Communicating Research to the General Public

At the March 5, 2010 UW-Madison Chemistry Department Colloquium, Prof. Bassam Z. Shakhashiri, the director of the Wisconsin Initiative for Science Literacy (WISL), encouraged all UW-Madison chemistry Ph.D. candidates to include a chapter in their Ph.D. thesis communicating their research to non-specialists. The goal is to explain the candidate's scholarly research and its significance to a wider audience that includes family members, friends, civic groups, newspaper reporters, program officers at appropriate funding agencies, state legislators, and members of the U.S. Congress.

Over 50 Ph.D. degree recipients have successfully completed their theses and included such a chapter.

WISL encourages the inclusion of such chapters in all Ph.D. theses everywhere through the cooperation of Ph.D. candidates and their mentors. WISL is now offering additional awards of $250 for UW-Madison chemistry Ph.D. candidates.

Wisconsin Initiative for Science Literacy

The dual mission of the Wisconsin Initiative for Science Literacy is to promote literacy in science, mathematics and technology among the general public and to attract future generations to careers in research, teaching and public service.

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Vapor deposition rate modifies order in highly structured glasses

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Chemistry)

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Chapter 2:

Communicating Research to Non-Expert Audience as a Part of the Wisconsin Initiative for Science Literacy Program

I have written this chapter of my thesis to explain my research to a broader audience of non-scientists, and scientists outside of my field. Many times, scientists' most important results and contributions are obscured by jargon and hidden behind paywalls, making it hard for others to know or understand what we did and why it is important. However, it is important that we can tell other people our stories clearly to show why our science is so important to ourselves and others. Therefore, I wanted to write a chapter so that my family, friends, and anyone else who may be interested in what I've done during my PhD has a document that is more accessible than a scientific paper. Thanks to all the members of the Wisconsin Initiative for Science Literacy at UW-Madison for providing this platform, and for sponsoring and supporting the creation of this chapter.

When I first came to graduate school, I wasn't sure what I wanted to study. I came in with some thoughts based on classes I had taken during my undergraduate chemistry major. I had enjoyed my physical and inorganic chemistry classes. My favorite part of my courses had always been learning visual explanations for how certain chemistry worked. I never really liked the equations and arrows of organic chemistry, but when I learned how the atoms moved around each other in physical space I became more interested. I never could have known that I would end up studying glass, and how visual and interesting it would be.

When I came to UW-Madison, I looked at all the groups without a clear idea of what I wanted to do (and, honestly, what research I even thought I was capable of doing). In college, I had worked in a lab that had recently moved from UW-Madison, and all of the graduate students told me "even if you think you're not interested in glasses, you *really* have to talk to Mark Ediger, at least for life advice." So, during the first week, I wound up in Mark Ediger's office, ready to learn about graduate school.

Glasses initially seemed like a boring research area to me. What more could there possibly be to learn about glasses? Windows are everywhere, and it doesn't seem like they're having any trouble doing their job. Eye doctors can precisely shape glass to make some people who are legally blind able to see with near 20/20 vision. You can sign up and get a Groupon for a glass-blowing class, and even your cousin took a glass-blowing class and made something semi-distinguishable. (Though, as shown in Figure 1, professional glassblowers can make some pretty complex creations).

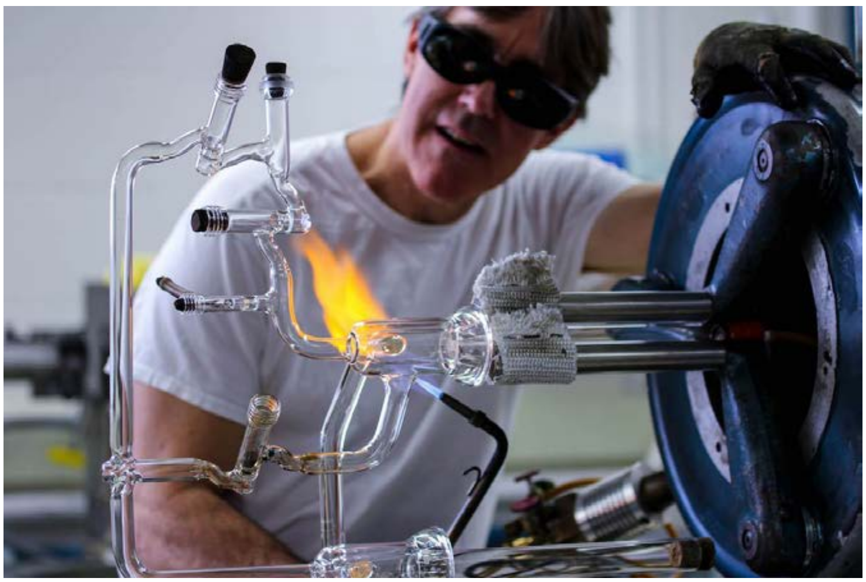

Figure 1. UW-Madison's very own resident glassblower, Tracy Drier, using a blowtorch to heat up an oxide glass to mold it into custom labware.[1]

What is a glass?

I quickly learned that the world of glasses is so much wider than all of the materials I mentioned above. Those materials are examples of glasses that are composed of oxygen in a particular ratio to other elements, and they are referred to as oxide glasses. While there is still active research on oxide glasses, I didn't realize that they were completely different from what the Ediger group works on. As I discovered, there is a wide range of materials that can form glasses, as long as their microscopic structure is disorganized in a particular way. For example, metallic atoms, polymers and plastics, pharmaceuticals, and sugar can all form glasses if they're prepared in the proper way, as shown in Figure 2.

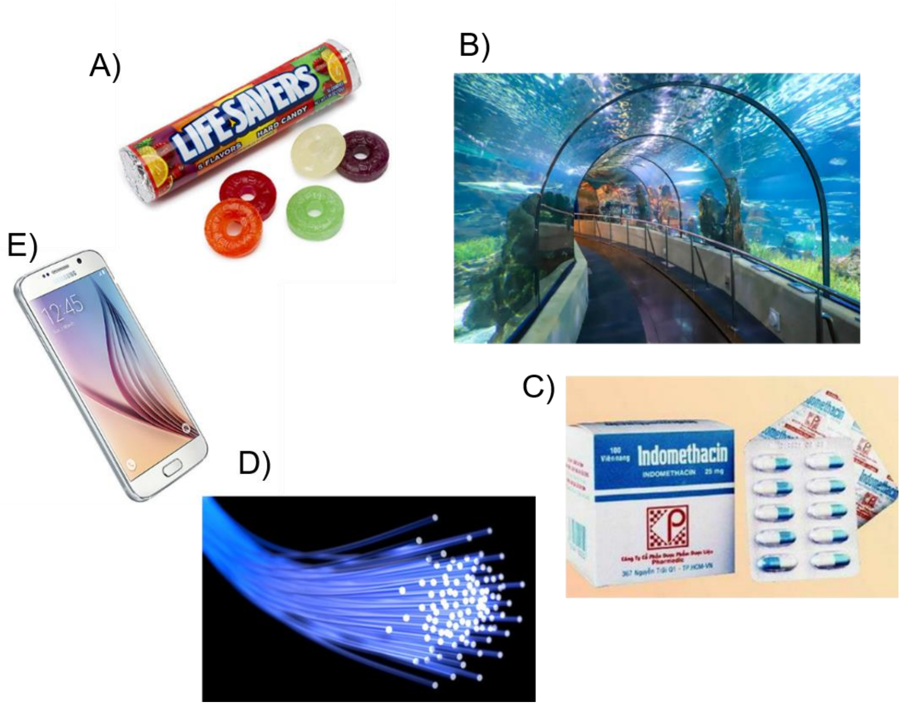

Figure 2. *Different types of glasses we encounter in our daily lives. Clockwise from top left: A) lifesavers, a sugar glass;*[2] *B) aquarium windows, a polymer glass;*[3] *C) indomethacin, an anti-inflammatory drug;*[4] *D) fiber optics, an oxide glass;*[5] *E) an OLED display, which contains a glassy emitter layer.*[6]

Traditionally, glasses are prepared by cooling a liquid fast enough that it will avoid crystallization. In crystals, which are solids, the atoms are arranged very regularly in a repeating pattern, illustrated in Figure 3A. Ice is one example of a crystal. Conversely, if that regular ordering is suppressed, a glass with a structure similar to the one shown in Figure 3B will form. Theoretically, everything can form a glass, but in practice, certain materials are better at forming glasses than others. In order for a liquid to become a solid crystal, its atoms or molecules need to carefully rearrange into a regular repeating pattern. If they cannot form a crystal, they will form a solid glass. Both atoms (single elements from the periodic table by themselves) and molecules (many atoms linked together by chemical bonds) can form glasses. Depending on the glass identity, the glass-forming parts may be single atoms or entire molecules that move as one. As a liquid cools, the atoms slow, making it harder for them to rearrange. Crystallization is a competition between how fast the atoms can move to rearrange themselves in the time before they are moving too slowly to rearrange any longer. If they're cooled fast enough, they'll be packed randomly in a structure that resembles the atomic arrangement of the original liquid, like the one shown in Figure 3B. When the solid structure resembles that of the liquid, with no regular repeating pattern, we refer to it as "amorphous."

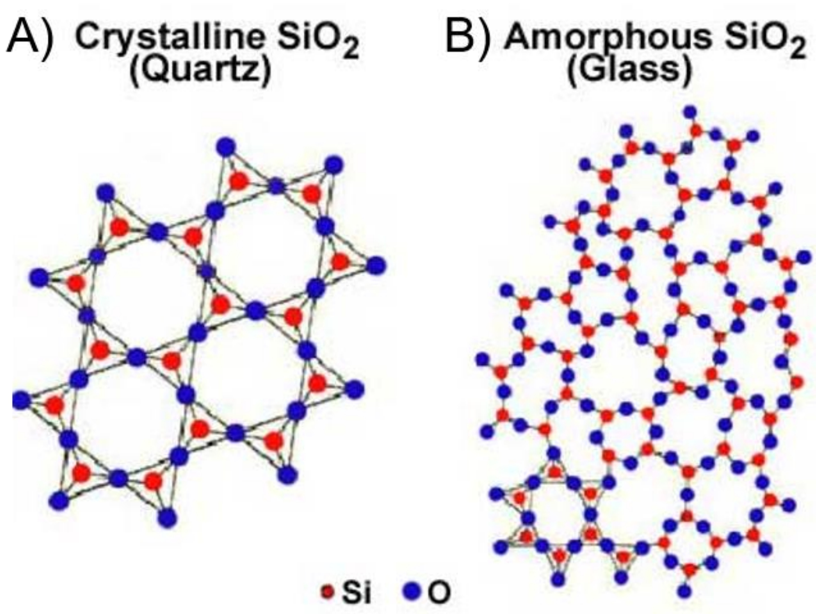

Figure 3. The difference between a silicon dioxide crystal and glass, the main component of familiar glass that you might find in a vase and a window. Both have the same ratio of atoms, but the A) crystal is regularly organized in a repeating pattern unlike the B) amorphous glass, in which the atoms are arranged rather randomly.[7]

As a side note, the fact that the glass structure looks so much like the liquid structure has led to a pervasive myth in our society that is not quite right. Perhaps you have heard before that "glass is actually a really slow-moving liquid," maybe even from a science teacher. This common myth stays around because the structure of a glass does look very much like a liquid. However, the atoms are rigidly jammed together, and the glass responds to stress and temperature the way a solid would.

Making better glasses with Physical Vapor Deposition

In my research, I prepare glasses using a technique called physical vapor deposition, or PVD. You may already be familiar with vapor deposition if you've ever come out to a frosted windshield in the morning, or taken something out of the freezer and had it frost over (like in Figure 4). The frost occurs when the water vapor molecules already present in the air hit the cold container, which has a temperature below the freezing point of water. The water molecules slow down and condense into a solid. In the frost shown in Figure 4, the molecules form crystals because they have time and space to rearrange into a perfect crystalline form.

Figure 4. Water vapor from the air that deposited into a (crystalline) solid on the outside of my frozen leftovers.

In my research, rather than having the glass-forming molecules deposit into a crystalline solid, they deposit into a glass. To perform PVD, we first evacuate all of the air from a chamber, aiming for a pressure similar to that of outer space – this way, there are less ambient molecules for the glass-forming molecules to run into. Next, we evaporate our chosen glass-forming molecules into a gas, and they deposit onto a cold substrate positioned above, as illustrated in Figure 5A. A substrate simply means a hard surface on which things condense or deposit; in my case, the substrate is usually a silicon wafer. There are a few reasons why my molecules form glasses instead of crystals. For one, the molecules we choose to work with are good glass-formers – for example, they may contain a big floppy part or have an asymmetric structure that gets in the way of the molecules rearranging neatly into a crystal, as illustrated schematically in Figure 6. We can also change two main variables: the temperature of the substrate, and the deposition rate (i.e. how many molecules hit the surface at once). PVD can be thought of like a game of Tetris. Lowering the temperature of the deposition is like making your keyboard really sticky and unresponsive – as each block comes down, it takes longer to rotate. If you raise the temperature, it's easier to rotate the blocks to get them into a better packing position. The deposition rate, which is how fast the molecules are evaporated and deposited, also matters. Going back to the Tetris analogy, a slow deposition rate is like the first level, where you have plenty of time to rotate the blocks coming down. A fast deposition rate is like playing at a high level where the blocks are flying in really fast, so there's not enough time to rotate them before they hit the other blocks. Therefore, raising the substrate temperature and lowering the deposition rate both result in a better-packed glass due to either easier rotation or more time. Essentially, it becomes a ratio between how much time it takes to rotate a block (temperature), and how much time you have to rotate the block (rate).

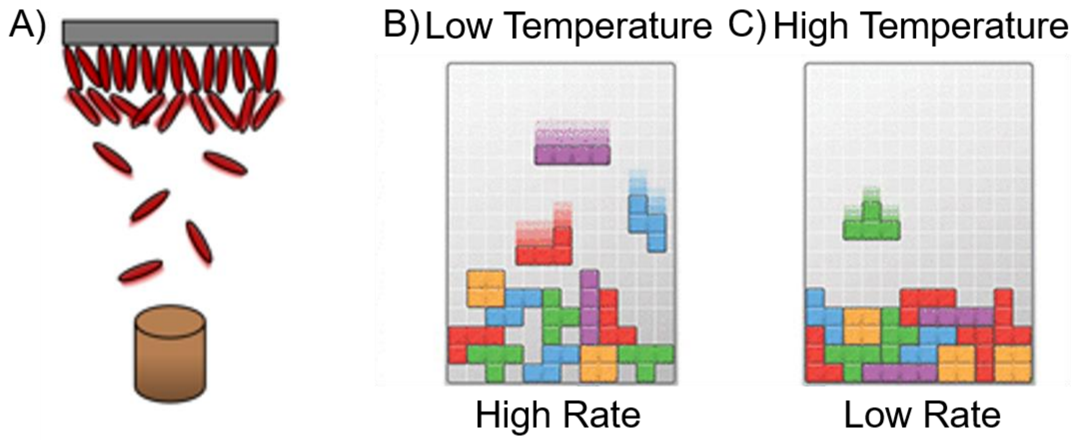

Figure 5. A) In PVD, the molecules are evaporated and deposit into a solid on a silicon substrate. B) and C) The game of Tetris provides a useful analogy for PVD. The temperature controls how "sticky" the keyboard is, and the rate controls how fast the blocks come down. Reprinted from L. Berthier, M.D. Ediger, Physics Today *69, 2016, 40, with the permission of AIP Publishing.*

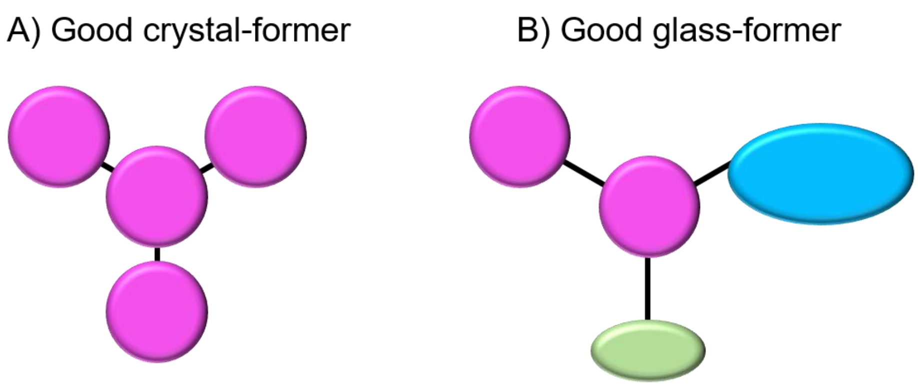

Figure 6. Schematic of molecular designs to enhance or limit crystallization. A) A molecule that is more likely to crystallize (and less likely to form a glass) is symmetric, so it is easy to pack regularly with its neighbors no matter what orientation it is. B) A good glass-forming molecule is asymmetric in size and shape, making it take more time to rearrange into a regular repeating structure.

Measuring the Properties of Vapor-deposited glasses

Because of the way we prepare our glasses, we study them as films that are about 500 nanometers thick – that's about 1/100th the thickness of a single human hair. Such thin films require very sensitive measurements. In my work, I did measurements with both optical light and X-rays. While they use two different types of radiation, the thin film characterization techniques operate off a similar principle to what is shown in Figure 7. In both techniques, a beam travels through the film and reflects off the substrate. Then, on the other side, the beam coming out is gathered in a detector. Based on how the beam changes after traveling through the film, we can learn about its properties.

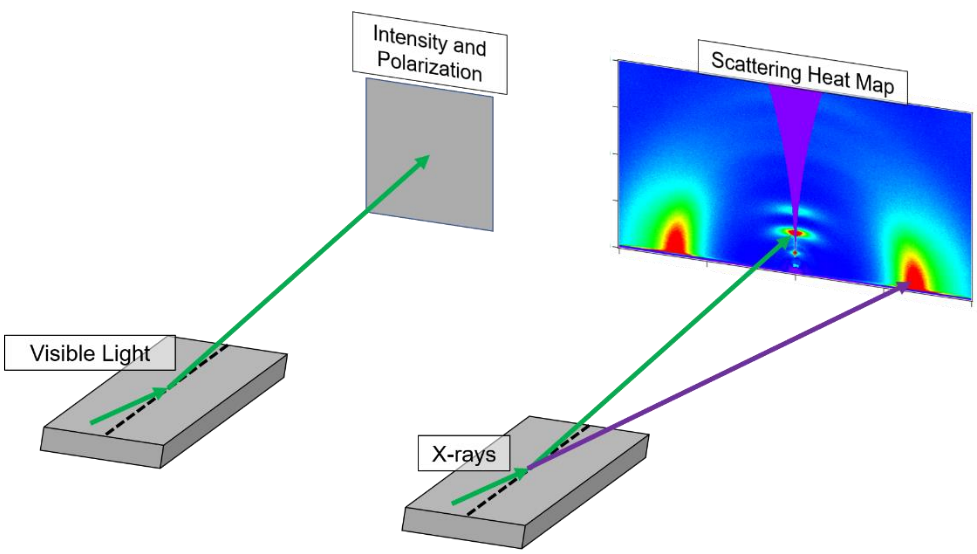

Figure 7. The geometry of the two types of characterization techniques I use. On the left is ellipsometry, which measures how fast light travels through the glass. On the right is X-ray scattering. Since the X-rays are nearly the same wavelength as the distance between molecules, they help us understand how far apart the molecules are.

Ellipsometry uses visible light to measure the speed of light through the film, and gives us information about how the molecules are oriented with respect to the substrate. X-ray scattering uses much shorter-wavelength X-rays to measure how the molecules pack with each other. Because their wavelength is close to the distance between molecules, X-rays work really well for studying how close together molecules are. From this information, we can also figure out whether the molecules are layering with one another. Combined with the ellipsometry, we can get a more complete picture of how the molecules are arranged in the vapor-deposited glasses.

What I have learned and contributed to my field

If I had to summarize the two biggest contributions that I've made to my field, it would be these two ideas: 1) We can significantly manipulate the structure of vapor-deposited glasses by changing the rate of deposition we use to make them, and 2) we can create glasses with extremely high levels of order from materials that look like they would create fairly uninteresting materials.

Controlling the Deposition Rate

In the introduction, I said that both the temperature and the rate at which glasses are deposited impacts whether they form a glass or a crystal. When they form a glass, the exact structure of the glass still depends upon both deposition variables. This had been previously known for some classes of materials, such as metallic glasses, but no one had really tested the theory of deposition rate on the types of organic (mostly carbon-containing) molecular systems that I study. One reason that scientists had not previously studied deposition rate effects is simply because changing the deposition rate can take a lot of time to study. Most differences in glass structure only become observable once you start decreasing the rate by factors of 10. Therefore, depositions that previously took about an hour can take up to 10 hours to complete.

If you were to talk to a glass scientist from twenty years ago and tell them that we can now control the structural order of a glass, they would call you crazy and say that glasses don't have structural order. About 15 years ago, my research group showed that vapor-deposited glasses can be made so that all of the molecules lie preferentially in one direction, as-shown in Figure 8. When the molecules are all arranged in one preferred orientation, they are "anisotropic" and when they are randomly arranged they are "isotropic" - like the sample on the right in Figure 8. Most liquids we encounter in daily life are isotropic, meaning that the molecules are randomly oriented. The reason that vapor-deposited glasses are anisotropic can be explained by thinking back to our game of Tetris. In the game, all of the blocks (molecules) want to have an organized surface structure. The amount of time (controlled by rate) and energy (controlled by temperature) the molecules have to rearrange determines if they will form a well-ordered structure or if they will only achieve partial ordering.

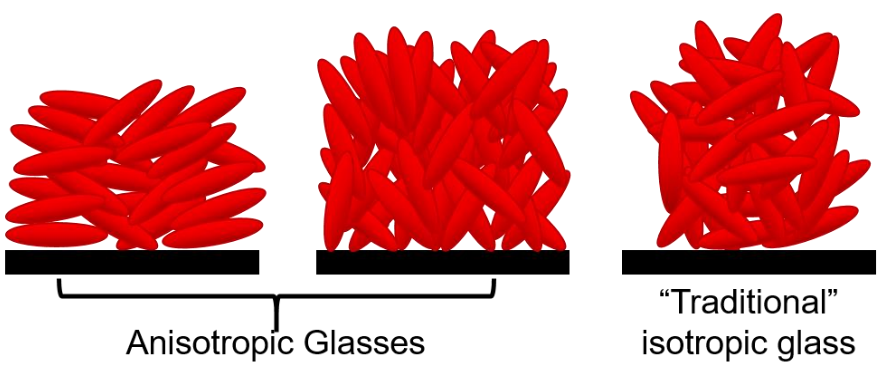

Figure 8. Schematics showing anisotropy and isotropy, where each ellipse represents a molecule. The two glasses on the left are anisotropic, like the glasses that we can produce by physical vapor deposition. The glass on the right is what scientists traditionally thought of as a glass that could be prepared by cooling a liquid, which is a solid with no preferred orientation.

As I was beginning my thesis work, my colleagues found a way to create even more structurally ordered glasses by vapor depositing a liquid crystal called itraconazole. Itraconazole is an organic molecule that is primarily used as an antifungal, but forms very interesting glasses, so glass scientists have used it as a model system. Primarily encountered in liquid crystal displays, liquid crystals flow like a liquid, but contain well-organized molecules. For example, the itraconazole used by my colleagues forms molecular layers. They found that they could alter the layer structure of similar-looking glasses by controlling the substrate temperature. Figure 9 shows what the liquid looks like, and what the resulting glasses look like.

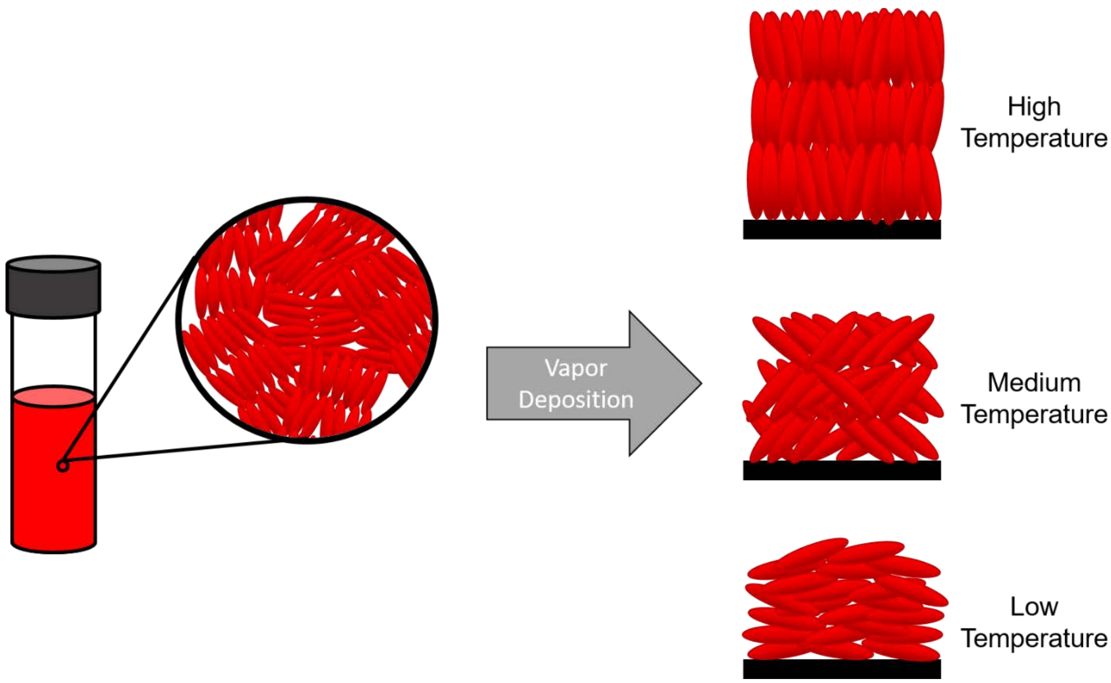

Figure 9. On the left, the liquid state of a layered liquid crystal contains molecules that are packed into bunches that organize into layers. Locally, they are layered, but the bunches are random throughout the liquid. The right shows the aligned structures that can be created by physical vapor deposition depending on the temperature at which the glass is maintained <u>during deposition</u>. The glasses prepared at low temperature have horizontally oriented molecules that do not form layers. As the temperature during deposition is increased, the molecules become more vertically oriented and begin to organize into layers that run parallel to the silicon substrate.

At the time, these itraconazole glasses were the most anisotropic glasses anyone had ever created. Since the range of structures that can be prepared is so wide, a small change in deposition conditions creates a substantial change in structure, as illustrated in Figure 9. We thought, then, that itraconazole would be a really good candidate to study the effect of deposition rate on the structure of vapor-deposited glasses. It seemed like a reasonable idea (based upon the Tetris analogy) that lowering the deposition rate would have the same effect as increasing the substrate temperature, but no one had actually proven it yet. In fact, there were some earlier reports in the scientific literature that found that deposition rate had no effect upon structure, but we suspected that couldn't be right, so we had to test it out.

I performed experiments where I changed both the deposition temperature and the deposition rate.. Using ellipsometry and X-ray scattering, I measured the orientation and packing of the molecules. I found that, indeed, lowering the deposition rate had the same effect on the structure of the vapor-deposited glass as raising the deposition rate, as shown in the schematic in Figure 10. I was able to quantitatively relate the two variables – raising the deposition temperature by 5 K (5 °C, or 9 °F) had the same effect as depositing the glass 10 times more slowly.

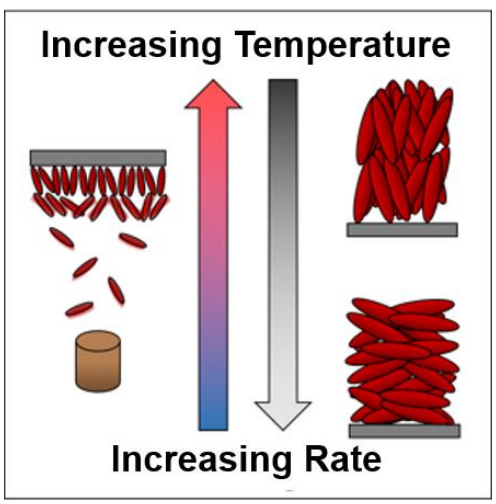

Figure 10. Vapor-depositing more slowly creates the same structure changes in vapor-deposited glasses as increasing the substrate temperature during deposition. Reprinted with permission from C. Bishop et. al. J. Phys. Chem. Lett. ***10****, 2019, 3536-3542. Copyright 2019 American Chemical Society.*

Why is this relationship between temperature and deposition rate important? For one, it gives industrial engineers more flexibility in how they make materials, such as organic light emitting diode (OLED) displays. Raising or lowering the substrate temperature away from room temperature can be inefficient and costly on a large scale. The deposition rate, on the other hand, is cheaper to control. Since it's estimated that about 500 million OLED display smartphones are created in a single year, those sorts of energy savings could really add up. Conversely, if an engineer wanted to prepare materials at a faster rate, they could now know to increase the substrate temperature to compensate for the reduced time that the molecules have to pack with one another.

Making Highly Ordered Glasses

The itraconazole glasses that I have discussed so far were the most highly ordered vapor-deposited glasses ever created. However, they were made from a highly ordered liquid, so one might not consider that too surprising. A lot of molecules don't have liquid crystal phases and are isotropic (completely disordered) in their liquid state, and we wondered if those liquids can also be used to prepare highly structured glasses.

The answer is yes, they can. The discovery came about by accident. When I was creating glasses of itraconazole, we identified a similar molecule, posaconazole, which another Ediger group member had worked with previously. Posaconazole has the same chemical structure as itraconazole, except 4 atoms (out of about 87) are different. We decided that I should deposit it as a control system to compare to itraconazole. It turned out that when it was vapor-deposited, it formed a glass that looked very similar to the liquid crystalline glasses! Similar to itraconazole, the oriented and layered vapor-deposited glass structure could be changed by changing both the substrate temperature and the deposition rate, as shown in Figure 11.

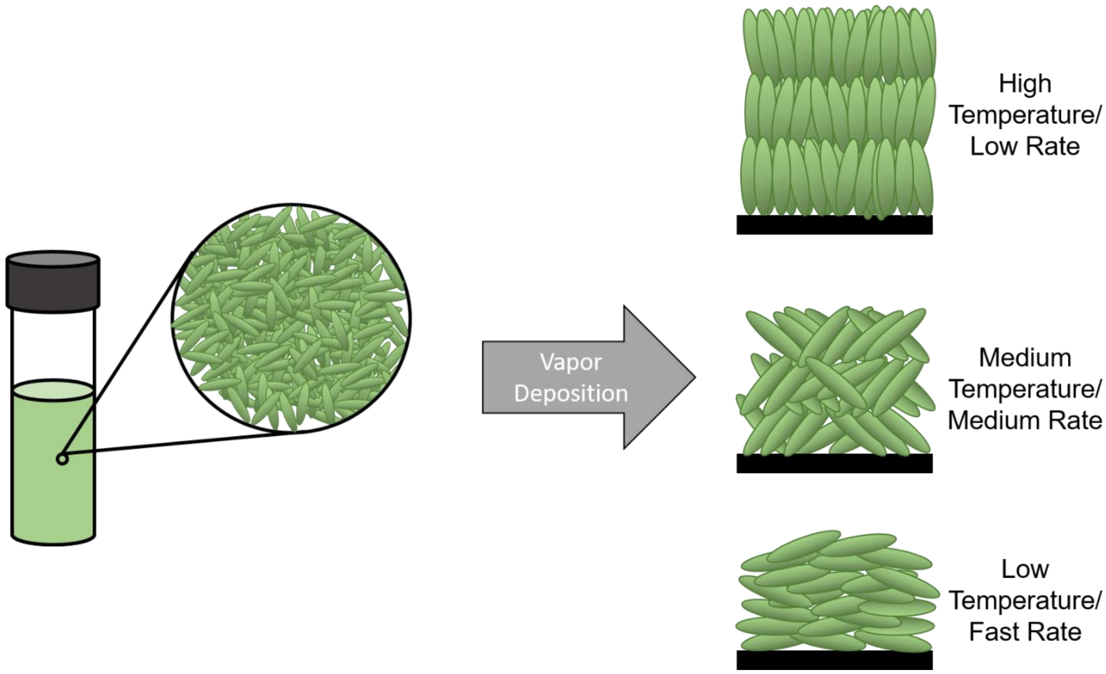

Figure 11. Posaconazole is an isotropic liquid with no liquid crystal phases, with a liquid structure that looks like the image on the left. However, when vapor deposited, it shows the same structure as the liquid crystal itraconazole.

Since this was a quite unexpected result, we needed to find out more. Since the structure of vapor-deposited glasses depends on the preferred structure at the surface of the liquid, we hypothesized that there must be something different about the surface of liquid posaconazole. To do this, we reached out to our collaborators at the National Institute of Standards and Technology (NIST), who then used a technique called X-ray absorption to study the surface structure of our liquid posaconazole. What they found was that, in contrast to the bulk of the isotropic liquid, the surface of the liquid posaconazole was highly structured. The bulk and surface structure are illustrated in Figure 12. We therefore concluded that the reason that this isotropic liquid can form such highly structured glasses is due to its unique surface structure.

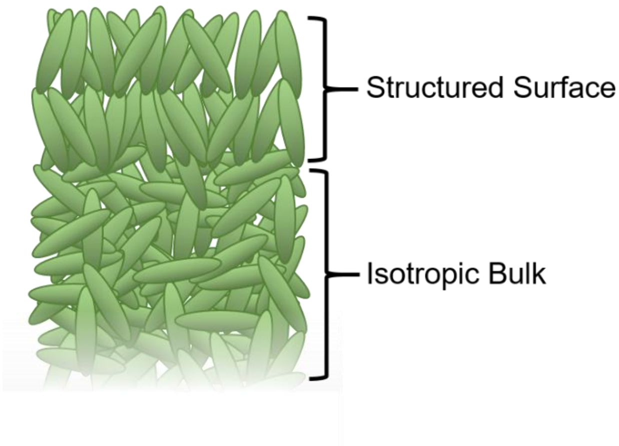

Figure 12. The surface of posaconazole is unexpectedly highly structured, as revealed by X-ray absorption. Molecules at the surface are vertically oriented, even though the bulk of the liquid is composed of randomly oriented molecules.

Since the structured free surface of posaconazole allows us to prepare highly structured glasses, we think there must be other molecules that we haven't discovered that could behave the same way. To figure out what other systems out there might behave like this, we'll need to collaborate with a lot of other chemists and physicists. A complete team to tackle this problem would consist of computational chemists who can simulate liquids and vapor deposition; organic chemists who can design new molecules; X-ray physicists, like our team at NIST, who can experimentally verify the surface structure of liquids; and finally, a group of physical chemists like ourselves who can test the hypotheses by vapor-depositing and characterizing new glasses.

Potential Applications of my Glasses

My PhD research has focused primarily on how to prepare, predict, and manipulate structural order in vapor-deposited glasses. We think that these glasses could be really useful for organic electronics that require similar materials. Since our glasses have unique properties that other processes can't produce, we think that they could be used to create new and exciting materials. Light, mechanical stress, and charge conductivity could all be modified by the structure of the glasses. All of these properties could be utilized in new organic electronics that require cheap, lightweight, and flexible materials, such as wearable screens and health monitoring devices. The processing principles we have established can be applied to more efficiently make the organic glasses used in these applications, and could be used to optimize non-organic glasses that are better suited, for example, to computer chips or wear-resistant coatings.

My next steps

After five years of my PhD, I learned a lot about what I want to do in the future. I learned that I definitely want to continue scientific research, collaborating with people, and creating new knowledge. By performing X-ray scattering at a national lab, I realized that I would like to work in that environment. Scientists at national labs are experts in specific measurement techniques, and collaborate heavily with other researchers so that they can more effectively perform their experiments.

One of my favorite parts of graduate school was learning what a social endeavor scientific research is. I learned to collaborate with other scientists, both within and outside of my research group, to learn more information about my samples and understand why their molecules are arranged the way they are. I traveled to conferences and met other graduate students, post-docs, and professors who worked on either the same things I did, or even completely different things, and learned more about life in other states and countries. I even had a unique opportunity to travel to Roskilde, Denmark for a month to learn how to do computer simulations of glasses and liquids (although turns out I really didn't like sitting at a computer all day coding – but at least I know that now, learned a lot, and met great people!)

I improved many skills that I never really thought about or expected to learn. I learned how to collaborate with other scientists, both within and outside of my research group, to further understand my glasses. I learned a lot about high vacuum systems and basic repair skills, like changing gaskets, using torque wrenches, and troubleshooting leaks. I learned to analyze data using many types of software and mathematical principles. I learned the surprisingly difficult skill of reading a scientific paper. They really are written in their own language, and it takes a lot of practice and helpful mentors to learn how to interpret the most important points and apply them to your own problems. Finally, I had lots of practice writing and presenting to effectively communicate my ideas to others and get comfortable talking in front of crowds.

As I was working on one of my papers with collaborators, I learned about a new X-ray technique that they are developing to more thoroughly examine the structure of polymer and molecular glasses. I liked it so much that I wrote a proposal with the lead investigator on that team, Dr. Dean DeLongchamp, and was awarded a post-doctoral fellowship to work on developing new X-ray techniques. I will be heading to Washington D.C. next year to work at NIST on developing the X-ray techniques to measure the structure of organic materials. Specifically, I will measure polymer glasses that are currently being directly used in organic solar cells and flexible electronics, to optimize their efficiencies with processing.

Graduate school was a long journey full of ups and downs, but I wouldn’t trade it in for any other experience. I’m grateful for everything I learned about glasses and scientific research, and that I was able to meet and learn from many amazing mentors and colleagues and make a lasting impact in a new scientific field.

Images

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