Anisotropic Vapor-Deposited Glasses: Hybrid Organic Solids

M. D. Ediger,*,[†] Juan de Pablo,[‡],[⊥] and Lian Yu[†],[§]

[†]Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, Wisconsin 53706, United States
[‡]Institute of Molecular Engineering, University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois 60637, United States
[§]School of Pharmacy, University of Wisconsin-Madison, 777 Highland Avenue, Madison, Wisconsin 53705, United States

CONSPECTUS: The term "organic solids" encompasses both crystals and glasses. Organic crystals are commonly grown for purification and structure determination and are being extensively explored for applications in organic electronics including field effect transistors. The ability to control the packing of one molecule relative to its neighbors is of critical importance for most uses of organic crystals. Often, anisotropic packing is also highly desirable as it enhances charge transport and optimizes light absorption/emission. When compared to crystals, the local packing in organic glasses is highly disordered and often isotropic. Glasses, however, offer two key advantages with respect to crystals. First, glasses typically lack grain boundaries and thus exhibit better macroscopic homogeneity. Second, glass composition can often be varied over a wide range while maintaining homogeneity. Besides electronic materials, many modern plastics used in a wide range of technologies are organic glasses, and the glassy state is being increasingly utilized to deliver pharmaceuticals because of higher bioavailability. In this article, we introduce vapor-deposited organic glasses as hybrid materials that combine some of the useful features of crystals and traditional liquid-cooled glasses. Physical vapor deposition produces glasses by directly condensing molecules from the gas phase onto a temperature-controlled substrate and allows film thickness to be controlled with nanometer precision. Just as liquid-cooled glasses, vapor-deposited glasses have smooth surfaces and lack grain boundaries. These attributes are critical for applications such as organic light emitting diodes (OLEDs), in which vapor-deposited glasses of organic semiconductors form the active layers. In common with crystals, vapor-deposited glasses can exhibit anisotropic packing, and the extent of anisotropy can be comparable to that of the typical organic crystal. For vapor-deposited glasses, in contrast to crystals, anisotropic packing can generally be controlled as a continuous variable. Deposition conditions can be chosen to produce glasses with significant molecular orientation (molecules "standing up" or "lying down" relative to the substrate), and π-stacking can be directed along different directions relative to the substrate.

Over the last five years, we have gained a fundamental understanding of the mechanism that controls the anisotropy of vapor-deposited glasses and learned how to control many aspects of anisotropic packing. Two key elements that enable such control are the high mobility present at the surface of an organic glass and the tendency of the surface to promote anisotropic packing of molecules. In contrast to traditional epitaxial growth, for vapor-deposited glasses, the free surface (not the substrate) acts as a template that controls the structure of a growing film. The structure of any given layer is decoupled from those beneath it, thereby providing considerable freedom in producing layered glassy structures.
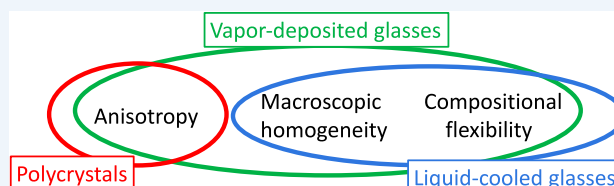
INTRODUCTION

Glasses have often been regarded as inferior to crystals. Crystals provide stability and are almost always the solid state of lowest free energy. Their long-range order makes crystals extremely useful for molecular characterization via X-ray diffraction. Crystals also provide anisotropic control over molecular interactions. In organic electronics, current research emphasizes the importance of polymorph selection and crystal orientation.[1] Often the goal is to make charge transport as efficient as possible in the direction that is important for a particular device.

At first glance, glasses seem deficient in every way with respect to crystals. Glasses are usually made by cooling a liquid. If crystallization does not occur, a glass forms when molecular motions slow to the point that the liquid cannot remain in equilibrium.[2,3] Such a glass inherits the disordered and isotropic structure of the liquid. The structure of a glass is hard to characterize with X-ray scattering, revealing only very broad peaks instead of the thousands of sharp reflections obtained from a high quality single crystal. Because they are out-of-equilibrium, glasses inconveniently evolve in time, either into a more stable glass (physical aging) or into a crystalline state.

However, glasses have advantages that make them the material of choice for certain applications. Unlike polycrystalline materials, glasses do not have grain boundaries, and thus, it is much easier to prepare glasses that are macroscopically homogeneous. Modern communication depends upon optical fibers that can transmit laser pulses over distances of 100 km without excessive attenuation; it is no surprise that these fibers are made of a glass (silicate) and not a crystal. A second

advantage of glasses is the ease with which they form single-phase mixtures.[4] While cocrystals require molecules that pack well together into a crystal lattice, glassy mixtures have much more relaxed requirements, similar to liquid mixtures.

Homogeneity and compositional flexibility are critical for some applications of glasses such as organic light emitting diode (OLED) displays. The active layers in OLEDs are vapor-deposited glasses of organic semiconductors.[5] Homogeneity ensures that all pixels have the same performance. The emitter layer in an OLED has multiple components, and good performance requires that these components be well-mixed. More than 300 million cell phone displays each year are made by this technology.

In this Account, we explain why organic glasses prepared by physical vapor deposition (PVD) can be viewed as hybrid organic solids that combine some of the best features of crystals and glasses. Figure 1 schematically introduces the PVD
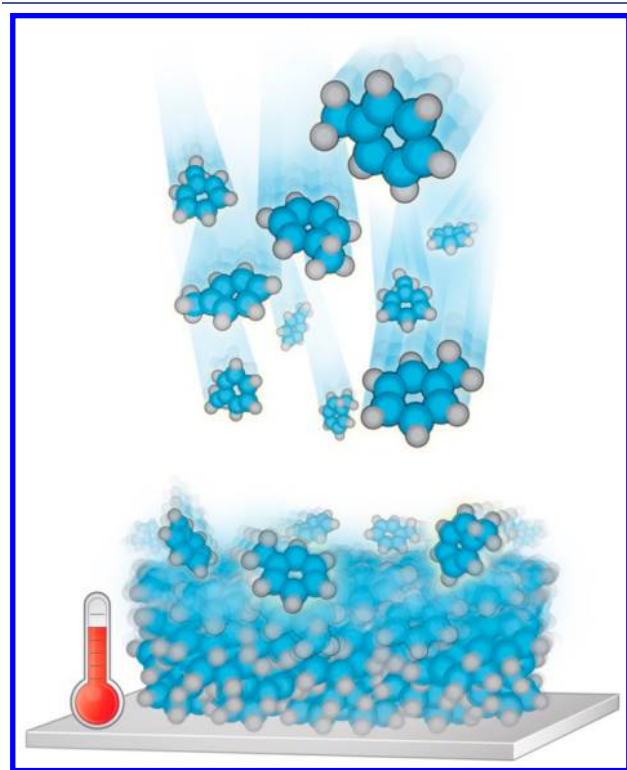

Figure 1. Schematic illustration of physical vapor deposition (PVD). A glass is prepared by condensation of a vapor onto a temperature-controlled substrate. Mobility at the glass surface has a strong influence on the glass properties. Adapted with permission from ref 6. Copyright 2016, AIP Publishing.

process. Typically a source material is heated in a vacuum chamber to provide the vapor. Multiple sources can be used to deposit layered glasses or to co-deposit mixed glasses. The thickness of the deposited layers can be controlled with nanometer precision; this is important in OLEDs, where an improper layer thickness diminishes light output as a result of interference effects.

We focus here on the ability of PVD to produce anisotropic glasses. In this respect, PVD glasses combine the glass-like property of macroscopic homogeneity with the crystal-like property of anisotropic packing. The anisotropy of PVD glasses can be substantial and similar to that in a typical organic crystal. The second key attribute of glasses, compositional

flexibility, is maintained in anisotropic PVD glasses. In addition, PVD glasses can be much more stable than liquid-cooled glasses[7−9] and thus are a hybrid material in this respect as well.

In this Account, we first discuss the characterization of anisotropy in solids and demonstrate how anisotropy in PVD glasses can be controlled by deposition conditions. The substrate temperature is a key variable for this purpose. We next explain how the structure of PVD glasses is controlled by mobility at the surface of the growing glass and by the anisotropic structures preferred by molecules at a free surface. This mechanism is the opposite of traditional crystal epitaxy where the substrate controls the structure of a growing film. Finally, we discuss strategies for maximizing anisotropy in PVD glasses. Throughout this article, we describe potential applications for these materials in the field of organic electronics.

■ ANISOTROPIC MOLECULAR ORIENTATION IN CRYSTALS

In this section, we take a broad look at molecular orientation in single crystals of organic molecules to enable a comparison with PVD glasses. We use the birefringence as a measure of anisotropy that can be conveniently obtained for both crystals and glasses. It is determined by the extent to which the index of refraction of a solid depends upon the polarization direction of light. The birefringence is closely related to molecular orientation. For a given molecule, the solid with the most anisotropic molecular orientation will almost always have the strongest birefringence. At the opposite extreme, for an isotropic sample such as a liquid-cooled glass, all molecular orientations are equally likely and the birefringence is negligible.

Winchell[10] compiled birefringence values (Δn) for more than 1600 organic crystals, and these are plotted in Figure 2.

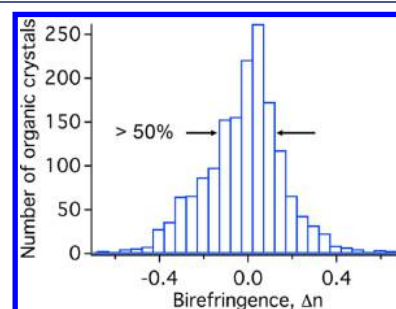**Figure 2.** Number of organic crystals plotted against birefringence for 1675 structures compiled by Winchell.[10] Of these crystals, 57% have Δn in the range from −0.125 to +0.125.

These data indicate that the absolute value of Δn for a typical organic crystal is below 0.125. As a point of reference, Δn = 0.11 for the inorganic crystal calcite, the textbook example to illustrate birefringence. The crystal structure determines the principal directions for the polarization of light, and, for many crystals, there are three independent indices of refraction. In constructing Figure 2, we use the largest and smallest indices of refraction to calculate Δn.

ANISOTROPIC MOLECULAR ORIENTATION IN PVD GLASSES

In this section, we show that PVD glasses of organic molecules can be as anisotropic as the typical organic crystal and that the anisotropy of PVD glasses can be continuously controlled over a wide range by choice of deposition conditions. As PVD glasses are typically thin films (10−1000 nm), two measures of molecular orientation can often be conveniently obtained from spectroscopic ellipsometry: the orientation order parameter S_z and the birefringence Δn. Both parameters are obtained by fitting ellipsometry data acquired over a wide wavelength range to optical models.[11] As an example, Figure 3 shows S_z and Δn
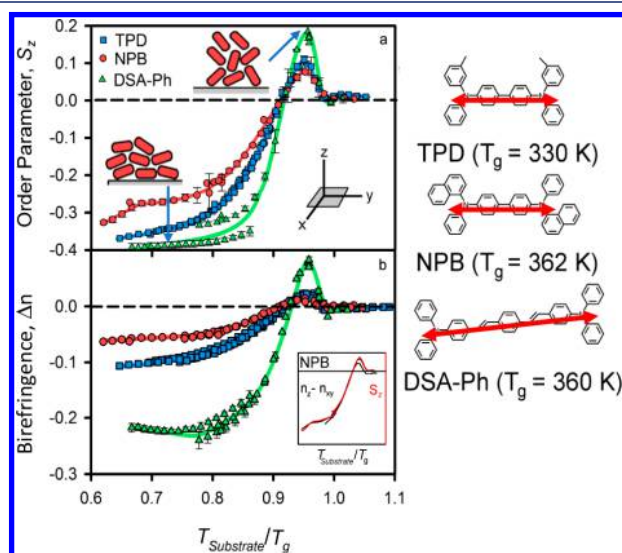

Figure 3. Orientation order parameter S_z and birefringence Δn for PVD glasses of three molecules used in OLEDs, as a function of the substrate temperature during deposition. Molecular structures and schematic representations of the anisotropic glasses are also presented. Adapted from ref 11.

for three molecules used in OLEDs; TPD and NPB are hole transport materials, while DSA-Ph is used as an emitter.[11] For these molecules, S_z is directly related to the average orientation of the molecular long axis with respect to the substrate normal. An S_z value of 1 would mean that all the molecules are perfectly standing up relative to the substrate, while an S_z value of −0.5 means that all the long axes lie in the plane of the substrate.

For each of the three molecules shown in Figure 3, hundreds of glasses were prepared using the temperature of the substrate ($T_{substrate}$) during deposition as the control variable. For DSA-Ph, S_z depends strongly on $T_{substrate}$ and varies over a substantial range, between −0.4 and +0.2. At low values of $T_{substrate}$, all three molecules show a pronounced tendency for their long axes to lie in the plane of the substrate (since S_z approaches the limiting value of −0.5). To a first approximation, birefringence values shown in Figure 3b tell the same story as the S_z parameter since the polarizability for these molecules is largest along the long axis. For vapor-deposited glasses, we define the birefringence relative to the substrate; here, $\Delta n = n_z − n_{xy}$ using the coordinate system defined in the inset to Figure 3a.

Figure 3 shows that a remarkable level of control over molecular orientation in PVD glasses can be obtained by controlling the temperature of the substrate during deposition.

For each of these three molecules, one can choose between a tendency for horizontal or vertical orientation. We emphasize that all the materials shown in Figure 3 are solids; once prepared, they can be used across a wide temperature range with no change in their anisotropic packing.[11] Furthermore, all these materials are glasses as they have broad X-ray diffraction patterns and transform into supercooled liquids at temperatures slightly above the glass transition temperature T_g.[12]

The observation that three rod-shaped molecules show a similar pattern of orientation versus $T_{substrate}$ suggests that the observed behavior is connected with molecular shape. The observation that normalizing the $T_{substrate}$ by T_g produces the same orientation trends suggests that some sort of molecular mobility is key because T_g is determined by molecular mobility. Independent experiments show that the observed molecular orientation is not influenced by the substrate material, at least for reasonably flat substrates, or by the thickness of the deposited film.[11,13] These observations are important for determining the mechanism by which molecular orientation is controlled in PVD glasses and will be discussed in the following section.

As a first comparison between anisotropy in crystals and PVD glasses, we compare the data in Figures 2 and 3. In Figure 3B, Δn for each molecule can be selected from a range of at least 0.08, with DSA-Ph showing the largest range (0.3). Thus, PVD glasses of organic molecules can be as anisotropic as the typical organic crystal shown in Figure 2.

For any given molecule, a more detailed comparison between anisotropy in PVD glasses and in a single crystal can be made through S_z. On the basis of the known crystal structure for TPD, in principle, one could produce S_z values between −0.5 and +0.85 if one could grow single crystals on a substrate with perfect control over crystal orientation. While this is a considerably larger range of molecular orientations than available from PVD glasses of TPD (Figure 3A), this level of control over crystal growth for organic molecules is extremely rare. For polycrystalline samples, the average S_z could be much smaller than the values calculated for a single crystal.

Observations of anisotropic glasses predate the work discussed above. Hellman showed that vapor-deposited inorganic glasses could be anisotropic,[14] while Lin was the first to show this for organic molecules,[15] and Yokoyama extended this to many molecules used in OLEDs.[16] More generally, it has long been understood that liquid-cooled glasses (such as Plexiglas) become anisotropic under stress. Anisotropic glasses can be formed by cooling an aligned liquid crystalline phase[17] or by cooling a liquid of polar glassformers in an electric field.[18] Thin films of some polymeric semiconductors can be viewed as anisotropic glasses.[19]

ROLE OF SURFACE MOBILITY FOR PVD GLASSES

In the next two sections, we describe the surface equilibration mechanism that controls the properties of PVD glasses. Key to this mechanism is the observation that the surfaces of organic glasses can be highly mobile. Figure 4 illustrates the surface and bulk diffusion coefficients for some representative organic glasses.[20] For o-terphenyl, for example, surface diffusion is 10^8 times faster than bulk diffusion at T_g, and very high surface mobility continues down to the temperatures below T_g where PVD glasses are prepared.

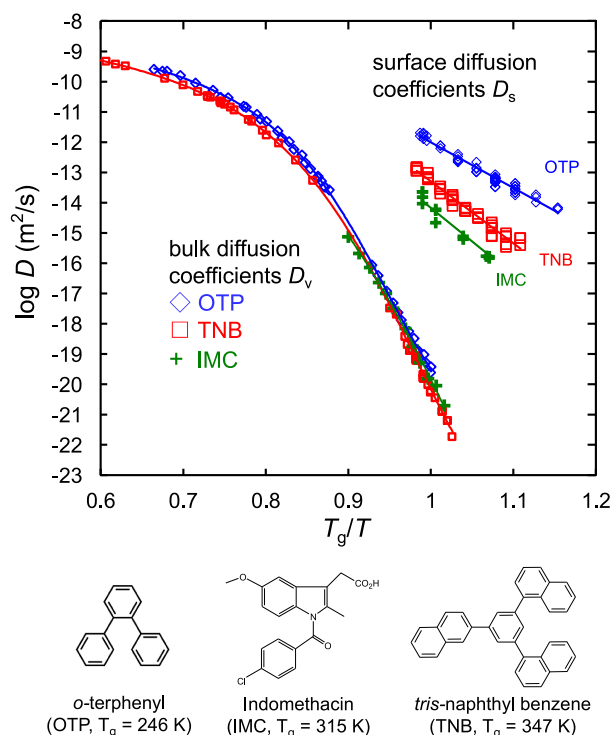During deposition at typical rates, molecules condensing on the surface have roughly 10 s to experience high surface

Figure 4. Surface and bulk diffusion coefficients for three organic glassformers.[21] Surface mobility can be very high even below T_g.

mobility before they are buried by more molecules. For substrate temperatures below T_g, this mobility results in equilibration toward the supercooled liquid (the amorphous state with the lowest free energy). Figure 5 shows the
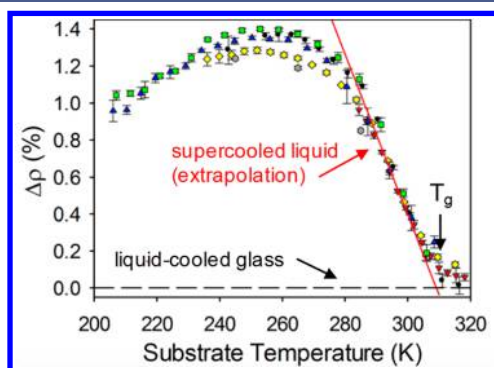

Figure 5. Densities of vapor-deposited glasses of indomethacin as a function of the substrate temperature during deposition, relative to a glass prepared by cooling the liquid at 1 K/min. Reproduced with permission from ref 23. Copyright 2017, AIP Publishing.

effectiveness of this equilibration.[22,23] Vapor-deposited glasses of indomethacin are denser than the liquid-cooled glass, as indicated by the y-axis. For a 30 K range below T_g, the measured density matches that expected for the supercooled liquid (but unattainable by a liquid-cooled glass); the molecules in these films have used surface mobility to equilibrate to the equilibrium density. At lower temperatures, surface mobility is not adequate for equilibration (for the given deposition rate). The high density of PVD glasses is associated with high thermal stability[7] and resistance to photochemical processes.[24] Similar to anisotropy, these properties are also

hybrid with respect to liquid-cooled glasses and crystals and are useful for OLEDs.

ORIGIN OF ANISOTROPY IN PVD GLASSES

Besides surface mobility, there is one additional feature of liquid surfaces that is essential to produce anisotropy in PVD glasses. While molecules in the bulk of a liquid adopt all orientations with equal probability, molecules at the free surface can be anisotropic. This result has been well-documented for water and alcohols and also applies to the organic semiconductors in Figure 3. During deposition, as molecules near the surface explore different packing arrangements, they equilibrate not only toward higher density packing (Figure 5), but also toward the anisotropic packing preferred near the surface. Further deposition traps these molecules in high density, anisotropic packing arrangements.

The connection between anisotropic surface structure and anisotropic glass structure was discovered by computer simulations.[11,25] Figure 6 shows results from computer
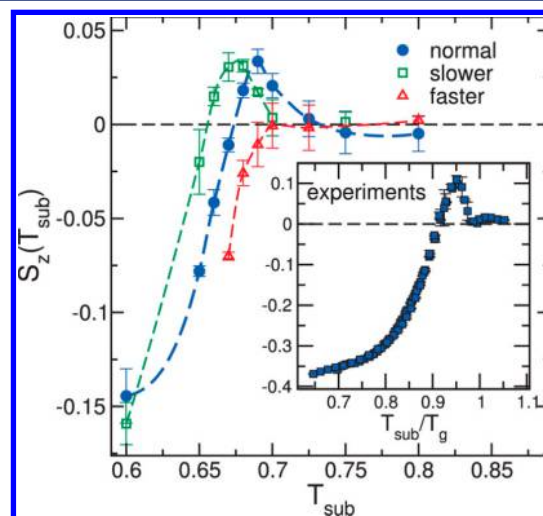

Figure 6. Orientation order parameter S_z for glasses of coarse-grained TPD from molecular simulations, as a function of substrate temperature (T_{sub}) during deposition, for three deposition rates. The inset shows experimental results for PVD glasses of TPD. Reproduced with permission from ref 25. Copyright 2015, AIP Publishing.

simulations that qualitatively reproduce the key features of Figure 3. In the simulations, a coarse-grained version of the TPD molecule was vapor-deposited onto a substrate held at a fixed temperature. The molecular orientation as a function of $T_{substrate}$ found in the simulations reproduces the trend seen in experiments.

Given the similarity between experiment and simulation in Figure 6, we used the simulations to understand the mechanism that controls anisotropy in PVD glasses.[25] While many quantitative details from the simulations support the mechanism below, here we present only a qualitative view of the deposition process (Figure 7). The equilibrium surface structure of the TPD liquid is shown on the left side, with each molecule represented as a short rod. The simulations show that while the bulk TPD liquid is isotropic, molecules right at the surface tend to lie flat and the molecules just below tend to orient vertically. At low substrate temperatures, only the top layer is able to equilibrate during deposition; as further
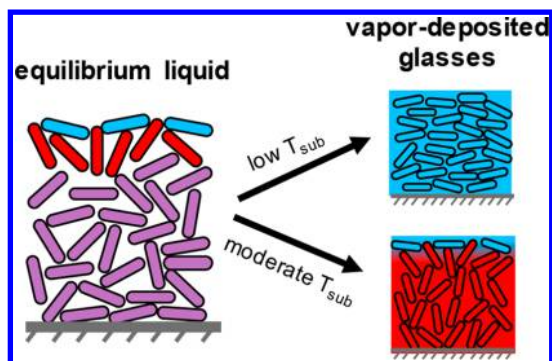
Figure 7. Illustration of how anisotropic structure present at the surface of an equilibrium liquid is trapped during deposition to produce anisotropy in the PVD glasses. Note that anisotropy extends throughout the glassy film. Reproduced with permission from ref 23. Copyright 2017, AIP Publishing.

Figure 8. Orientation order parameter S_z for DSA-Ph in mixed PVD glasses with Alq3. DSA-Ph orientation is nearly independent of composition when the substrate temperature is scaled to the mixture T_g. Reproduced with permission from ref 31. Copyright 2016, Royal Society of Chemistry (Great Britian); permission conveyed through Copyright Clearance Center, Inc.

deposition continues, these horizontal molecules would like to reorient toward the equilibrium surface structure but lack the mobility to do so. Thus, a glass results in which all molecules are trapped lying in the plane of the substrate. At moderate $T_{substrate}$, the top two layers are able to equilibrate during deposition. Molecules just below the surface thus evolve toward vertical orientation and are trapped into this orientation by further deposition. Simulations in which the deposition rate was varied support this mechanism, as shown in Figure 6. Slower deposition allows equilibration of the second layer down to lower temperature, and thus, the peak vertical orientation occurs at lower $T_{substrate}$.

The surface equilibration mechanism described above is quite different from the epitaxial growth process often used to control anisotropy in thin films of crystalline materials. While epitaxial growth is templated by the underlying substrate, the structure of PVD glasses thicker than a few monolayers is templated from the free surface. This provides a practical advantage since a desired glass structure need not constrain the choice of underlying substrates. As an illustration, we note that a single component glass can be produced in alternating stacks of vertical and horizontal orientation by cycling $T_{substrate}$ during deposition.[26]

If the molecule being deposited has a dipole moment, it is possible to produce a glass with macroscopic dipole orientation. Such a glass has a surface potential that grows linearly with film thickness, as each layer of molecules adds a small net dipole to the solid. Surface potentials as large as ±5 V for 100 nm films have been reported,[27] and these potentials influence charge injection in organic electronic devices.[28] The surface equilibration mechanism allows a prediction of the sign of the surface potential and predicts how $T_{substrate}$ will modulate its magnitude.[29]

COMPOSITIONAL FLEXIBILITY IN ANISOTROPIC PVD GLASSES

Figures 3 and 6 show that the PVD process provides considerable control over anisotropic packing for glasses with one component. Given that a key technological advantage of glasses is their compositional flexibility, we and others[30] have investigated whether highly anisotropic glasses can be prepared to contain multiple components without phase separation. In Figure 8, we show the results of experiments in which DSA-Ph was codeposited with Alq3 (tris(8-hydroxyquinoline)-
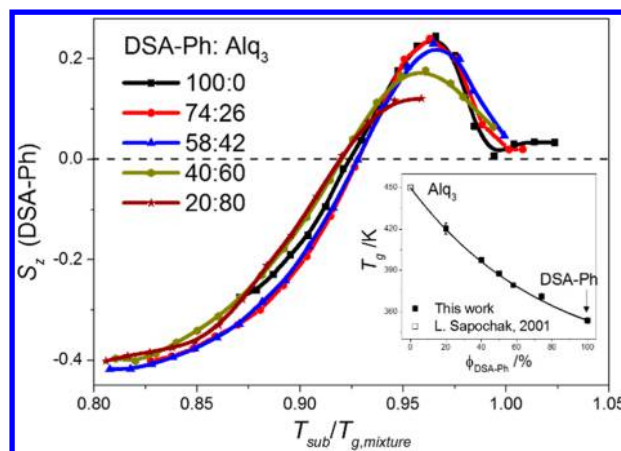
aluminum);[31] Alq3 has been used as an electron transport material and emitter layer in OLEDS. Remarkably, the same pattern of molecular orientation for DSA-Ph is found in all the glasses, nearly independent of composition. For this system, the two components are well mixed in the glass, as indicated by a single T_g that shifts smoothly between the values for the two pure components. This example clearly establishes that highly anisotropic PVD glasses can be prepared without sacrificing compositional flexibility; this wide range of miscibility would be difficult to achieve for a crystalline material.

Control over molecular orientation allows the absorption and emission of light from thin films to be modulated. For example, the emitter layer in OLEDs requires well-mixed components and control over anisotropic packing. As a result of device geometry, an OLED with the transition dipoles of all emitter molecules lying in the substrate plane will emit 50% more light than the same device with randomly oriented emitters.[16] Very recent work on emitter orientation in two-component systems is consistent with the surface equilibration mechanism.[32] Another recent study established that deposition of the densest glass (as illustrated in Figure 5) increased the efficiency of an OLED as a result of increased emitter quantum yield.[33] Presumably, the densest glass packing inhibits nonradiative relaxation processes.

MOLECULAR PACKING IN ANISOTROPIC PVD GLASSES

Molecular orientation is just one aspect of the structure of a solid, and a more comprehensive view of molecular packing can be obtained through X-ray scattering.[34] For anisotropic glasses, two-dimensional scattering patterns, such as the ones shown in Figure 9, can be particularly useful.[12] Here we show grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns obtained for vapor-deposited glasses of TPD. For these synchrotron experiments, the incident X-ray beam enters a thin film from one side, at roughly 0.2° relative to the substrate plane, with the detector placed on the opposite side of the film. Scattering from structure along the surface normal (q_z) is shown in the vertical direction, while scattering from in-plane structure is shown in the horizontal direction (q_{xy}). For
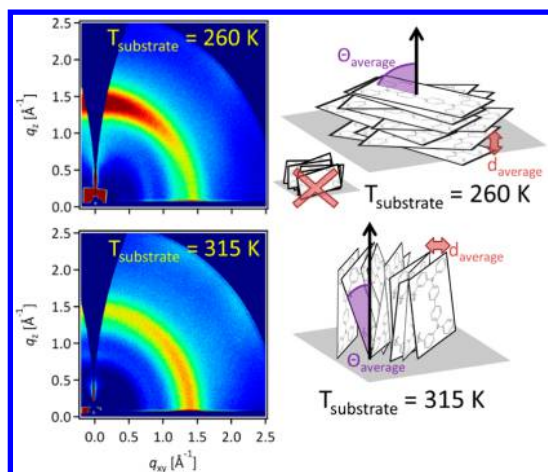
Figure 9. GIWAXS patterns for glasses of TPD vapor-deposited at two different substrate temperatures, with simplified illustrations of packing. Adapted with permission from ref 12. Copyright 2015, American Chemical Society.

reference, a liquid-cooled glass has a scattering pattern that is radially symmetric as a result of its isotropy, that is, the same scattering pattern is observed along q_z and q_{xy} and all other directions.

The upper panel in Figure 9 shows a glass of TPD vapor-deposited onto a low temperature substrate. The scattering with $|q| \approx 1.4$ Å^{-1} is indicative of contacts between carbon atoms on adjacent TPD molecules. The more intense scattering along q_z is reasonably interpreted as a tendency toward "face-on" packing, as shown in the schematic. This is consistent with Figure 3, which shows that the long-axis of TPD tends to lie in the plane. The lower panel in Figure 9 shows scattering for a glass of TPD vapor-deposited at 0.95 T_g. The slight excess scattering observed along q_{xy} is consistent with a mild tendency toward vertical orientation and edge-on packing.

Some have viewed the scattering in Figure 9 and wondered if these anisotropic samples might be better described as nanocrystalline. All the glasses shown in Figures 3 and 9 become isotropic liquids when heated a few degrees above T_g. In contrast, crystal nuclei would be expected to grow into larger crystals under these conditions. In addition, PVD glasses are molecularly smooth, in contrast with typical crystalline films, and optical and AFM experiments show no indications of grain boundaries. Thus, these PVD films are macroscopically homogeneous, as expected for glasses.

The cartoons in Figure 9 suggest the idea that charge mobility might be enhanced by controlling the anisotropy in PVD glasses of organic semiconductors. While experiments have shown that charge mobility can be modulated by deposition conditions (by at least an order of magnitude), it is not yet clear whether anisotropic packing or dense packing will generally be the key factor controlling charge mobility.[16,35,33]

■ MAXIMIZING THE ANISOTROPY OF PVD GLASSES

On the basis of Figure 3, one might anticipate that even more anisotropic glasses might be prepared with even more anisotropic molecules. This is indeed the case, but there is a new feature to consider here, as rod-like molecules of sufficiently large aspect ratio are mesogens, that is, molecules that form liquid crystals. Itraconazole (shown at the bottom of

Figure 10) is an interesting example.[36] As the liquid of itraconazole is cooled from high temperature, it undergoes
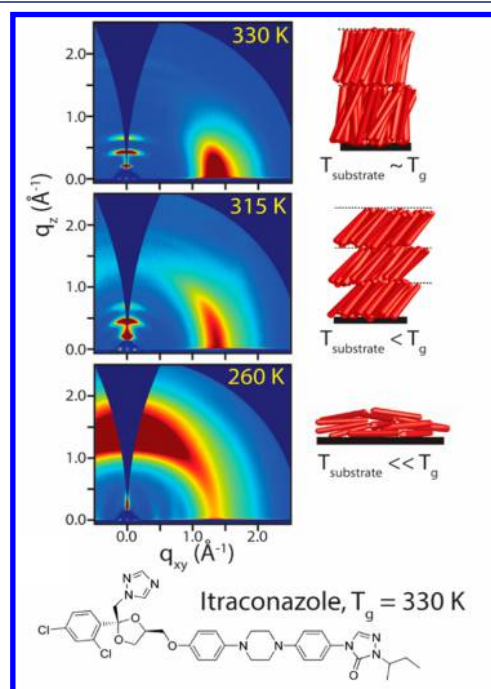

Figure 10. GIWAXS scattering patterns for vapor-deposited glasses of itraconazole, with sketches of molecular packing in the films. Adapted with permission from ref 36. Copyright 2017, American Chemical Society.

transitions from an isotropic phase to a nematic phase and then a smectic phase. Further cooling results in the formation of a glass that inherits its structure from the equilibrium smectic liquid. A wide range of structures are formed when itraconazole is vapor-deposited onto substrates with different temperatures, as illustrated with the GIWAXS scattering patterns in Figure 10. We describe these materials as glasses with liquid−crystalline order.

The top panel of Figure 10 shows the scattering pattern characteristic of an aligned smectic liquid crystal and was obtained by depositing onto a substrate at T_g. The in-plane scattering with $q_{xy} \approx 1.4$ Å^{-1} is consistent with nearly vertical rods, indicating a high degree of nematic alignment. The three orders of diffraction along q_z (0.2, 0.4, and 0.6 Å^{-1}) indicate strong smectic ordering, with layers running parallel to the substrate. It is remarkable that such a highly aligned and ordered structure can be directly formed by deposition as conventional methods usually require annealing and a careful selection of contact surfaces. Why did deposition produce this structure? Most rod-like mesogens prefer to orient perpendicular to a liquid surface at equilibrium. If we assume that itraconazole has this property, and that it also has enhanced mobility at its free surface, then the observed structure is consistent with the surface equilibration mechanism. During deposition near T_g, surface mobility allows all the surface molecules to orient vertically. When one layer is complete, the next layer begins to form, eventually allowing construction of an aligned smectic. We have verified that the observed structure is independent of the underlying substrate, as expected from the surface equilibration mechanism.[13]

The second and third panels in Figure 10 can also be understood in terms of surface equilibration. The middle panel shows the structure of a sample deposited onto a substrate held somewhat below T_g. Again, strong indications of smectic order are observed, but the rods are less vertical and the smectic layers are closer together. We interpret this to mean that the top monolayer did not have quite enough time to equilibrate during this deposition. At even lower temperatures, the molecules get trapped parallel to the substrate. We imagine that this is the initial structure upon deposition and that there is insufficient mobility to evolve away from it before the structure is trapped by further deposition.

Discotic liquid crystals (formed from disc-shaped molecules) have been extensively investigated for organic electronics; the stacking of π-systems can result in very high charge mobility.[37,38] For a few discotic systems, PVD has been used to prepare glasses with liquid crystalline order including highly ordered columns running parallel to the free surface.[39] It is of interest to determine whether deposition conditions can be found that result in discotic materials with high charge mobility.

SUMMARY AND FUTURE PROSPECTS

Because of their nonequilibrium nature, glasses have structures that depend upon the method of preparation. Because cooling from the isotropic liquid is the most common route of glass formation, and because this route yields an isotropic glass, the idea of "anisotropic glasses" has not received much attention and is sometimes regarded as an oxymoron. However, once one envisions routes of preparation beyond liquid cooling, it is clear that many (perhaps all) molecules could have anisotropic amorphous forms. Glass preparation by vapor deposition is inherently an anisotropic process and currently provides the most important route to anisotropic glasses. On the basis of our results, we expect that for many organic compounds, there are a very wide range of anisotropic glasses with sufficient stability for applications.

Returning to the theme of PVD glasses as hybrid organic solids, we summarize the ways in which PVD glasses combine attributes of crystals and liquid-cooled glasses. PVD glasses are more flexible with respect to composition than crystals and are generally macroscopically homogeneous. While single crystals can certainly be more anisotropic than PVD glasses, vapor-deposited glasses can be strongly anisotropic with deposition parameters allowing continuous control over anisotropy. While the underlying substrate is critically important for controlling crystal orientation, the structure of PVD glasses is independent of the substrate for films thicker than a few monolayers. In addition, it is much easier to obtain a smooth, pinhole-free film of a PVD glass than for a crystalline material. In comparison to liquid-cooled glasses, it is clear that PVD glasses offer a wide-range of anisotropic packings, with the added benefit of enhanced thermal and chemical stability.

Anisotropic glasses offer potential advantages for applications. Control over molecular orientation in any organic solid provides the ability to modulate the absorption and emission of light. The improved efficiency of OLEDs as a result of emitter orientation is a key example. In addition, control over molecular packing in principle allows modulation of the interactions responsible for charge transport. While charge mobility in glasses is generally much lower than in single crystals, appropriate deposition conditions for PVD glasses can increase charge mobility.

There are exciting avenues for future work with anisotropic glasses. The direct deposition of discotic liquid crystal mesogens should be further explored; for this case, order of magnitude increases in charge mobility might be expected relative to isotropic glasses. It is possible that glasses with the extreme anisotropy of an aligned liquid crystal might be obtained even without using liquid crystal mesogens, as suggested by recent work.[13] If this is general, it would significantly expand the set of molecules for which very highly organized glasses can be obtained. There are intriguing questions about macroscopic homogeneity and compositional flexibility in highly organized anisotropic glasses: will these advantageous properties be increasingly difficult to obtain as the level of anisotropy increases? Will there be local segregation of components during deposition driven by different surface energies and molecular mobilities? And more generally, can preparation routes beyond PVD be identified for producing anisotropic glasses?

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: ediger@chem.wisc.edu.

ORCID ⊙

M. D. Ediger: 0000-0003-4715-8473
Juan de Pablo: 0000-0002-3526-516X

Present Address

⊥Division of Materials Science, Argonne National Laboratories, Lemont, IL 60439, United States.

Notes

The authors declare no competing financial interest.

Biographies

Mark Ediger is Professor of Chemistry at the University of Wisconsin-Madison. He received a B.A. degree in chemistry and mathematics from Bethel College, Kansas, and a Ph.D. degree in physical chemistry from Stanford University under the direction of Michael Fayer. His laboratory studies supercooled liquids, polymer glasses, and vapor-deposited glasses.

Juan de Pablo is Professor of Molecular Engineering at the University of Chicago. He received a degree in chemical engineering from the National Autonomous University of Mexico (UNAM), and a Ph.D. degree in chemical engineering from the University of California-Berkeley under the direction of John Prausnitz. His laboratory studies supercooled liquids, organic glasses, polymeric materials, liquid crystals, and biological macromolecules.

Lian Yu is a Professor of Pharmaceutical Sciences and Chemistry at the University of Wisconsin-Madison. He received a B.S. degree in chemistry from Peking University, China, and a Ph.D. degree in physical chemistry from The Ohio State University under the direction of Terry A. Miller. His laboratory studies crystallization, polymorphism, and the amorphous state of molecular solids.

■ REFERENCES

(1) Giri, G.; Park, S.; Vosgueritchian, M.; Shulaker, M. M.; Bao, Z. N. High-Mobility, Aligned Crystalline Domains of TIPS-Pentacene with Metastable Polymorphs Through Lateral Confinement of Crystal Growth. *Adv. Mater.* **2014**, *26*, 487−493.

(2) Angell, C. A.; Ngai, K. L.; McKenna, G. B.; McMillan, P. F.; Martin, S. W. Relaxation in glassforming liquids and amorphous solids. *J. Appl. Phys.* **2000**, *88*, 3113−3157.

(3) Debenedetti, P. G.; Stillinger, F. H. Supercooled liquids and the glass transition. *Nature* **2001**, *410*, 259−267.

(4) Pandey, R.; Holmes, R. J. Graded Donor-Acceptor Heterojunctions for Efficient Organic Photovoltaic Cells. *Adv. Mater.* **2010**, *22*, 5301−5305.

(5) Sasabe, H.; Kido, J. Recent Progress in Phosphorescent Organic Light-Emitting Devices. *Eur. J. Org. Chem.* **2013**, *2013*, 7653−7663.

(6) Berthier, L.; Ediger, M. D. Facets of glass physics. *Phys. Today* **2016**, *69*, 40−6.

(7) Swallen, S. F.; Kearns, K. L.; Mapes, M. K.; Kim, Y. S.; McMahon, R. J.; Ediger, M. D.; Wu, T.; Yu, L.; Satija, S. Organic glasses with exceptional thermodynamic and kinetic stability. *Science* **2007**, *315*, 353−356.

(8) Liu, T. Y.; Cheng, K.; Salami-Ranjbaran, E.; Gao, F.; Li, C.; Tong, X.; Lin, Y. C.; Zhang, Y.; Zhang, W.; Klinge, L.; Walsh, P. J.; Fakhraai, Z. The effect of chemical structure on the stability of physical vapor deposited glasses of 1,3,5-triarylbenzene. *J. Chem. Phys.* **2015**, *143*, 084506.

(9) Leon-Gutierrez, E.; Garcia, G.; Lopeandia, A. F.; Clavaguera-Mora, M. T.; Rodriguez-Viejo, J. Size Effects and Extraordinary Stability of Ultrathin Vapor Deposited Glassy Films of Toluene. *J. Phys. Chem. Lett.* **2010**, *1*, 341−345.

(10) Winchell, A. N. *The Optical Properties of Organic Compounds*, 2nd ed.; Academic Press: New York, 1954; p 487.

(11) Dalal, S. S.; Walters, D. M.; Lyubimov, I.; de Pablo, J. J.; Ediger, M. D. Tunable molecular orientation and elevated thermal stability of vapor-deposited organic semiconductors. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 4227−4232.

(12) Gujral, A.; O'Hara, K. A.; Toney, M. F.; Chabinyc, M. L.; Ediger, M. D. Structural Characterization of Vapor-Deposited Glasses of an Organic Hole Transport Material with X-ray Scattering. *Chem. Mater.* **2015**, *27*, 3341−3348.

(13) Gomez, J.; Gujral, A.; Huang, C. B.; Bishop, C.; Yu, L.; Ediger, M. D. Nematic-like stable glasses without equilibrium liquid crystal phases. *J. Chem. Phys.* **2017**, *146*, 054503.

(14) Hellman, F.; Gyorgy, E. M. Growth-Induced Magnetic-Anisotropy in Amorphous Tb-Fe. *Phys. Rev. Lett.* **1992**, *68*, 1391−1394.

(15) Lin, H. W.; Lin, C. L.; Chang, H. H.; Lin, Y. T.; Wu, C. C.; Chen, Y. M.; Chen, R. T.; Chien, Y. Y.; Wong, K. T. Anisotropic optical properties and molecular orientation in vacuum-deposited ter(9,9-diarylfluorene)s thin films using spectroscopic ellipsometry. *J. Appl. Phys.* **2004**, *95*, 881−886.

(16) Yokoyama, D. Molecular orientation in small-molecule organic light-emitting diodes. *J. Mater. Chem.* **2011**, *21*, 19187−19202.

(17) Liu, S. H.; Lin, M. S.; Chen, L. Y.; Hong, Y. H.; Tsai, C. H.; Wu, C. C.; Poloek, A.; Chi, Y.; Chen, C. A.; Chen, S. H.; Hsu, H. F. Polarized phosphorescent organic light-emitting devices adopting mesogenic host-guest systems. *Org. Electron.* **2011**, *12*, 15−21.

(18) Wortmann, R.; Poga, C.; Twieg, R. J.; Geletneky, C.; Moylan, C. R.; Lundquist, P. M.; DeVoe, R. G.; Cotts, P. M.; Horn, H.; Rice, J. E.; Burland, D. M. Design of optimized photorefractive polymers: A novel class of chromophores. *J. Chem. Phys.* **1996**, *105*, 10637−10647.

(19) Gujral, A.; Yu, L.; Ediger, M. D. Anisotropic organic glasses. *Curr. Opin. Solid State Mater. Sci.* **2018**, *22*, 49−57.

(20) Zhang, W.; Brian, C. W.; Yu, L. Fast Surface Diffusion of Amorphous o-Terphenyl and Its Competition with Viscous Flow in Surface Evolution. *J. Phys. Chem. B* **2015**, *119*, 5071−5078.

(21) Ruan, S.; Zhang, W.; Sun, Y.; Ediger, M. D.; Yu, L. Surface diffusion and surface crystal growth of tris-naphthyl benzene glasses. *J. Chem. Phys.* **2016**, *145*, 064503.

(22) Dalal, S. S.; Fakhraai, Z.; Ediger, M. D. High-Throughput Ellipsometric Characterization of Vapor-Deposited Indomethacin Glasses. *J. Phys. Chem. B* **2013**, *117*, 15415−15425.

(23) Ediger, M. D. Perspective: Highly stable vapor-deposited glasses. *J. Chem. Phys.* **2017**, *147*, 210901.

(24) Qiu, Y.; Antony, L. W.; de Pablo, J. J.; Ediger, M. D. Photostability Can Be Significantly Modulated by Molecular Packing in Glasses. *J. Am. Chem. Soc.* **2016**, *138*, 11282−11289.

(25) Lyubimov, I.; Antony, L.; Walters, D. M.; Rodney, D.; Ediger, M. D.; de Pablo, J. J. Orientational anisotropy in simulated vapor-deposited molecular glasses. *J. Chem. Phys.* **2015**, *143*, 094502.

(26) Gomez, J.; Jiang, J.; Gujral, A.; Huang, L.; Yu, L.; Ediger, M. D. Vapor deposition of a smectic liquid crystal: Homogeneous, highly anisotropic glasses with tunable molecular orientation. *Soft Matter* **2016**, *12*, 2942−47.

(27) Osada, K.; Goushi, K.; Kaji, H.; Adachi, C.; Ishii, H.; Noguchi, Y. Observation of spontaneous orientation polarization in evaporated films of organic light-emitting diode materials. *Org. Electron.* **2018**, *58*, 313−317.

(28) Noguchi, Y.; Miyazaki, Y.; Tanaka, Y.; Sato, N.; Nakayama, Y.; Schmidt, T. D.; Brutting, W.; Ishii, H. Charge accumulation at organic semiconductor interfaces due to a permanent dipole moment and its orientational order in bilayer devices. *J. Appl. Phys.* **2012**, *111*, 114508.

(29) Bagchi, K.; Jackson, N. E.; Gujral, A.; Huang, C. B.; Toney, M. F.; Yu, L.; de Pablo, J. J.; Ediger, M. D. Origin of Anisotropic Molecular Packing in Vapor-Deposited Alq3 Glasses. *J. Phys. Chem. Lett.* **2019**, *10*, 164−170.

(30) Yokoyama, D.; Sakaguchi, A.; Suzuki, M.; Adachi, C. Horizontal orientation of linear-shaped organic molecules having bulky substituents in neat and doped vacuum-deposited amorphous films. *Org. Electron.* **2009**, *10*, 127−137.

(31) Jiang, J.; Walters, D. M.; Zhou, D.; Ediger, M. D. Substrate Temperature Controls Molecular Orientation in Two Component Vapor-deposited Glasses. *Soft Matter* **2016**, *12*, 3265−70.

(32) Jurow, M. J.; Mayr, C.; Schmidt, T. D.; Lampe, T.; Djurovich, P. I.; Brutting, W.; Thompson, M. E. Understanding and predicting the orientation of heteroleptic phosphors in organic light-emitting materials. *Nat. Mater.* **2016**, *15*, 85−91.

(33) Rafols-Ribe, J.; Will, P. A.; Hanisch, C.; Gonzalez-Silveira, M.; Lenk, S.; Rodriguez-Viejo, J.; Reineke, S. High-performance organic light-emitting diodes comprising ultrastable glass layers. *Science Advances* **2018**, *4*, No. eaar8332.

(34) Richter, L. J.; DeLongchamp, D. M.; Amassian, A. Morphology Development in Solution-Processed Functional Organic Blend Films: An *In Situ* Viewpoint. *Chem. Rev.* **2017**, *117*, 6332−6366.

(35) Esaki, Y.; Komino, T.; Matsushima, T.; Adachi, C. Enhanced Electrical Properties and Air Stability of Amorphous Organic Thin Films by Engineering Film Density. *J. Phys. Chem. Lett.* **2017**, *8*, 5891−5897.

(36) Gujral, A.; Gomez, J.; Jiang, J.; Huang, C. B.; O'Hara, K. A.; Toney, M. F.; Chabinyc, M. L.; Yu, L.; Ediger, M. D. Highly Organized Smectic-like Packing in Vapor-Deposited Glasses of a Liquid Crystal. *Chem. Mater.* **2017**, *29*, 849−858.

(37) Feng, X. L.; Marcon, V.; Pisula, W.; Hansen, M. R.; Kirkpatrick, J.; Grozema, F.; Andrienko, D.; Kremer, K.; Mullen, K. Towards high charge-carrier mobilities by rational design of the shape and periphery of discotics. *Nat. Mater.* **2009**, *8*, 421−426.

(38) Eccher, J.; Zajaczkowski, W.; Faria, G. C.; Bock, H.; von Seggern, H.; Pisula, W.; Bechtold, I. H. Thermal Evaporation versus Spin-Coating: Electrical Performance in Columnar Liquid Crystal OLEDs. *ACS Appl. Mater. Interfaces* **2015**, *7*, 16374−16381.

(39) Gujral, A.; Gomez, J.; Ruan, S. G.; Toney, M. F.; Bock, H.; Yu, L.; Ediger, M. D. Vapor-Deposited Glasses with Long-Range Columnar Liquid Crystalline Order. *Chem. Mater.* **2017**, *29*, 9110−9119.