the most important property in distinguishing those four states mentioned and depicted above. In the liquid state all of the consisting molecules are seen to have random directions. Each molecule's direction does not have any relationship to one another. This is called isotropy, and we describe the liquid as isotropic. Traditionally, having isotropic characteristics indicates that measured physical and optical properties remain identical even after applying any types of electromagnetic field, such as light. Materials in the liquid phase are truly isotropic in the concept of this definition. Simply stated, we can say that all molecules travel in random directions in the liquid phase, so the directionally averaged properties show no differences with changes in directions of measurements. On the contrary, in the solid state molecules do not change their direction as shown in **[Fig 1].** In other words the molecules in the solid state are frozen to occupy specific positions in a specific direction. This is called anisotropy, the opposite of isotropy. This means the values of the measured physical properties will change according to the directions in which measurements are done. If we change the direction in which the measurement is done, the out-coming result will change. Even if we use the same technique of measurement or the same equipment, the values measured in that session of the experiment will vary. In liquid crystals molecules are a bit more flexible in their motion when compared to a solid state, but they definitely have a preferred direction. If each direction of all molecules are averaged, we can find the averaged direction of the molecules. This averaged or preferred direction is called the **director**.

Liquid crystal materials have some interesting characteristics; rod-like molecular structures, rigidness of long axis, and strong dipole and/or easily polarizable substituents. If we rotate the director exactly by 180 degrees, there is no change in physical meaning. Those two positions are considered exactly the same. If we measure dielectric constant of a material and then change the direction in which the measurement was done, the second measured value of dielectric constant will be exactly the same as the first. Like this all measured properties turn out to be the same with the 180 degrees of rotation of the sample under investigation.

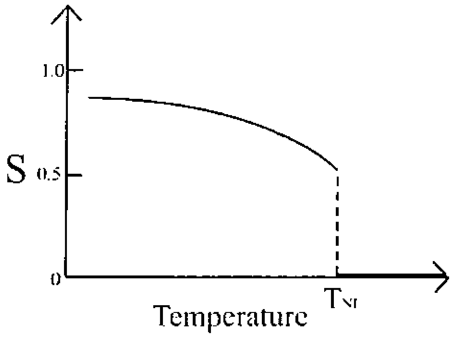
When it comes to an individual molecule of liquid crystal, it is not always in the same direction with the director because of its thermal motion. Unless the temperature reaches to the absolute zero, molecules are vibrating and rotating. There must be a deviation of each molecule's direction from the preferred direction or director. Here we can introduce an order parameter to find out how much the individual molecule deviates from the director. The simplest order parameter can be written like this. $\mathbf{S=(1/2)\langle 3\cos^2\theta-1\rangle}$, here θ is the angle between director and the long axis of each molecule which eventually means the deviation angle from director as described in **[Fig 2]**, and the brackets around **$3\cos^2\theta-1$** mean the averaged value of $3\cos^2\theta-1$. For example, if all the molecules are in the same direction with the director, θ becomes zero, thus the order parameter S becomes 1. 1 is the maximum value of order parameter and it means all of the molecules are in a totally ordered state. In other cases, order parameter always has a value less than the unity. Typical values for the order parameter of a liquid crystal range between 0.3 and 0.9.

The order parameter has a tendency to decrease when the temperature increases, because the temperature growth activates the thermal motion of the molecules, which means molecules became more random and violent in their motion. Being random is the same as being less ordered. **[Fig 3]** illustrates this dependence of the order parameter and at the phase transition point there is a distinctive jump in the value of the order parameter.



[Fig 2] A detailed feature of a single liquid crystal molecule

(This picture plus **[Fig 3]**, **[Fig 10]**, **[Fig 15]**, **[Fig 16]**, and **[Fig 17]** were quoted from http://abalone.cwru.edu. This website has the best web tutorial of liquid crystals and the concept of **chapter 1** was somewhat influenced by this tutorial.)

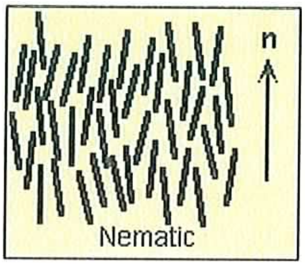


[Fig 3] The dependence of the order parameter on temperature

1.2 Classification of Liquid crystals

Liquid crystals can largely be divided into two categories, lyotropic liquid crystals and thermotropic liquid crystals. If mesomorphism occurs in a phase by the influence of thermal process, that phase can be called a thermotropic liquid crystal. Lyotropic liquid crystals can show mesomorphism under the influence of solvents, for example the concentration of the solution. As thermotropic liquid crystals rather than lyotropic liquid crystals are used in the display industry I will focus only on thermotropic liquid crystals in this thesis from now on.

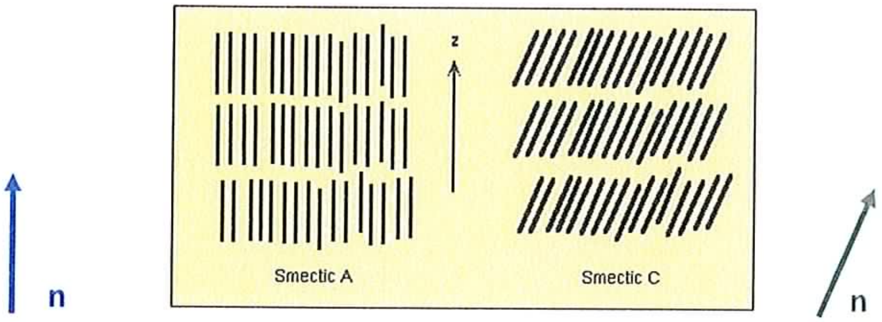
In thermotropic liquid crystals there are two main phases, nematics and smectics according to the dimensional order. Nematic liquid crystals are the dominating materials in the display industry. Most of the monitors of laptop computers are made of this, and nowadays many of HDTVs (high density televisions) are being made with this material. As a matter of fact, in the display industry nematic liquid crystal material is essential. The constituent molecules of nematic liquid crystals have orientational order but do not have positional order. Molecules can move around from place to place, but they still have orientational order. In the following picture we can imagine their features. The orientational order is designated by unit vector **n** in the picture.



[Fig 4] A schematic of nematic liquid crystal

Smectic liquid crystal materials have layers unlike nematics and they have orientational order also. Smectic liquid crystal materials can be utilized in the display devices. And they have some advantages over nematic display using nematic liquid crystals. Those advantages are: fast switching, wide viewing angle, high resolution, low price, etc. Smectic liquid crystal display also has some problems to be solved; however, despite the problems they are the most futuristic materials for the display industry. There are a lot of smectic liquid crystal materials, and new ones are being synthesized. Some of them possess positional order together with orientational order. In this report I will take a look at only three major kinds of smectic liquid crystals.

There are three representative types of smectic liquid crystals. They are smectic A (SmA), smectic C (SmC), and smectic random (SmR) phases. (For the moment I will not consider chirality, and chirality will be discussed after description of those three phases mentioned above.) In smectic A (SmA) phase molecules have orientational order, which can be indicated by a director; unit vector **n**, and they form layers among the molecules as the molecules of the other smectic liquid crystals do. In every single layer molecules can travel around, but between the layers there is no pass through of molecules. In other words, molecules are constrained in one layer; however, they can move from one place to another in that layer. This is why smectic liquid crystals are called two-dimensional liquid. If we consider a liquid, for example, water, the molecules feel free to move in any direction (x, y and z direction in Cartesian coordinate system); this is a three-dimensional liquid. However if we put smectic liquid crystal molecules in Cartesian coordinate, the molecules can move in just two directions (say x and y direction), so we can call smectic liquid crystals two-dimensional liquids or they can be called 1-dimensional solids. In the following picture the left side is a schematic of a smectic A phase.



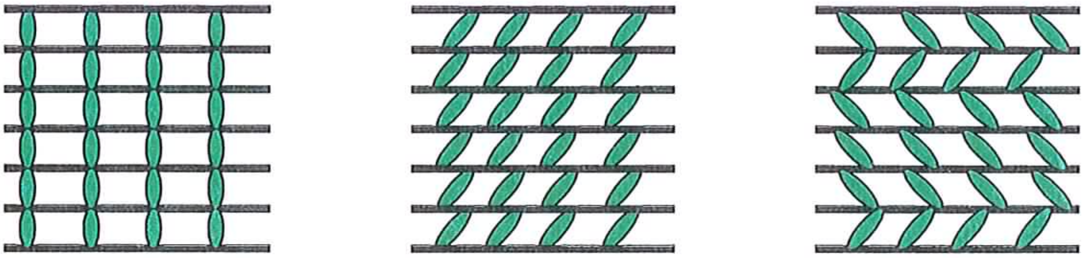
[Fig 5] Pictures of two smectic liquid crystal structures

(From the left pictures represent smectic A and smectic C, respectively.)

Smectic C phase has a similar look compared to smectic A. Most of the out looking features are very similar except in smectic C phase all the molecules are tilted away from normal vector (**z** unit vector) with a certain degree. The normal vector is a vector, which is normal to the layers. In **[Fig 5]** there are two directors. The blue colored director, which is a director of smectic A, is located in the same direction as the layer normal vector **z**. However, if we look at the direction of the green colored director of smectic C, the layer normal vector **z** and the director are not in the same direction any more. The angle between the two unit vectors (layer normal vector and director) is called the tilt angle, and the tilt angle is one of the most basic and important parameter in investigating liquid crystals.

Smectic random phase also has layers. Molecules in the layers are oriented in a preferred direction, but the preferred direction differs from layer to layer without any correlations among layers. That is why people call them smectic random phases. Therefore in smectic random category, there are lots of smectic random phases.

As a summary of smectic liquid crystal phases, here follows a simplified picture.

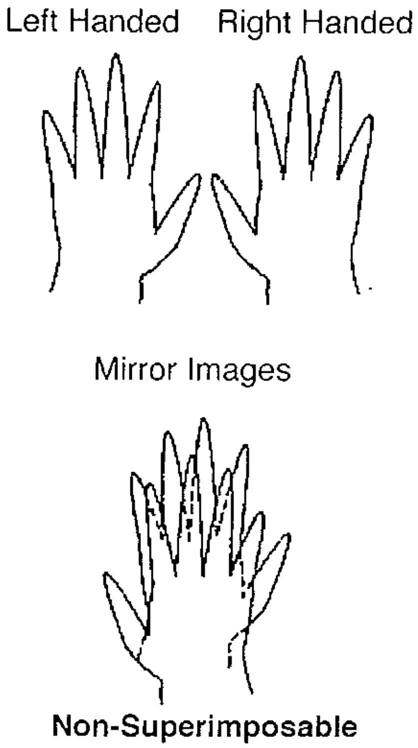


[Fig.6] Smectic phases

(Smectic A, Smectic C, and Smectic Random from the left. In SmA phase the molecules are stacked in a vertical way to the layers, in SmC phase molecules are stacked with a tilt but in one direction, and in Smectic random phase molecules are stacked with a tilt but the direction of tile varies randomly from layer to layer.)

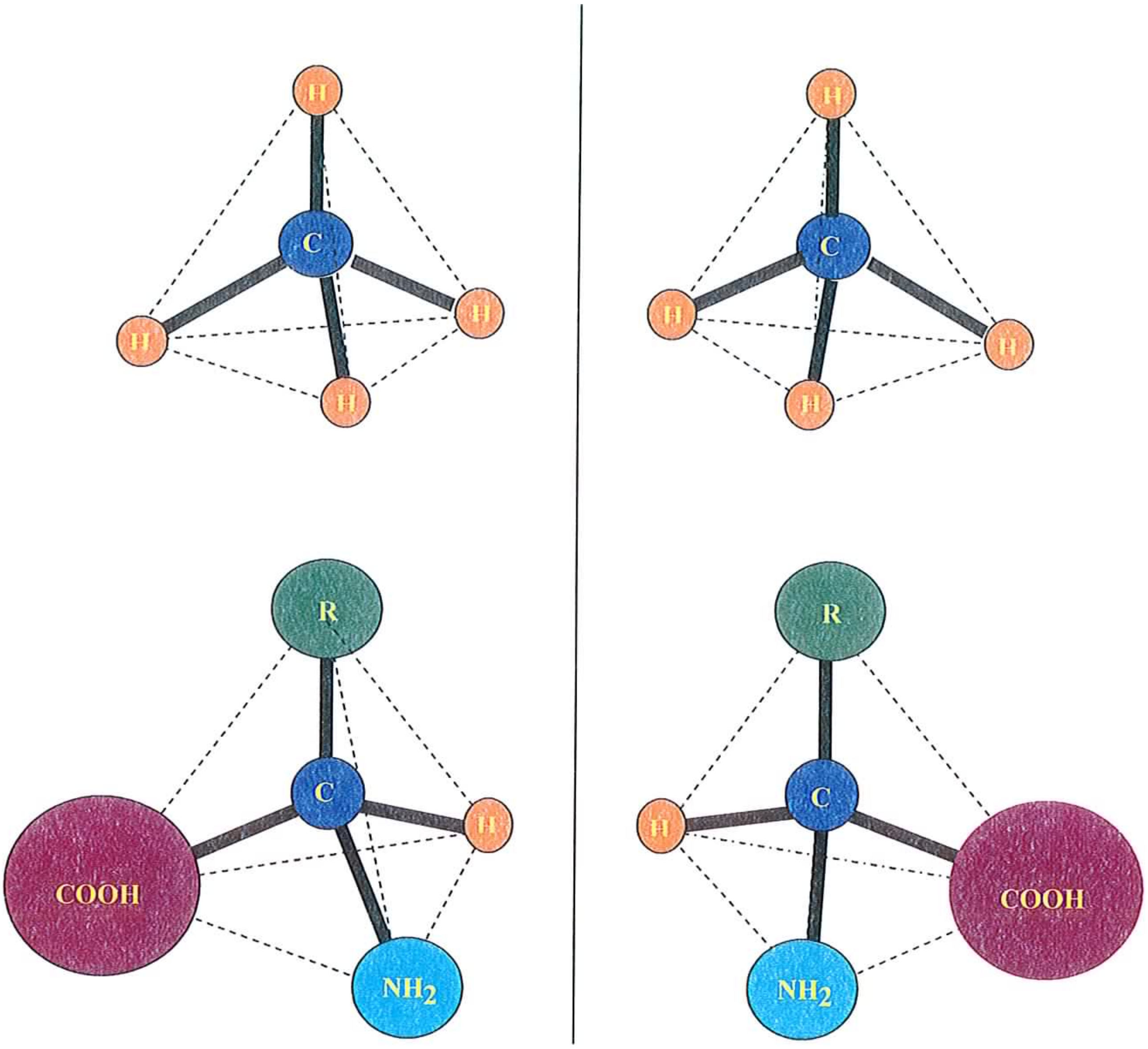
Now it is time to consider chirality [2]. Chirality means ‘handedness’. When we take a look at the image of our hand – one of either side can be an example -

reflected in the mirror we can find that the image and our real hand cannot be superimposed. In that case we say our hand is chiral.



[Fig 7] Picture of our hand and its mirror image

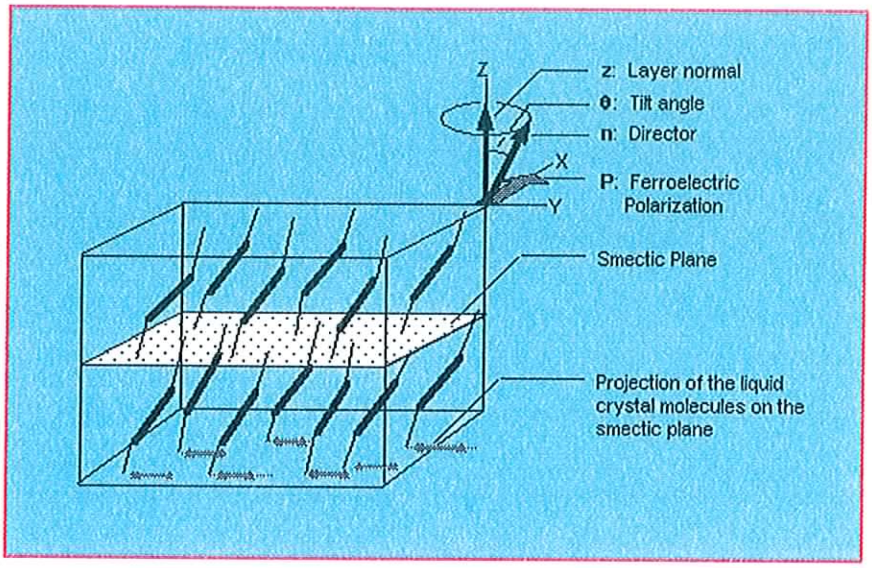
Here follows a good example in the next page explaining chirality with a sample of chemical structures of simple molecules.



[Fig. 8] Two different molecules and their mirror images

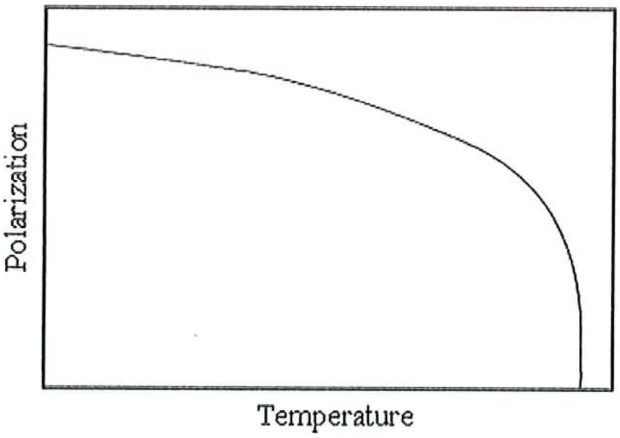
In **[Fig 8]** there are two different molecules. In this figure ‘R’ means any alkyl group. The first molecule is methane, and it is exactly tetrahedral. Every single distance from the central atom carbon to each of hydrogen is the same. As we can easily see it is possible to superimpose methane molecule and its mirror image. On the contrary when we see the second molecules in the figure even if we rotate the image we cannot superimpose the molecule and its mirror image.

If the molecules of liquid crystals are chiral, they have a spontaneous polarization with them. The spontaneous polarization is caused because of the difference of electronegativity of the molecule’s constituent atoms. Spontaneous polarization is one of the most important features of liquid crystals and more explanations of the spontaneous polarization will be discussed in the following section. Measuring spontaneous polarization can be found in some papers, for example reference [3], [4], [5], and [6]. In these cases we can represent the chirality by * right after their names. For example, if a certain smectic C phase consists of chiral molecules, we can write Sm C^* instead of Sm C. In **[Fig 9]** director, layer normal, tilt angle, and spontaneous polarization can be seen together. The phase in the picture is smectic C^* phase.

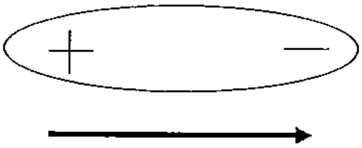


[Fig 9] Geometry of a simplified smectic C^* phase

The spontaneous polarization has a dependence on temperature. If the temperature is increased, the spontaneous polarization is decreased. The following picture (**[Fig 10]**) summarizes the feature of spontaneous polarization under temperature changes.



[Fig 10] Temperature dependence of spontaneous polarization

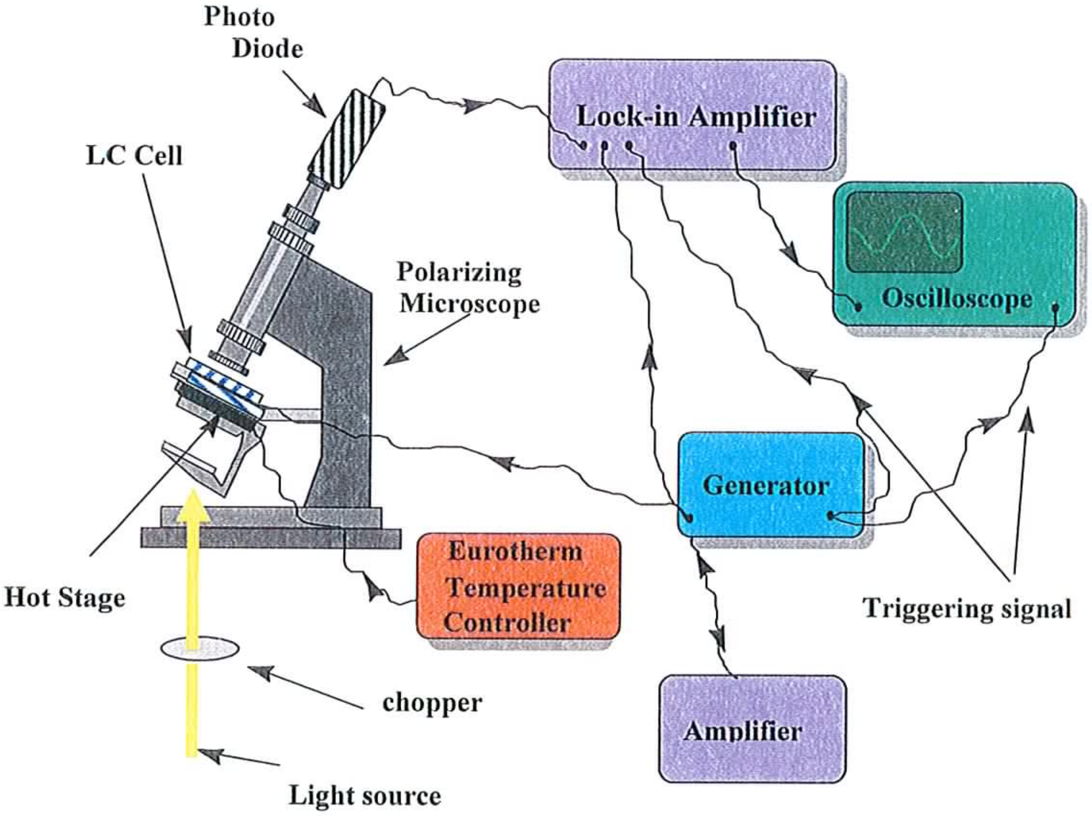


[Fig 11] Spontaneous polarization and applied electric firld

The direction of spontaneous polarization changes along with electric field. Spontaneous polarization is designated by an arrow. If you apply electric field, the direction of the spontaneous polarization will follow the same direction of applied electric field. This phenomenon is an important fact in electro-optic measurement. We have to consider simple optics concerned with polarizers together with this phenomenon to see an interesting electro-optic effect in liquid crystals, which has been the major part of our research. In the experiments, I investigated the behaviors of liquid crystals under the change of frequency and amplitude of electric field. In **chapter 2.1 Making a Network of Experimental Devices** more details will be discussed.

Chapter 2

Making a Network of Experimental Devices



[Fig 12] Schematic picture of experimental setup

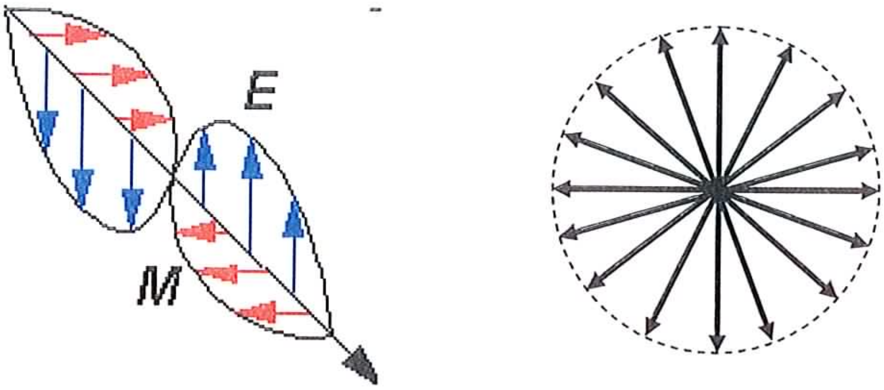
The powerful method of measuring properties of liquid crystals is dielectric spectroscopy. By using dielectric spectrometer we can get some useful information such as dielectric constants [7], relaxation time, etc. These parameters, their temperature, and electric field dependence can be used to characterize microscopic properties of the materials under investigation as well as their structural arrangement. However, for liquid crystal materials such as dendrimers dielectric spectroscopy was not successful. There can be some reasons for these unsuccessful results. The problems existing here can be high conductivity / high density of the sample or the size of the LC molecules. An experimental setup to overcome the weak points of the dielectric spectroscopy was designed by Dr. Yuri Panarin and after a couple of months of hard work finally I could establish the optoelectronic experimental setup. **[Fig 12]** is the schematic of the optoelectronic experimental device network. As can be seen easily this setup is composed of eight main devices. They are a polarized microscope, photodiode, lock-in amplifier, temperature controller, generator, oscilloscope, amplifier, and choppers. The unique function of every single device will be explained in the following chapter.

2.1 Making a Network of Experimental Devices

2.1.1 Polarized Microscope

A polarized microscope is definitely the most important device in any experiment concerned with an investigation on the properties of liquid crystal as birefringent materials. The very unique feature of the polarized microscope is that there are two polarizers usually crossed by 90 degrees to one another. We can examine the phase changes or polymorphism from the figures appearing in the polarized microscope visually, and we can also identify phase transition temperature by investigating the textures of the liquid crystals from the microscope. To understand more of how the polarized microscope works in reality I delightfully introduce the simple and basic optics.

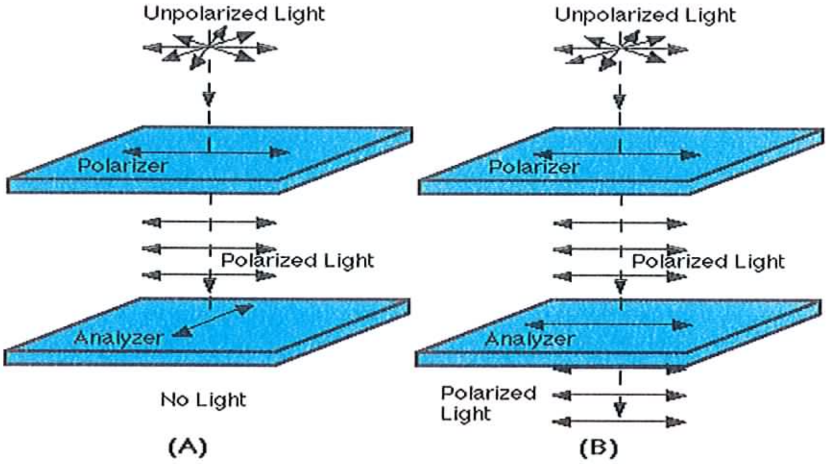
Light is composed of two vector quantities. One is the electric field vector and the other is the magnetic field vector. Those two vector components are orthogonal to each other, and both also make exactly 90 degrees angle to the direction of the light's propagation. This conformation is depicted in **[Fig 13]**. In the research I only consider the electric field component because the magnetic field component is essentially the same.



[Fig 13] Schematic of an electromagnetic wave

(In the left side, the blue arrows represent electric field (E) and the red arrows represent magnetic field (M). One big black arrow represents the direction of the light's propagation. The right side picture is taken when we see the light in the propagation direction. The thin black lines indicate electric field and/or magnetic field.)

Ordinary white light is made up of a number of waves that fluctuate at all possible angles (See the right side picture in **[Fig 13]**.). Light is considered to be linearly polarized when it contains waves that fluctuate only in one specific plane. It is as if the rope is strung through a picket fence - the wave can move up and down, but motion is blocked in any other direction. A polarizer is a material that allows only light with a specific angle of vibration to pass through. The direction of fluctuation passed by the polarizer is called the 'easy axis'. After the light has passed the first polarizer, it has only one directional component fluctuating with a specific angle, which is the same as the angle of the polarizer. When the light then comes to the second polarizer (crossed by 90 degrees to the first polarizer) none of the light components can pass through it. This simple optical phenomenon is sketched in the following picture.

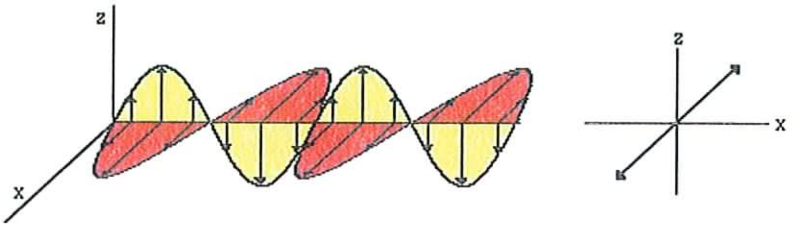


[Fig 14] Simple interpretation of the phenomenon between the two polarizers (Light enters from the top of this picture and passes the first polarizer, and then the second polarizer (it is often called an analyzer.). In case (A) none of the light's components can survive after passing those two polarizers so the image, which can be obtained after the analyzer, is absolutely black. In case (B) two polarizers are in the same direction (they are not crossed at all), so the very specific component of the light which are in the same direction of the polarizers can survive even after passing through the analyzer and we can see a bright image.)

If we put liquid type materials between the two crossed polarizers, there would be no change of the phenomenon treated above because liquid has nothing to do with the change of the state of the light's polarization. However if we put some novel crystalline materials between those two crossed polarizers, very interestingly enough, some components of the light can survive even after passing both polarizers crossed by 90 degrees. That means there must be a change of the state of the light's polarization. It has been believed that only solid materials can exist in crystalline form, but some extraordinary liquid-like materials were found to exist forming crystalline structures, so the name liquid crystals were given to those materials.

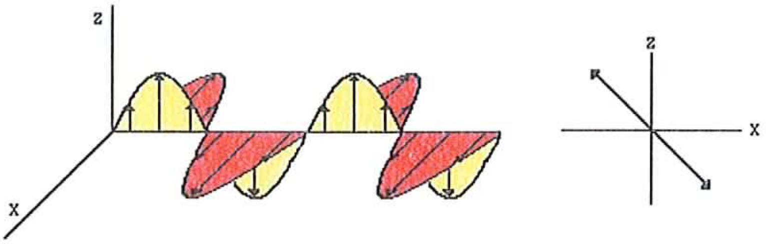
To make a short description of how the crossed polarized microscope works, let us take a look at **[Fig 14]** with this paragraph. If the director of the liquid crystal material is in the same direction of the first polarizer, there will be no change caused by putting the liquid crystal material between the two polarizers. This is because all components of the light passed the first polarizer will be blocked by the second polarizer (analyzer). However, if the director is not in the same direction of the first polarizer there must be some components which are not exactly linearly polarized in the direction of the first polarizer. Some of those components will finally survive after passing through the second polarizer (analyzer).

Linear polarization is merely a special case of circularly polarized light. Consider two light waves, one polarized in the YZ plane and the other in the XY plane. If the waves reach their maximum and minimum points at the same time (People usually say that those two different waves are in phase), their vector sum leads to one wave, linearly polarized at 45 degrees. This is shown in the following diagram.



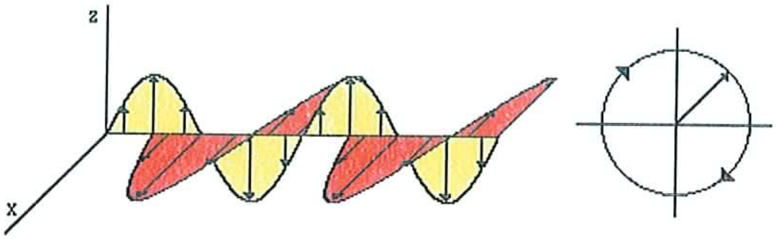
[Fig 15] Two light waves in phase

Similarly, if the two waves are 180 degrees out of phase, the resultant is linearly polarized at 45 degrees in the opposite sense.



[Fig 16] Two light waves out of phase by 180 degrees

If the two waves are 90 degrees out of phase (one is at an extremum and the other is at zero), the resulting wave is circularly polarized. In effect, the resultant electric field vector from the sum of the components rotates around the origin as the wave propagates. The following diagram shows the sum of the electric field vectors for two such waves.



[Fig 17] Two light wave out of phase by 90 degrees

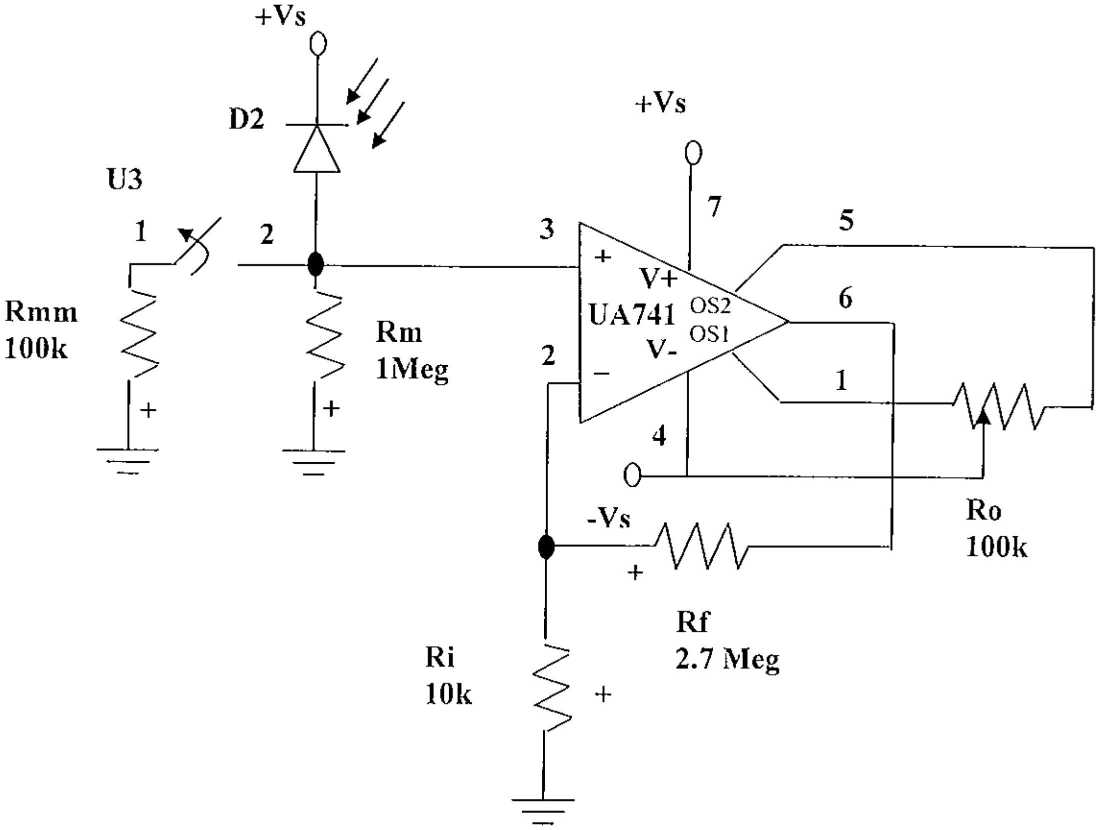
The most general case is when the phase difference is at an arbitrary angle (not necessarily 90 or 180 degrees.). This is called elliptical polarization because the electric field vector traces out an ellipse (instead of a line or circle as before.) [8].

The crossed angle between the two polarizers can be changed by rotating one of either polarizer. Usually the angle is fixed by 90 degrees, but sometimes changing of the angle between the two polarizers is needed to find out what the structure of the liquid crystal cell looks like.

A sample, which contains liquid crystal material, is placed in the hot-stage mounted on the crossed polarized microscope. The table on which the hot-stage is mounted can be rotated by hand. By rotating the table we can find tilt angle of the liquid crystal sample. This will be discussed in **chapter 2.1.1 Tilt Angle Measurement** section.

2.1.2 Photodiode

Photodiode is attached to the top of the polarized microscope where passed light comes out. The light from the illuminating source passes through the two polarizers in the microscope and then arrives at the photodiode. The function of the photodiode is to change the optical signal into the electrical signal. The converted electric signal is proportional to the intensity of the light. The more light passes, the higher the electric signal will be. Finally the converted electric signal leaves the photodiode and then enters the lock-in amplifier. I made the circuit of the photodiode manually from a circuit diagram.



[Fig 18] Circuit Diagram of the photodiode

2.1.3 Lock-In Amplifier

The electric signals from the photodiode enter the lock-in amplifier, and the lock-in amplifier shows the value of the electric signals. It usually displays in a small window in units of mV. Another important information given by the lock-in amplifier is the phase difference between the originally applied electric field and the electric signal from the sample. For better understanding of how it works, refer to text from the manual of the lock-in amplifier.

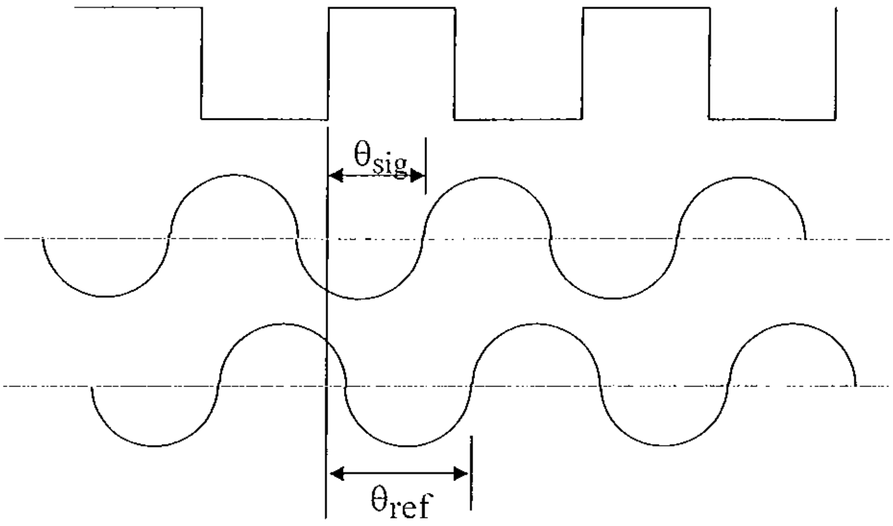
> *Lock-in amplifiers are used to detect and measure very small AC signals – all the way down to a few nanovolts. Accurate measurements may be made even when the small signal is obscured by noise sources many thousands of times larger.*
>
> *Lock-in amplifiers use a technique known as phase-sensitive detection to single out the component of the signal at a specific reference frequency AND phase. Noise signals at frequencies other than the reference frequency are rejected and go not affect the measurement.*
>
> *Let's consider an example. Suppose the signal is a 10 nV sine wave at 10 kHz. Clearly some amplification is required. A good low noise amplifier will have about 5* $\mathrm{nV}/\sqrt{\mathrm{Hz}}$ *of input noise. If the amplifier bandwidth is 100 kHz and the gain is 1000, then we can expect our output to be* $10\mu\mathrm{V}$ *of signal (1o nV × 1000) and 1.6 mV of broadband noise (*$5\ \mathrm{nV}/\sqrt{\mathrm{Hz}} \times \sqrt{100\ \mathrm{kHz}} \times 1000$*). We won't have much luck measuring the output signal unless we single out the frequency of interest.*

If we follow the amplifier with a band pass filter with a Q=100 (a VERY good filter) centered at 10 kHz, any signal in a 100 Hz bandwidth will be detected (10 kHz/Q). The noise in the filter pass band will be 50 μV (5 nV/$\sqrt{Hz}$ × $\sqrt{100}$ Hz × 1000) and the signal will still be 10 μV. The output noise is much greater than the signal and an accurate measurement cannot be made. Further gain will not help the signal to noise problem.

Now try following the amplifier with a phase-sensitive detector (PSD). The PSD can detect the signal at 10 kHz with a bandwidth as narrow as 0.01 Hz. In this case, the noise in the detection bandwidth will be only 0.5 μV (5 nV/$\sqrt{Hz}$ × $\sqrt{0.1}$ Hz × 1000) while the signal is still 10 μV. The signal to noise ratio is now 20 and an accurate measurement is possible.

Lock-in measurements require a frequency reference. Typically an experiment is excited at a fixed frequency (from an oscillator or function generator) and the lock-in detects the response from the experiment at the reference frequency. In the diagram below, the reference signal is a square wave at frequency ω_r. This might be the sync output from a function generator. If the sine output from the function generator is used to excite the experiment, the response might be the signal waveform shown below. The signal is $V_{sig}\sin(\omega_r t + \theta_{sig})$ where V_{sig} is the signal amplitude.

The SR830 generates its own sine wave, shown as the lock-in reference below. The lock-in reference is $V_L\sin(\omega_r t + \theta_{ref})$.



[Fig 19] A diagram of a reference and signal wave used in the lock-in amplifier

The SR830 amplifies the signal and then multiplies it by the lock-in reference using a phase-sensitive detector or multiplier. The output of the PSD is simply the product of two sine waves.

$$V_{psd} = V_{sig}V_L \sin(\omega_r t + \theta_{sig}) \sin(\omega_L t + \theta_{ref})$$

$$= \tfrac{1}{2} V_{sig}V_L \cos([\omega_r - \omega_L]\, t + \theta_{sig} - \theta_{ref}) -$$

$$\tfrac{1}{2} V_{sig}V_L \cos([\omega_r + \omega_L]\, t + \theta_{sig} - \theta_{ref})$$

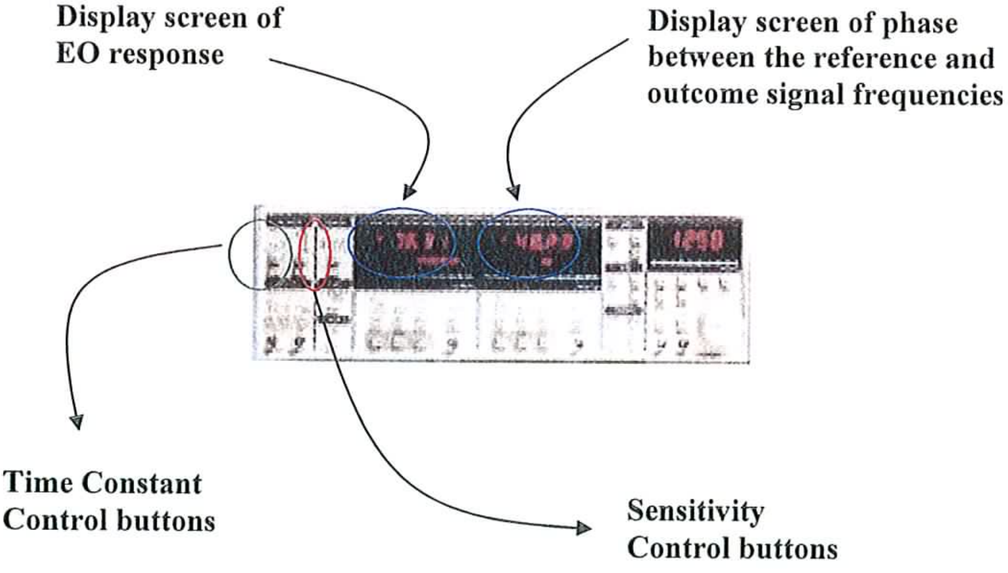
The PSD output is two AC signals, one at the difference frequency ($\omega_r - \omega_L$) and the other at the sum frequency ($\omega_r + \omega_L$).

If the PSD output is passed through a low pass filter, the AC signals are removed. What will be left? In the general case, nothing. However, if ω_r equals ω_L, the difference frequency component will be a DC signal. In this case, the filtered PSD output will be

$$V_{psd} = \tfrac{1}{2} V_{sig} V_L \cos(\theta_{sig} - \theta_{ref})$$

This is a very nice signal – it is a DC signal proportional to the signal amplitude.

A picture of the real lock-in amplifier follows next.



[Fig 20] Picture of the lock-in Amplifier
(SR830 model from SRS, Stanford Research Systems)

2.1.4 Temperature Controller

The temperature controller is connected to the hot stage, which is mounted on the table for liquid crystal cell on microscope, and the temperature of the hot stage is governed by the temperature controller. It can control the temperature with an accuracy of $0.1^{o}C$ from $0\ ^{o}C$ to $200\ ^{o}C$ (In order to go below room temperature a special attachment with liquid nitrogen facilities has to be mounted.). Once the temperature is set by the controller it is very stable during every session of experiments. The controller used in our experiment is Eurotherm 2216e.

2.1.5 Generator

The generator used in this optoelectronic experimental setup is the same one as usually used in normal electronic laboratories. It can apply an electric field to the small sample cell under investigation. In the experiment two main properties of the electric field can be varied. One is the frequency of the electric field and the other is the amplitude of the electric field. The frequency range varies from 0.2 Hz to 100,000 Hz. The cell is made up with two glasses coated with Indium Tin Oxide (ITO) conduction layer, which acts as an electrode. The cell is connected to the generator by wires and the electric field from the generator is applied to the cell. We can change the form of the waves applied to the liquid crystal cell; they are square wave, sinusoidal wave, and triangular wave. The generator used in this work is a 33120A from Agilent.

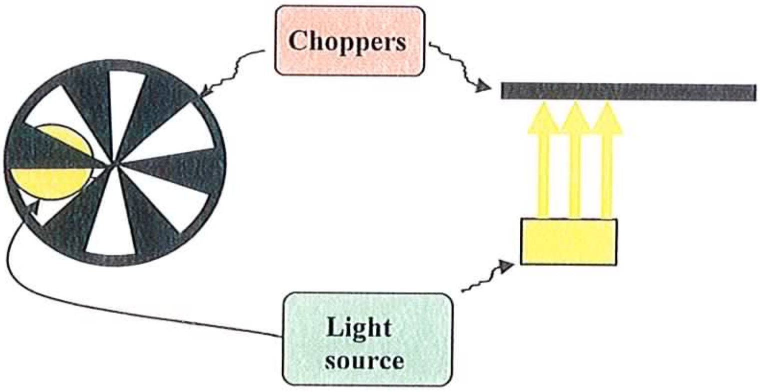
2.1.6 Amplifier

A simple amplifier is connected to the generator. The function of the amplifier is the same as the usual amplifiers. It magnifies the amplitude of the electric field from the generator. I also designed an amplifier with a draft of the circuit and the substantial amplitude (with amplification coefficient of 20) of the electric field is from 0.1 mV to 200 V.

2.1.7 Oscilloscope

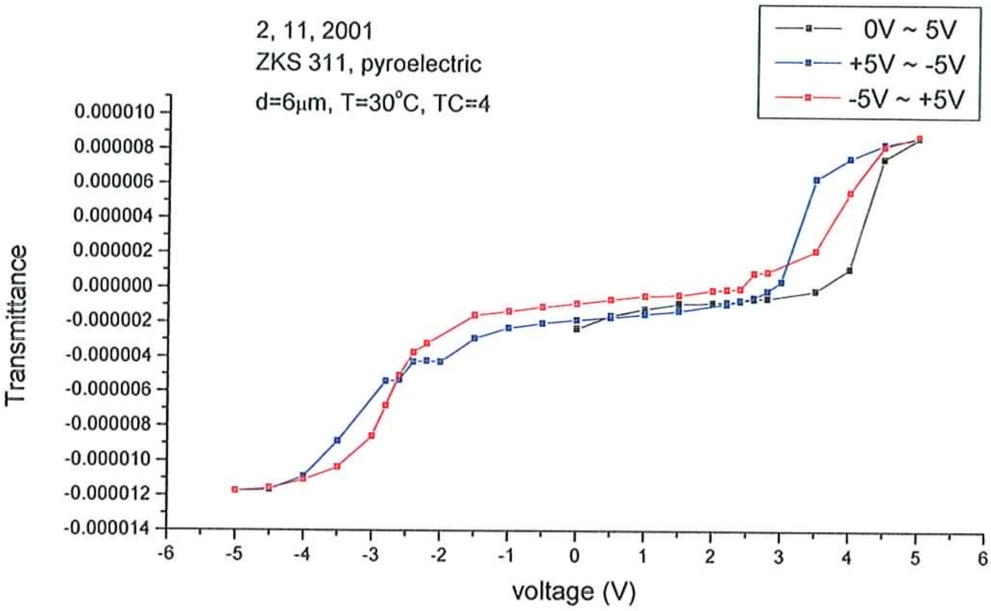
All signals are displayed in the window of the oscilloscope and from the distinctive oscillograms we can easily find what is going on during the session of the experiments. A 54603B from Hewlett Packard was used.

2.1.8 Choppers



[Fig 21] A rough sketch of the choppers
(The left is a view seen from the top and the right is a view from the lateral.)

Choppers rotate regularly with a specific frequency, which is made to vary by a controller. They block and unblock the light repeatedly. This device can be used for measuring small signals, for example, pyroelectrics. The repetitions of blocking and unblocking the light cause a little change of the temperature; light is a source of heating rather than an optical source. Pyroelectrics are so sensitive to the temperature changes that they can respond to those changes easily. This setup will be used for the further investigation and a result of the test experiment is shown below.



[Fig 22] A graph showing hysteresys of pyroelectric material

2.1.9 Automation of the Experimental Setup

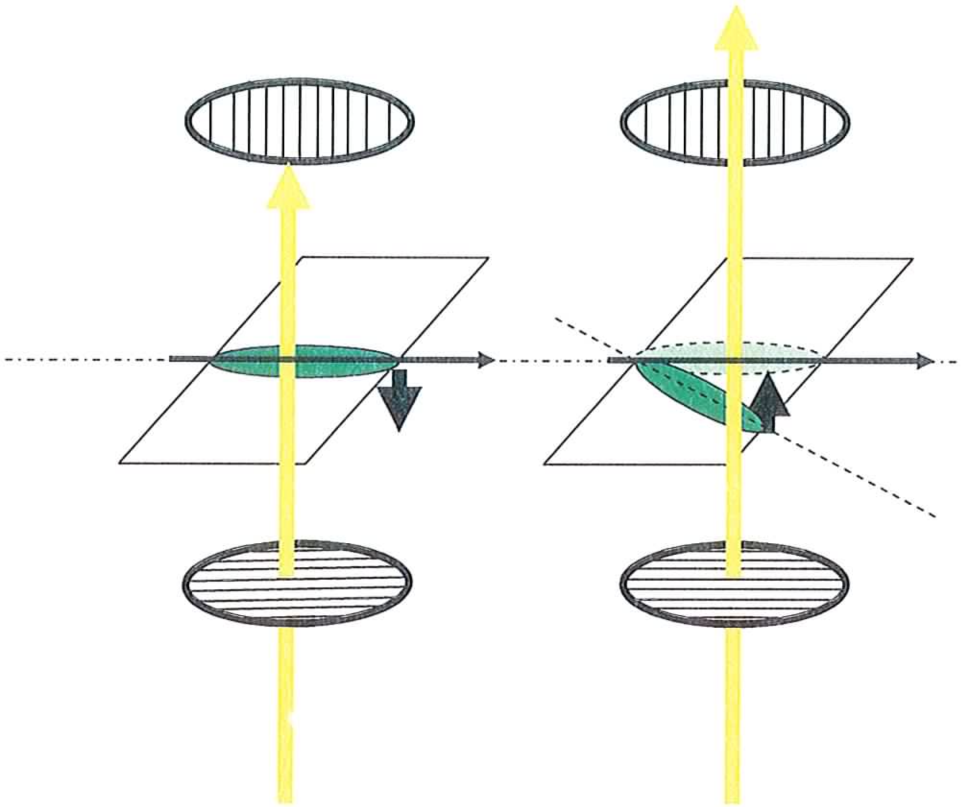
All devices are virtually connected to the computer and a program in Visual Basic to control the devices was developed with Dr. Yuri Panarin's help. We can change any properties generated from any devices by that program, and we can also design a long period time-consuming experiment by just adjusting some parameters used in the program. This automation of the experimental setup saved unnecessary time and effort.

2.2 Measuring Techniques

2.2.1 Tilt Angle Measurement

Tilt angle is one of the most basic information of liquid crystal materials structure. Tilt angle is defined as an angle between the layer normal vector and the director, which is the averaged direction of all molecules. It is explained in **Chapter 1.1** and the picture of the geometric structure is depicted in **[Fig 2]**. By measuring the tilt angles we can understand how much the molecules are tilted away from the layer normal vector, and this understanding is somewhat important in the point that tilt angles can show directly or indirectly that there is a phase change. For example, the tilt angles have something to do with the layer thickness. If the tilt angle grows large, that means the layer thickness gets smaller. Layer shrinkage happens. It is easily understood if we take a short look at the **[Fig 6]**. In the opposite case, if the tilt angle becomes smaller, that indicates the layer thickness gets bigger. Let us consider a phase transition from the smectic C to the smectic A. It is usually done by cooling down the liquid crystal material. As we understand and discussed so far, in the smectic C phase molecules are aligned in one preferred direction, which is called director with a tilt from the layer normal vector. On the contrary, in smectic A phase all molecules are aligned along the same direction of the layer normal and perpendicular to the smectic layers. In short, they have two different tilt angles before and after the phase transition. Because of this difference it is possible to find out when and under what conditions this phase transition is happening by simply measuring the difference of the tilt angles.

By applying the electric field two configurations of the molecules can be obtained. As shown already in **Chapter 1.2** (**[Fig 11]**) in chiral liquid crystal phases all molecules have to follow the direction along which the electric field is applied. Usual generators used in most electronic experiment generate an oscillating voltage, for example, sinusoidal wave, square wave, etc. When the direction of the applied electric field changes, molecules also change their directions according to the fact given in **[Fig 11]**. The basic features are sketched in the following picture.

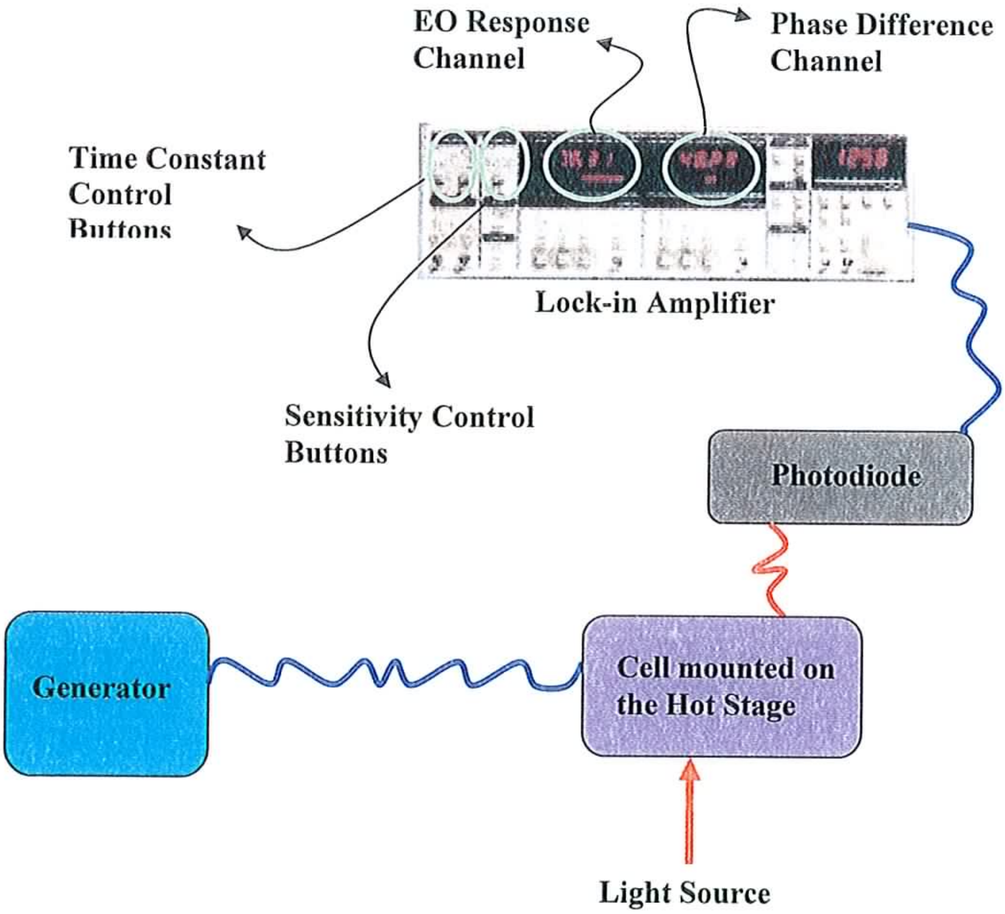

a) b)

[Fig 23] Change of director under external oscillating electric field

Picture a) represents the state when positive voltage is applied and b) represents the state when negative voltage is applied. Short black arrows indicate the spontaneous polarization of the molecules and it changes the direction when the sign of the applied electric field changes. Hence the molecules have to change their positions. Long black arrows represent layer normal vector.

2.2.2 Relaxation Time Measurement

In this section how to measure relaxation time will be discussed using the electro-optic technique. Here a short explanation about how to get an electro-optic response from the liquid crystal cell is presented. Other devices involved in the setup were discussed throughout **chapter 2.1.1** to **chapter 2.1.8**.



[Fig 24] Schematic of a set of devices presenting what “electro-optic” means

The technique employs two devices, which are worth additional mention. They are photodiode and lock-in amplifier. As the name "Electro-optic" suggests, there are two signals: electric signal and optical signal. In **[Fig 24]** the orange line means optical signal, and the blue line means electric signal. The unique function of the photodiode is changing the properties of the signals. In this case the photodiode changes optical signal from the light source into electric signal. The more the light source illuminates, the bigger the signal from the photodiode. The circuit diagram is included in **chapter 2.1.2**.

The converted electric signal from the photodiode goes into the lock-in amplifier. In this setup SR830 model from SRS (Stanford Research Systems) was used. The powerful function of the lock-in amplifier is that it can catch small signals out of big noises efficiently. When we suppose that the important signal, which we have to catch, is small, but the noise is comparatively big, it is hard or even impossible to catch that small signal which has an important meaning in that session of the experiment out of the noise.

When the signal gets into the lock-in amplifier computer store the information received from the lock-in amplifier as a data file. Using Origin program a plot of electro-optic signal versus frequency can be obtained. After making a plot Cole-Cole equation was used to fit the data and finally to get relaxation time τ.

$$u(\omega)=\sum_{i=1}^{2}\frac{u_i}{(1+j\omega\tau_i)^{\alpha_i}}+u_\infty$$

Here u_i and τ_i are an amplitude and relaxation time of *i-th* relaxation process and u_∞ is offset. Following the procedure described above the relaxation time could be determined.

2.3 Cell Preparation

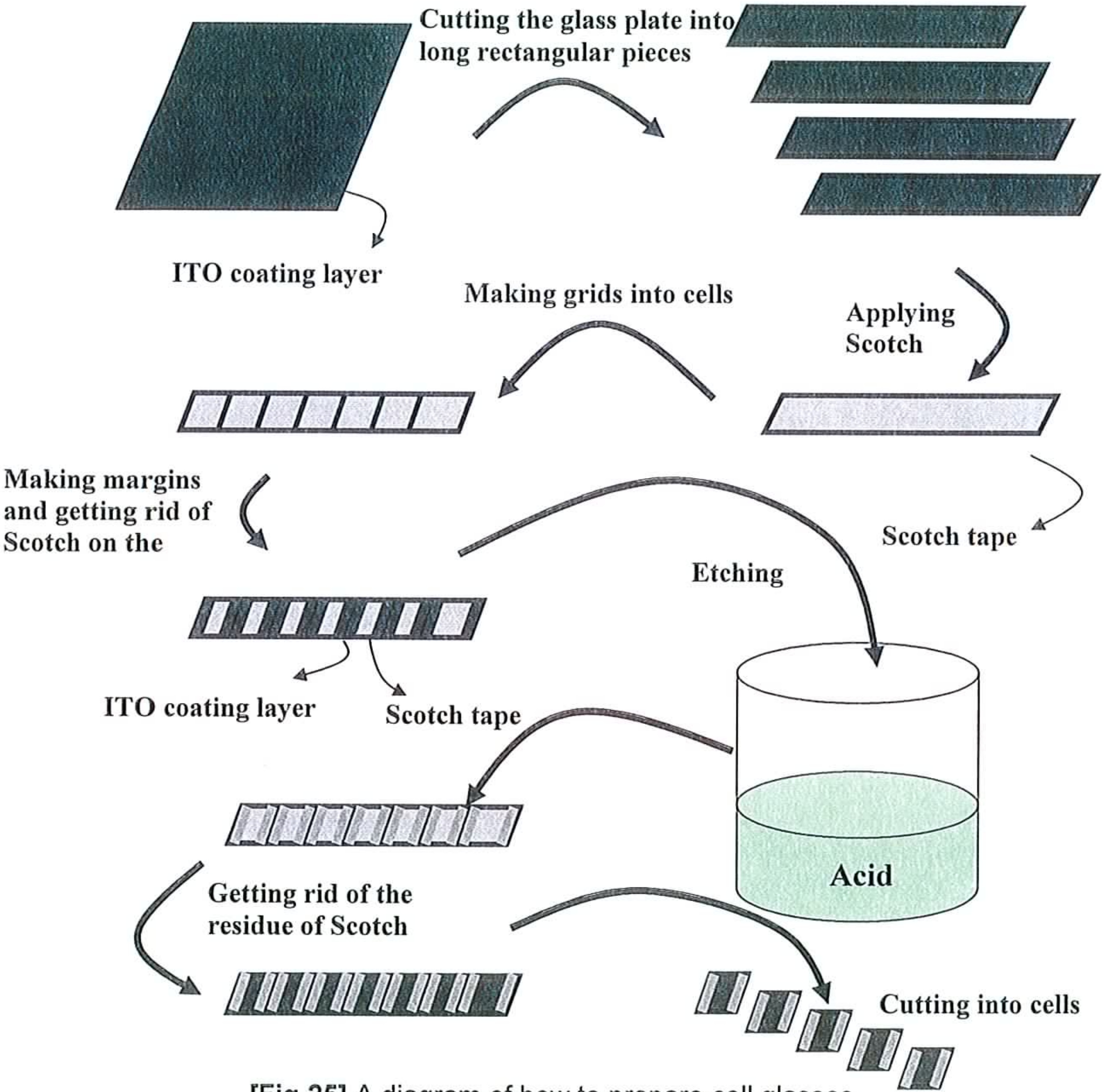
To make a liquid crystal cell several things are needde: 1. two glass slides coated with Indium Tin Oxide (ITO), 2. Scotch tape and cutter, 3. weak acid, 4. rubbing rod, 5. spin coating device, 6. polymer material for coating. 7. liquid crystal material and spacers, 8. glue, solder, etc. Items 1 to 6 are used in **chapter 2.3.1 Preparing Two Glass Slides** and items 6 to 8 belong to **chapter 2.3.2 Making a Cell.**

2.3.1 Preparing Two Glasses

Before cutting, a large glass plate coated with Indium Tin Oxide (ITO) was mounted on the grid paper, which helps us place and cut the glass accurately. To make two glass slides cutting the large glass using a diamond knife into many parts must be done. Along the grid line we first cut the glass into long (with one side 1 cm long) rectangular pieces. After that Scotch tape on the surface of those pieces of glass was applied. Finishing sticking Scotch tape, one piece of glass was picked up and at this time only the Scotch tape (not the glass) was cut into 1 cm by 2 cm (usual size of a liquid crystal cell glass plate) rectangles. Following the procedure I could have our own grid line on the glass, which means many cells, by the scars on Scotch tape. Making margins of 1 millimeter to each grid line have followed after that.

Only the central part of the cell is needed for conducting layer so the ITO layer on the margins of each rectangular cell was scratched off. To scratch off the ITO layer which adhered to the marginal area of each cell, the first step is taking off Scotch tape which is on the marginal area of the cell, and the next step is etching the whole long rectangular glass in a beaker filled with a weak acid.

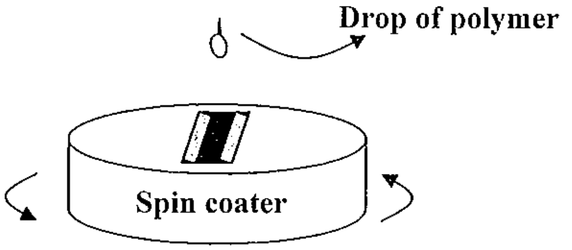
After washing off the acid residue and discharging the Scotch tape, which still remained in the central part of each cell, by cutting the glass into 1 cm by 2 cm pieces finally glass slides are prepared with ITO conducting layer only on the central part of each glass. The schematic of this procedure is depicted in **[Fig 24]**.



[Fig 25] A diagram of how to prepare cell glasses

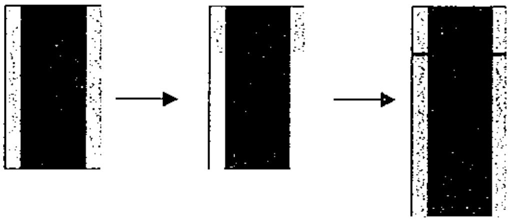
2.3.2 Making a Cell

With two pieces of glass I prepared in **chapter 2.3.1**, polymer for surface coating, spacer, solder, wire, glue, and liquid crystal material I prepared some liquid crystal cells. The detailed procedure follows with a diagram.



1. Put a piece of glass and drop some polymer on the surface of the glass.

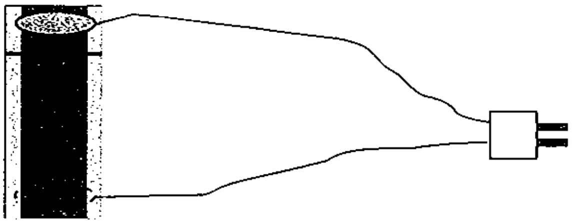
2. Coat the surface of the glass by spinning.



1. Prepare two spacers and put them on the margin of the glass.

2. Superimpose another piece of glass with 70% of the area covered by each other. (Two glasses must face their ITO coated surface.)

3. Glue two longer sides and one shorter side. (Leave one shorter side for capillary action when we put liquid crystal between two glasses.)



1. Put the liquid crystal material between the two glasses using capillary action.

2. Apply little glue at both sides of the end of the cell and solder them.

3. Connect wires with one end to the cell and the other end to a connector, which will be connected to the generator.

[Fig 26] A diagram of making a liquid crystal cell with explanation

Chapter 3

Dendrimer LC Showing Ferroelectric Properties

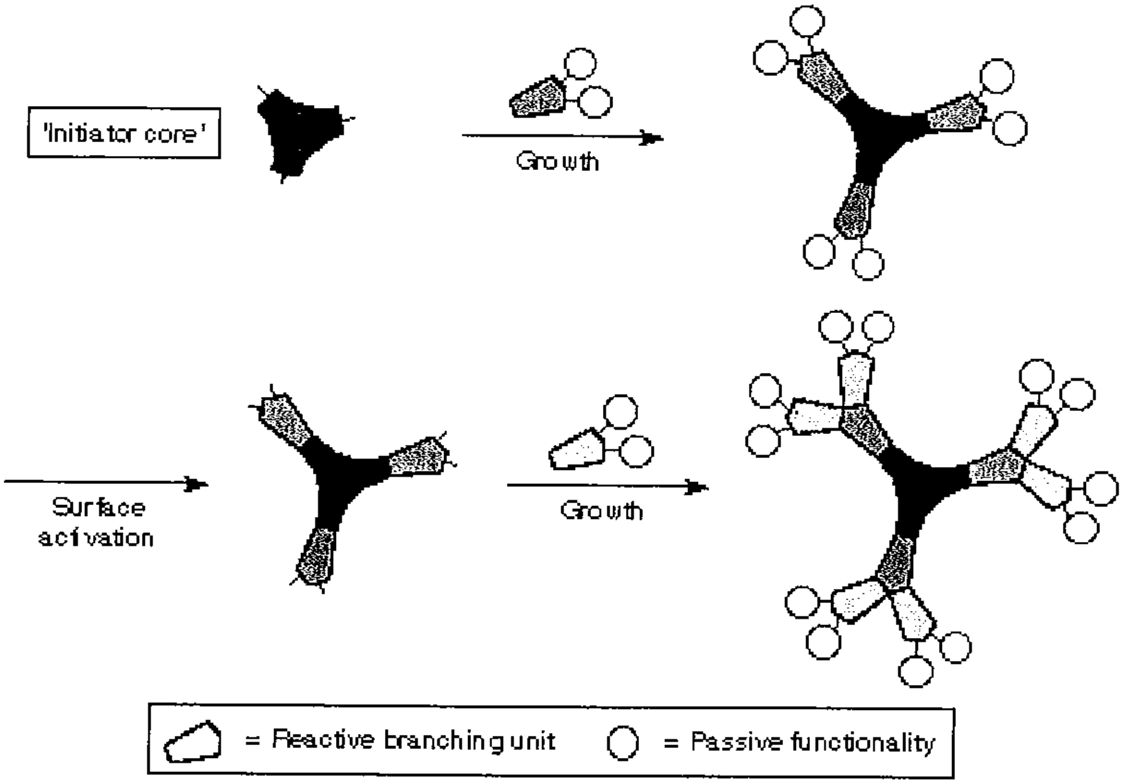
The ferroelectric properties of dendritic materials were investigated. Dendrimers themselves are quite interesting materials, and their useful applications in modern industry are no doubt attractive. Recently it is reported that dendritic materials can possibly show the properties of liquid crystals, and with the increasing scientific curiosity I investigated the properties of dendrimers, as I am sure they show ferroelectric properties.

3.1 Background of Dendrimers

The word "dendrimer" came from Greek (dendros = tree, meros = tail). It means the way of synthesizing dendrimers looks like trees are growing with branches. A good introduction to dendrimers can be found in reference [9].

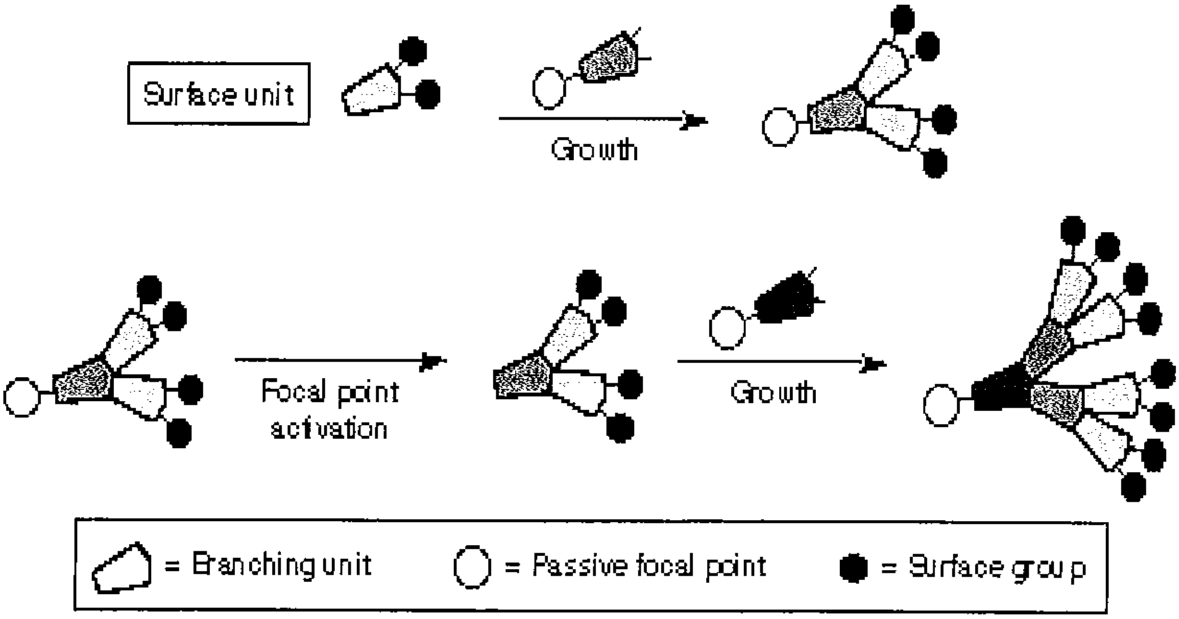
There are two main ways of synthesizing dendrimers. One is a divergent method and the other is a convergent method.

Divergent growth [10], as the name suggests, initially starts with one active core. Starting from a reactive core, a generation is grown, and then the new periphery of the molecule is activated for reaction with more monomers. The two steps can be repeated. This synthesis method has been used since the first appearance of dendrimers. Large dendritic materials can be made simply by repeating those two sessions. The weak point of this method is that incomplete generation growth and side reactions can occur during the synthesizing process, and purifying the product is somewhat difficult. However, it's popular even now because of its simplicity. **[Fig 27]** shows how divergent growth occurs in synthesizing dendrimers.



[Fig 27] Divergent synthesis of dendrimers

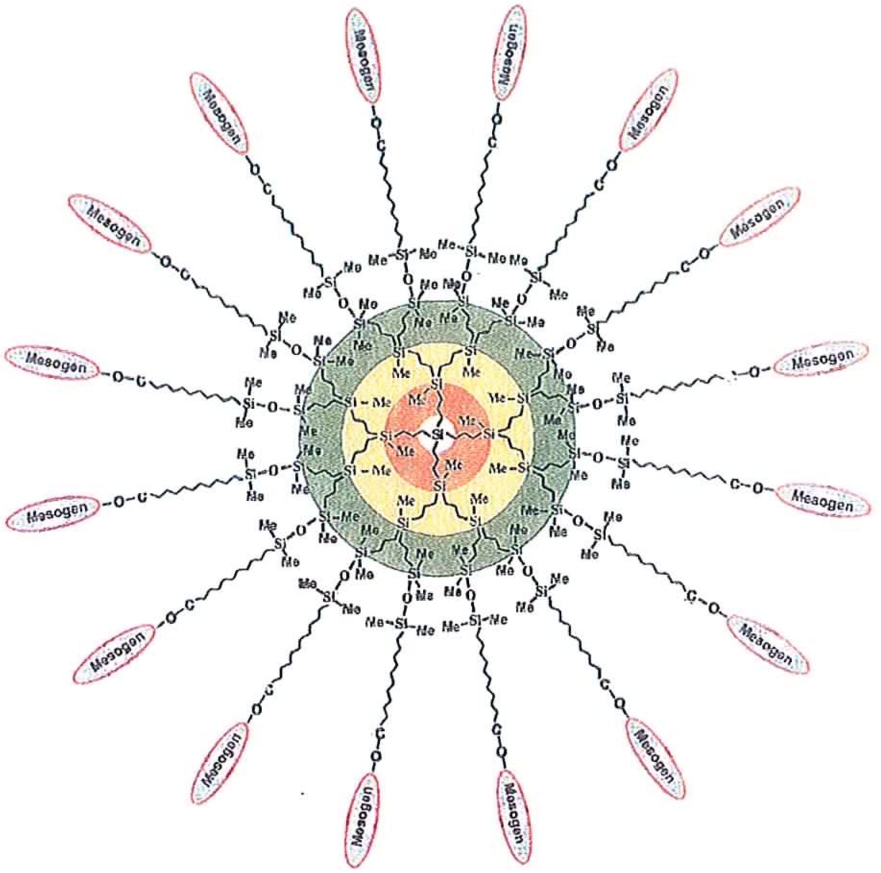
The convergent synthesizing method was developed due to the difficulty of the purification process in divergent synthesis. The procedure is totally reverse compared to divergent synthesis. It starts from the part, which will eventually be the surface of dendrimers. When the branches grow big enough, they are combined into one proper core. This method is considered to be more efficient than divergent one, because purifying the final product is easy. There are some problems using convergent synthesis also. It's not easy to make large dendrimers, and the final yield is low. **[Fig 28]** represents convergent synthesizing method for dendrimers.



[Fig 28] Convergent synthesis of dendrimers

The applications of dendrimers are various. The following lists are today's main and potential applications of dendrimers.

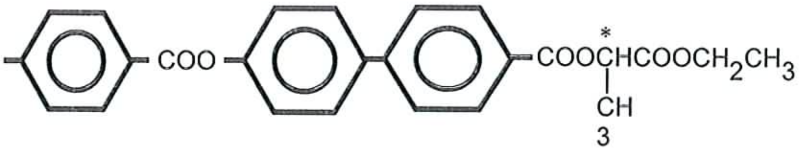
- Liquid crystal materials
- Heterogeneous catalysis
- Inks
- Immunology
- Agro chemistry
- Chemical sensor, biosensor
- Medicine (diagnosis / therapeutic agent)



n = 1, 2, 3, etc. generation number

m = 8, 16, 32 = $8 \times 2^{n-1}$ number of terminal mesogenic groups

Mesogen =



[Fig 29] A schematic of a dendritic structure
(Asterisk on the carbon atom right of this picture represents the chirality.)

The picture demonstrated above is a rough schematic of a dendritic structure. The main features of dendritic materials are the following. They are composed of two main parts, the core and their branches – structural mesogenic unit. A good example can be found in reference [11]. The core is located in the center of the molecules, and all of the branches are connected with the core part. Dendrimers have received a great interest by scientists recently, because they can possibly have a property of liquid crystalline materials ([12] and [13]), and ultimately it can be used in the display industry as a liquid crystal material.

The growth of a dendrimer is quite interesting, which is accompanied by an increase in the number of branching points. In the above picture, the orange-colored part means it has a generation number of one, that is, there has been one growth of branch. The yellow-colored and green-colored parts mean 2nd generation and 3rd generation, respectively. The bigger the generation number is the larger the molecule is.

During the investigation a series of liquid crystalline dendrimers were used with a generation number of 1, 2, 3, 4 containing 8, 16, 32, 64 terminal methoxyphenyl benzoate mesogenic groups respectively as our samples (G-1 (PBL), G-2 (PBL), G-3 (PBL)). These materials show ferroelectric properties due to the presence of chiral mesogens.

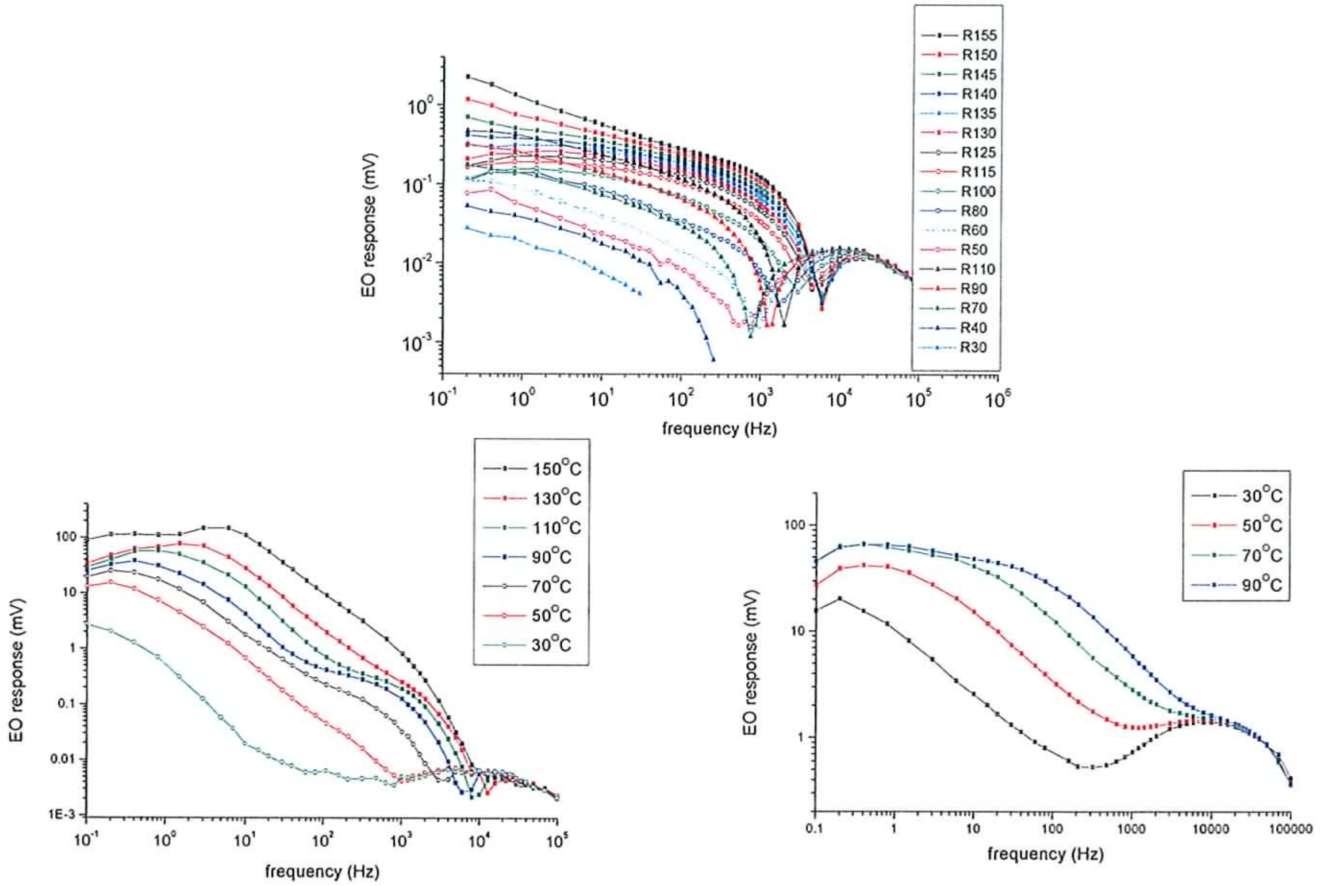
3.2 Experiments and Results

3.2.1 Alignment and Textures

The molecules of dendrimers are very large, and because of their high conductivity, and high density, it's not easy to get a good alignment of a dendrimer cell. In order to get a linear elcetro-optic response, the samples with cell thickness of 15 μm were aligned by shearing together under simultaneous application of high (100 - 200V) and low-frequency (~ 1 Hz) voltage. Two types of texture are finally found in the same cell. The first one with high electro-optic response is shown on the top part of photos in **[Fig 30]** and the other type of texture without electro-optic response (shown on the bottom part of the photos). The ratio between these two textures is considered to depend on the temperature of the sample.

[Fig 30] Pictures taken from crossed polarized microscope
((a), (b), and (c) were taken when I applied –100V, 0V, and +100V, respectively.)

3.2.2 Dependence of Electro-optic Spectra on Temperature



[Fig 31] The temperature dependence of electro-optic spectra forG-1 (PBL)$_8$, G-2 (PBL)$_{16}$, and G-3 (PBL)$_{32}$ at fixed voltages, 1V, 1V, 100V, respectively.

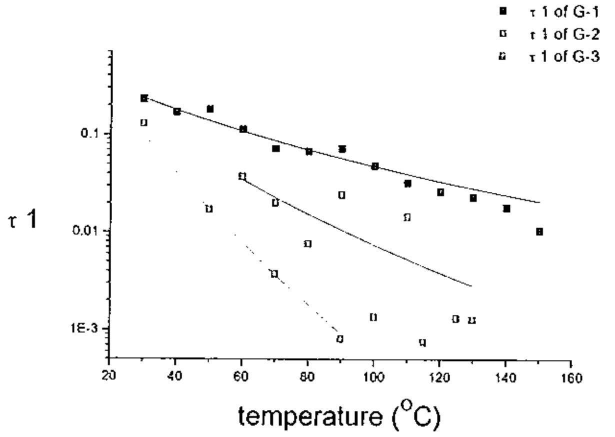
I found that as the temperature goes up, the relaxation time of electro-optic response moves to the high frequency area. This means relaxation frequency moves to the right side of the graph (high frequency area) when the temperature increases.

The electro-optic spectra have been fitted to the sum of Cole-Cole equations:

$$u(\omega) = \sum_{i=1}^{2} \frac{u_i}{\left(1 + j\omega\tau_i\right)^{\alpha_i}} + u_\infty$$

where u_i and τ_i are an amplitude and relaxation time of *i-th* relaxation process and u_∞ is offset.

The following Figures present the temperature dependence of the relaxation time of the low-frequency process.



[Fig 32] The dependence of relaxation time of low frequency process (1st relaxation process) on the temperature

(G-1 (PBL) at V=1V, G-2 (PBL) at V=1V, G-3 (PBL) at V=200V, respectively. G-2 (PBL) and G-3 (PBL) are shown small because of the space efficiency.)

The temperature dependences of relaxation times (τ 1 and τ 2) were fitted to Arhenius law (red lines in the above page) and the values of the activation energy were obtained.

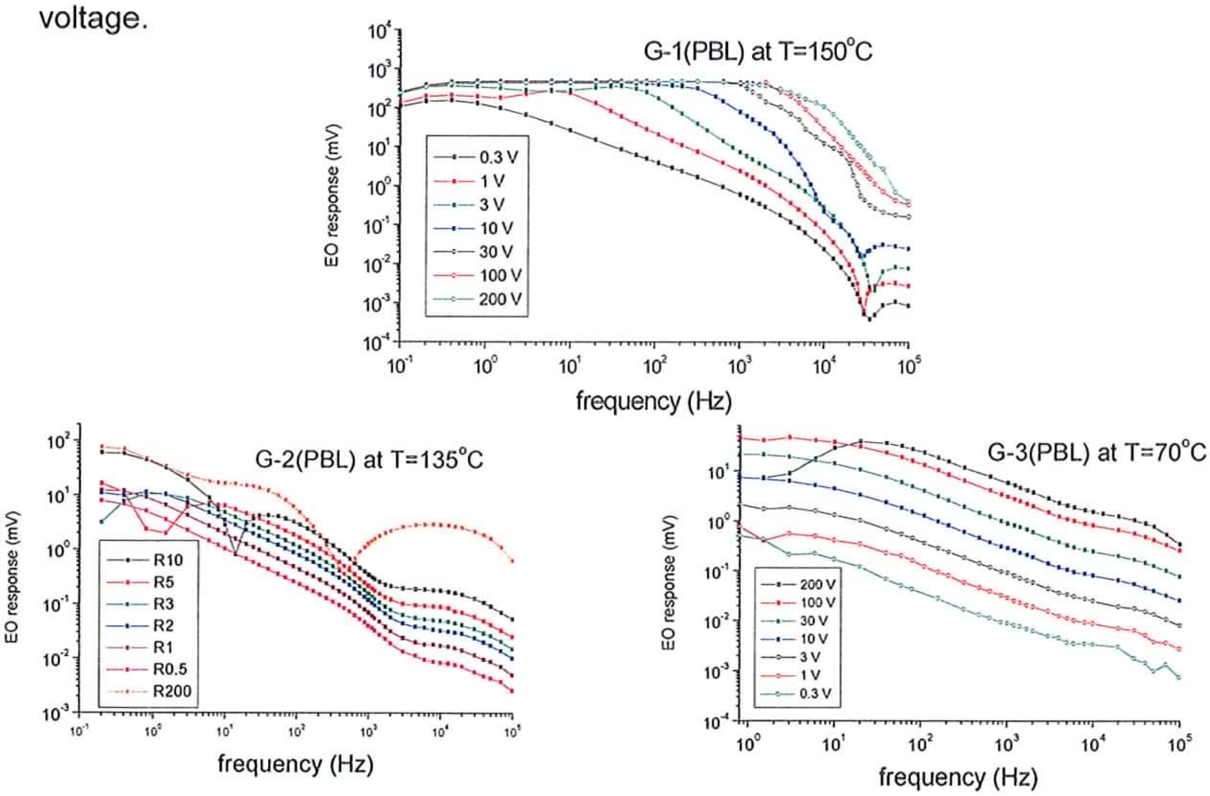
	G-1 (PBL)	**G-2 (PBL)**	**G-3 (PBL)**
Activation energy (1st process, Joules)	3.5767×10^{-20}	6.6136×10^{-20}	1.1825×10^{-19}
Activation energy (2nd process, Joules)	3.7696×10^{-20}	3.5409×10^{-20}	

[Table 1] Activation energies of 1st and 2nd relaxation processes of G-1 (PBL), G-2 (PBL), G-3 (PBL)(2nd process activation energy of G-3 (PBL) was not possible to calculate.)

3.2.3 Dependence of Electro-optic Spectra on Applied Voltage

As we can infer from the data of section 2.2.1.1, there is a dependence of electro-optic spectra of dendrimer on applied voltage as well. The applied voltage was changed step by step at fixed temperature.

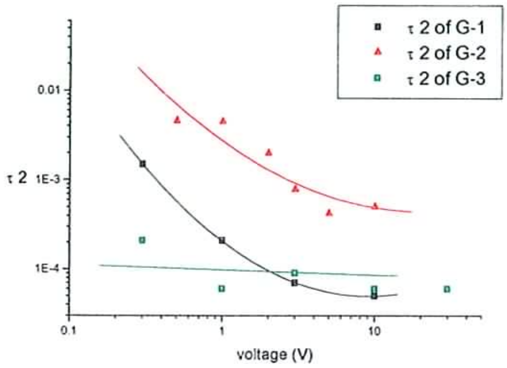
The following graphs show the dependence of electro-optic spectra on applied voltage.



[Fig 33] The dependence of electro-optic spectra on applied voltage at fixed temperature

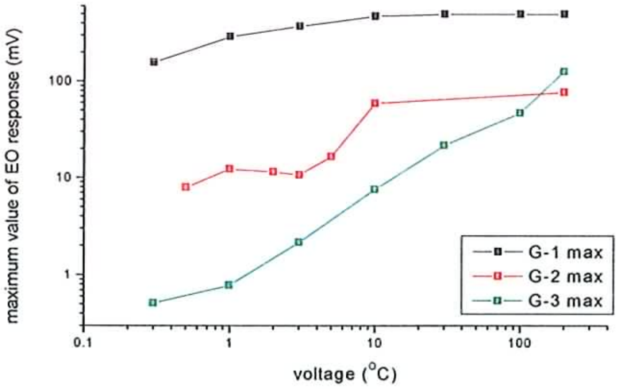
(G-2 (PBL) and G-3 (PBL) are shown small because of the space efficiency.)

The following picture represents the dependence of relaxation time of G-1 (PBL), G-2 (PBL), and G-3 (PBL) on applied voltage measured at fixed temperature.



[Fig 34] The dependence of relaxation time (high frequency process, 2nd process) of G-1 (PBL), G-2 (PBL), and G-3 (PBL) on applied voltage measured at fixed temperature

Finally, I can find a very interesting fact when I compare the maximum amplitude of electro-optic response of G-1, G-2, and G-3 together.



[Fig 35] The dependence of electro-optic response of three different dendrimer samples on applied voltage.

There is a significant difference between behaviors of the amplitude of the electro-optic response. The amplitude of electro-optic response of G-1 dendrimer is higher than others and is almost independent of the applied voltage. This means that I have a complete switching even at a low applied voltage.

The opposite situation applies for the G-3 dendrimer. The amplitude is changing linearly with applied voltage while the relaxation time is almost independent of voltage. This is typical for pure relaxation (not switching) processes. G-2 dendrimer shows intermediate behavior.

From the comparison of the electro-optic response I state with confidence that smaller molecules of first-generation dendrimer (G-1) are more amenable to the influence of the electric field than bigger molecules of the second- and, especially, third-generation dendrimers.

The contents of **chapter 3** were posted on the conference (8th International Conference of Ferroelectric Liquid Crystals), which was held in Georgetown University, Washington DC from August 5th to 10th with the name of the writer of this thesis as the first author.

Chapter 4

Two Different De Vries Smectic A Phases

As can be determined, the molecules in the smectic A phases are roughly perpendicular to the smectic layers. However in 1979 Andrian De Vries suggested that all molecules are already tilted in the SmA phases. After De Vries' suggestion there were loads of discussion about the appropriate structures, which can explain properly the pre tilt phenomena in the SmA phases. In the following I will take a deep and critical look into the De Vries smectic A phases.

4.1 Background of De Vries Smectic A Phases

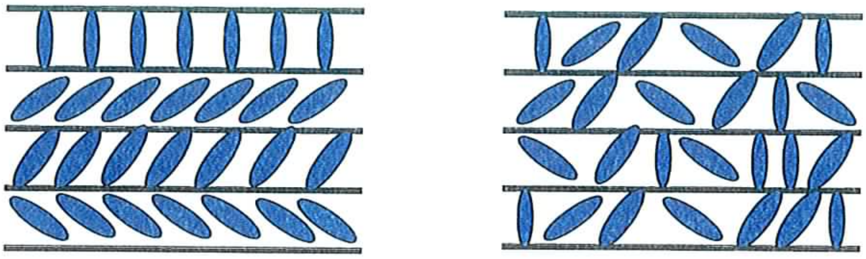
The idea of the pre tilt in the SmA phases is very important. So here I quote an abstract from the first paper of De Vries SmA phases.

> *Even though the average molecular direction in smectic A phases is perpendicular to the smectic planes, most molecules in these phases have rather large tilt angles because the orientational order parameter S in all smectic A phases is significantly less than unity. This molecular tilt*

> *inherent to all A phases accounts for the observed differences between layer thickness d and molecular length l of four quite different compounds, without any need for assuming additional tilt, interdigitation, or kinking of chains. From the differences between d and l, S values from 0.78 to 0.84 are obtained, which yield average molecular tilt angles from 20 to 17. It is predicted that all smectic A phases with monomolecular layers will follow the same pattern. The concept of "inherent tilt" should apply to all orthogonal smectic phases, thermotropic as well as lyotropic. (from the abstract of Mol. Cryst. Liq. Cryst. Vol. 49(Letters), p. 143~152)*, [14]

As the abstract says, all of the transitions from smectic A to smectic C have shrinkage in the layer thickness because of the molecular tilt. However, we can find no shrinkage of the layer thickness in some smectic A materials. They undergo the transition from smectic A to smectic C without any shrinkage [15], [16], and [17]. In this thesis I tried to find out the origin of the transition without any shrinkage and also the possible structure for the explanation of the properties of De Vries smectic A liquid crystals.

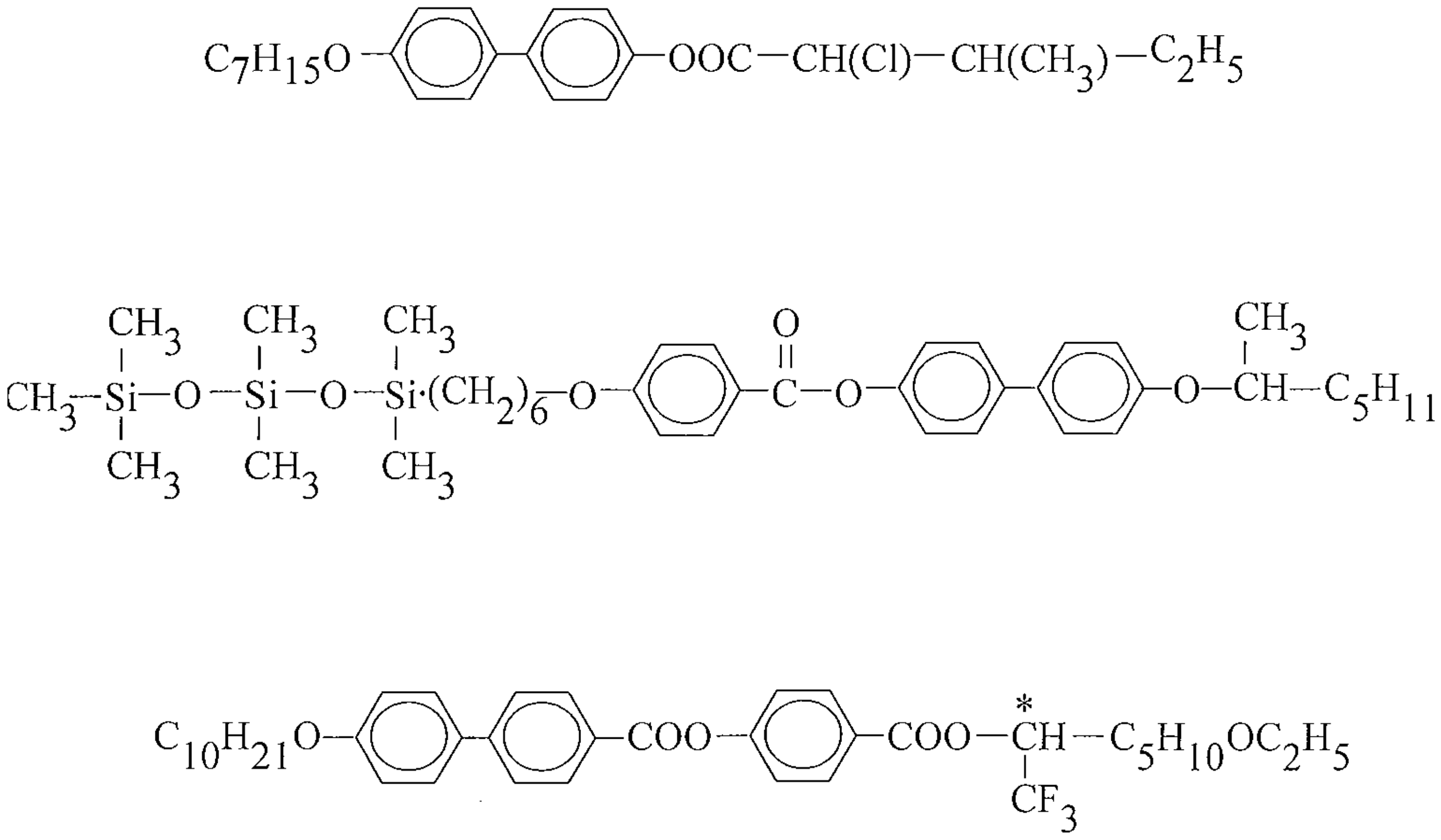
In this research I used three different liquid crystal materials as De Vries smectic A liquid crystals. I measured electro-optic response of these three liquid crystals and fit the data I got with a function of $k/(T-T_{AC})^{a}$, where T_{AC} is the temperature of smectic A to smectic C transition. Satisfactorily I found that two of these three liquid crystals have different a value in the fitting function from one of the three. The two most understandable structures for the different De Vries smectic A liquid crystals follow in the next page.



[Fig 36] Two possible structure for different De Vries smectic A liquid crystals (I call the left structure type I and the right one type II. In type I molecules are aligned in a single direction in each layer, but the directions change from layer to layer. In type II molecules have no relation with one another in aligning themselves even in one layer, so they are random in terms of directions.)

Those two structures are the most acceptable explanation for the two different De Vries smectic A liquid crystals [18] and [19]. A lot of research and experiments were done to figure out which type is proper to explain which liquid crystal, however, it has been a very tough subject. Even laser technique is useless, because laser just can find the thickness of the liquid crystal layer, but the thicknesses of these two different structures are the same. With the previously done research and this experiment I satisfactorily conclude which structure is appropriate to which type of De Vries liquid crystal.

C7 ([20]), TsiKN65 ([21] and [22]), and MC513 were used as our experimental materials. Here follow the chemical structures of the three different De Vries liquid crystals.

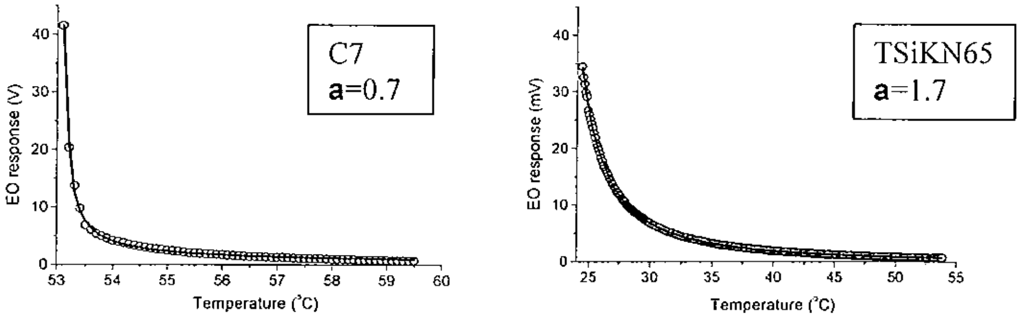


[Fig 37] The chemical structure of three different De Vries liquid crystals (C7, TsiKN65, and MC513, respectively from the top)

4.2 Experiments and Results

The liquid crystal cells were prepared with two pieces of glasses coated with ITO conducting layer. After rubbing the glass I put the liquid crystal material between the two pieces of ITO coated glass, and by the rubbing effect I can make the alignment of the molecules easy. Finally I soldered the two ITO glasses and put the cell on the mount of the microscope equipped with hot stage.

I first measured the electro-optic response and then fit the data obtained from the lock-in amplifier to the function, $k/(T-T_{AC})^{a.}$. Here k is constant, T is the temperature of the current time in the session of the experiment, T_{AC} is the transition temperature from smectic A to smectic C phase, and **a** is the most important factor in this experiment. I tried to fit data of three different De Vries smectic A liquid crystals to the function, $k/(T-T_{AC})^{a}$ and got very satisfactory results.



[Fig 38] Electro-optic data of C7 and TsiKN65 fitted to $k/(T-T_{AC})^{a}$

(C7 and MC513 have a value of 0.7, but TsiKN65 sample has 1.7. Fitting data of MC513 was omitted from the consideration of space in the thesis format.)

As can be see easily, the values of **a** in $k/(T-T_{AC})^a$ are different. They have two different values of **a**. When I consider this with the previous works done, for example [23], I can find out that each case refers to type I and type II, respectively.

The contents of **chapter 4** will be posted on the 19th International Liquid Crystal Conference which will be held in Edinburgh from 30th of June, 2002 to 5th of July, 2002 with the author of this thesis as a third author.

Chapter 5

Conclusion

5.1 Conclusion for Ferroelectric Dendrimers

Though dendrimers show the possible properties for a liquid crystal display material, it has been hard to explicitly demonstrate the ferroelectric properties of them. After finishing all the experiment in **chapter 3**, finally the possibilities for dendrimers to be used as LCD material were shown. **[Fig 35]** definitely shows that as the generation number grows up, the electrooptic response goes down, and within the same generation number as the applied voltage goes up the electrooptic response goes up, except for generation number 1, which is quite sensitive, so it keeps high electrooptic response regardless of the magnitude of applied voltage. These properties are the basic requirements for LCD materials and a series of experimental results described in **chapter 3** proved that dendrimers can be used as LCD materials.

5.1 Conclusion for De Vries Smectic A Phases

There still remains considerable discussion about this issue, however, according to the work done in **chapter 4** I could fairly conclude that there are two kinds of De Vries Smectic A liquid crystals called type Ⅰ and type Ⅱ (Conceptual pictures are given in **chapter 4**, **[Fig 36]**). In this thesis I presented experimental result from electrooptic technique which shows different **a** values of $k/(T-T_{AC})^a$. Those different **a** values mean that C7 belongs to type Ⅰ and TSiKN65 belongs to type Ⅱ when considered with [23]. Hopefully this could be a period mark at the end of the long lasting discussion about De Vries Smectic A phases.

Publications

Dynamic properties of ferroelectric dendrimers investigated by electro-optic spectroscopy, *Abstract of 8th International Conference on Ferroelectric Liquid Crystals* (2001), p234

Electro-optic and dielectric properties of random SmC phase in bulk and confined geometries, *Abstract of 8th International Conference on Ferroelectric Liquid Crystals* (2001), p196

Structure and electro-optic response of De Vries SmA phases, *proceeding 19th International Liquid Crystal Conference* (2002)

References

[1] *Liquid Crystals*, Peter J. Collings, Princeton University Press, Princeton (1990)

[2] *Organic Chemistry 6th Edition*, T. W. Graham Solomon, Wiley, New York (1996)

[3] V. M. Vaksman, and Yu. P. Panarin, *Mol. Mats.*, **1**, 147-154 (1992)

[4] L. M. Blinov, L. A. Beresnev, N. M. Shtykov and Z. M. Elschvili, *J. Phys. (Paris)*, **40**, C3-269 (1979)

[5] J. Hoffmann, W. Kuczynski and J. Malecki, *Mol. Cryst. Liq. Cryst.*, **44**, 287 (1978)

[6] S. Kimura, S. Nishiyama, Y. Ouchi *et al.*, *Jap. J. Appl. Phys.*, **26**, L255 (1987)

[7] *Principles of Dielectrics*, Oxford Science Publications (1998)

[8] *Physical Chemistry 5th Edition*, P. W. Atkins, Oxford University Press, (1994)

[9] O. A. Matthews, A. N. Shipway, J. F. Stoddart, *Prog. Polym. Sci.* 1-56, (1998)

[10] Chungkyun Kim, Eunmi Park, and Eunju Kang, *Bull. Korean. Chem. Soc.*, **17**, 419 - 424 (1996)

[11] S. Ponomarenko, N. Boiko, E. Rebrov, A. Muzafarov, I. Whitehouse, R. Richardson and V. Shibaev, *Mol. Cryst. Liq. Cryst.*, **332**, 43-50 (1999)

[12] S. A. Ponomarenko, E. A. Rebrov. A. Yu. Bobrovsky, N. I. Boiko, A. M. Muzafarov and V. P. Shibaev, *Liquid Crystals*, **21**, No. 1, 1-12 (1996)

[13] R. M. Richardson, S. A. Ponomarenko, N. I. Boiko and V. P. Shibaev, *Liquid Crystals*, **26**, No. 1, 101-108 (1999)

[14] A. De Vries, A. Ekachai, and N. Spielberg, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 143-152 (1979)

[15] P. A. Williams, N. A. Clark, M. B. Ros, D. M. Walba, and M. D. Wand, *Ferroelectrics*, **121**, 143-146 (1991)

[16] M. Buivydas, S. T. Lagerwall, I. Dierking, F. Gouda and A. Mochizuki, *Ferroelectrics*, **212**, 67-78 (1998)

[17] F. Giesselmann, P. Zugenmaier, I. Dierfking, S. T. Lagerwall, B. Stebler, M Kaspar, V. Hamplova, and M. Glogarova, *Phys. Rev. E*, **60**, 598-602 (1999)

[18] C. S. O'Hern, T. C. Lubensky and J. Toner, *Phys. Rev. Letts.*, **83**, 2745-2748 (1999)

[19] N.A. Clark, T. Bellini, R.-F. Shao, D. Coleman, S. Bardon, D.R. Link, J.E. Maclennan, X.-H. Chen, M.D. Wand, D.M. Walba , P. Rudquist, and S.T. Lagerwall, *Phys. Rev. Letts.*, to be published (2001)

[20] Ch. Bahr, and G. Heppke, *Mol. Cryst. Liq. Cryst.*, **151**, 69-73 (1987)

[21] M. S. Spector, P. A. Heiney, J. Naciri, B. T. Weslowski, D. B. Holt, and R. Shashidhar, *Phys. Rev. Lett.*, **61**, 1579-1584 (2000)

[22] J. V. Selinger, P. J. Collings, and R. Shashidhar, *Phys. Rev. E*, **64**, 061705 (2001)

[23] O. E. Kalinovskaya, Yu. P. Panarin and J. K. Vij, *Europhys. Lett.*, **57**, 184 (2002)

Curriculum Vitae

Minseok Chang was born in Seoul, Korea on January 12, 1975. He attended Sehwa High School in Seoul, Korea, graduating in February, 1994. He received a Bachelor's Degree in Chemical Engineering and Industrial Chemistry from Hanyang University in Seoul, Korea on February, 2001. As a full time postgraduate research student of the engineering department at Dublin Institute of Technology, he is now submitting this thesis for his MPhil degree in March, 2004. He has been registered as a graduate student and teaching assistant of physics department at San Diego State University as of September 2002.