

STUDIES ON ORIENTATION OF ORGANIC FLUORESCENT DYES
IN STRETCHED POLYMER FILMS

by

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STUDIES ON ORIENTATION OF ORGANIC FLUORESCENT DYES
IN STRETCHED POLYMER FILMS

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INTRODUCTION

Fluorescence spectroscopy has quickly become an important technology in studying the macromolecular environment, molecular interactions in cuvette (in-vitro), and physiological environment such as cells and tissue. Detecting fluorescence with the microscope (fluorescence microscopy) makes this technology extremely sensitive with the capability to detect single molecules. This sensitivity has stimulated a profound development in biomedical imaging in cellular and tissue environment with the additional benefit of fascinating growth of biomedical applications of fluorescence. Fluorescence is now the leading technology for studying numerous biological processes such as biomolecular transport, ligands binding, protein– protein and donor - receptor interaction on the cellular level. Many significant achievements and the growing needs for understanding biological processes motivate the development of new water-soluble fluorophores that emit in the red and near infrared spectral range to help minimized the background of the biological components. Researchers have been synthesized many new dyes and tested them for biological applications, but in most cases the fundamental physico-chemical properties of the new dyes have not been tested yet and still remain unknown. This lack of knowledge, as a result, slows down the development of new probes.

The research that we propose focused on studying fundamental properties of new fluorescent dyes. In order to study the relationship between fluorophore chemical structure/geometry and its spectroscopic properties, we developed a method for immobilizing and orienting of dye molecules on a solid support, such as polymer film, for example. To achieve this, we embedded fluorescent dyes in oriented poly vinyl alcohol

(PVA) film. PVA is a high molecular weight polymer that forms matrices while stopping (freezing) molecular mobility at room temperatures. The reasons that PVA had been chosen as the hosting material, as compared to other polymers, are due to both polar and hydrophobic properties. Also, PVA films are relatively easy to process, while they maintain good thermo-stability, chemical resistance and transparency. In the next step we developed the new experimental set-up for studying the transition moment direction of organic fluorescent dyes oriented in stretched polymer films. The structure of transition moments in the molecular framework is one of the fundamental properties of a molecular system responsible for the molecules' interaction with light and other molecules. These films were stretched up to 4-fold compared to their original lengths. Such stretching very effectively oriented the organic molecules in between aligned polymer chains. Various properties of fluorescence such as absorption, emission, and excitation were measured with both vertical and horizontal light polarization as compared to the stretching direction of the film. Different concentrations of each particular fluorescence dye in the PVA film were also studied. By measuring absorption and emission of dyes that were oriented in stretched PVA films with polarized light we determined the orientation of molecular transition moments as compared to film stretching direction and molecular frame of the fluorophore.

The first part of this project we designed and prepared proper PVA films. We used commercially available highly purified PVA powder available from Sigma Aldrich. The powder without any further purification was dissolved in de-ionized water and was heated to about 100 °C upon stirring for several hours. The PVA (about 10% PVA/water) formed a homogeneous aqueous solution. The liquid PVA was very carefully poured into

a Petri dish and dried overnight to form a clear uniformed film without any air bubble and impurity. We made several samples of PVA film using different molecular weight PVA to determine the film that give us the best result (spectral properties). Also, different thicknesses of PVA films were made. To produce PVA films with different dyes, we used some known fluorescent dyes such as Styryl 11 (LDS 798), Acridine Orange (AO) and Polyenes fluorescent dyes such as 1,6-Diphenyl-1,3,5-hexatriene (DPH) and 1,8-Diphenyl-1,3,5,7-octatetraene (DPO) that are broadly used in biomedical imaging; however, their polarized spectroscopic properties have never been studied. Dyes were dissolved into hot aqueous solution of PVA and DI water and poured into the petri dish and left to dry overnight. For stretching, we built the apparatus that helped us stretch the PVA films up to 4-fold. In our final stage, we built the adapter that helped us hold the PVA film and appropriately oriented the films in respect to the polarization of incoming light. The spectrophotometer system was equipped with the polarizer (wire polarizer that is capable to work with UV/VIS and NIR light). The apparatus for mounting and holding the films was integrated with the spectrophotometer. The photo-physical properties of the PVA films and PVA films containing dyes were measured with our system and appropriate comparison and calculations were made.

CONCEPT AND THEORY

1. Light and Light Interaction with Matter

Unlike the other energy such as heat or sound that can be characterized in a straightforward manner, light is an electromagnetic radiation that carries both wave and particle properties. The light particle, which is called a photon, was discovered in 1900 by Paul Villard and it was named by Ernest Rutherford 3 years later. In 1914, Rutherford

and Edward Andradeshowed the electromagnetic radiation nature of light. This dual nature of light is often a source of confusion; however, various experiments had confirmed the fact that they both exist. For example, the single photon double-slit interference and the photoelectric effect showed the wave and the particle nature respectively. A photon is a quantum, and is the smallest possible part of an electromagnetic wave, called a quantum of electromagnetic radiation of light.

Light is often characterized by its brightness and color. The brightness of light is intensity dependent. The intensity of light, denoted as I , is also called photon flux through a certain surface area, which is orthogonal to the direction of light propagation. The number of photons that hit a detector, such as the human retina, CCD, and photodiode per unit time is directly related to the brightness of the incident light. In **Figure 1**, the color of light (wavelength) on the other hand is related to the period of the electromagnetic radiation, or equivalently, the frequency of the energy of light.

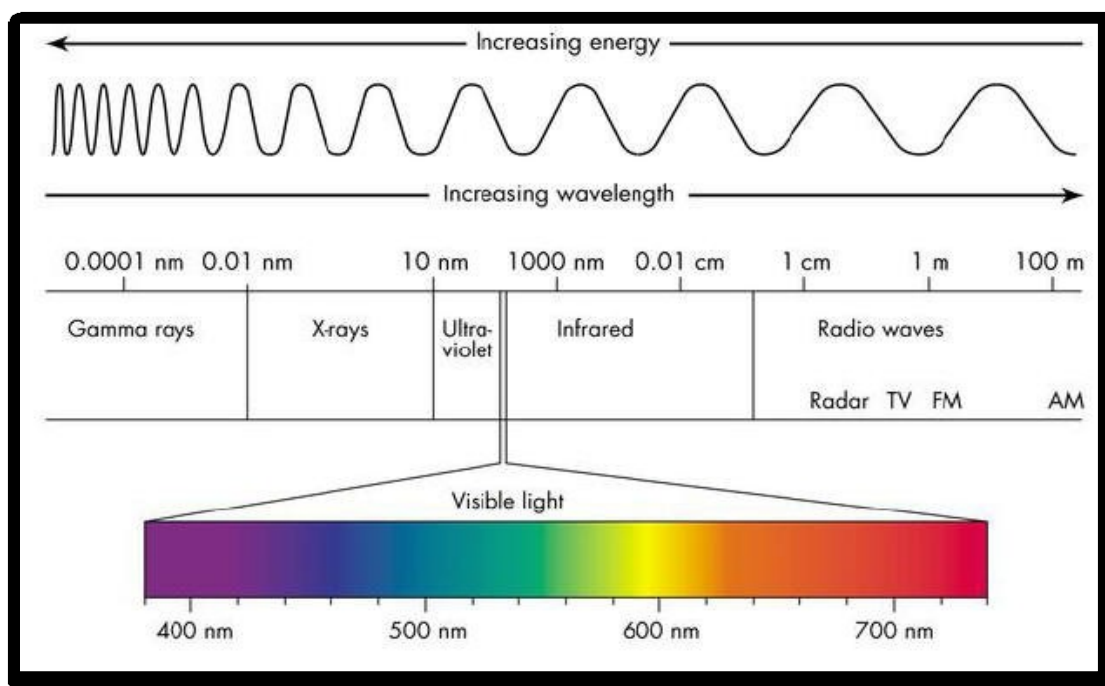


Figure 1: Electromagnetic Radiation Spectrum

In free space, light is a transverse electromagnetic wave. The electromagnetic field is depicted as orthogonal electric magnetic field E and B. In **Figure 2**, E and B are not truly expressed to scale. In fact, the electric field E and the magnetic field B differ by a scalar c, which is the speed of light.

$$E = c * B$$

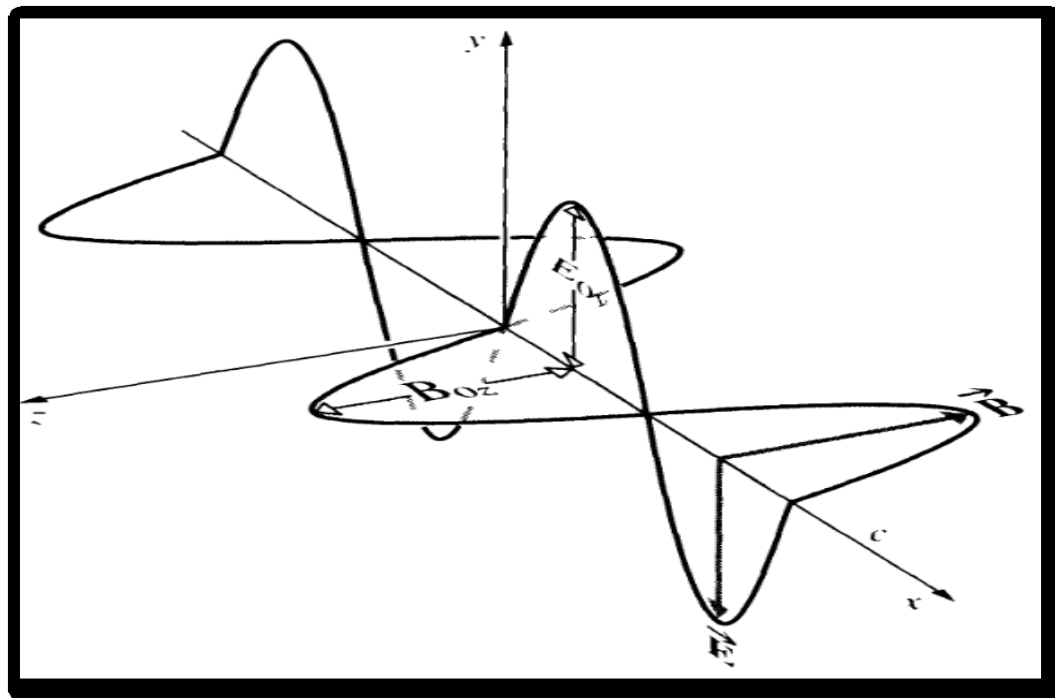


Figure 2: Light Wave

It is important to notice that light waves have the properties of mutually perpendicular electric and magnetic fields, which oscillate at right angles to the direction of propagation. **Figure 3** shows the cross product of electric field and the magnetic field, followed by the right hand rule, which yields the direction of propagation of light.

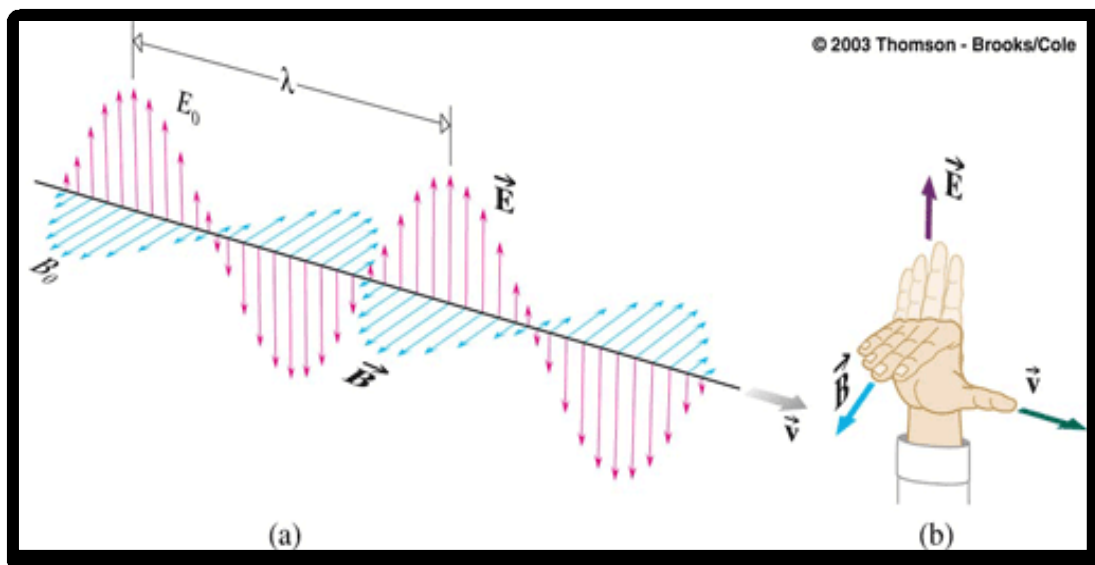


Figure 3: Propagation of Light

Let us now look at the interaction of light and matter. When light strikes an object it will interact in one or more of the following ways, such as transmission, refraction, reflected, scattering or absorption; these will also depend on the properties of an object, i.e., whether or not the object is transparent, translucent, opaque, smooth, rough or glossy, the interaction with light can be wholly or partially.

Transmission happens when light passes through an object without being altered. The object is said to be transparent. The alteration in this case is related to the refractive index of the material through which the light is transmitted. The refractive index of a material is the ratio of the speed of light – electromagnetic wave in vacuum to that in matter.

$$n = \frac{c}{v}$$

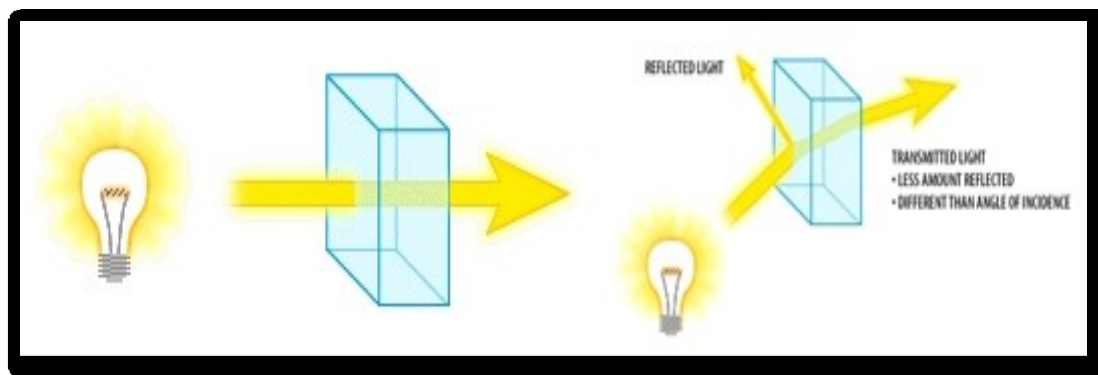


Figure 4: Transmission of Light with Refraction and Reflection

At the boundary surface, the surface when two different refractive index matters meet, if light strikes the surface straight on, the direction of light will remain unchanged. However, if light meets the boundary surface at an angle α , the beam of transmitted light will change direction according to the difference in refractive index and, of course, the angle of incident light beam that strikes the surface. This is called the refraction of light. In addition, the beam will be partially reflected.

The above case of reflection is when light interacts with transparent objects. In the case of opaque object as in **Figure 5**, the object surface will determine the condition of reflection. It can be either fully reflected, fully diffused or scattered, or both. Also when the substance contains different size and different refractive index particles, the amount of light scattered will also be altered. An example of this is the color of the sky. During the day when the distance from the sun to the observer is shortest the blue-violet light of the spectrum in **Figure 1** is scattered by particles in the air such as water, oxygen and nitrogen gases, thus producing the blue sky. Then later at dawn when the sun is at the horizon, the distance of the sun to the observer increases; the short blue-violet wavelengths are lost and the longer orange-red wavelengths of light are scattered giving the sky the fiery color of sunset.

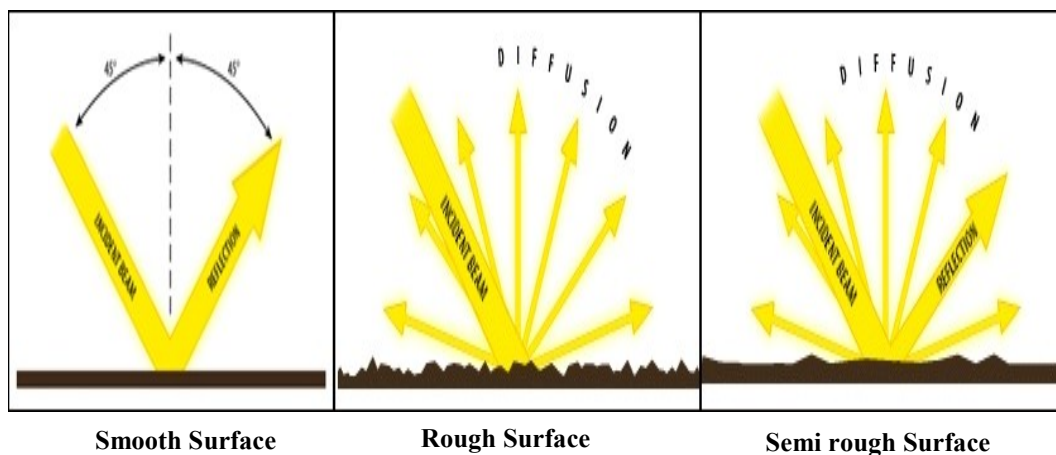


Figure 5: Reflection of Light on Different Surfaces

Finally, light can be absorbed within objects that contain pigmentation. Pigments are natural or artificial colorants that absorb some or all the wavelengths of light. As shown in **Figure 6**, the color that we see from the object is the reflection of the wavelengths that are not absorbed.

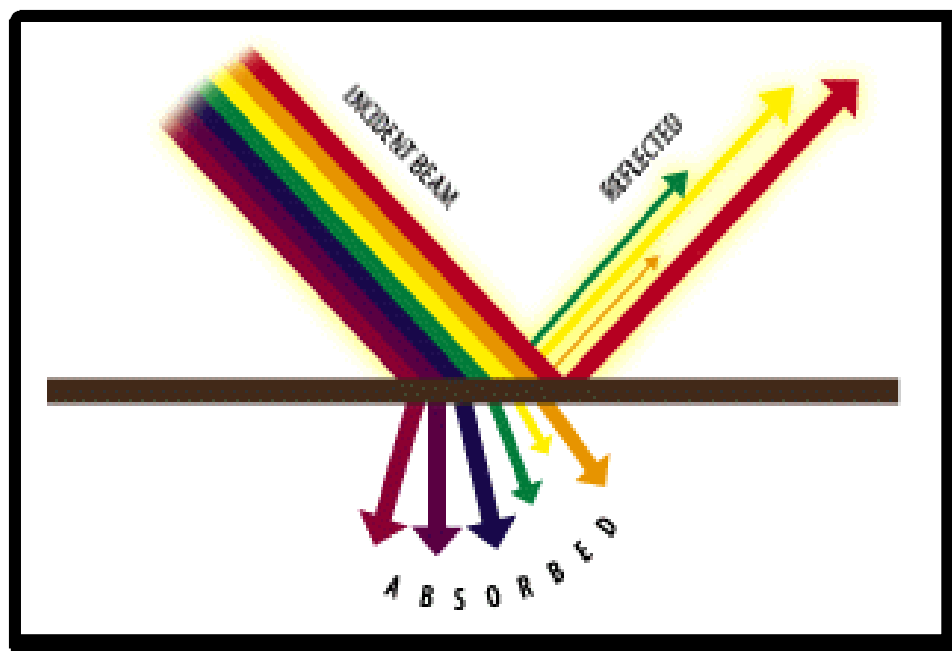


Figure 6 Absorption of Light

2. Polarization of Light

As light is electromagnetic radiation that contains the electric and magnetic fields as in **Figure 3**, the magnitude of the magnetic field is relatively small compare to the electric field (differs by a scalar factor $c = 3 * 10^8$). Therefore, the polarization of light is determined by its electric field direction. Assuming a light wave is polarized in \hat{r} direction, thus its electric field vector points in the same direction \hat{r} . Ambient light in everyday life is non-polarized which has a random distribution of electric field. This is so called isotropic light. We can treat any isotropic light as light that has two components of polarization, one vertical and one horizontal, after taking an average of all the directions of polarization. Any light wave for which the orientation of the electric field is constant is considered to have linear polarization. In this paper we are concerned mostly with linearly polarized light.

Polarizer is a device that only allows light of a certain polarization to be transmitted. When light passes through the polarizer, it may lose some or all of its intensity depending on the polarization of the incident light. Let's say we have a polarizer that polarizes in \hat{r} direction and a light wave passes through it. If the electric field E of the light wave points along the direction \hat{r} of the polarizer, no intensity of light is lost. If direction of E (\hat{e}) is perpendicular to \hat{r} , all intensity is lost. If \hat{e} and \hat{r} are neither parallel nor perpendicular, the amount of transmitted is determined by Malus's Law

$$I = I_0 \cos^2 \left(\frac{\mathbf{E} \cdot \hat{r}}{|\mathbf{E}| |\hat{r}|} \right) = I_0 \cos^2(\hat{r} \cdot \hat{e}) = I_0 \cos^2(\theta)$$

Where θ is the angle between the polarization direction of \hat{e} and \hat{f} . Isotropic light which has random polarization loses half of its intensity through a polarizer since we consider the angle of average \hat{e} to be 45 degree.

Figure 7 shows common sheets of polarizer that was invented in 1938 by Edwin Land. The polarizer contains free moving charges on parallel conducting wires. Light with electric field parallel to those wires is absorbed and perpendicular will pass through.

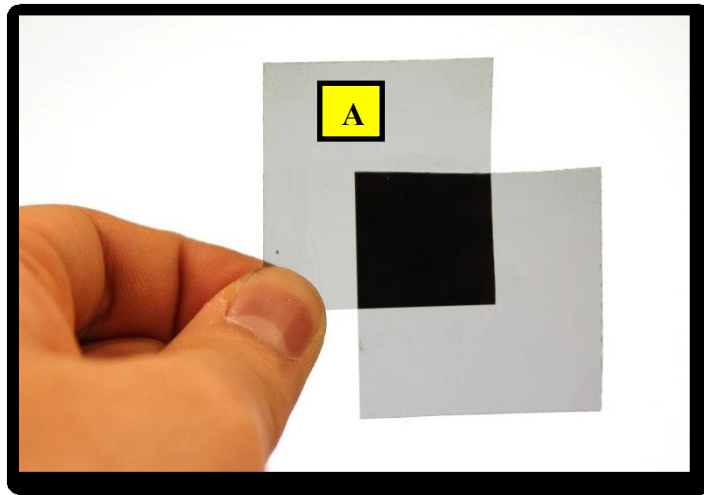


Figure 7: Polarizer

It is obvious in the **Figure 7** that isotropic light loses half on its intensity through the polarizer (region A). The perpendicular cross section of two polarizers does not allow light to pass through since the equation $I = I_0 \cos^2(\theta)$ is zero at 90 degrees. The limitation of these common polarizer sheets is that they only work with visible light (light in the wavelength range of 350nm-700nm). In this research we use a Wire-Grid polarizer, in which very thin metallic wires are layered between fused silica or quartz. Such a polarizer will allow us to obtain the spectrum in the range from UV to near IR.

3. Fluorescent dyes' absorption and emission of light

Fluorescent dyes, which are also known as chromophores, are chemical molecules that are responsible for giving the color to a substance through absorption and emission of light wave at certain wavelengths. The interaction of light with molecules taking place through the molecular orbitals that are formed by loosely bound electrons shared between atoms in the outer shell. Light carries energy with magnitude proportional to the frequency ν of the light wave:

$$\varepsilon = h\nu$$

If the fluorescent molecule does not have access to extra energy, the electrons in the molecular orbital are in a relaxed state called the ground state. When interacting with light, the molecule may absorb light and the energy from the photon is transferred to an electron in the outer shell. From here a transition to a higher energy state might occur and the molecule is said to be in an excited state. The excitation to the first stage requires the smallest discrete amount of energy that the molecule need to absorb, and each consequent excitation state requires an elevated amount of energy. The electron states are discrete, meaning that the electron is either in one state or another but not in between. Only a discrete amount of energy from absorbing light is taken by the molecule. The energy of the electron is also quantized and corresponds to an Eigenstate of a wave function ψ . The electronic energy of a molecule is symbolized by ε_n , in which the subscript n denoted the excited state of the molecule. The ground state is corresponding to $n=0$.

In general, the energy of a real molecule is determined by the summation of its electronic energy state ε_i^e , vibration state ε_i^v and rotational state ε_i^r respectively

$$\varepsilon_i = \varepsilon_i^e + \varepsilon_i^v + \varepsilon_i^r$$

The electrons will stay for a specific amount of time in the excited state before it makes the transition back to the ground state and emits photons. The wavelength of the emitted photons is proportional to the energy different $\Delta\mathcal{E} = \mathcal{E}_i - \mathcal{E}_0$

$$\lambda = \frac{hc}{\Delta\mathcal{E}}$$

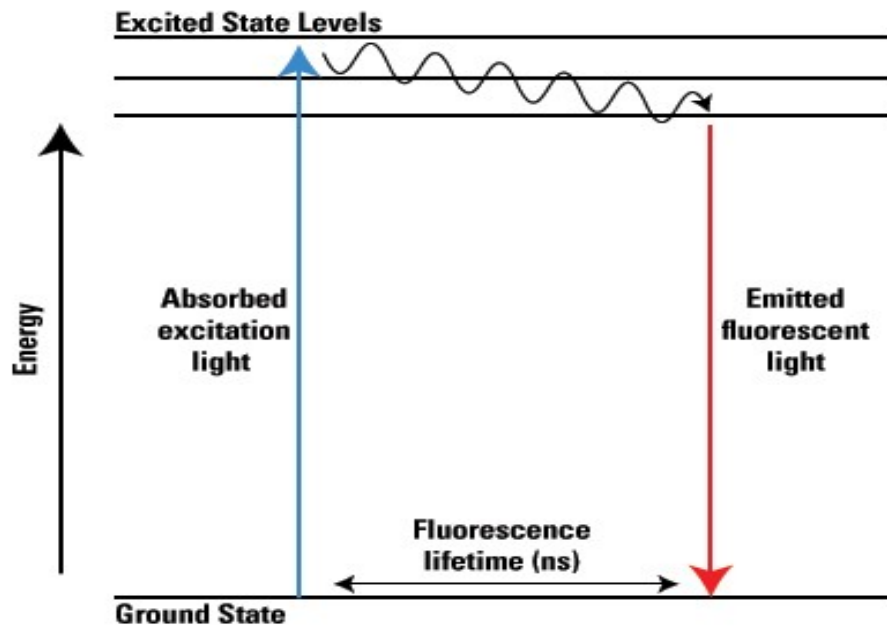


Figure 8: JablonskiDiagram

4. Polarized Absorption - Linear Dichroism

In general, the term Linear Dichroism is referred to as the selective absorption of one of the two orthogonal polarization states of an incident beam. The dichroic polarizer itself is an anisotropic device that produces a preferential absorption of one particular field component while being relatively transparent to the other field component. As mentioned above, one of the simplest application devices is the Wire-Grid Polarizer containing parallel conducting wires as shown in the **Figure 9** below.

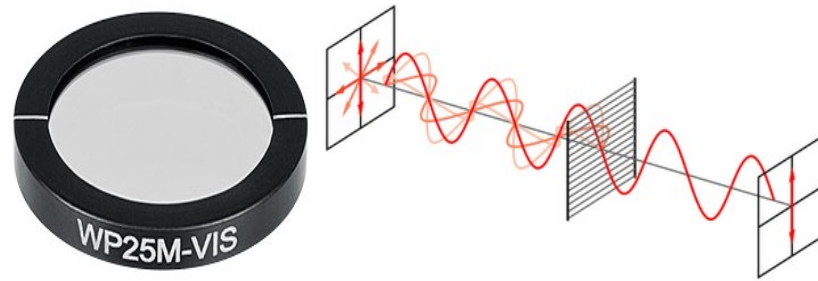


Figure 9: Wire-Grid Polarizer

In this figure, a non-polarized electromagnetic wave approaches the grid from the left. The electric field can be resolved into the usual two orthogonal components, one parallel to the wires and the other perpendicular to them. The parallel component of the field interacts with the conduction electrons along the length of each wire and generates a current. As a result the electrons collide with the lattice atom and transfer energy to them, thus heating up the wires. Energy is transferred from the field to the grid. Furthermore, the electrons accelerate along the parallel component of the field in both directions, forward and backward. Thus, the incident wave turns out to be eliminated by the wave reradiated in the forward direction. The wave that reradiates in the backward direction appears as a reflected wave. On the other hand, the electrons are not able to move significantly from the perpendicular direction of the wires. As we expected, the corresponding field component of the wave is basically unchanged as it propagates through the grid polarizer. This is crucial for not making an incorrect assumption by saying that the component of the field parallel to the grid somehow slips through the slits between the wires but instead, the transmission axis of the grid is perpendicular to the wires.

MATERIALS, METHOD AND INSTRUMENTATION

1. Chemicals

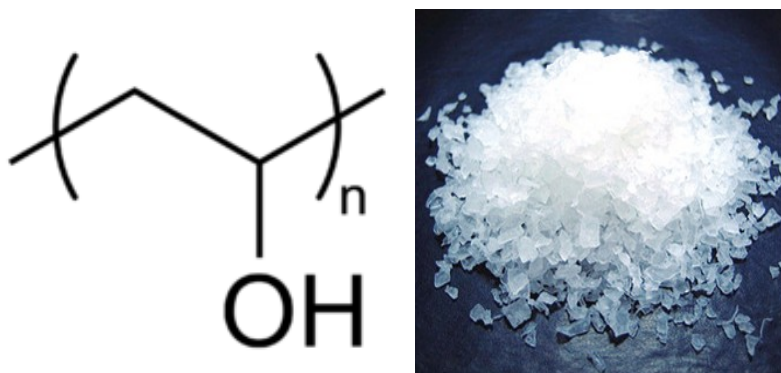


Figure 10: Structure and Physical Appearance of PVA

Polyvinyl alcohol (PVA) is a water soluble polymer forming by a chain of monomer with molecule structure shown in **Figure 10**. PVA has outstanding film forming properties, and it is also odorless and nontoxic. It is normally supplied in powder form with several grades and molecular weights. All the experiments in this project were performed using PVA obtained as a powder from Sigma Aldrich without further purification.

The fluorescent dyes that were investigated are known fluorescent dyes such as LDS and Acridine Orange (AO), and Polyene fluorescent dyes such as DPH and DPO. Those dyes are obtained from Exciton, Inc (OH) with high purity. The molecular structures are shown in **Figure 11**. One must realize the rod-like structures of those dyes and the conjugated double bond system which gives the molecule its fluorescent property. Those fluorescent dyes have visible absorption spectrum band and excitation which are at very convenient wavelength for the laser diodes excitation that are generally available with today's microscopy systems. Fluorescent dyes such as LDS and

Acridineare soluble in water, while DPH and DPO are not. The solvent for DPH and DPO was Methanol, which was also obtained from Sigma Aldrich Laboratory.

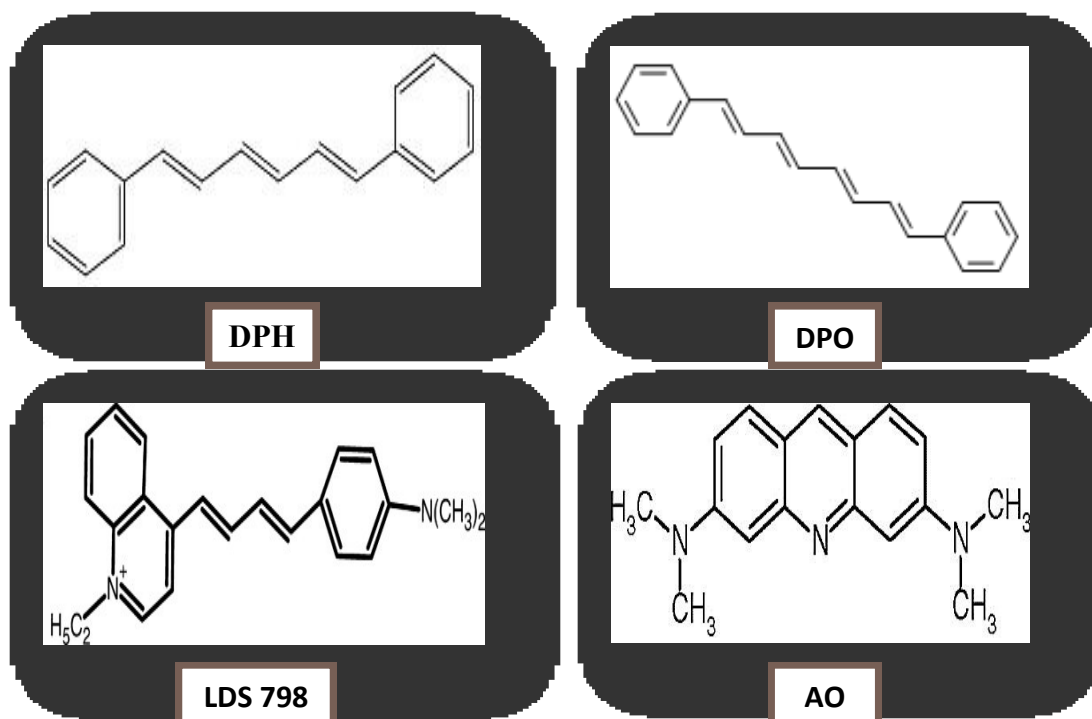


Figure 11: Structures of DPH, DPO, LDS and AcridineOrange(AO)

2. Method

The first part of this experiment was to create PVA film. 10% PVA films were prepared by dissolving PVA powder in DI (deionized) water heated to nearly 100°C (Figure 12a). To prevent overheating of the PVA from directly contact with the hot plate, a water bath was used to submerge the portion of the flask that contains PVA solution and the temperature of the water in the water bath was r checked by the electric thermometer regularly. Small portions of PVA powder were added to the heated water in the flask over periods of time under stirring continuous for 2-3 hours. For efficiency the stirring was performed by the stirring rod placed inside the PVA solution flask. The water

bath – PVA solution flask system was heated by the hot plate stirrer. Hot PVA solution was then poured into glass vials. During heating, air bubbles were generated inside the solution. In order to get rid of the air bubbles, those glass vials were sonicated for few minutes before pouring out to the Petri dish for drying. Usually it took 3-4 days for the PVA films to be completely dry at room temperature.

PVA films with fluorescent dyes were made similarly. However, depending on the solubility of the dyes, different solvents were used to dissolve the dyes into PVA solution. LDS and AO were dissolved in water before mixing with hot PVA solution in the glass vials. The mixing was performed upon stirring. DPH and DPO were insoluble in water, so they were dissolved in methanol before entering the PVA solution. After mixing and getting rid of the air bubbles, the PVA-Dyes solutions were poured into petridishes and left overnight for drying (**Figure 12b,c**).

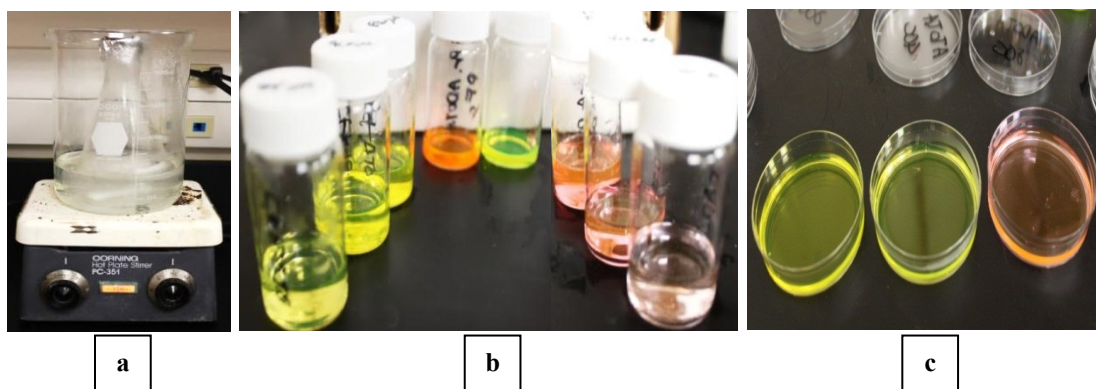


Figure 12: Procedure of Making PVA Films

After drying, those films were removed from the Petridishes and cut into rectangular pieces (30mm x 10mm to produce the un-stretched films. For stretched films, larger rectangular pieces were cut (30mm x 20mm). Such pieces were placed into the stretching apparatus that was built for this project. In **Figure 13**, the PVA strip was put

into positions A and B. The knob C upon rotation brought B away from A; thus stretching the PVA film. The films were stretched up to 4 times their original length. In the stretching process, the PVA films were heated and the stretching force was adjusted to assure a smooth film elongation. Before stretching, two marks of distance 5mm were placed in the center of the strip. The stretching procedure was done when the distance between those two marks was 20mm. For correctly prepared stretched films, the center of the stretching should be very uniform. We prepared PVA films without fluorescent dyes with different thickness. Also the PVA films with dyes were prepared with different concentration of the dyes solution. One of the main reasons for preparing different concentration of PVA with dyes is to prevent recrystallization during the drying process.

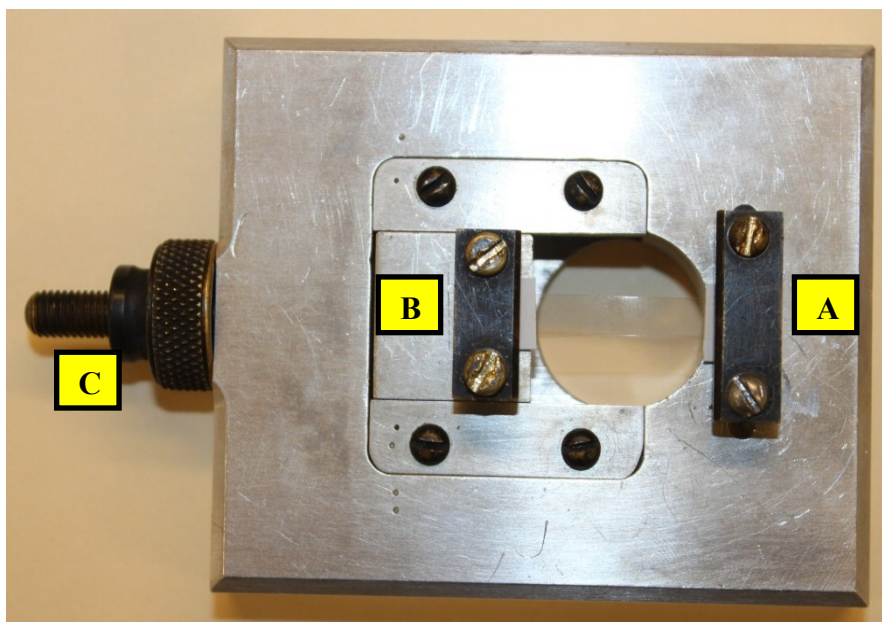


Figure 13: Stretching Apparatus

Figure 14 showed the un-stretched and the stretched PVA films with and without fluorescent dyes under white light and UV light.

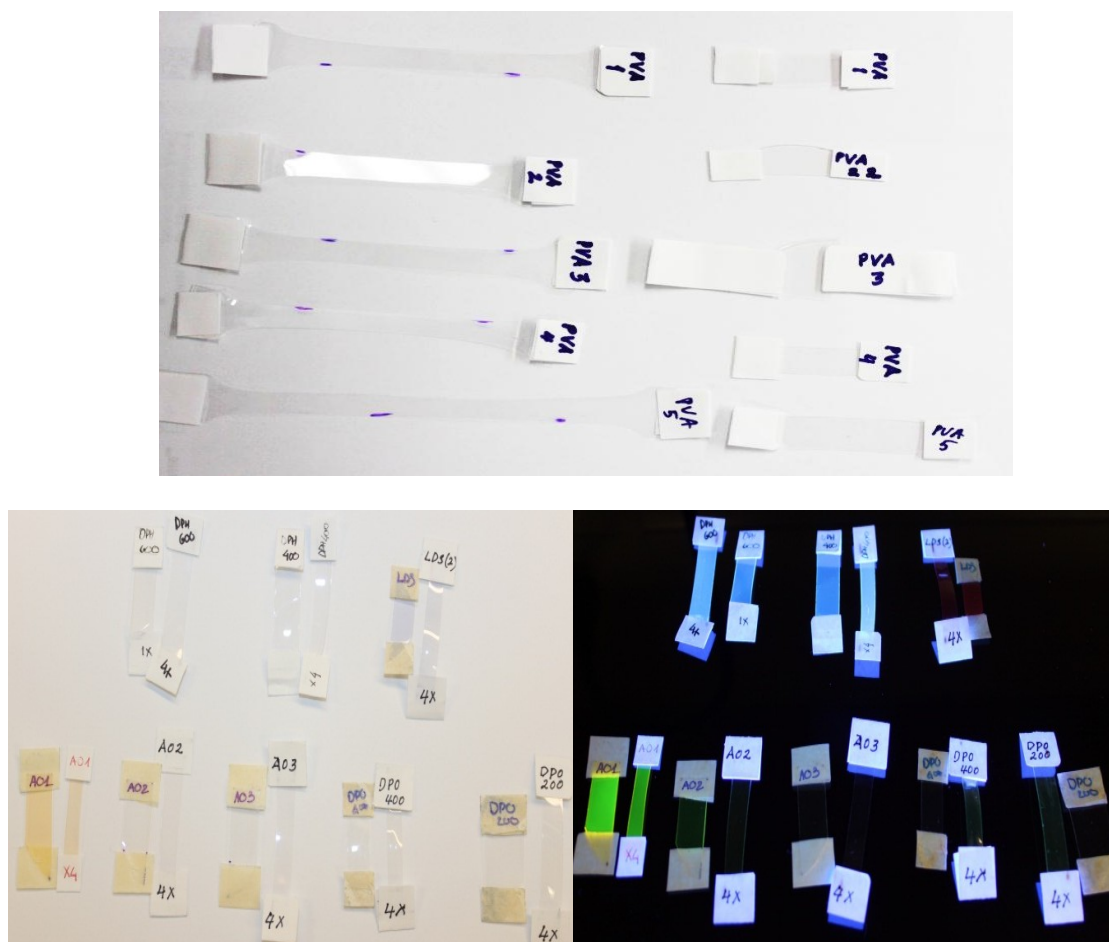


Figure 14: PVA Isotropic Films and PVA-Dyes Films in White Light and UV Light

3. Instrumentation

Absorption spectra were recorded using a Cary 60 UV-VIS spectrophotometer (**Figure 15**). The instrument originally came with the cuvette adapter, so we had to build the adaptor to hold and position the films.

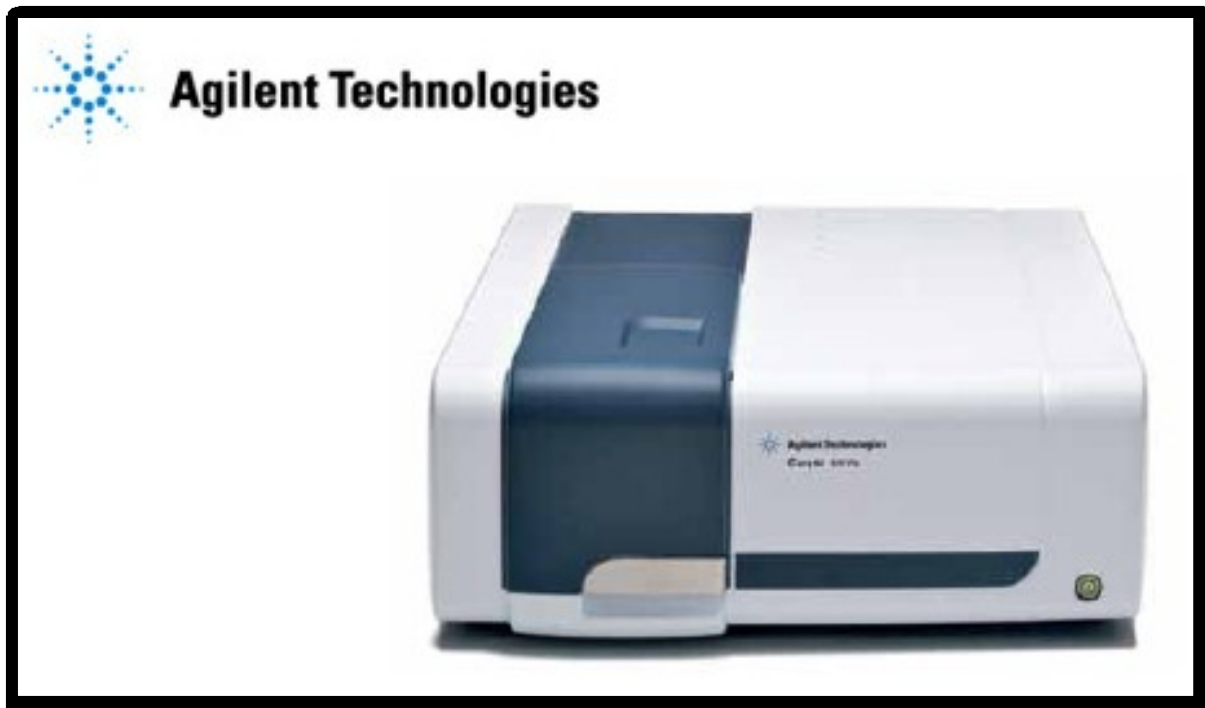


Figure 15: Cary 60 UV-VIS

The apparatus in **Figure 16** has two components. The first component is the part used to position the PVA films. The films were placed under the two aluminum bars and passed through the center of the internal hole. The second part of this apparatus has the rotational hole with 3.5mm diameter which has the same center as the internal hole of the first part. The first part is attached to the second part by the screw at position S. Also the position of the hole could be manually positioned up, down, left, and right by rotational knobs A and B, and tilted to assure the light beam is shot straight perpendicular through the hole by knobs X,Y and Z. The holding apparatus is aligned to fit perfectly into the chamber of the Cary 60 instrument and the light beam goes into the hole perpendicular to the surface area of the PVA films attached to it. The Wire-Grid polarizer was placed in front of the detector window of the spectrophotometer.

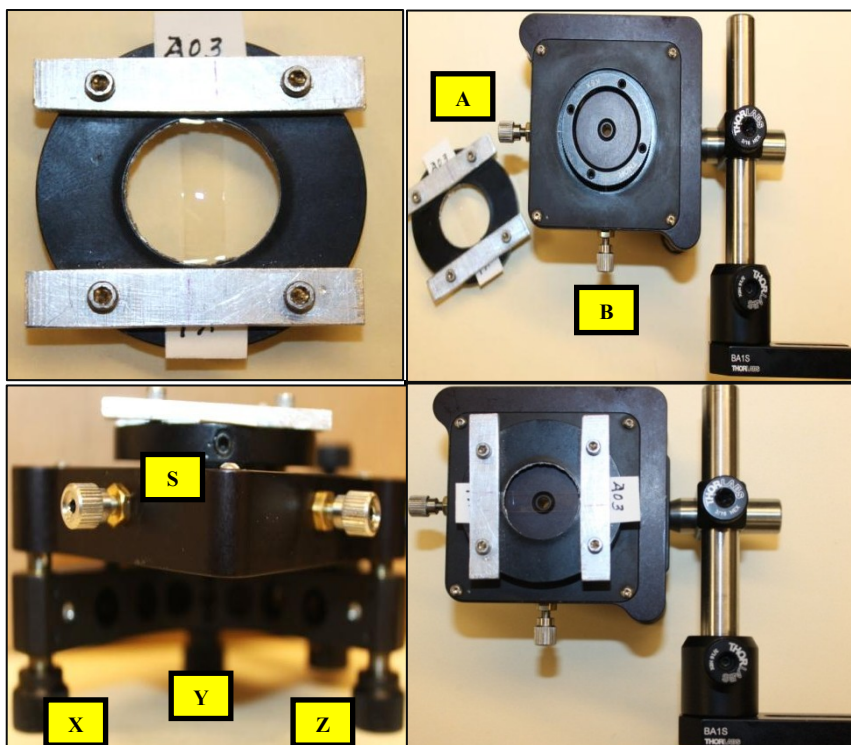


Figure 16:PVA Holding Apparatus

Figure 17 below demonstrates the complete setup of the system.

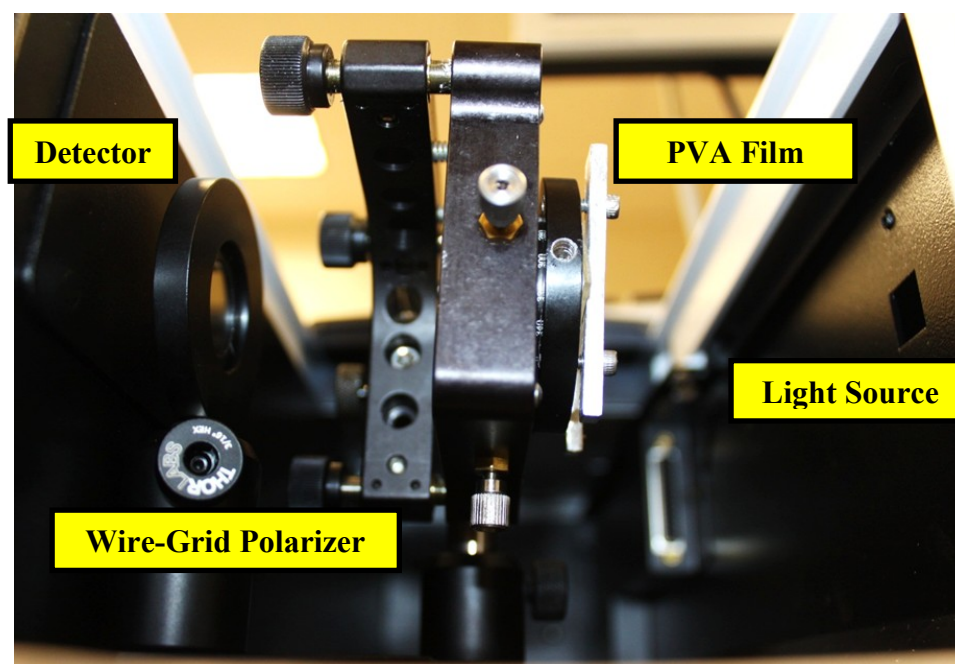


Figure 17: Complete Setup of the Cary 60 UV-VIS System

RESULTS AND DISCUSSION

We have chosen three isotropic PVA films, with different thickness. The absorption of those films was dependent on the thickness of the film (**Figure 18**). The thicker the film, the more absorption it had. The thickness of the film increased from PVA1, PVA2 and PVA3. Also, the absorption of those films was independent of the direction of polarization. For the sake of convenience, the polarizer was fixed with the polarization direction being horizontal; the films were rotated while measuring the parallel (horizontal) and perpendicular (vertical) absorption.

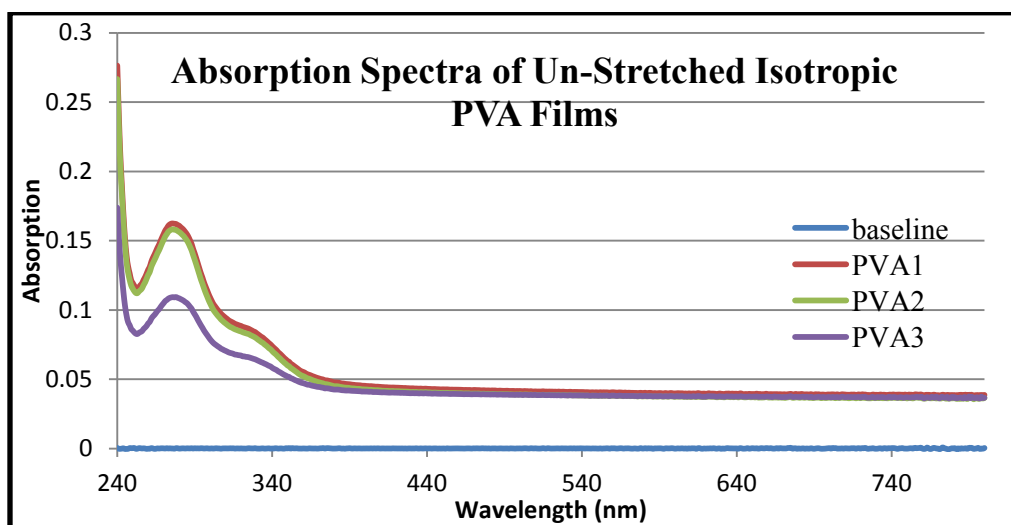


Figure 18: Absorption Spectra of Un-Stretched Isotropic PVA Films

For each isotropic film, we stretched it and obtained the absorption spectra. We observed that the absorption is dependent on the polarization of light. Each graph has 2 different absorption lines, one for the stretched (S) film that was positioned parallel (H), and the other for the stretched film that was perpendicular (V) to the fixed horizontal axis of the polarizer. The stretched films oriented along the polarizer absorbed more than the ones that were perpendicular to the polarizer as shown in **Figure 19**. The PVA chains themselves were re-aligned along the stretching direction during stretching, and thus

absorbed more when the polarization of the incident beam paralleled the stretching direction.

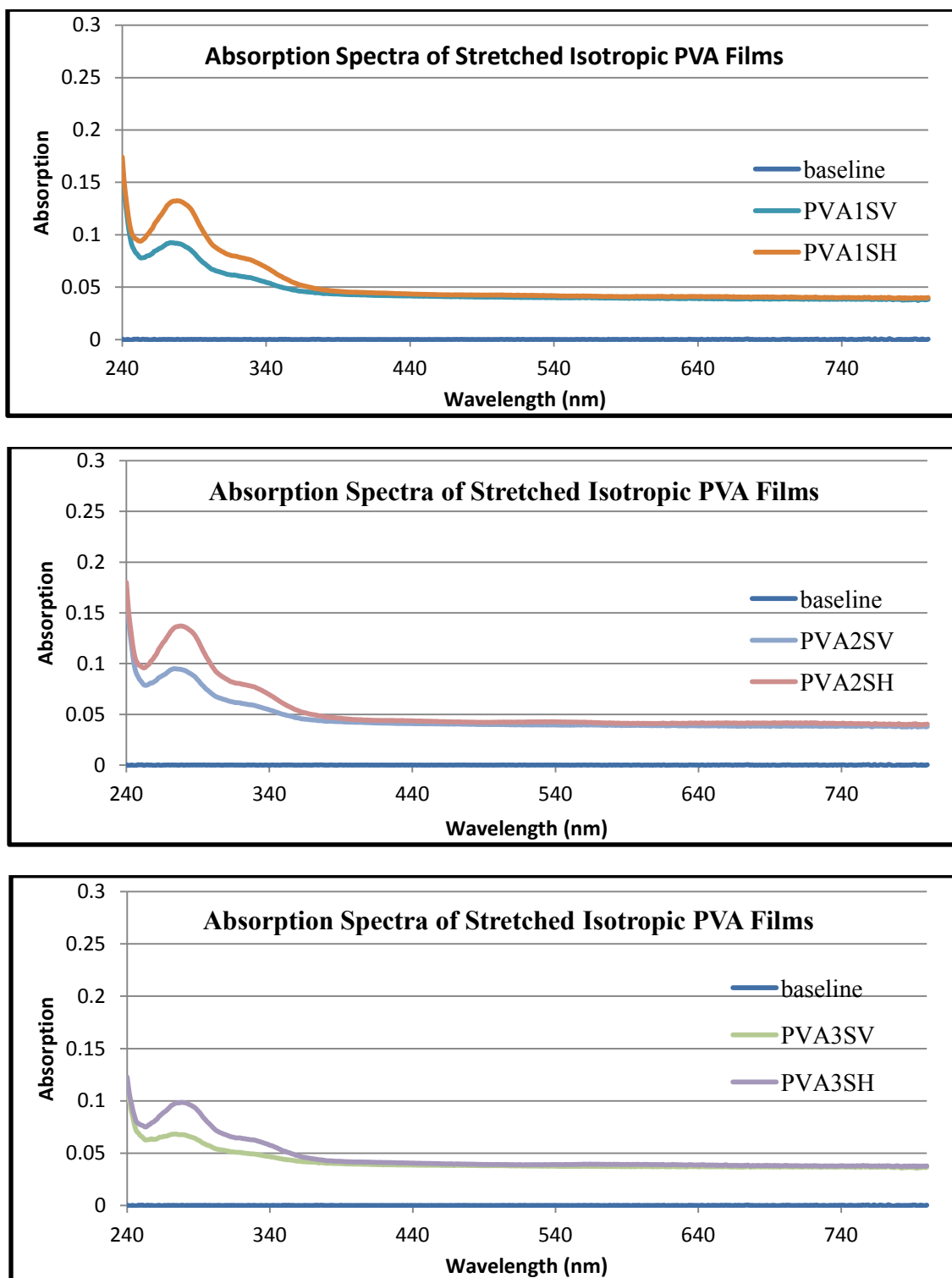


Figure 19: Absorption Spectra of Stretched Isotropic PVA Films

Observed under the polarizer sheet, we see the difference in emission of the stretched PVA films with different polarization of light. In the **Figure 20a1** and **b1**, the first film in each picture had intensity of emission light that is independent of the polarization of light labeled with the red arrow. Those are un-stretched films that had random distribution of fluorescent dyes in them. The second film in each picture was the stretched film. What was observed is that the intensity of emission of the film that has the stretching direction parallel to the polarization of incident light was higher than the one that was stretched perpendicular to the polarization of incident beam. Thus, the film that was stretched parallel to the horizontal light absorbed more. The same results were achieved with the other films (**Figure 20a2,b2,a3** and **b3**). The different in the rest of the films were not being able to observe by human eyes; therefore they were measured with the spectrophotometer.

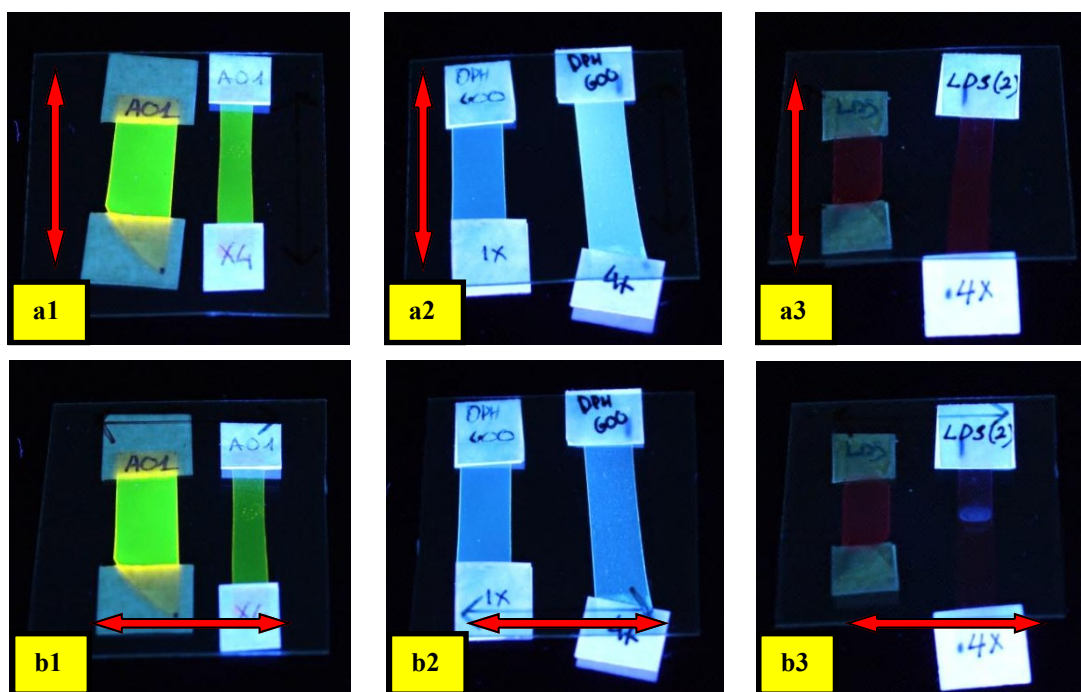


Figure 20 Linear Dichroism of PVA Film Observed under Polarizer

Figure 21 contains the absorption spectra of PVA-DPH film. Each graph has 3 different absorption lines, one for the un-stretched film, and the other two for the stretched film that was positioned parallel (H) and perpendicular (V) to the fixed horizontal axis of the polarizer. By comparing the absorption of the stretched film, it was evident that greater absorption in the stretched film that was positioned parallel to the polarizer axis in the region between 340nm-385nm, which was the signature of the absorption band of DPH, as compared to the film that was positioned perpendicular to the polarizer axis. Different concentrations of DPH in PVA films showed the common trend.

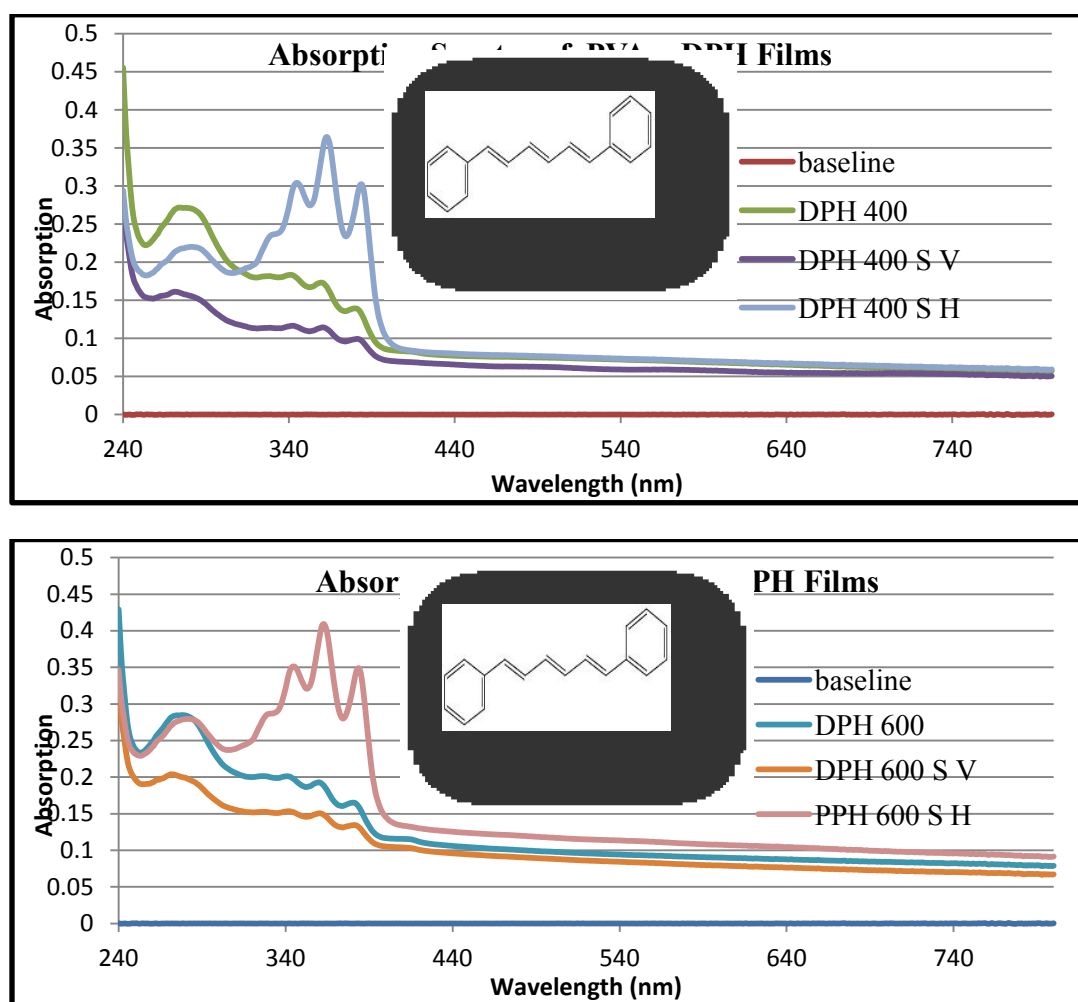


Figure 21: Absorption Spectra of PVA - DPH Films

DPO in PVA films showed the same result with the greater absorption of the stretched film in the parallel (H) position, compare to the vertical position (H) in the range of 340nm-390nm, which is the absorption band signature of DPO. **Figure 22** shows the absorption spectra of DPO in PVA films.

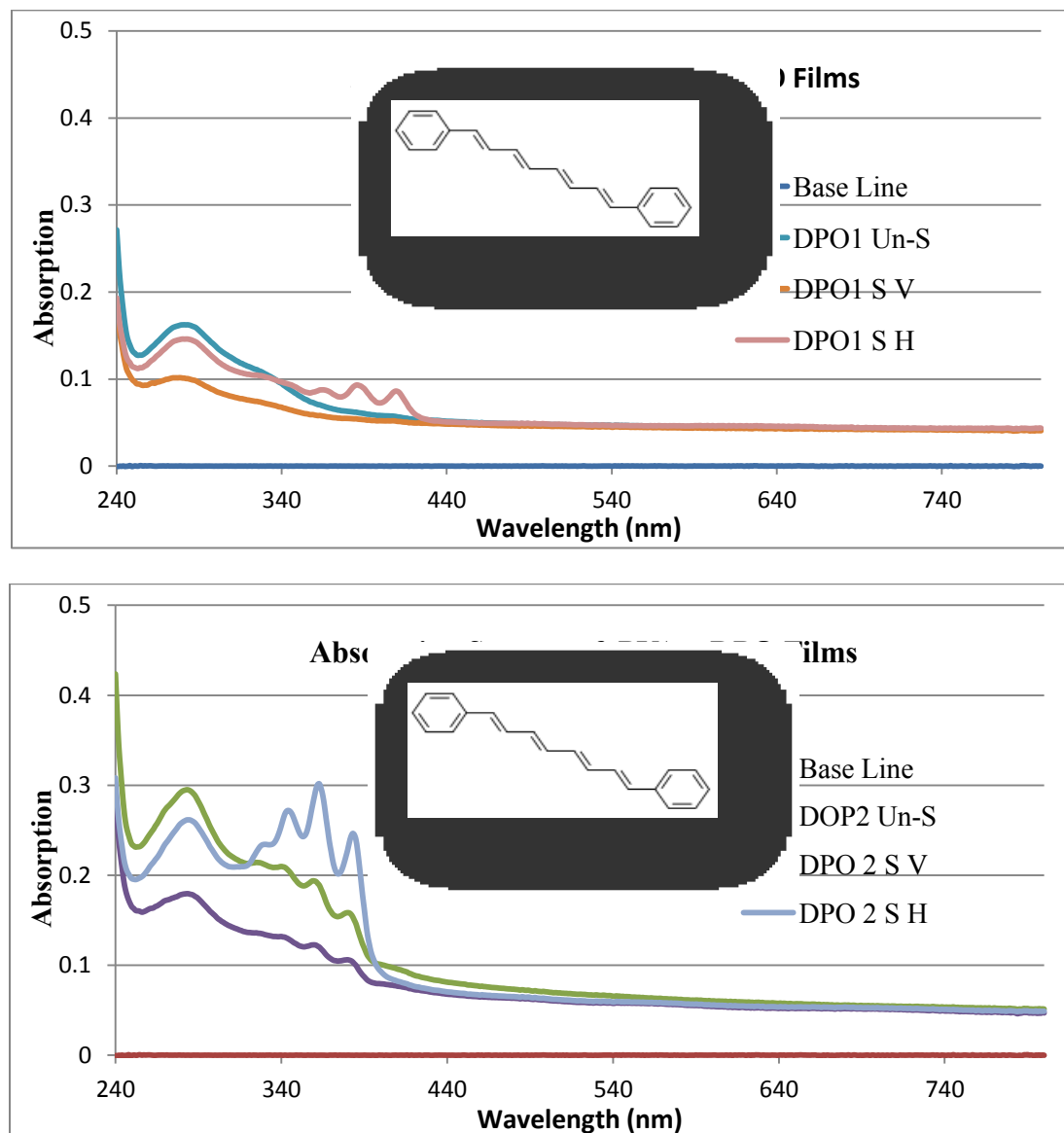


Figure 22: Absorption Spectra of PVA - DPO Films

The absorption band of LDS 798 was in the range of 500nm to 700nm. The absorption of LDS in PVA films did not depend on the concentration of LDS in the film.

Figure 23 shows the absorption spectra of LDS in PVA films.

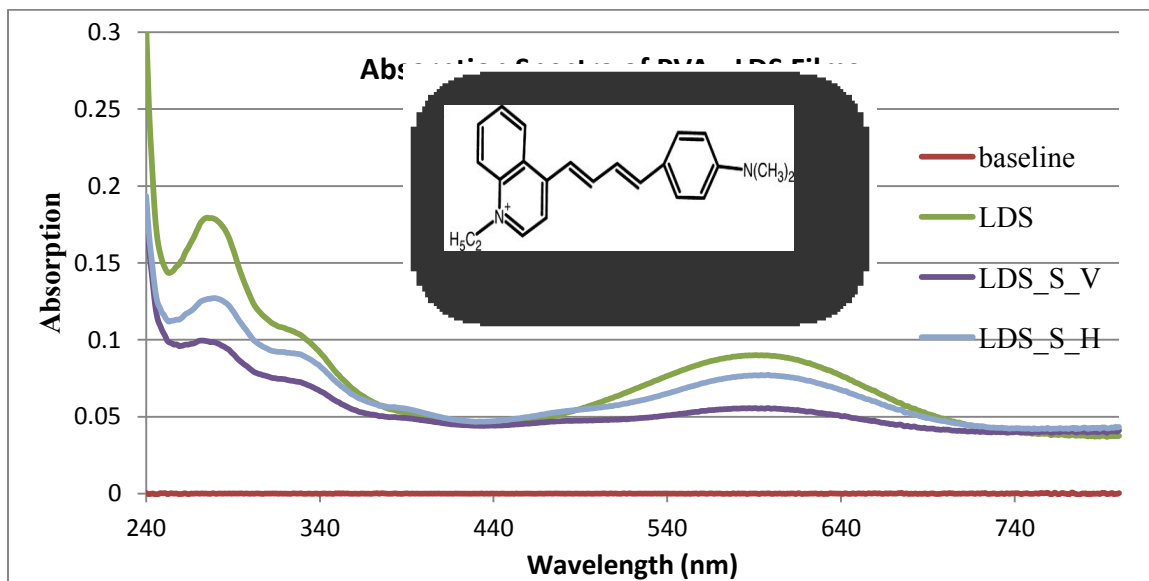


Figure 23: Absorption Spectra of PVA - LDS Films

In the case of Acridine Orange (AO), the highest concentration of dye in the film showed a significant absorption band of AO between 450nm-530nm. Similarly, greater absorption was observed in the stretched film that was positioned parallel to the polarizer axis as compared to the film that was positioned perpendicular to the polarizer axis. The lower concentration of AO in PVA film did not show clearly the difference in absorption range of AO.

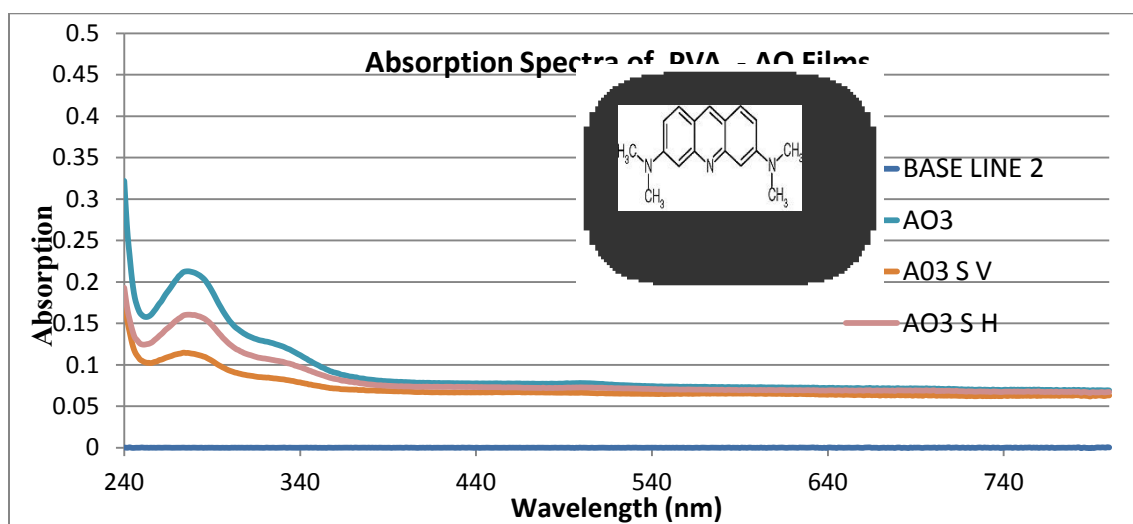
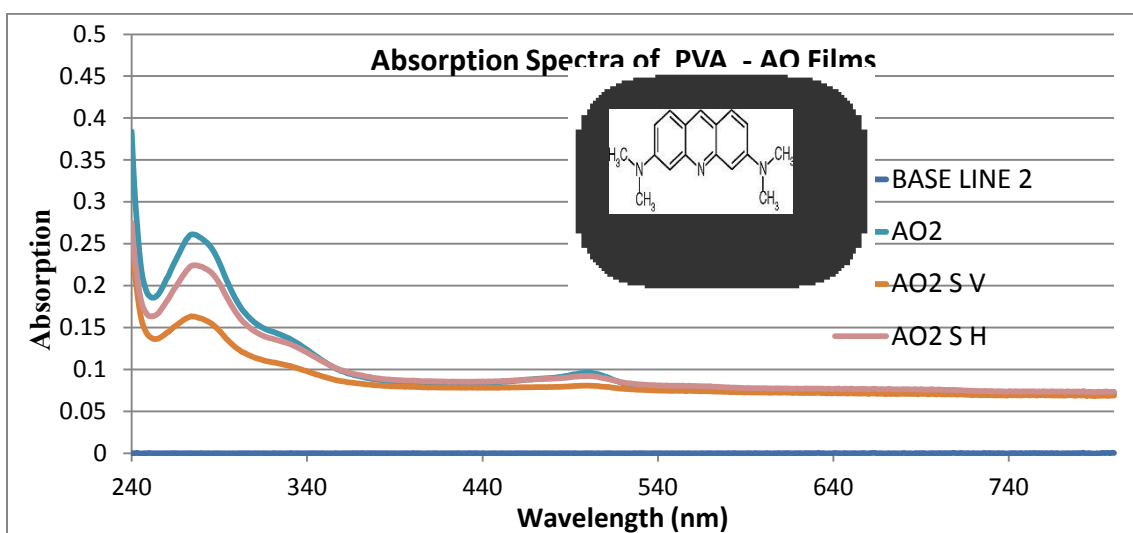
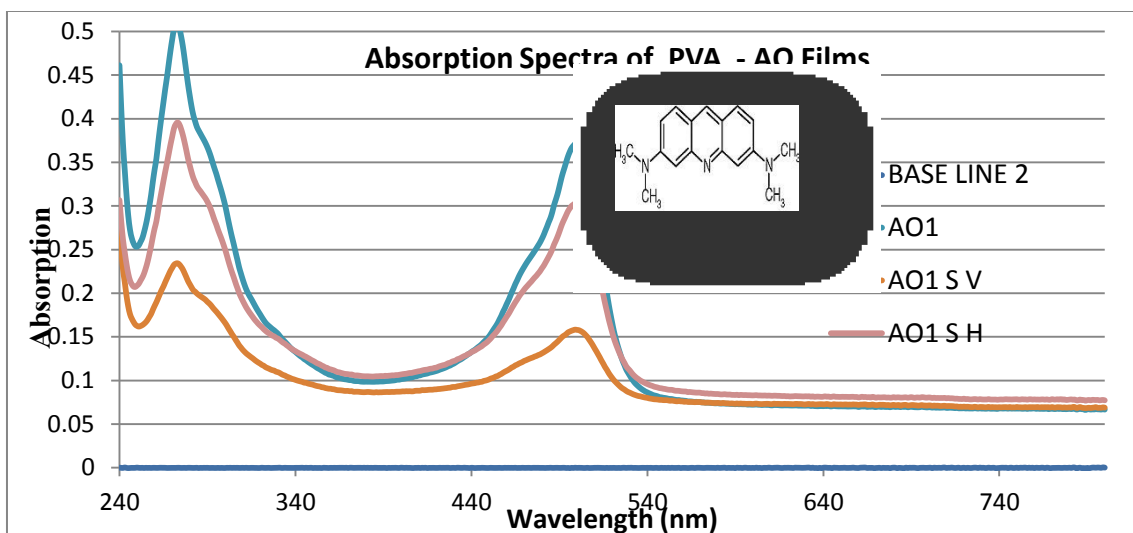
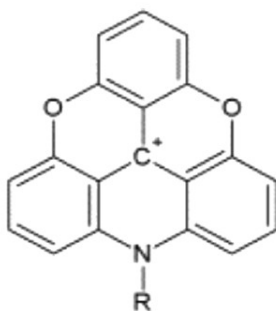


Figure 24: Absorption Spectra of PVA - AO Films

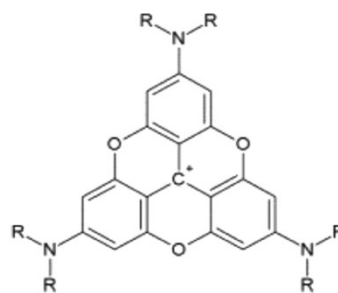
CONCLUSIONS

We have established the technology for measuring polarized absorption (Linear Dichroism) of organic dyes in oriented media such as stretched polymer films. Our experiment indeed showed excellent orientation of elongated molecules like LDS, DPH and DPO and AO along the stretching direction of the polymer matrices. Thus, we observed significant higher absorption when the polarization of the incident light is parallel to the stretching direction of the PVA films than when they are perpendicular. The orientation of planar molecules like AO was less effective when compared to the other rod-like molecule structures. By applying of the orientation model we were able to estimate the orientation of electronic transition moments in the frame of the molecules. Molecules like LDS, DPH and DPO have transition moments oriented along the long molecular axis. On the other hand, AO showed much more complicated distribution of transition moments orientations.

In light of our results, the next step will be to determine the direction of the emission transition moment for those fluorescent dyes. Also we will apply this method to study different fluorescent dyes with different molecular structures and different symmetrical orientations such as ADOTA and ATOTA to find their absorption and emission transition moment directions.



ADOTA



ATOTA

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ABSTRACT

We present a method for immobilizing and orienting organic fluorescent dyes in transparent poly(vinyl alcohol) (PVA) matrix. Dyes were introduced into the water solution of PVA that was slowly dried in a Petri dish, thus forming a uniform thin polymer film that trapped dye molecules in a rigid polymer matrix. These films were stretched up to 4-folds compared to their original length, a process that was very effectively oriented organic molecules in between aligned polymeric chains. Such immobilized and oriented molecules were used for studying the direction of electronic transition moment. Structure of transition moments in the molecular framework is one of the fundamental properties of a molecular system responsible for its interaction with light and other molecules. Spectroscopic properties such as absorption, emission, and excitation were measured with both vertical and horizontal light polarization as compared to the stretching direction of the film. A mathematical model was used to analyze observed dichroism and to determine directions of absorption and emission transition moments. Different concentration of each particular fluorescence dye in the PVA film was also be studied.