Anisotropic organic glasses

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Abstract

While the last decades have seen considerable efforts to control molecular packing in organic crystals, the idea of controlling packing in organic glasses is relatively unexplored. Glasses have many advantageous properties that crystals lack, such as macroscopic homogeneity and compositional flexibility, but packing in organic glasses is generally considered to be isotropic and highly disordered. Here we review and compare four areas of recent research activity showing control over anisotropic packing in organic glasses: 1) anisotropic glasses of low molecular weight organic semiconductors prepared by physical vapor deposition, 2) the use of mesogens to produce anisotropic glasses by cooling equilibrium liquid crystal phases, 3) the preparation of highly anisotropic glassy solids by vapor-depositing low molecular weight mesogens 4) anisotropic films of polymeric semiconductors prepared by spin-coating or solution casting. We delineate the connections between these areas with the hope of cross-fertilizing progress in the development of anisotropic glassy materials.

1. Introduction

Organic glasses have a considerable impact on society in areas including food,[1] pharmaceuticals,[2] and organic electronic devices.[3] Organic glasses form the active elements in organic light emitting diodes (OLEDs) that are being used in nearly one billion cellphone displays[4] and increasingly in television displays[5]. Newer technologies based on organic materials, both glassy and crystalline, are also being developed with recent advances in organic field effect transistors (OFETs)[6–9] and organic photovoltaics (OPVs)[10–18] leading towards flexible and printable electronics. Organic materials are well-suited for these applications as molecular structures can be manipulated to prepare optimal n-type and p-type semiconductors.[19] Glassy organics within the active layers in devices have a number of advantages over their crystalline counterparts. Glasses are macroscopically homogeneous which means that glassy thin films can be fabricated over large surface areas without grain boundaries that act as charge traps[20] or lead to differences in performance between individual devices. In comparison to crystalline solids, the composition of glasses can be varied over a wide range[21,22] allowing for homogeneous multicomponent

films with tunable dopant concentration. Finally, because glasses are non-equilibrium solids, their process of formation plays an important role in producing structures tailored for specific applications, including anisotropic packing motifs. It is the last of these advantages, the preparation of anisotropic molecular packing structures in glasses that is the focus of this article.

Anisotropic molecular packing in organic electronic devices plays a crucial role in device performance, in both crystalline and glassy systems. A single crystal of pentacene, for example, exhibits quite different charge carrier mobilities along different crystallographic directions, varying by up to a factor of 4.[23] Charge transport in molecular systems depends on electron orbital overlap between adjacent molecules to facilitate charge transfer.[19] For instance, in pentacene it was shown that the charge transport is highest along the herringbone structure in the crystal lattice. For sexithienyl, it was found that a co-facial molecular packing arrangement exhibited most efficient charge mobility along the π−π stacking direction.[24] The highly reproducible local packing arrangements in organic crystals can lead to very high charge mobilities[23–25] but grain boundaries often act as deep traps that severely limit overall device performance. Glasses typically exhibit a broad distribution of nearest-neighbor interactions that lower charge mobility in comparison to the perfect crystal, but in favorable circumstances deep trap states can be avoided, improving the overall performance. In addition to charge mobility, it is often important to control light absorption and emission properties in organic electronics devices and anisotropic packing is an important tool for accomplishing this. For emitters in OLEDs, careful control of molecular orientation of the dilute emitter molecule in the matrix can increase light outcoupling efficiency by 40% when compared to an isotropic film.[26,27] This enhancement is due only to geometry (in-plane transition dipoles emit light along directions that more efficiently escape the device) and not due to a modification in the electronic states of the film.

While glasses are generally thought of as isotropic materials, structural anisotropy is not incompatible with a lack of crystalline order. The most common route of preparing a glass, by cooling a supercooled liquid as described in Figure 1a, does result in an isotropic material. As the system is cooled,

molecular motions eventually become so slow that the liquid can no longer remain in equilibrium. We define the temperature of kinetic arrest as the glass transition temperature T_g. For typical cooling rates, this corresponds to a structural relaxation time $\tau_\alpha \sim 100$ s and often to a viscosity $\eta \sim 10^{12}$ Pa s;[28] for comparison, the viscosity at T_g is about 10^{15} times that of water. For this route of preparation, an isotropic glass is formed since the glass inherits its structure from the isotropic liquid.

Since glasses are non-equilibrium solids, the details of preparation (such as thermal history and the presence of external forces) are important in determining the structure and properties of the glass. If a glass is produced or processed in an anisotropic environment, the resulting structure will likely be anisotropic. For example, when a polymer glass is plastically deformed in tension, the polymer chains can be stretched by a factor of two or more.[29] Upon release of the tension, the anisotropy is kinetically trapped in the glass as molecular motions are very slow. Another way to produce an anisotropic glass is first to apply an electric field to the liquid of a polar molecule, resulting in an anisotropic liquid.[30] Upon cooling with the field on, the anisotropic structure of the liquid gets trapped into a glassy state that is maintained even after the field has been removed. For the purposes of this article, we will focus on three routes to the preparation of anisotropic glasses, as described in the lower panels of Figure 1. Condensing a vapor onto a substrate, as shown in Figure 1b, can lead to glasses with anisotropic molecular packing as the anisotropic structure at the free surface (vacuum interface) gets trapped into the bulk glass. An anisotropic glass can also be prepared by cooling a liquid crystal to the temperature of kinetic arrest, as described in Figure 1c. The glass formed in this manner inherits its structure from the anisotropic liquid crystalline phase. Lastly, Figure 1d describes spin-coating[31] as a means to induce anisotropic structures into polymeric films. Shear flow during spin-coating and in related solution processing methods acts to orient the polymer chains and this orientation is kinetically trapped as the solvent evaporates.

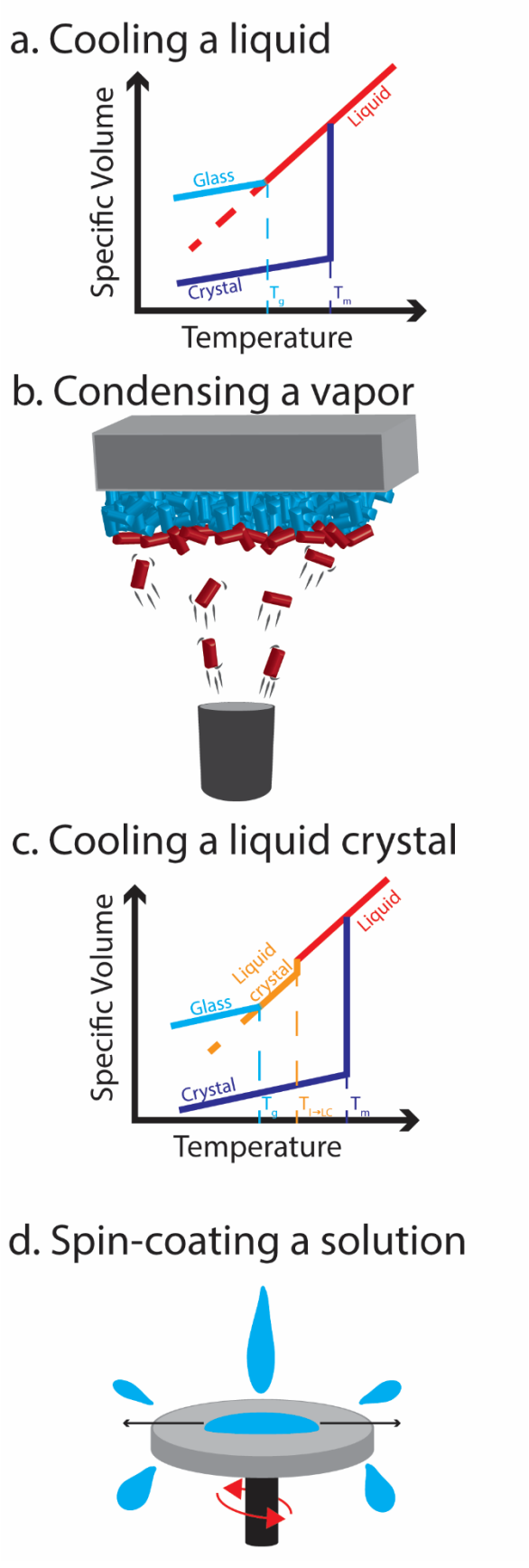

Figure 1. Routes to preparing isotropic and anisotropic glasses, as described in the text. a) cooling a liquid leads to a glass with an isotropic structure inherited from the supercooled liquid, b) condensing a vapor onto a substrate may lead to a glass with an anisotropic structure as a result of partial equilibration towards the anisotropic surface of the equilibrium liquid, c) cooling a liquid crystal can form a glass that inherits its structure from the anisotropic liquid crystal, and d) spin-coating a solution leads to anisotropic glassy structures due to the shear flow acting upon the film as it vitrifies.

Our goal in this brief review is to summarize work involving four different types of anisotropic organic glasses: 1) anisotropic glasses of low molecular weight organic semiconductors prepared by physical vapor deposition, 2) the use of mesogens to produce anisotropic glasses by cooling equilibrium liquid crystal phases, 3) the preparation of highly anisotropic glassy solids by vapor-depositing low molecular weight mesogens, 4) anisotropic films of polymeric semiconductors prepared by spin-coating or solution casting. Our discussion is general but will emphasize optimization of structure in the context of organic electronics. Of course, factors other than structure such as electric field, impurities, charge carrier density amongst many others also influence the performance of organic electronic devices.[32] In this review, we attempt to delineate connections between spheres of activity which have proceeded along largely independent paths. We acknowledge that what we label as "anisotropic organic glasses" have often been referred to by other names, such as "poorly ordered" or "amorphous" solids, or liquid crystalline solids. While not arguing against the utility of these descriptions, we respectfully ignore these previous categorizations in order to emphasize what we see as the common features of these materials in hopes that a cross-fertilization of ideas can lead to further progress in all of these areas.

2. Physical vapor deposition as a route to anisotropic glasses

In this section, we will describe physical vapor deposition as a route for preparation of structurally anisotropic glasses, discuss a proposed mechanism for the origin of this anisotropy, and provide examples of enhanced device performance in OLEDs resulting from anisotropic packing. Physical vapor deposition has been shown to prepare organic glasses with structural anisotropy as well as remarkable kinetic stability. These properties can be controlled by the substrate temperature during deposition ($T_{substrate}$) and to a lesser extent by the deposition rate. These effects have been explored for a number of organic molecules with varying molecular weight and functional groups, [26,33–43] including a number of organic semiconductors. For instance, Gujral et al.[35] prepared vapor-deposited glasses of TPD, *N,N′*-bis(3-

methylphenyl)-*N,N′*-diphenylbenzidine, a rod-shaped p-type (hole) transport material, with good glass-forming ability (T_g = 330 K). When deposited onto a low temperature substrate ($T_{substrate}$ = 0.79 T_g), the TPD molecules exhibit a tendency towards face-on packing, while deposition at higher temperature ($T_{substrate}$ = 0.95 T_g) prepared glasses with a tendency towards end-on packing.[35,38] (Here "end-on" indicates the long axis of the TPD molecule is perpendicular to the substrate). A grazing incidence X-ray scattering pattern and a schematic structure of a glass deposited at $T_{substrate}$ = 0.79 T_g is reproduced in Figure 2; the tendency towards face-on packing can be inferred from the observation that scattering near q ~ 1.4 $Å^{-1}$ (corresponding roughly to the correlation between carbon atoms in adjacent molecules) occurs predominantly in the out-of-plane direction. Vapor-deposited glasses of TPD also have remarkably high density and kinetic stability when compared to a liquid-cooled glass of TPD.[38] For vapor-deposited TPD, the designation of the material as an anisotropic *glass* is unambiguous. When vapor-deposited TPD glasses are heated to ~ 10 K above T_g, they transform into the same isotropic supercooled liquid that one obtains upon heating a liquid-cooled glass. In Section 5, we point out the similarity between the scattering pattern of vapor-deposited TPD and those observed for thin films of several polymeric semiconductors with very high charge mobility.

Figure 2.

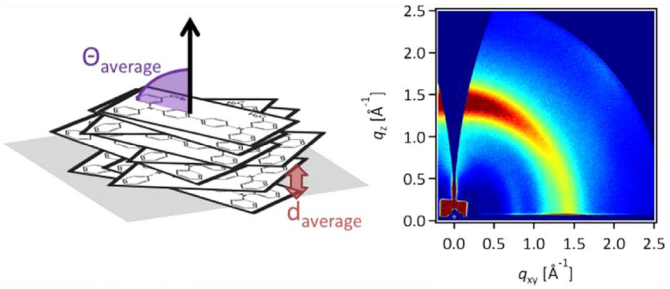

Figure 2. A glass of TPD prepared by physical vapor deposition at $T_{substrate} = 0.79\ T_g$, exhibiting a tendency towards face-on molecular packing. The right panel shows scattering data obtained by grazing incidence X-ray scattering, with vector q_z corresponding to out-of-plane scattering and q_{xy} corresponding to in-plane scattering. The left panel schematically illustrates packing consistent with x-ray and optical experiments. For this glass, $d_{average} = 4.5$ Å and $\theta_{average} = 69^\circ$ (measured from substrate normal). Reproduced with permission from Gujral et al., *Chem. Mater.* **2015**, *27*, 3341-3348. Copyright 2015 American Chemical Society.[35]

A mechanism[38,44] has been proposed to explain the structural anisotropy and kinetic stability of vapor-deposited glasses. The mechanism relies on the system exhibiting two properties: 1) molecular mobility at the free surface of the glass that is significantly enhanced in comparison to bulk glass, and 2) an anisotropic structure at the free surface of the equilibrium supercooled liquid. When depositing a film onto a substrate maintained at $T_{substrate} < T_g$, every molecule that is deposited is at the free surface of the glass for a brief residence time before getting buried by further deposition. During this residence time, the molecule uses the enhanced mobility at the free surface to partially equilibrate to a lower energy configuration before being buried by the oncoming set of molecules.[44] This leads to a bulk glass in which every molecule has partially equilibrated during the deposition process, and thus the glass has enhanced kinetic stability (and lower enthalpy). To explain the anisotropy, one must consider the preferred orientations of the molecules at the free surface as they are equilibrating. According to coarse-grained and atomistic molecular dynamics (MD) simulations,[38,45] molecules in the very top monolayer of the liquid adopt a face-on orientation while in the next layer down a slight end-on orientation is preferred. Below the second layer, the molecules exhibit an isotropic distribution of orientations, as expected in a bulk liquid of TPD. Returning back to our description of the deposition, at very low $T_{substrate}$, only the very top monolayer has the mobility to rearrange and partially equilibrate, leading to a preferred face-on orientation being trapped into the bulk of the film upon further deposition. This mechanism is consistent with the experimental findings reproduced here in Figure 2, with the sample deposited at $T_{substrate} = 0.7\ T_g$ exhibiting face-on packing. At somewhat higher $T_{substrate}$, the mobility is sufficiently high in the second monolayer, allowing every molecule deposited to equilibrate to the end-on orientation.

Several studies have reported that anisotropy in vapor-deposited organic semiconductors leads to enhanced charge carrier mobility. Yokoyama et al.[46] used vapor deposition to prepare glasses of a rod-shaped organic semiconductor, BSB-Cz [4,4'-bis[(N-carbazole)styryl]biphenyl] on indium tin oxide (ITO) substrates. The films were found to be either optically isotropic or anisotropic depending on $T_{substrate}$, as determined by spectroscopic ellipsometry. Consistent with the low deposition temperature and the

mechanism described above, the anisotropic glass exhibited a strong tendency for the long axes of the molecules to lie in the plane of the device. The researchers found that the charge carrier mobility increased roughly threefold in time-of-flight (TOF) measurements in the highly anisotropic material when compared with the isotropic film, to about 10^{-3} $cm^2V^{-1}s^{-1}$. This enhancement was attributed to an overall increase in the overlap between the HOMOs and LUMOs of adjacent molecules in the anisotropic film; Marcus theory[47] was used to describe thermally-activated hopping between molecules. While organic crystals can have charge carrier mobilities that are several orders of magnitude higher,[23] the ability to improve charge mobility in an amorphous film is important for organic electronics.

Similarly, Xing et al.[48] compared vapor-deposited and solution-processed films of TCTA [tris(4-carbazoyl-9-ylphenyl)amine], a p-type (hole) organic semiconductor. Preferential face-on packing, with a nearest-neighbor distance corresponding to a π-π stacking motif, was observed in the vapor-deposited film while the solution-processed film exhibited isotropic packing. The anisotropic vapor-deposited film consistently outperformed the solution-processed film, with higher current density across the entire range of voltages measured by the authors. Similar to the work on Yokoyama et al.,[46] the authors rationalized their results as being due to increased overlap between π orbitals in the anisotropic samples.

Without the advantage of facile charge transport along the backbone of a polymeric chain, low molecular weight glasses rely solely on charge hopping between molecules. The two studies discussed above have been interpreted to indicate that anisotropic packing can be used to enhance charge mobility. Another factor that may play a role in the enhanced performance of vapor-deposited glasses is the increased density of deposited glasses (by up to ~1.5%)[34,38,49] An increase in density would also be expected to increase charge transfer integrals between neighboring molecules.[50] Both the density and anisotropy explanations for enhanced device performance are consistent with the idea that charge mobility can be improved by control of molecular packing in glassy materials. The general advantages of disordered glassy materials, such as the lack of grain boundaries, can therefore be exploited while simultaneously increasing charge carrier mobility. It is also possible that the increased density of vapor-

deposited glasses will lead to increased chemical and photochemical stability,[51] resulting in increased device lifetime. Further investigation of the impact of anisotropic structure and increased density on device performance would be useful.

Anisotropic packing is also important for two-component systems that play a key role in OLED design. In many OLED devices, the light-emitting molecules are a dilute component within a charge carrier matrix.[52] The overall efficiency of an OLED can be increased by controlling the molecular orientation of the emitter molecules as explained by Yokoyama[26] and illustrated in Figure 3. Transition dipoles oriented vertically preferentially emit light into the plane of the film; because the device has a much greater index of refraction than air, almost all of this light is totally internally reflected and is wasted from a device perspective. In contrast, a horizontal transition dipole emits light that has a much higher probability of leaving the device in a useful manner. Several groups have observed an increase in OLED efficiency that correlates with in-plane orientation of the transition dipoles, with the efficiency increasing by up to a factor of 1.4.[26,53,54] This enhancement is remarkable as it requires no modification of the chemistry or geometry of the device.

Jiang et al.[21] recently studied two-component glasses of Alq_3 [aluminum-tris(8-hydroxyquinoline) and DSA-Ph [1,4-di-[4-(N,N-diphenyl)amino]styryl-benzene] with the goal to understand what controls molecular orientation during co-deposition by physical vapor deposition. Alq_3 is a roughly spherical molecule used as an electron transport material. DSA-Ph is a rod-shaped molecule used as an emitter that has previously been reported to exhibit quite anisotropic structures in single-component glasses[38] prepared by vapor deposition. These authors vapor-deposited mixtures of four different compositions across a wide range of substrate temperatures and measured the orientation of the DSA-Ph molecules in all of these glasses. They showed that, regardless of the composition of the mixture, the orientation of the DSA-Ph molecules had the same dependence on the reduced substrate temperature ($T_{substrate}/T_{g,mixture}$). It is encouraging that molecular orientation in vapor-deposited emitter/host mixtures has this simple relationship with the vapor-deposited glasses of the neat emitter, since the latter can be understood by the

surface equilibration mechanism discussed above. It is worth emphasizing that the control of the orientation of a dilute emitter in a host matrix would be an extremely challenging problem if crystalline materials were to be utilized, as it would often be impossible to find a co-crystal that incorporates the emitter and the host. In contrast, for vapor-deposited glasses, many different combinations of emitters and hosts can readily be used without being limited to a small number of available polymorphs or co-crystals.

Figure 3.

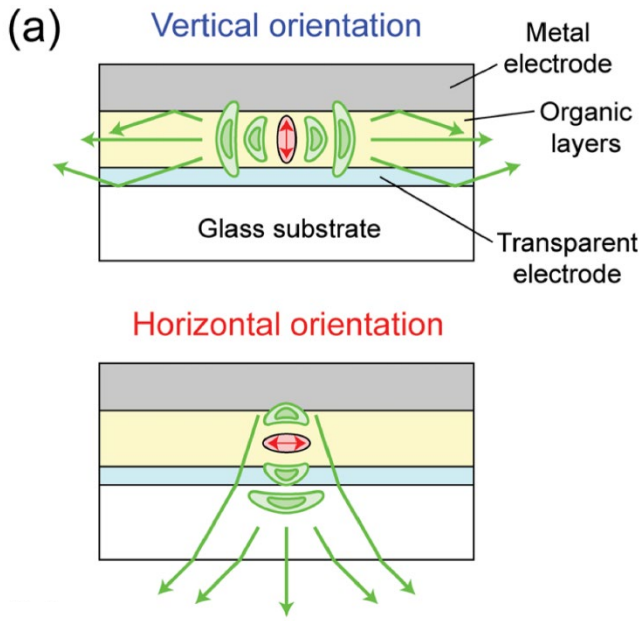

Figure 3. Schematic illustrating the different fates for photons emitted in an OLED device, for molecules whose transition dipoles are oriented vertical or horizontal with respect to the glass substrate. Horizontal orientation results in a much higher probability of light successfully leaving the device. Reproduced from Yokoyama *J. Mater. Chem.* **2011**, *21*, 19187-19202[26] with permission from The Royal Society of Chemistry.

3. Glasses of liquid crystals

Liquid crystalline systems, with their tendency to self-assemble, provide a very promising route for the preparation of organic solids with anisotropic molecular packing. For applications that require high charge mobility, columnar discotic mesogens are particularly attractive.[55–57] These systems form columnar superstructures in which π electron-rich aromatic cores are stacked upon each other in close proximity. For tunable optical properties, chiral mesogens have been exploited.[58] Many liquid crystals, however, tend to crystallize upon undercooling.[56] While this has been explored as a route for the preparation of crystals that preserve elements of the packing of the liquid crystal,[59] often polycrystalline solids result, potentially causing problems associated with grain boundaries such as poor charge transport and light scattering. As we describe below, rational molecular design principles have been utilized to counter this through the synthesis of mesogens that have difficulty packing into three-dimensional crystals. The liquid crystal phases formed from these mesogens can be trapped into a kinetically arrested solid at room temperature as shown in Figure 1c. As these systems undergo a glass transition upon cooling from an equilibrium liquid crystalline phase, they form a glass with liquid crystal-like structure.

In this section, we first explore how liquid crystalline systems have been used to develop a fundamental understanding of the relationship between molecular packing and charge transfer. We will then provide examples of glasses formed from liquid crystals that exhibit high carrier mobility for organic electronic applications and optimized optical properties for photonic devices.

Molecular design principles were used in one recent study of discotic molecular systems by Feng et al.[60] to achieve a charge mobility of 0.5-2 $cm^2\ V^{-1}\ s^{-1}$ (using time-domain microwave conductivity). The authors argue that mobility in excess of 10 $cm^2V^{-1}s^{-1}$ might be achievable with liquid crystals if defect-free films can be prepared. To highlight the importance of nearest-neighbor packing arrangements, Feng et al. synthesized discotic systems with different peripheral functional groups attached to a coronene core. The peripheral groups were either hydrophobic or hydrophilic, and positioned to control the azimuthal rotation

angle between nearest neighbors in a column. The measured charge mobility showed a clear dependence upon the azimuthal angle, even for systems with very similar nearest-neighbor distances along the column, in agreement with quantum mechanical calculations. This study highlights both the importance of carefully controlling molecular packing anisotropy to optimize device performance and the potential for extremely high charge mobility in material with liquid-crystalline packing.

Kelber et al.[61] recently explored the synthesis of discotic liquid crystals, with the goal of producing highly ordered liquid crystalline mesophases that could be cooled into a glassy state at room temperature. Additionally, they wanted to keep the molecular weight of the mesogens low enough to allow the system to be vapor-deposited, since this a common route for preparation of thin films for organic electronic devices. The researchers achieved these goals by preparing a phenanthroperylene ester with an aromatic core that is slightly distorted due to steric hindrance. This material forms large domains (roughly 0.1 mm across) of a columnar liquid crystal when cooled from the isotropic liquid. Upon further cooling, a glass is formed that locks the columnar packing into place, with the spacing between rings determined to be 3.5 Å. The researchers note the ability to tune the electronic properties of the product, for example by synthetically replacing a subset of the electron-withdrawing carbonyl groups with electron-donating amines.

Chiral nematic liquid crystals are potentially useful for optical applications as polarizers, optical notch filters, and reflectors;[62,63] in chiral nematics, the nematic director rotates along a right-handed or left-handed helix with periodicity on the order of hundreds of nanometers. To illustrate the importance of the glassy nature of these materials, we will discuss an optical reflector developed by Chen that is based upon a mixture of the two stereoisomers of a mesogen, i.e., the two components of the mixture differ only in their stereoconfiguration around a single carbon atom.[64] The system investigated had a 1,3,5-benzenetricarboxylic acid core allowing the attachment of three nematic groups, one of which was chiral. Figure 4 shows the optical reflectance spectra of one of the pure stereoisomers and two of the mixtures; the two chiral components are denoted **I**-*S* and **I**-*R*. When the two stereoisomers are mixed in different

proportions, the pitch of the chiral nematic helix is systematically altered in the equilibrium liquid crystal; these phases were then trapped into glassy solids by cooling. As the pitch of the helices is varied, different wavelength regions are selected for reflectance. This type of solid-state device relies on the compositional flexibility of the liquid crystal phases and the glasses formed from them, and would be difficult to reproduce with crystalline materials. For these applications, the macroscopic homogeneity of a glassy film is also essential.

Figure 4.

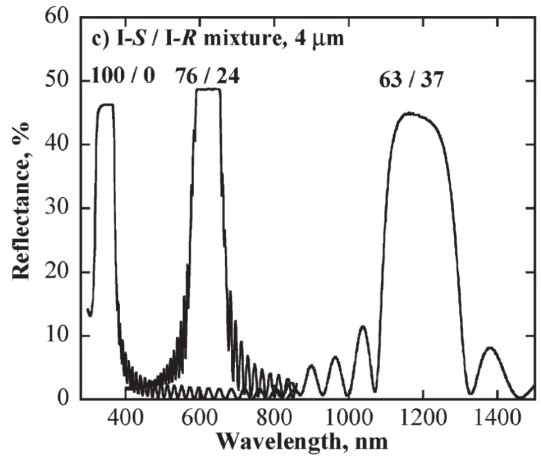

Figure 4. Reflectance spectra of mixtures of two stereoisomers of a chiral nematogen with a benzenetricarboxylic acid core (the two components are denoted I-S and I-R). The reflectance spectrum of one of the pure compounds is also shown. The wavelength region of reflectance can be controlled by the composition of these glassy mixtures. Reproduced from Chen, *J. Soc. Inf. Disp.* **2004**, *12*, 205-211 with permission from John Wiley & Sons.[64]

4. Vapor-deposited glasses of liquid crystalline mesogens

In Sections 2 and 3, we discussed two different strategies for the preparation of glasses of non-polymeric organic molecules with anisotropic molecular packing. The first strategy, physical vapor deposition, relied on anisotropic packing of molecules that occurs at the free surface of the film during deposition. Vapor deposition leads to bulk materials with anisotropic structures that vary from face-on to slightly end-on, depending on deposition conditions. The second strategy relied on equilibrium self-assembly of liquid crystalline moieties in the bulk material; upon quenching into a kinetically arrested glass, this leads to structures very similar to the equilibrium liquid crystal. In this section, we will discuss a third approach that combines elements from both of these strategies. We show that physical vapor deposition of the molecules that form liquid crystals can directly produce highly anisotropic organic without going through a bulk liquid state.

Recently, Gujral et al.[65] compared the packing motifs accessible by vapor deposition for two disc-shaped mesogens that form columnar discotic liquid crystals: a phenanthroperylene-ester (T_g = 392 K) and a triphenylene-ester (T_g ~ 310 K). The GIWAXS scattering patterns and accompanying structural representation are shown in Figure 5. For both mesogens, the researchers found that glasses prepared with $T_{substrate} \sim T_g$ exhibited highly ordered columnar packing, with the columns propagating in-plane (i.e., parallel to the free surface). Deposition at $T_{substrate} \sim 0.75\ T_g$ resulted in face-on packing for both systems. The researchers found that highly ordered vapor-deposited films of the phenanthroperylene-ester showed some evidence of electron delocalization, at least on a local level, as inferred from the redshift of visible absorption for a highly ordered vapor-deposited film. These highly ordered as-deposited films have domains of roughly 100 nm which presumably describes the size over which columnar structures propagate in a single direction. The researchers found that the vapor-deposited films exhibited properties expected for glasses (and not 3D crystals) by observing structural evolution toward the equilibrium liquid crystal phase just above T_g (and over 100 K below the crystalline melting point). In addition, the lack of mixed-index peaks in the X-ray scattering of the films, and the comparison with powder diffraction

collected from the equilibrium crystalline solids indicates that these deposited films are structurally dissimilar to the crystalline material. The scattering patterns shown in Figure 5 are similar to those observed for the ordered anisotropic polymeric systems (such as P(NDI2OD-T2)) discussed in Section 5 below. In both cases the scattering patterns lack mixed index peaks and are indicative of an anisotropic packing that is less-ordered than that which occurs in a three-dimensional crystal.

Figure 5.

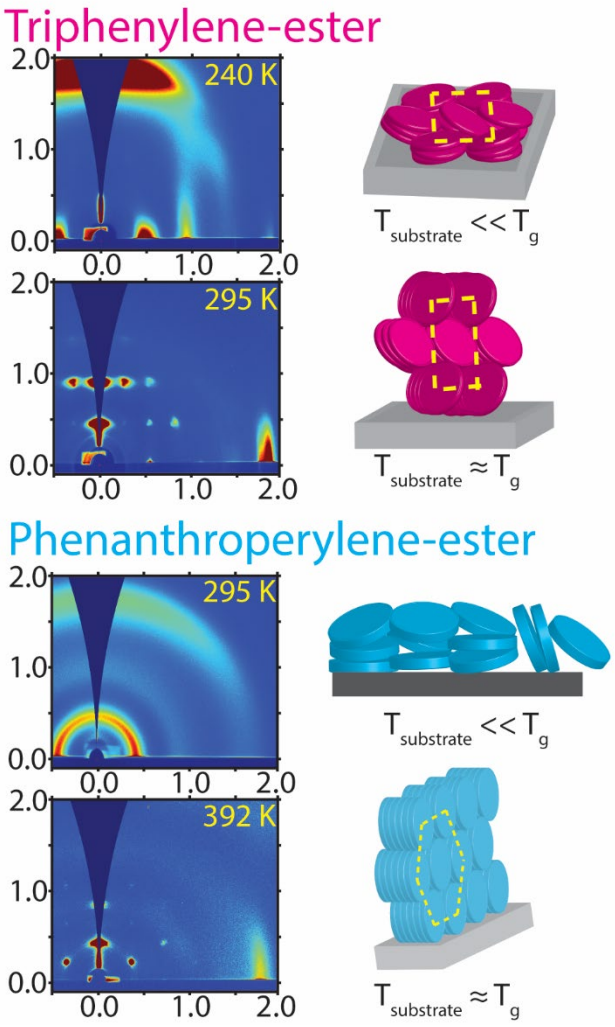

Figure 5. Two-dimensional X-ray scattering patterns alongside structural schematics for glasses of a triphenylene-ester and a phenanthroperylene-ester vapor-deposited at two different values of $T_{substrate}$. Each colored disk represents a single mesogen. For both mesogens, deposition near T_g produces glasses with highly ordered columnar structures that propagate in the plane of the substrate. Adapted with permission from Gujral et al., Chem. Mater,, **2017**, Article ASAP.[65] Copyright 2017 American Chemical Society.

The structures shown in Figure 5 were explained in terms of the surface equilibration mechanism that was introduced in Section 2.[38] deposition occurs at high $T_{substrate}$,, enough mobility exists near the free surface for the mesogens to achieve edge-on packing which is known to be the preferred structure at the surface of the equilibrium liquid crystal. It is reasonable to assume that these edge-on molecules at the surface pack into columns that propagate parallel to the free surface. As additional molecules are deposited on top of these columns, they form additional columns in registry. The end result of this process is a bulk sample of tightly packed in-plane columns, as shown in Figure 5. For depositions at sufficiently low $T_{substrate}$ values, molecules landing on the free surface do not have time to reach edge-on packing before being trapped into the bulk by further deposition. One can infer from the observed bulk packing that the molecules initially adopt a face-on orientation at the surface which is trapped into the bulk upon further deposition.

Eccher et al.[66] prepared discotic liquid crystalline films by vapor deposition and spin-coating that were incorporated into devices. From the observed device performance, the researchers extracted a charge carrier mobility for the films. In this study, a diimidodiester derivative of benzo[*ghi*]perylene deposited onto a room temperature substrate led to a slightly disordered edge-on packing. Even though the deposition conditions were not optimized for a specific packing motif, the vapor-deposited films gave a similar electric response to the annealed spin-coated films. Both of these films outperformed the highly disordered spin-coated films.

The structure of vapor-deposited glasses of a smectic mesogen, itraconazole,[36,67] was studied as a function of $T_{substrate}$ during deposition. It was found that glasses of itraconazole with smectic-like layering could be attained by depositing onto substrates near and below T_g. At the highest substrate temperatures, deposition formed a smectic monodomain with layers oriented parallel to the free surface; the smectic order in these systems was very similar to the equilibrium smectic liquid. Interestingly, just below T_g, the layered smectic structure persisted in the as-deposited glasses with a layer spacing that decreased monotonically with falling $T_{substrate}$. At the lowest $T_{substrate}$ investigated, a quite different structure was

observed as the rod-like molecules preferentially lie in the plane of the substrate. These results can also be rationalized with the surface equilibrium mechanism. The preferred orientation for itraconazole at a vacuum interface is perpendicular to the surface (homeotropic anchoring). For the highest $T_{substrate}$ glasses investigated, mobility is high enough during deposition for the free surface to completely equilibrate into a single smectic layer. Subsequent deposition then builds further layers on top of the existing layers; the glass prepared under these conditions has the same layer spacing as the equilibrium smectic liquid. At intermediate $T_{substrate}$, the molecules partially equilibrate and self-assemble towards the equilibrium smectic-like layering, but do not quite achieve the equilibrium structure before getting buried by oncoming molecules. For the very lowest $T_{substrate}$ glasses that the researchers prepared, the molecules do not have the mobility required to make any progress towards the preferred vertical orientation before further deposition buries them into the bulk; for these samples, the bulk glass consists of molecules lying very nearly in the plane of the substrate.

The three studies described in this section suggest that the surface equilibration mechanism can at least qualitatively account for the glassy structures formed by vapor deposition of smectic and columnar mesogens. This suggests that the mechanism might generally apply to additional classes of liquid crystals, including chiral systems. These ideas may be used by researchers to engineer films with molecular packing motifs tailored for specific applications.

5. Anisotropic structures in polymeric semiconductor films

Since the 1977 discovery by Heeger, MacDiarmid and Shirakawa[68] of conductivity in polyacetylene (for which they were awarded the Nobel Prize in Chemistry in 2000), there has been considerable research activity aimed to optimize charge carrier mobility in organic materials. For polymeric glasses, experimental investigations and theoretical models[32] indicate that there are two key processes in charge transport: the fast charge transport mechanism along the covalently-bonded chain, and

the slower molecular hopping between chains. It is, therefore, important to prepare materials with interchain structures that increase delocalization by π-conjugation between chains. While it was considered obvious for decades that highly crystalline materials would optimize charge mobility, recent work shows that very high charge mobility can be achieved with anisotropic packing arrangements that have very subtle nearest-neighbor correlations.

To explore how short-range interactions lead to long-range charge transport, Noriega et al.[13] compiled data from 13 high molecular weight polymeric semiconductors. The systems were categorized by the researchers into three broad classifications: 1) "semi-crystalline," 2) "poorly ordered" or anisotropic, and 3) "amorphous" or isotropic. Scattering patterns from representative systems across these classes have been reproduced from their work in Figure 6. The semi-crystalline patterns shown at the top feature sharp diffraction peaks with harmonic progressions indicating the presence of highly ordered structures. The scattering patterns at the bottom show only broad peaks with no radial variation in intensity (indicating isotropic packing); these features are characteristic of many liquid-cooled glasses. The scattering patterns in the middle are characteristic of the "poorly ordered" systems; they exhibit coexistence of very broad (but anisotropic features) with a small number of sharper features. We suggest that the materials referred to as "poorly ordered" by Noriega et al. can also be reasonably described as anisotropic glasses, based on similarities to the low molecular weight anisotropic glasses described above.

The analysis of Noriega et al.[13] indicates that the highest charge mobility among the 13 polymeric semiconductors were those in the "poorly ordered" category. The high performance of the "poorly ordered" systems is also reflected in low activation energies for transport in the films (derived from temperature-dependent FET measurements). Prior to this study, and similar ones,[69] the prevailing wisdom indicated that semi-crystalline systems exhibited the highest carrier mobility due to highly ordered domains of materials. But according to this analysis, charge transport in semi-crystalline systems is limited by barriers associated with the transitions between highly crystalline regions and less ordered regions. This type of barrier may be absent in the "poorly ordered" systems as a result of more homogeneous packing

throughout the film. Isotropic films had a much lower charge mobility and also higher activation energies for transport, ruling them out as efficient charge transport materials. Presumably the isotropic materials lack the effective paths for charge hopping between chains that are present in the anisotropic "poorly ordered" materials. To illustrate the ideas laid out by Noriega et al., we will explore two examples of poorly ordered systems below.

Figure 6.

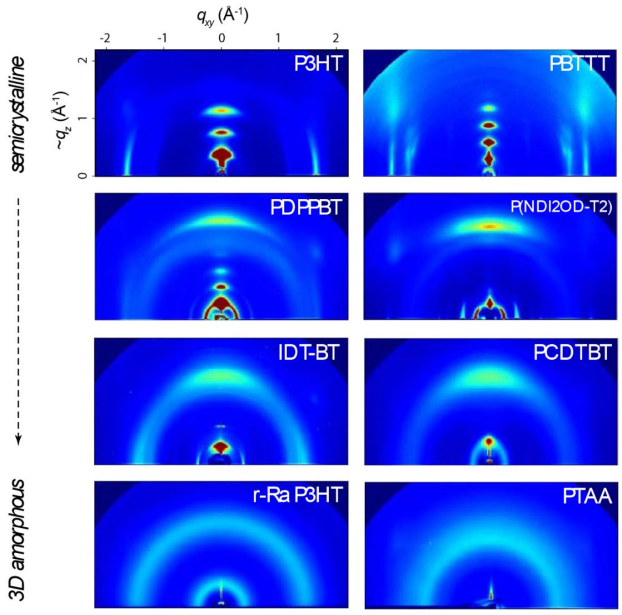

Figure 6. Two-dimensional grazing incidence x-ray scattering patterns obtained from thin films of various polymeric semiconductors. The vector q_z represents scattering out-of-plane while q_{xy} represents scattering in-plane. The systems, from top to bottom, are representative of different degrees of order, ranging from semi-crystalline to amorphous. The systems in the middle, which we characterize as anisotropic glasses, show very high charge mobility. The eight systems displayed are (left to right, top to bottom): regioregular poly(3-hexyl thiophene), poly (2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2,-b]thiophene), poly(diketopyrrolopyrrole-alt-benzothiadiazole), Poly{[N,N-9-bis(2-octyldodecyl)naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt5,59-(2,29-bithiophene)}, indacenodithiophene-co-benzothiadiazole, Poly[N-9′′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′benzothiadiazole)], regiorandom poly (3-hexyl thiophene), Poly(triarylamine). Reprinted by permission from Macmillan Publishers Ltd: *Nature Materials*, **2013**, *12*, 1038-1044, copyright 2013.[13]

Beiley et al.[70] showed the importance of weak short-range anisotropic interactions in a "poorly ordered" film of poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)], abbreviated to PCDTBT; the scattering pattern for PCDTBT is shown in Figure 6. The as-cast film exhibits a very broad out-of-plane peak at q_z = 1.5 Å^{-1} corresponding to a spacing of d = 4.0 Å, and is interpreted as π-π stacking which is preferentially oriented out of the plane of the substrate (face-on packing). The authors estimate that the coherence length for this peak is less than 14 Å; as this is only ~3 times that stacking distance, this indicates a quite disordered structure. In spite of this disorder, the films exhibited very high hole mobility with a low activation energy. The x-ray scattering pattern for the vapor-deposited TPD sample shown in Figure 2 is remarkably similar to that of the PCDTBT film shown in Figure 6, reinforcing the idea that both can be considered as anisotropic glasses. In each case, scattering near q ~ 1.5 Å^{-1} occurs predominantly in the out-of-plane direction, consistent with face-on packing of aromatic ring structures; it appears that the vapor-deposited TPD glasses and the PCDTBT sample have similar levels of anisotropy and similarly short coherence lengths.

When the as-cast films of PCDTBT were annealed well above T_g, the peak at 1.5 Å^{-1} became even broader and the coherence length decreased; these morphological changes were accompanied by a decrease in hole mobility.[70] This annealing test not only supports the connection between weak anisotropic interactions and efficient charge transport, but also provides a key insight into the nature of the material. When semicrystalline films are annealed above T_g, they generally become more ordered[29] as thermal motion allows the quality of packing in the crystalline regions to be perfected. When anisotropic glasses of low molecular weight organics (such as the one shown in Figure 2) are annealed above T_g,[38] they become more isotropic as they equilibrate towards the (isotropic) liquid state. Thus the morphological changes observed upon annealing PCDTBT are also consistent with the idea that "poorly ordered" PCDTBT films can be viewed as anisotropic glasses.

Similarly, Zhang et al.[71] investigated a rigid copolymer based on indacenodithiophene-benzothiadiazole backbone (IDT-BT). Although they designed the monomer to limit crystallinity, they

reported very high charge mobility. The GIWAXS scattering pattern for the as-cast IDT-BT is shown in Figure 6. Similar to the PCDTBT example discussed above, the π-π stacking feature indicates considerable disorder with a preference for face-on packing. The structure of IDT-BT films was investigated in greater detail in a later publication by Zhang et al.[72] This work revealed a common orientation for the polymer chains in the non-crystalline and more ordered regions, which the authors attribute to the rigidity of the polymer backbone. They argue that because of the rigid backbone, most transport occurs along the backbone with high delocalization. Interchain interactions with short range and relatively disordered π-stacking can effectively bridge the gaps between the chains. The rigid backbone additionally acts to suppresses crystallization,[71] leading to the preparation of anisotropic glassy films. Our description of these films as glasses is consistent with the absence of observable thermal transitions in these films.[71]

Concluding remarks

In this article, we have reviewed several categories of anisotropic glasses, their structural features, and their technological relevance. The studies highlighted here relied heavily on powerful characterization techniques that could evaluate the extent of anisotropy and guide the optimization of materials. The development of new structural characterization techniques is an important frontier. Resonant scattering of polarized soft x-rays (P-SoXS) is increasingly providing important information about anisotropy in organic films by characterizing the length scales over which orientational order persists.[73] Advanced transmission electron microscopy has recently succeeded in finding unexpected correlations in the orientations of neighboring chains in some materials for which GIWAXS indicates low levels of order.[74,75] As a final example, fluctuation electron microscopy provides access to information about higher order structural correlations that are absent in most scattering experiments.[76]Further application of these methods and new developments will significantly aid efforts to understand anisotropic organic glasses and related materials.

The recent increase in interest in anisotropic organic glasses has enriched the materials community, not only from the viewpoint of fundamental glass science, but also from an engineering perspective, as organic electronic devices penetrate further into the marketplace. Physical vapor deposition, already used in large-scale manufacture of OLEDs, has played an important role in this development. There is the potential for further advances, for example by combining the surface equilibration feature of vapor deposition with other self-assembly techniques. One can imagine the use of external fields during deposition or possibly combining some aspects of substrate control with the surface equilibration mechanism.

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