

Deposition of Oriented Molecular Thin Films Relevant for Organic Electronics

Stephanie Milazzo

(*Department of Physics, Rhodes College
2000 North Pkwy, Memphis, Tennessee, 38112*)

August 12, 2011

Abstract

Organic thin films have many potential applications in the field of organic electronics. To be electronically viable, films must have strong molecular orientation to enable maximum electron sharing and mobility through the film. In this study, simple, solution-based film deposition techniques are tested on several highly solvable polycyclic aromatic hydrocarbons with the goal of obtaining excellent molecular orientation using simple methods. Good orientation was obtained growing anthracene films from evaporation and solution shearing deposition techniques, and reasonable orientation was obtained growing pyrene films with the same methods. To further determine the level of orientation of these films, x-ray diffraction analysis will be done at the Cornell High Energy Synchrotron Source (CHESS). Further suggestions for continuing exploration of organic thin films are also discussed.

1 Introduction to Organic Thin Films

The use of organic materials in electronics is a field of much exploration today. Creating electronics from organic materials could enable scientists to create large-area, low-cost, flexible electronics or displays, such as cell phones, car instruments, or personal computers. Organic thin films are essential in the creation of organic electronics, and are used as either Organic Field Effect Transistors (OFETs) or Organic Light Emitting Diodes (OLEDs). Organic electronics can be produced via solution-based processes - offset printing, inkjet printing, and many more are currently investigated - and as such would require less energy and less production cost than similar products based on silicon. Moreover, organic electronics will facilitate other low-cost, energy-efficient, and environmentally friendly technologies such as organic solar cells and room lighting based on highly efficient OLEDs.

Materials formed of benzene rings are of particular interest in organic thin films because of their interesting electrical properties. Benzene rings are formed of a ring of 6 carbon atoms, each with a hydrogen atom adjoined to it. The carbon atoms in these rings exhibit a pi bond, meaning their individual p orbital electrons are delocalized into a ring of shared electrons. This allows easy sharing and mobility of the electrons within the material, making these materials interesting for electrical conductivity. One class of these materials, Polycyclic Aromatic Hydrocarbons, or PAHs, is composed of materials made of multiple fused benzene rings. The specific PAHs used in this study can be seen in Figure 1. The lattice structure of the anthracene and pyrene can be seen in Figures 2 and 3, respectively.

The electron mobility is also a function of the molecular packing within the crystal structure as well as of the grain boundaries between crystals. If material is deposited on an isotropic substrate by dropcasting or spin coating, grain orientations are random and form the most serious limitation of the achieved mobilities. A way to improve this situation is anisotropic growth to get the material to form either elongated grains enabling single grain devices, or at least orient the material so that only small-angle grain boundaries are formed. Film deposition processes creating oriented films from solution have previously been demonstrated to create well-oriented films with relatively simple means [1, 2, 3]. The purpose of this project was to test simple deposition methods of organic thin films from solution with the goal of obtaining high molecular alignment on isotropic substrates such as glass slides or wafers covered with a thick gate oxide.

2 Introduction to Crystal Growth

To obtain good crystalline alignment of organic molecules, deposition processes with directionality must be used. The isotropic symmetry of crystal growth must be broken in deposition to obtain oriented crystalline structure within the crystal. In the methods studied in this project, a sweeping meniscus across an isotropic substrate is used to obtain orientation of molecule within the crys-

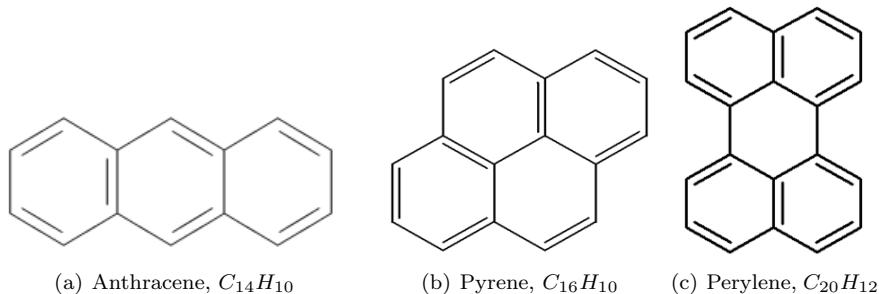


Figure 1: Polycyclic Aromatic Hydrocarbons studied in this work

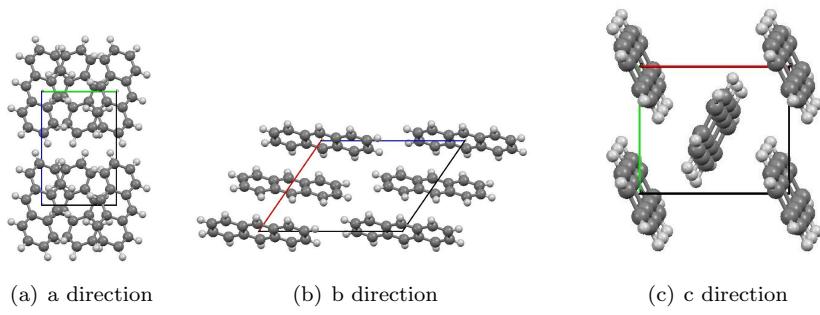


Figure 2: 3 dimensional views of the packing structure of anthracene.

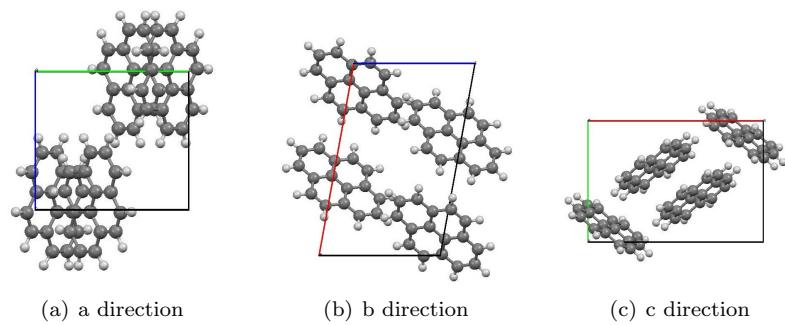


Figure 3: 3 dimensional views of the packing structure of pyrene.

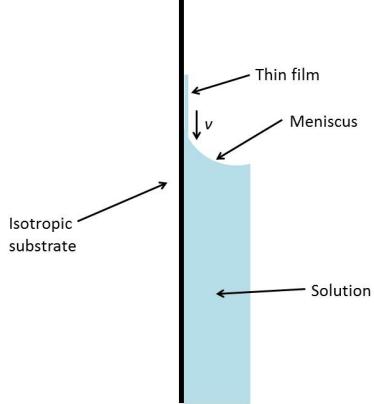


Figure 4: Diagram of vertical shearing motion in thin film deposition.

talline structure. The shearing motion of the sweeping meniscus at a controlled velocity, v , creates a preferential direction of nucleation and crystallization on the isotropic substrate in the direction of the shearing motion. Diagrams of this process using vertical and horizontal shearing processes are shown in Figures 4 and 5, respectively. In both horizontal and vertical film deposition, we would like to leave a solid crystalline thin film behind the sweeping meniscus. The crystallization of the thin film directly behind the sweeping meniscus is caused by a convective flow of organic material to the drying regime [5, 6], and well as a shearing force created by the shearing surface at quicker velocities. If, however, the meniscus is swept too quickly across the substrate, a liquid film is left on the substrate in what is called the Landau-Levich regime of film deposition [4]. In this regime, a layer of liquid adheres to the surface below. When this occurs, the molecules of organic material lose the directional orientation given to them by the sweeping meniscus due to randomization from Brownian motion. Thus, the thin film crystallizes into an isotropic and unoriented structure. Because we want highly oriented crystalline structure in our thin films, we will strive to obtain shearing velocities that avoid the Landau-Levich regime of thin film growth. Through these shearing deposition methods, we aim to break the isotropic symmetry of the crystalline structure of these thin films and obtain good molecular alignment.

3 Crossed Polarizer Microscopy

To analyze the domain orientation of thin films, a cross-polarized microscope will be used. The organic materials in this study polarize light, so this analysis technique is an effective way to test the anisotropy of these films. This type of microscope places the polarizing specimen to be studied between two crossed

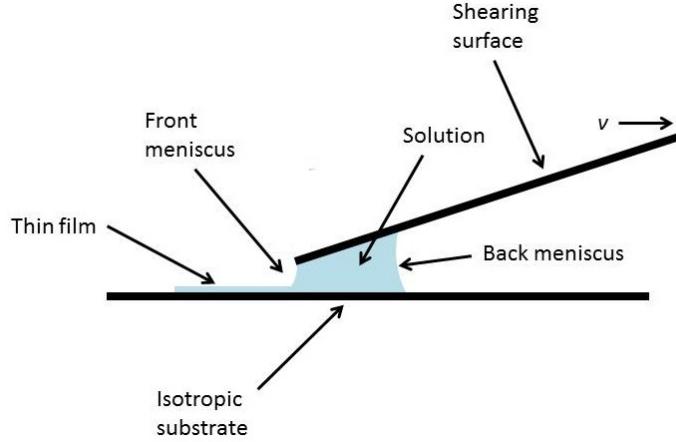


Figure 5: Diagram of horizontal shearing motion in thin film deposition.

polarizers. The light transmitted by subsequent polarizers with polarization directions θ apart is described by the Law of Malus ($I = I_0 \cos^2(\theta)$). The amount of light transmitted between two polarizers as a function of the angle between them (θ) is shown in Figure 6. If subsequent polarizers have a parallel component of their polarization directions ($\cos(\theta) \neq 0$), some light is transmitted. While two crossed polarizers transmit no light ($\cos(90^\circ) = 0$), the addition of a third polarizer (parallel to neither initial polarizer) creates non-zero cosines between each set of subsequent polarizers. This phenomenon is shown in Figure 7. So, a third polarizer, parallel to neither crossed polarizer, will allow the transmission of some light through the set of three polarizers. We will treat the thin film as a third polarizer placed between the two crossed polarizers. The actual experimental setup can be seen in Figure 8.

The light produced by the microscope undergoes a loss in intensity as it passes through the first filter. If we define I_0 as the initial intensity of light hitting the first polarizer and I_1 as the intensity of light after the first polarizer, then we know that

$$I_1 = \frac{1}{2} I_0$$

because a factor of half the intensity is lost from going from unpolarized light to linearly polarized light. From here, we define I_3 is the final intensity after the third polarizer and θ as the angle between the polarization directions of the first polarizer and of the film. Then by the Law of Malus, we can determine that:

$$I_3 = \frac{1}{2} I_0 \sin^2(\theta) \cos^2(\theta)$$

Or, alternatively,

$$I_3 = \frac{1}{8} I_0 \sin^2(2\theta)$$

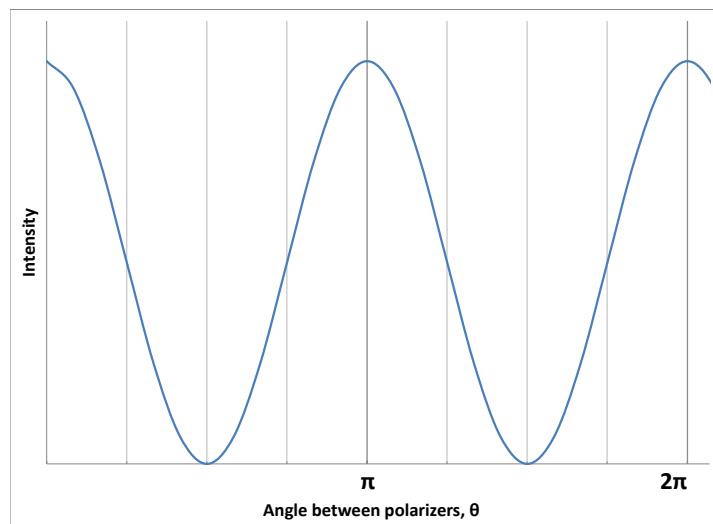


Figure 6: The intensity of light passed through two polarizers as a function of the angle between them, θ , according to the Law of Malus: $I = I_0 \cos^2(\theta)$.

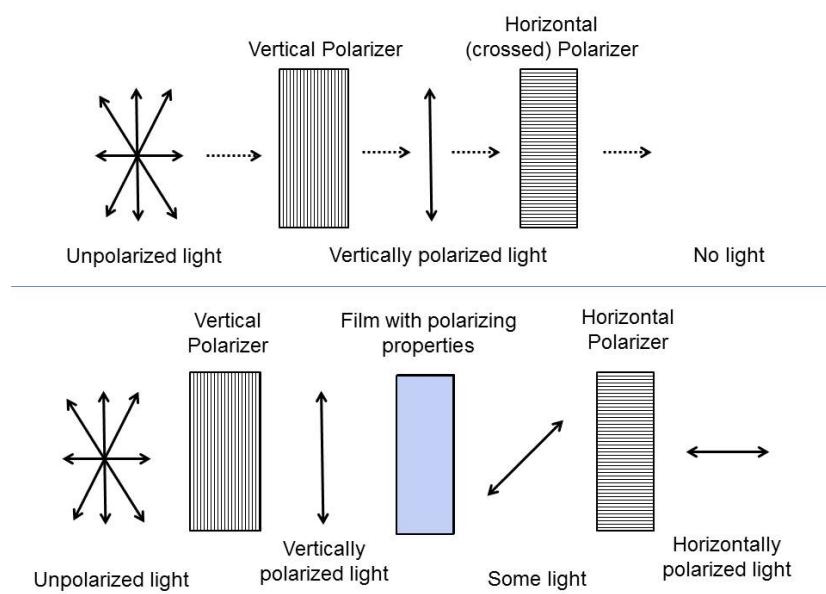


Figure 7: Properties of crossed polarizers used by a crossed polarizer microscope. No light passes through crossed polarizers, but some light is allowed through when a third polarizer is added between the crossed polarizers (and is not parallel to either polarizer).

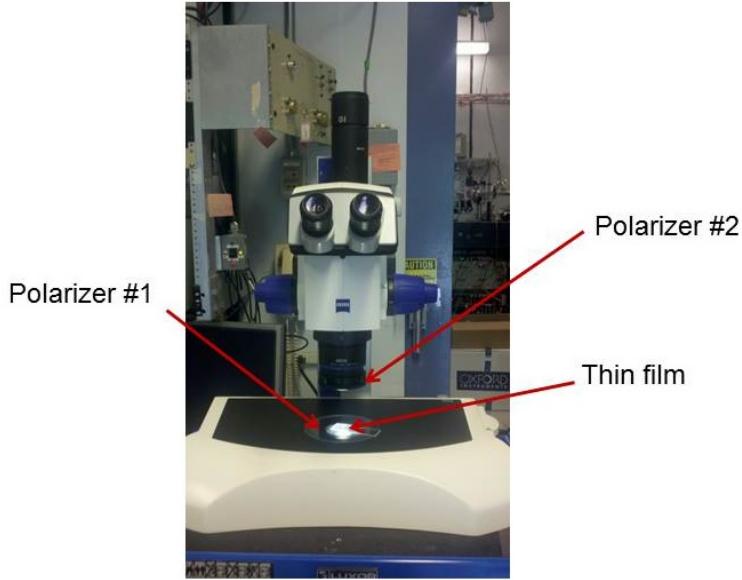


Figure 8: A picture of a thin film placed in the crossed polarizer microscope.

A graph of intensity as a function of angle θ between the polarization directions of the first polarizer and a particular domain in the thin film can be seen in Figure 9. Minima in intensity occur at every $\pi/2$ radians, where the polarization direction of that domain in the film is parallel to one of the polarizers in the microscope (and thus perpendicular to the other). When this occurs, there is no light transmitted because the assembly of polarizers is functioning again as a setup of crossed polarizers. However, it is interesting to note that, although we know when the polarization direction of the sample lines up with one of the polarizers in the microscope, we do not know which polarizer with which we have aligned. That is to say, we don't know the absolute polarization of the domains in our sample. In theory, this dilemma could be solved with the removal of one of the original crossed polarizers. The sample's polarization direction must be either parallel or perpendicular to that of the remaining polarizer, which can be easily determined by the transmission (or lack thereof) or light through the remaining two polarizers. However, although this model is theoretically sound, we realized our thin films are not strong enough polarizers to allow determination of ultimate polarization direction. But, although this analysis system leaves some ambiguity in absolute polarization direction, it is still an excellent and highly sensitive way to determine alignment and polarization of domains in the thin films.

To study the domains via polarization, pictures can be taken on the polarization microscope and analyzed visually. Because the human eye responds to

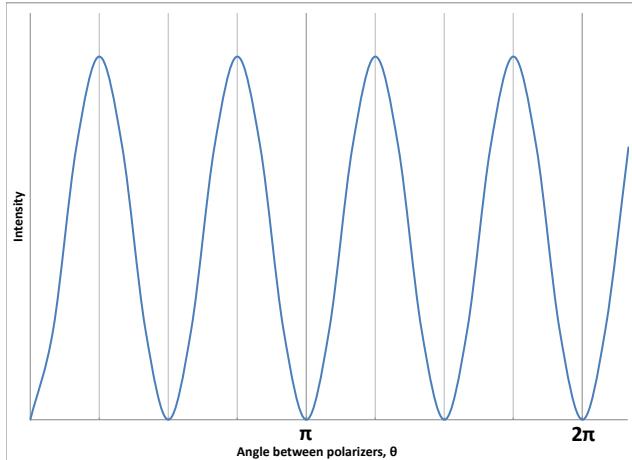


Figure 9: Graph of intensity of light transmitted through three polarizers (the first and third being crossed) as a function of the angle between the first and second polarizers.

intensity logarithmically according to Weber's Law:

$$\frac{\Delta S}{I} = k$$

or

$$S = k \ln \frac{I}{I_0}$$

it will be easier to detect minima in intensity than maxima. Or, said another way, the human eye is able to detect much smaller intensity variations in light when the initial intensity is low. This is shown in Figure 10, a function of the perceived intensity of light by the human eye as a function of actual intensity. Clearly, differences in intensity are easier to perceive at lower intensities. Absolute minima in intensity will be more successfully perceived than absolute maxima. Therefore, polarizing domains will be found by when they become dark under the crossed polarizer microscope.

4 Anthracene films by solvent evaporation

One method of growing organic thin films from solution is through evaporation. In this method, a substrate is placed vertically into a beaker of the solution of organic material. As the solvent evaporates from the solution, a film is grown on the substrate. Variations on this basic method include addition of a heating

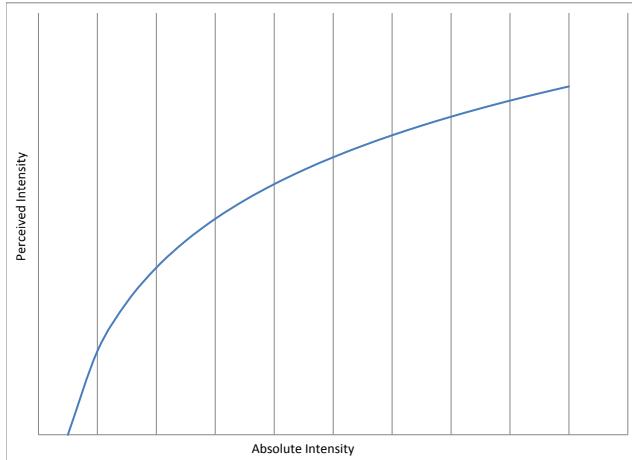


Figure 10: A graph of perceived intensity of light by the human eye as a function of actual intensity, according to Weber’s Law.

element, or pumping the solution out at a controlled rate. This method is shown in Figure 11. The evaporation method was first test on anthracene films to maximize orientation.

4.1 Effect of solution concentration on film growth

One method of optimizing thin film growth in the evaporation method is variation of the solution concentration. We tested several concentration of anthracene in ethyl acetate, ranging from 0.123-3.498 mg/mL. The saturated concentration of anthracene in ethyl acetate at room temperature is 8.773 mg/mL [7]. Films were grown from these solution at room temperature (21°C) with no external pumping. We achieve good film growth and domain orientation for films grown at higher concentrations (see Figure 12). However, for solution concentrations below 0.5 mg/mL, only small films are grown on the substrate. This is because nucleation, or the beginning of crystal growth on the substrate, occurs at points of supersaturation in the solution. At very low concentrations, little film is grown because little oversaturation occurs in the solution. The film that does grow at these low concentrations grows towards the bottom of the substrate, when the concentration of the solution has increased due to solvent evaporation. From this, we can conclude that to grow useful films from solution, the concentration of the solution needs to be high enough to allow sufficient supersaturation and nucleation on the substrate surface, to allow crystallization to occur.

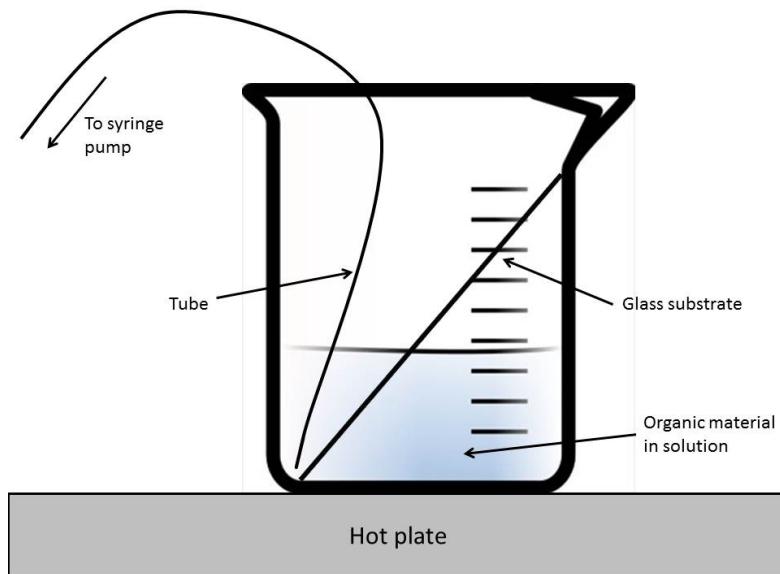
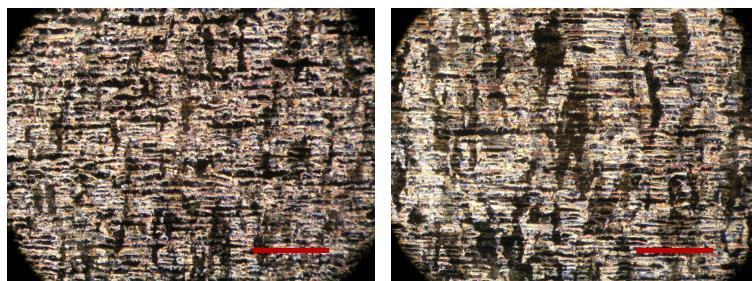


Figure 11: Evaporation method. The substrate is placed into a beaker of the organic material in solution. Optional variations on this method include the addition of heat via a hot plate, and the controlled removal of the solution via a syringe pump. The angle of the glass slide from the bottom of the beaker is 77.5° .



(a) Film grown from 3.498 mg/mL solution of anthracene in ethyl acetate (b) Film grown from 2.285 mg/mL solution of anthracene in ethyl acetate

Figure 12: Polarized optical micrographs of anthracene films at high concentration levels. The scale bar in each is 3 mm, and the growth direction is vertical.

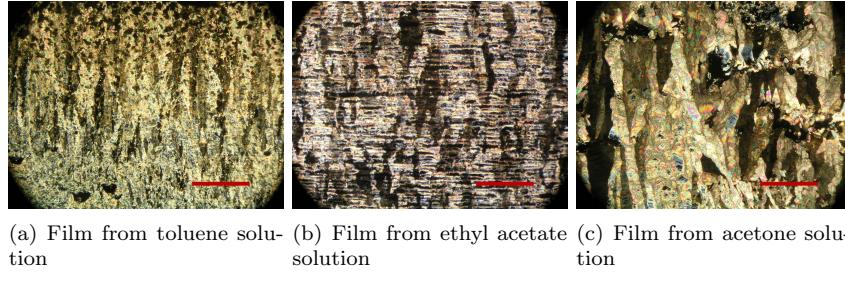


Figure 13: Polarized optical micrographs demonstrating the effects of vapor pressure on film growth. Vapor pressures from left to right: 3.8 kPa, 12.7 kPa, 30.7 kPa. Scale bar is 3 mm, growth direction is vertical.

4.2 Effect of vapor pressure on film growth

Another way to vary film growth in the evaporation method is to change the solvent used to place the organic material in solution, thus changing the vapor pressure and the evaporation rate of the solution.

Solutions with similar concentrations (2.119-2.407 mg/mL) of anthracene were prepared in three solvents of varying vapor pressures. The solvents used were Acetone (vapor pressure of 30.7 kPa at 25°C), Ethyl Acetate (vapor pressure of 12.7 kPa at 25°C), and Toluene (vapor pressure of 3.8 kPa at 25°C). Film domain orientation tends to increase with increasing vapor pressure. The domains grow in length and width when a solvent with higher vapor pressure (see Figure 13). This indicates that higher evaporation rate contributes to higher orientation in crystallization in film growth.

4.3 Effect of pumping on film growth

One variation on the evaporation method with previously documented success is pumping the solution out of the beaker at a controlled rate [3]. In our experimental setup, a syringe pump was used to pump out the liquid, using a small tube inserted in the beaker of solution to gradually remove the solution. For a high concentration of anthracene in ethyl acetate (3.6 mg/mL), a slow pumping rate (10 mL/hr) improved domain orientation. However, a higher pumping rate (20 mL/hr) showed a decline in the orientation of crystalline domains within the thin film. This is likely due to the higher deposition rate resulting in the deposition of a liquid film. The molecules randomize their orientation before they dry, causing a decline of crystalline orientation in the growth direction. This data can be seen in Figure 14.

4.4 Effect of heating on film growth

Another way to control the speed of film deposition onto the substrate is through varying the temperature, and thus the rate of evaporation. Films grown from an-

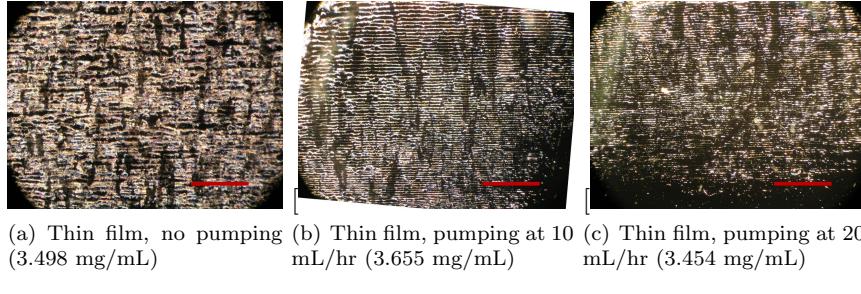


Figure 14: Comparison of domain orientation from anthracene in ethyl acetate solution as a function of controlled pumping of solution. Scale bar is 3 mm, Growth direction is vertical.

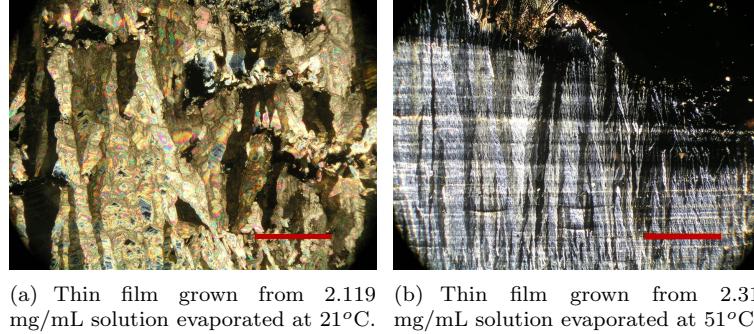
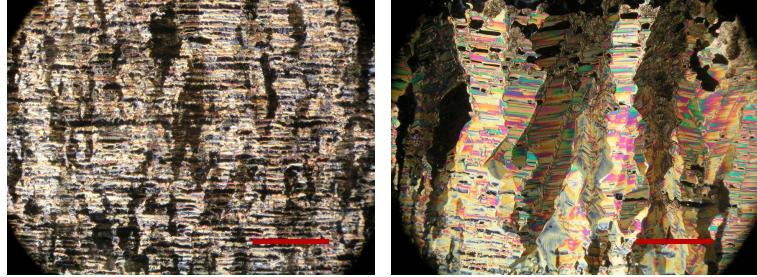


Figure 15: Polarized optical micrographs of films grown from anthracene solution in acetone showing the effects of temperature of film growth. Scale bar is 3 mm, growth direction is vertical.

anthracene in solution in acetone demonstrate higher orientation when evaporated at higher temperatures (see Figure 15). Similar effects of higher temperature can be seen in films grown from anthracene in ethyl acetate solution (see Figure 16).

4.5 Effect of simultaneous heating and pumping on film growth

Since heat and controlled pumped removal of solution have positive effects on crystalline orientation in film growth, it logically follows that the two manipulations in tandem may have an even more positive effect. For films grown from ethyl acetate solution, pumping at higher temperatures does have increase crystalline orientation in thin films. Figure 17 shows a comparison of films grown from ethyl acetate with no pumping or heating, with just pumping, with just heating, and with both pumping and heating. Figure 18 demonstrates domain switching in different orientations in the films in Figure 17 grown with heat and



(a) Thin film grown from 2.285 mg/mL solution evaporated at 21°C. (b) Thin film grown from 3.046 mg/mL solution evaporated at 53°C.

Figure 16: Polarized optical micrographs of films grown from anthracene solution in ethyl acetate showing the effects of temperature on film growth. Scale bar is 3 mm, growth direction is vertical.

with heat and pumping. Notice the domains switch at a rotation of approximately 45° . We expect 90° symmetry of our domains because each polarized domain will cross one of the fixed crossed polarizer directions at every 90° . This domain switching at around 45° is consistent with this model of 90° symmetry.

4.6 Further analysis of evaporation variations in anthracene film growth

To further explore the effect of heat and pumping on film growth, domain analyses were performed on the four films shown in Figure 17. For further analysis, we will define them as Films A (no pumping or heating), Film B (pumping, no heating), Film C (heating, no pumping), and Film D (heating and pumping). Figure 19 shows histograms for the deviation of the orientation of the domains in each film from the growth direction of the film. Although the Gaussian shape appears better in the first two films, the angular spread decreases significantly in the final histogram, demonstrating the higher orientation present in films grown with heating and pumping. Table 1 shows further data on the orientation of domains in these films. Notice the lengths of the domains in the films increase with the addition of heat and pumping, showing higher domain orientation. Additionally, smaller angular spread with the addition of heating and pumping shows higher orientation of domains. From this data, we can conclude that heating and pumping both contribute to higher domain orientation in thin films of anthracene grown via evaporation.

4.7 Effect of vibrations on film growth

The films studied thus far were grown in a fume hood in a chemistry lab. Although this evaporation location is good for controlling fumes from the evaporation process, there are many sources of vibration in this room which may affect

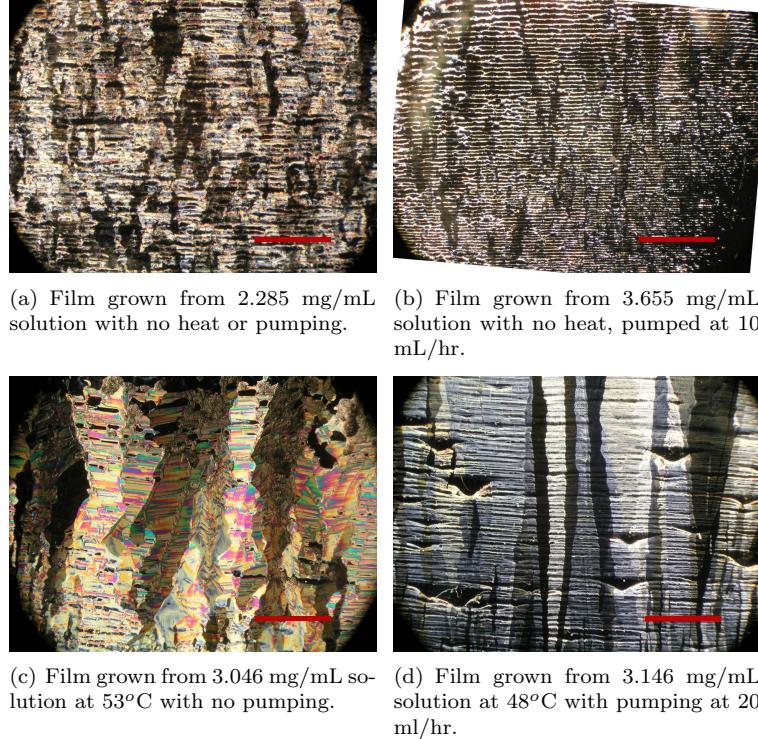
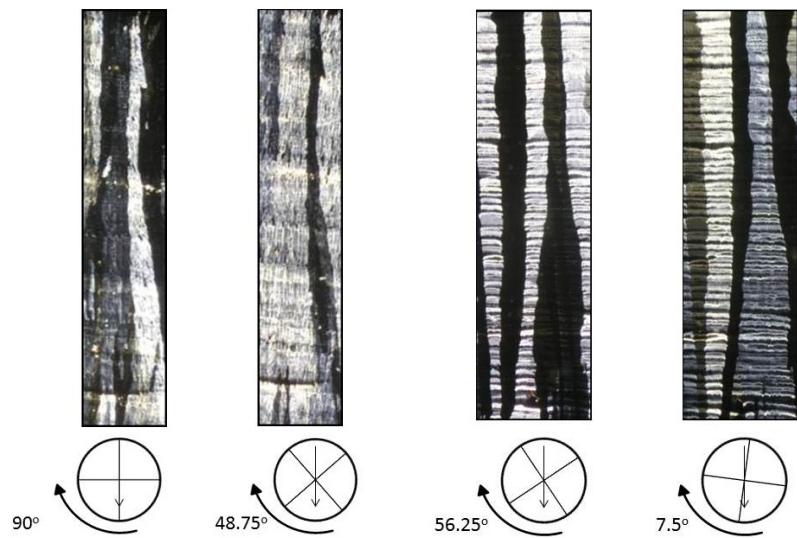


Figure 17: Polarized optical micrographs of films grown from ethyl acetate solution with various evaporation conditions as specified. Scale bar is 3 mm, growth direction is vertical.

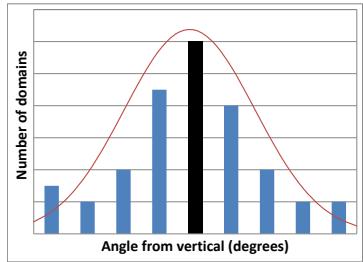
Film	Max Length (mm)	Mean Length (mm)	Mean Angle	Angle Std Dev
A	5.43	3.18	-0.47°	5.47°
B	5.97	3.43	-3.16°	5.33°
C	8.48	5.13	7.79°	5.43°
D	9.90	6.23	-2.91°	3.44°

Table 1: Data showing the domain orientation in films grown with varying parameters in the evaporation deposition method.

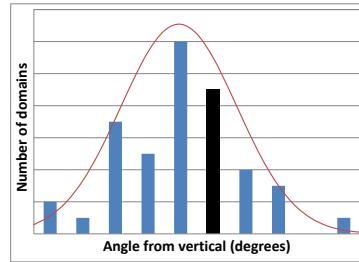


(a) Film grown from 3.046 mg/mL solution of anthracene in ethyl acetate, evaporated at 53°C with no pumping. (b) Film grown from 3.146 mg/mL solution of anthracene in ethyl acetate, evaporated at 48°C with pumping at 20 mL/hr.

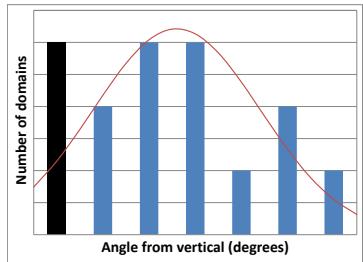
Figure 18: Polarized optical micrographs of domain switching. The growth direction is represented by the downwards vertical arrow, and the orientation of the crossed polarizers is shown by the crossed lines. Film 2 images are 1.46 mm wide each and Film 3 images are 2.88 mm wide.



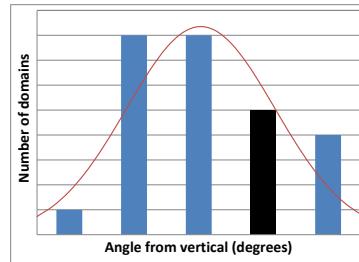
(a) Film A



(b) Film B

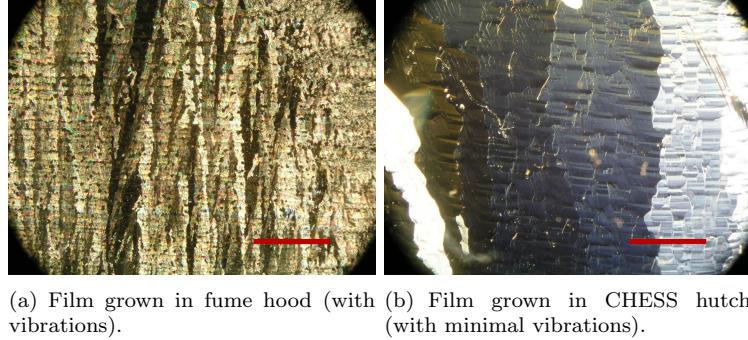


(c) Film C



(d) Film D

Figure 19: Histograms of angular deviation of domains in the thin films from the vertical (growth) direction. Each bar in the histograms represents a spread of 3° , and the black bar signifies the 0° mark. A Gaussian curve based on the mean and standard deviation of the data is also shown on each graph for comparison.



(a) Film grown in fume hood (with vibrations).
(b) Film grown in CHESS hutch (with minimal vibrations).

Figure 20: Films grown from 2.008 mg/mL solution of anthracene in acetone demonstrated the effects of vibration on film growth. Scale bar is 3 mm, growth direction is vertical.

film growth. To test this, we placed one evaporation setup in the fume hood as usual, and another in a very vibrationally quiet and stable room (the D1 hutch in the Cornell High Energy Synchotron Source) with the same solution of anthracene. From the films obtained, we determined that vibrations do have an effect on the growth of the thin films (see Figure 20). The domains become much wider and longer in the film grown with no vibration.

5 Pyrene films by solvent evaporation

The evaporation method was also tested in deposition of pyrene films

5.1 Evaporation without heat

Obtaining well-oriented films of pyrene proved to be more difficult than those of anthracene. This is likely due to the more complicated lattice structure of pyrene. The lattice structures can be seen in Figures 2 and 3. Anthracene has a simpler packing structure, so it is easier for crystals to grow and form well defined orientations of crystals. Films grown from straight evaporation (no heating or pumping) from solutions of 1.38 mg/mL and 0.36 mg/mL of pyrene in acetone produced films that were thick and flaky, with no polarized domains visible. Processes of low concentrations of pyrene in benzene with straight evaporation and pumped at 10 mL/hr and 20 mL/hr produced either no films left on the substrate or a very small film at the very bottom of the substrate. Similarly, a film grown without pumping from a 0.71 mg/mL solution in toluene produced nearly no film. However, a successful film was grown from 1.52 mg/mL solution of pyrene in ethyl acetate at room temperature with no pumping. The strong polarizing domains in this film can be seen in Figure 21.

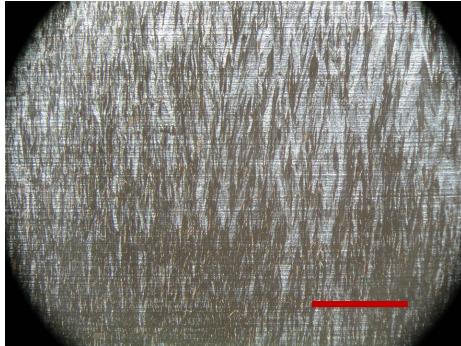
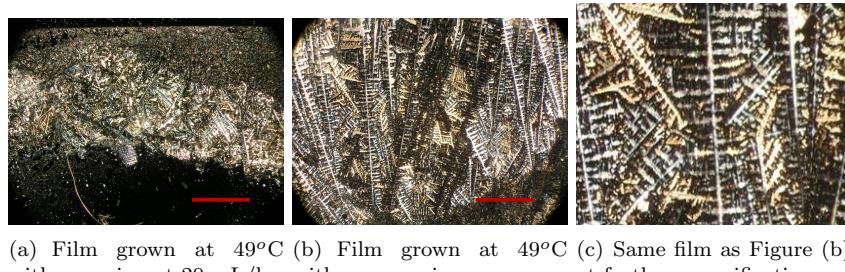


Figure 21: Polarized optical micrograph of a pyrene film grown from ethyl acetate solution. Scale bar is 3 mm, growth direction is vertical.

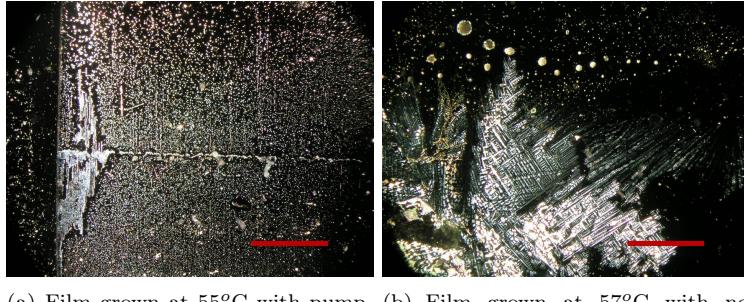


(a) Film grown at 49°C (b) Film grown at 49°C (c) Same film as Figure (b)
with pumping at 20 mL/hr. with no pumping. at further magnification.

Figure 22: Films grown from 2.42 mg/mL solution of pyrene in acetone with heat added. Dendritic structure is present in both films. Notice the small dendrimers are perpendicular to the large branches, signifying a very precise and well defined growth structure. Scale bar is 3 mm, growth direction is vertical. The third picture is about 3 mm wide.

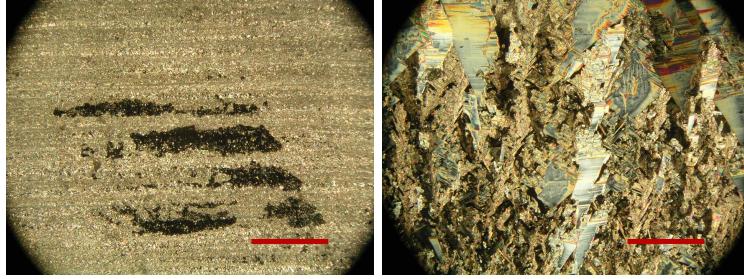
5.2 Evaporation with heat

More oriented domains in pyrene films were obtained when films were grown at higher temperatures, with and without pumping. In all cases, heating in evaporation created a dendritic structure in the crystal growth in the thin films, implying a higher level of supersaturation in the solution, forcing faster crystallization on the substrate surface. Films were successfully grown from solution of pyrene in acetone and ethyl acetate evaporated with heat added. Films were also grown from these solutions, heated and pumped out at 20 mL/hr. The pumped processes produced much less film on the substrate, and the films showed dendritic morphology. The films grown from acetone and ethyl acetate can be seen in Figures 22 and 23, respectively.



(a) Film grown at 55°C with pumping at 20 mL/hr. (b) Film grown at 57°C with no pumping.

Figure 23: Films grown from 1.41 mg/mL solution of pyrene in ethyl acetate with heat added. Dendritic structure is present in both films. Scale bar is 3 mm, growth direction is vertical.



(a) Film grown in fume hood (with vibrations). (b) Film grown in D1 CHESS hutch (with minimal vibrations).

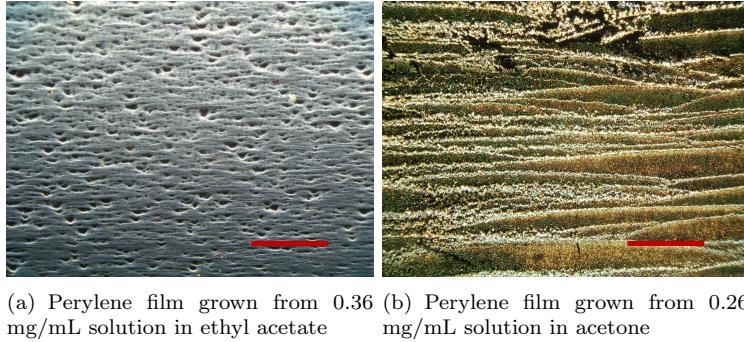
Figure 24: Pictures showing the effects of vibrations on film growth. The film grown with vibrations demonstrates no polarization orientation, and the film grown without vibrations shows strong orientation. Scale bar is 3 mm, growth direction is vertical.

5.3 Effects of vibration on film growth

Like the anthracene (see Section 4.7), the pyrene films were tested for the effects of room and fume hood vibration on film growth. Again, we see great improvement in orientation in the films that are grown with minimal vibrations, as demonstrate in Figure 24.

6 Perylene films by solvent evaporation

Several films were grown from perylene in solution in both acetone and ethyl acetate. Films were grown in the chemistry lab fume hood and the CHESS hutch (where previous films with minimal vibrations in growth had been grown). No polarized orientation was viewed with this films, as can be seen below in Figure



(a) Perylene film grown from 0.36 mg/mL solution in ethyl acetate
 (b) Perylene film grown from 0.26 mg/mL solution in acetone

Figure 25: Perylene films grown from the evaporation method, with no heating or pumping. The growth direction is vertical and the scale bars are 3 mm.

25.

7 Anthracene solution shearing films

A different method of growing organic thin films from solution is known as solution shearing, doctor blading or knife coating. In this method, a drop of solution is placed on the substrate, and a shearing surface at a fixed height above the substrate spreads the solution at a fixed rate to grow a film. A schematic of this experimental setup can be seen in Figure 26, and a picture of the actual experimental setup can be seen in Figure 27. Small amounts of solution, typically 30-50 μL , can be deposited quickly and efficiently.

7.1 Anthracene solution shearing films from acetone solution

Films were grown from a 2.589 mg/mL solution of anthracene in acetone at speeds varying from 1 cm/hr (2.78 $\mu\text{m/s}$) to 200 cm/hr (556 $\mu\text{m/s}$). Because of the high vapor pressure (and thus quick evaporation) of acetone, solutions spread at slow speeds dried out before being spread laterally, resulting in uninteresting film growth. However, beginning at around 10 cm/hr (27.78 $\mu\text{m/s}$), good polarized orientation can be seen in the grown films (see Figure 28). Histograms of the angular deviation of the polarized domains from the vertical (growth) direction can be seen in Figure 29. Although neither demonstrates exceptional orientation like the evaporation films did, there is reasonable angular orientation about the growth direction.

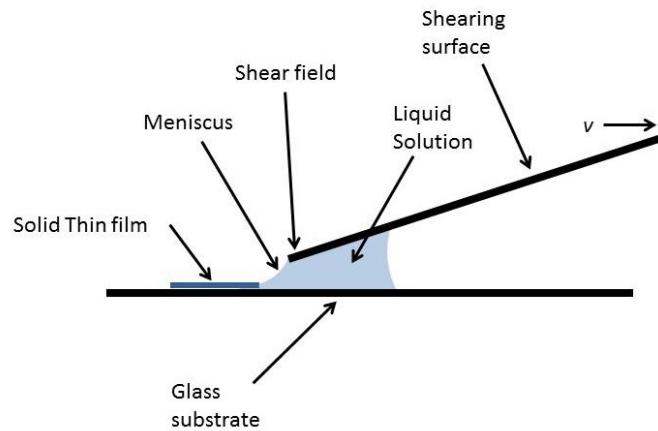


Figure 26: A diagram of the solution shearing method. A drop of solution is spread at a fixed rate by a shearing surface a fixed height above the substrate.

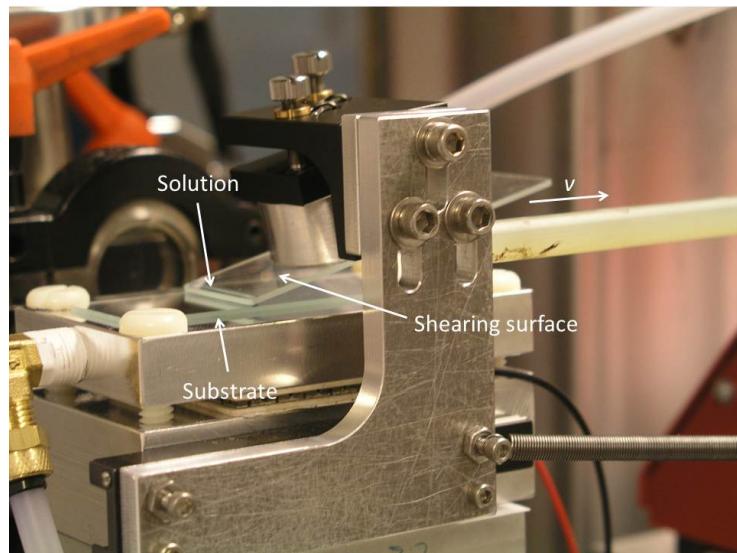
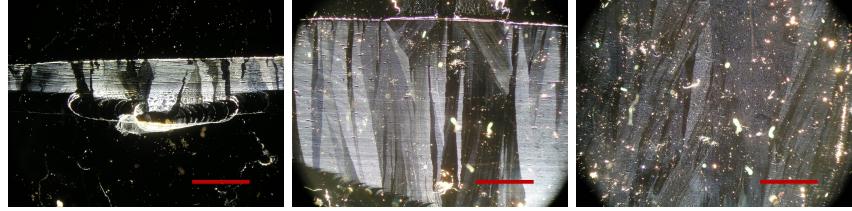
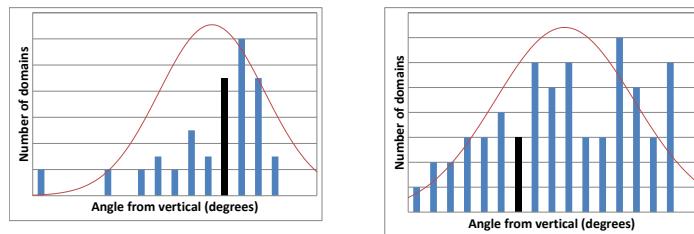


Figure 27: A picture of the experimental setup for the solution shearing method.



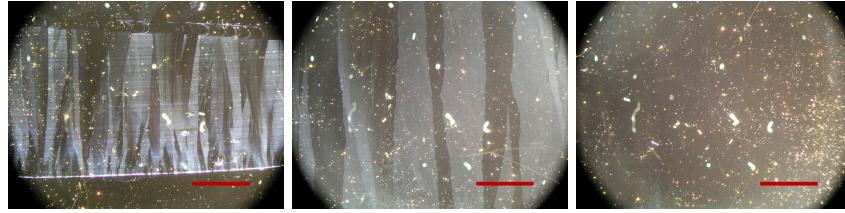
(a) Film grown at 10 cm/hr (b) Film grown at 50 cm/hr (c) Film grown at 200
(27.78 $\mu\text{m/s}$) (138.89 $\mu\text{m/s}$) cm/hr (556 $\mu\text{m/s}$)

Figure 28: Films grown at varying speeds from 50 μL drops of a 2.589 solution of anthracene in acetone. Scale bar is 3 mm, shearing (growth) direction is vertical.



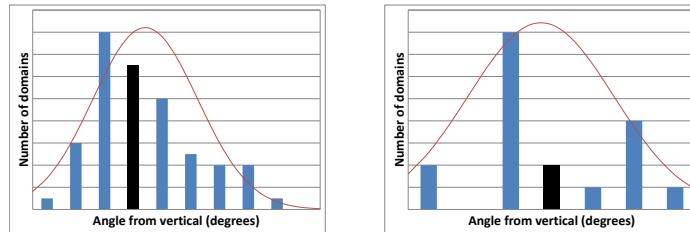
(a) Histogram of film grown at 50 (b) Histogram of film grown at 200
cm/hr (138.89 $\mu\text{m/s}$) cm/hr (556 $\mu\text{m/s}$)

Figure 29: Histograms of angular deviation of polarized domains from the vertical (growth) direction. In each histogram, each bar represents an angular spread of 3 degrees, and the black bar indicates the bar centered at 0 degrees.



(a) Film grown at 10 cm/hr (b) Film grown at 50 cm/hr (c) Film grown at 100 (27.78 $\mu\text{m/s}$) from a 40 μL (138.89 $\mu\text{m/s}$) from a 40 μL cm/hr (277.8 $\mu\text{m/s}$) from a 30 μL drop

Figure 30: Films grown from 2.193 solution of anthracene in ethyl acetate at speeds indicated. Notice higher orientation at lower speeds, and no visible domains in the highest speed. Scale bar is 3 mm, shearing (growth) direction is vertical.

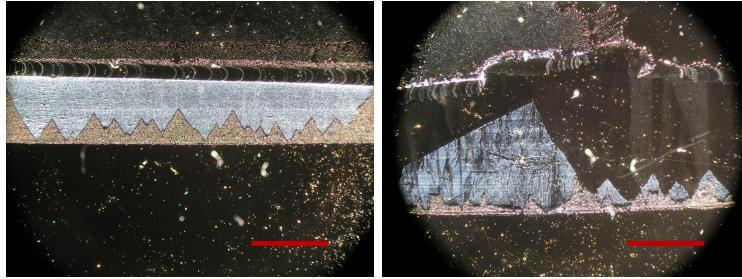


(a) Film grown at 10 cm/hr from a 40 μL drop(27.78 $\mu\text{m/s}$) (b) Film grown at 50 cm/hr from a 40 μL drop(138.89 $\mu\text{m/s}$)

Figure 31: Histograms of angular deviation of polarized domains away from the growth direction. Each bar in the histograms represents a spread of 3° , and the black bar signifies the 0° mark. A Gaussian curve based on the mean and standard deviation of the data is also shown on each graph for comparison.

7.2 Anthracene solution shearing films from ethyl acetate solution

Films were grown from a 2.193 mg/mL solution of anthracene in ethyl acetate at speeds varying from 10 cm/hr ($27.78 \mu\text{m/s}$) to 100 cm/hr ($277.8 \mu\text{m/s}$). Good molecular alignment can be seen at the slower speeds in this range, but no alignment is seen in higher speeds (entering the Landau-Levich regime of liquid film deposition). Figure 30 shows photographs of films grown at 10 cm/hr, 50 cm/hr and 100 cm/hr to show the contrast in orientation. Figure 31 further exemplifies the relation of molecular alignment to speed through histograms of angular deviation of domains from the growth direction.



(a) Film grown at 10 cm/hr (27.78 $\mu\text{m/s}$) from a 40 μL drop of a 1.77 $\mu\text{m/s}$ mg/mL solution of pyrene in acetone (b) Film grown at 10 cm/hr (27.78 $\mu\text{m/s}$) from a 30 μL drop of a 1.93 mg/mL solution of pyrene in ethyl acetate

Figure 32: Films grown from pyrene solution at low speeds, showing jagged growth with no polarized domains. Scale bar is 3 mm, shearing (growth) direction is vertical.

8 Pyrene solution shearing films

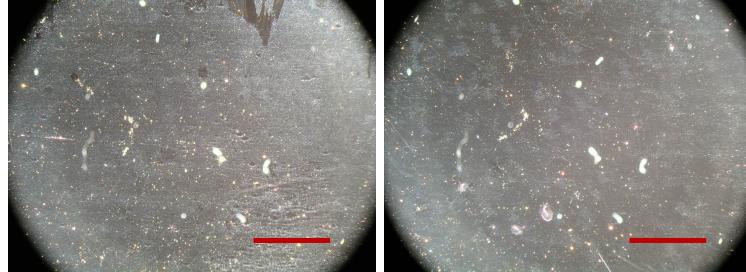
Pyrene films were grown from a 1.77 mg/mL solution of pyrene in acetone with speeds ranging from 10 cm/hr (27.78 $\mu\text{m/s}$) to 200 cm/hr (555.56 $\mu\text{m/s}$), and from a 1.93 solution of pyrene in ethyl acetate with speeds ranging from 10 cm/hr (27.78 $\mu\text{m/s}$) to 100 cm/hr (277.8 $\mu\text{m/s}$). At lower speeds, jagged and disoriented films are grown (see Figure 32), and at higher speeds, films are grown with no visible domains, most likely due to entering the Landau-Levich regime of film growth (see Figure 33). However, some oriented film growth can be seen in the film grown from acetone solution at 50 mL/hr (138.89 $\mu\text{m/s}$). Figure 34 shows a picture of this film.

9 Perylene solution shearing films

Films were grown from 0.75 mg/mL solution of perylene in acetone at speeds 10 cm/hr (27.78 $\mu\text{m/s}$) and 50 cm/hr (138.89 $\mu\text{m/s}$). No polarized orientation was seen in these films. Figure 35 shows these films in a crossed-polarizer microscope.

10 Film stability

Analysis of films over time revealed that films grown from the solution shearing method tend to disappear off of their substrates fairly quickly. The original films grown disappeared over about a week. To determine the cause of this phenomenon, multiple films were made with identical processes with solution shearing and left in different locations. The first test used films placed in the CHESS G-Line area (where the original films had disappeared) and the CHESS D-Line hutch. D-Line has fewer vibrations and less air flow than G-Line, and



(a) Film grown at 200 cm/hr (555.56 $\mu\text{m/s}$) from a 40 μL drop of a 1.77 $\mu\text{m/s}$) from a 40 μL drop of a 1.77 mg/mL solution of pyrene in acetone (b) Film grown at 100 cm/hr (277.8 mg/mL solution of pyrene in ethyl acetate

Figure 33: Films grown from pyrene solution at high speeds, showing no polarized domains in the growth direction, due to entering the Landau-Levich regime of film growth. Scale bar is 3 mm, shearing (growth) direction is vertical.

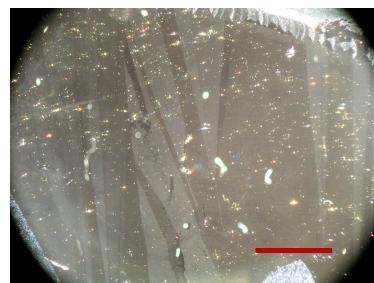
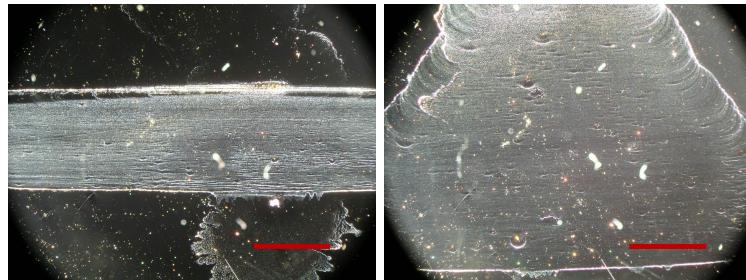


Figure 34: Film grown from a 40 μL drop of a 1.77 mg/mL solution of pyrene in acetone at 50 mL/hr (138.89 $\mu\text{m/s}$). Scale bar is 3 mm, shearing direction is vertical.



(a) Film grown at 10 cm/hr (27.78 $\mu\text{m/s}$) (b) Film grown at 50 cm/hr (138.89 $\mu\text{m/s}$)

Figure 35: Films grown from perylene solution in acetone using the solution shearing method at speeds indicated. Scale bar is 3 mm, shearing (growth) direction is vertical.

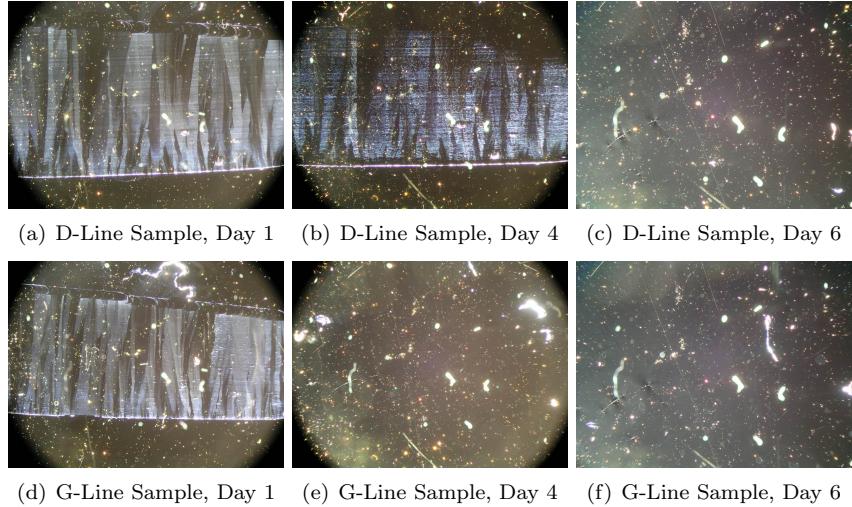


Figure 36: Polarized optical micrographs of identical samples left for days in D-Line and G-Line.

a slightly lower ambient temperature (20°C , where G-Line is 24°C). Figure 36 shows a comparison of the films left in D-Line and G-Line. Notice that, although the D-Line sample is stable for slightly longer, both samples eventually deteriorate in these environments.

To further test the nature of this phenomenon, identical solution sheared samples of anthracene were made to be left in G-Line, D-Line, and the MAC-CHESS refrigerator (3°C). The results of these trials over time can be seen in Figure 37.

11 Future Work

There is much that can be added to this project. X-ray scattering analysis on the crystal structure of these films will likely be done by Detlef Smilgies in October of 2011 in the G2 beamline in CHESS. To determine if the film growth has resulted in oriented crystalline film growth, grazing incidence wide angle x-ray scattering at D1 station or surface diffraction at G2 station will be used to analyze the bright reflections off of the crystalline surface and consequently determine if there is strong molecular alignment within the crystal structure. Figure 38 shows an example of a an x-ray diffraction pattern taken from a thin film with strong orientation.

Further exploration is necessary to determine the best way to produce films which do not deteriorate over time as ours have. One possibility is to use Tri-isopropylsilyl ethynyl (TIPS) pentacene to grow films. Pentacene is larger than anthracene (5 rings as opposed to 3), so will be stable over time. However, pentacene is insoluble, making our solution-based deposition techniques ineffective.

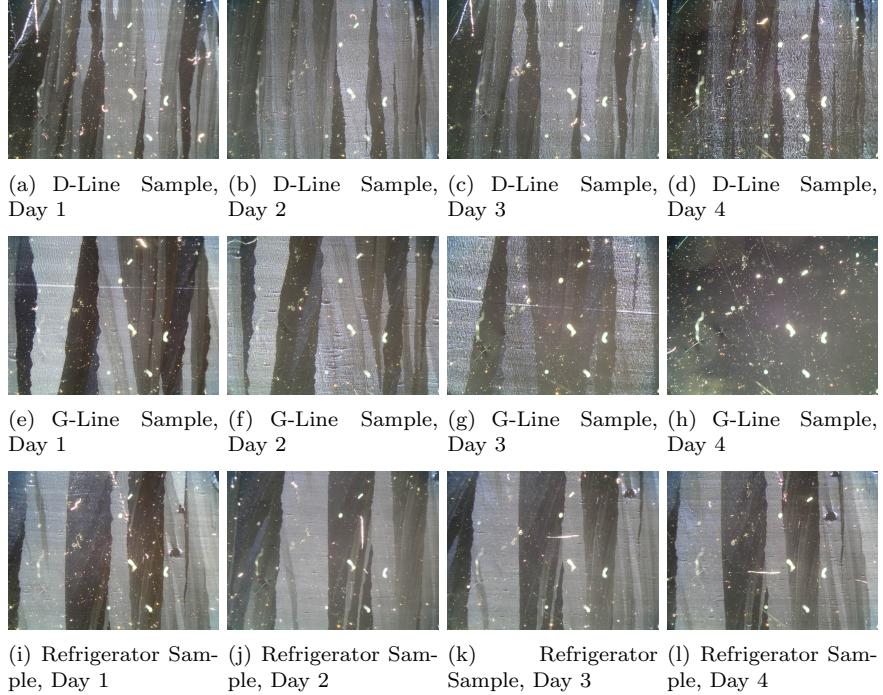


Figure 37: Identical samples left in three different environments over several days. Ambient temperature are, respectively, 20°C, 24°C, and 3°C.

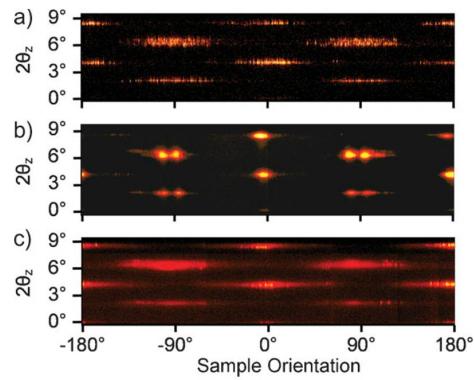


Figure 38: X-ray diffraction pattern from a TIPS pentacene film obtained from Sele et al [1]. The strong intensity peaks indicate strong crystalline orientation of the thin film. Ideally, the x-ray diffraction patterns from our thin films will demonstrate similar crystalline orientation.

However, the addition of other groups onto the primary pentacene molecule (as in TIPS pentacene) enables solubility of pentacene. So, this could be a worthwhile exploration.

In addition, another molecule possibly worth exploring is tetracene. Tetracene is composed of four benzene rings in a line, so is effectively halfway between anthracene and pentacene. Its being larger than anthracene could add stability to the films over time, and its being smaller than pentacene could potentially enable solubility. More preliminary research needs to be done to determine if this is a viable option.

12 Conclusions

The results from the films grown this summer are very promising for potential relevance in the field of organic electronics. Good orientation was obtained using a variety of simple, solution-based film deposition techniques, and future applications of these deposition procedures could be very important for directed growth of thin films for organic electronics. Future work will be necessary for industrially relevant films, but growth with these model molecules has proved very promising for future applications.

13 Acknowledgements

I would like to acknowledge my advisor, Detlef Smilgies, whose guidance and teaching have been extremely helpful throughout the summer. In addition, I would like to thank the organizers of the Cornell REU Program: Georg Hoffstaetter, Ivan Bazarov, Monica Wesley, and Lora Hine. This work is based upon research conducted at the Cornell High Energy Synchrotron Source (CHESS) which is supported by the National Science Foundation and the National Institutes of Health/National Institute of General Medical Sciences under NSF award DMR-0936384.

References

- [1] Christoph W. Sele, B. K. Charlotte Kjellander, Bjoern Niesen, Martin J. Thornton, J. Bas P. H. van der Putten, Kris Myny, Harry J. Wondergem, Armin Moser, Roland Resel, Albert J.J. M. van Breemen, Nick van Aerle, Paul Heremans, John E. Anthony, and Gerwin H. Gelinck, *Controlled Deposition of Highly Ordered Soluble Acene Thin Films: Effect of Morphology and Crystal Orientation on Transistor Performance*, *Adv. Mater.* 2009, **21**, 4926-4931.
- [2] Jonathan Rivnay, Leslie H. Jimison, John E. Northrup, Michael F. Toney, Rodrigo Noriega, Shaofeng Lu, Tobin J. Marks, Antonio Facchetti, and Alberto Salleo, *Large modulation of carrier transport by grain-boundary molec-*

ular packing and microstructure in organic thin films, Nature Materials 2009, 8, 952-958.

- [3] Randall L. Headrick, Hua Zhou, Binran Wang, Yiping Wang, Greggory P. Carpenter, Alex C. Mayer, Matthew Lloyd, George G. Malliaras, Alexander Kazimirov, John E. Anthony, *Growth of macroscopic-area single crystal polyacene thin films on arbitrary substrates*, <http://arxiv.org/abs/1107.3277>.
- [4] Mael Le Berre, Yong Chen, and Damien Baigl, *From Convective Assembly to Landau-Levich Deposition of Multilayered Phospholipid Films of Controlled Thickness, Langmuir*, 2009, 25, 2554-2557.
- [5] Zhen Yuan, D. Bruce Burckel, Plamen Atanassov and Hongyou Fan, *Convective self-assembly to deposit supported ultra-thin mesoporous silica films, J. Mater. Chem.*, 2006, 16, 46374641.
- [6] Brian G. Prevo and Orlin D. Velev, *Controlled, Rapid Deposition of Structured Coatings from Micro- and Nanoparticle Suspensions, Langmuir*, 2004, 20 (6), 2099-2107.
- [7] Abolghasem Jouyban, Jamshid L. Manzoori, Vahid Panahi-Azar, Jafar Soleymani, Mohammad A. A. Fakhree, Ali Shayanfar, and William E. Acree, Jr., *Solubility of Anthracene in Binary and Ternary Mixtures of Cyclohexanone, Ethyl Acetate, and Methanol at 298.2 K, J. Chem. Eng. Data* 2010, 55, 26072609.