Glassy phases in organic semiconductors

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ABSTRACT

Organic semiconductors may be processed from fluids using graphical arts printing and patterning techniques to create complex circuitry. Because organic semiconductors are weak van der Waals solids, the creation of glassy phases during processing is quite common. Because structural disorder leads to electronic disorder, it is necessary to understand these phases to optimize and control the electronic properties of these materials. Here we review the significance of glassy phases in organic semiconductors. We examine challenges in the measurement of the glass transition temperature and the accurate classification of phases in these relatively rigid materials. Device implications of glassy phases are discussed. Processing schemes that are grounded in the principles of glass physics and sound glass transition temperature measurement will more quickly achieve desired structure and electronic characteristics, accelerating the exciting progress of organic semiconductor technology development.

1. Introduction

Organic semiconductors have been pursued with great interest and substantial investment over the last several years because they are elementally abundant, they enable new processing approaches and product form factors, and their properties can be tuned using synthetic chemistry. Intramolecular transport in these materials occurs through delocalized valence orbitals that are realized via extensive conjugation. Steady advances in synthetic chemistry, materials characterization, and device physics over the last several decades have led to a mature understanding of how to control important aspects of organic semiconductors, such as the highest occupied molecular orbital (HOMO) level (analogous to valence band), lowest unoccupied molecular orbital (LUMO) level (analogous to conduction band), and bandgap. A large materials library is now accessible commercially, and new materials with superior properties are frequently announced.

One of the key advantages of organic semiconductors is that they are readily dissolved and processed as solutions or via low-temperature vapor deposition. Such approaches are possible because these materials form weak van der Waals solids rather than covalent crystals. These characteristics enable additive manufacturing approaches such as ink-jet printing, screen printing, and slot-die coating. The flexible and conformable form factors enabled by organic semiconductors may also open new applications that are inaccessible to more traditional inorganic semiconductor technologies.

With a few notable exceptions, optimal electrical transport is achieved in highly-ordered, crystalline material; however, most polymeric or even small molecule organic semiconductors, when processed as thin films, exhibit polycrystalline or paracrystalline structure. Most polymeric semiconductor films are semicrystalline or glassy, and in many cases the crystals themselves contain significant packing defects or dynamic disorder. The amount of order within the films is expected to affect their semiconducting properties. Specifically, there is a connection between structural disorder and "electronic disorder," where the latter refers to a distribution of HOMO/LUMO levels resulting in a complex density of states for charge carriers. From a molecular charge transport perspective, there are two types of energetic disorder. In *diagonal disorder*, the local intramolecular HOMO level and LUMO level of a material will vary spatially at the nanoscale [1]. The most common origin of diagonal disorder is conformal freedom - rotation about sp^2 bonds in a conjugated molecule to form different conformers, which may be planar or nonplanar. In *off-diagonal disorder*, variations in the regular intermolecular spacing or orientation lead to a distribution of different electronic couplings between molecules [1]. This type of disorder occurs in glassy phases and also to various extents within defective crystals. Several approaches have been developed to evaluate the impact of energetic disorder on the device physics of organic electronics devices, such as transistors, with significant connections to the thermally-activated charge transport that is typically observed in such systems [2]. Molecular dynamics simulations reveal strong impacts of molecular conformation on hole transport rates [3]. For these reasons, there has been a significant investment in developing and adapting materials structure measurements that can be applied to organic semiconductors [4–7].
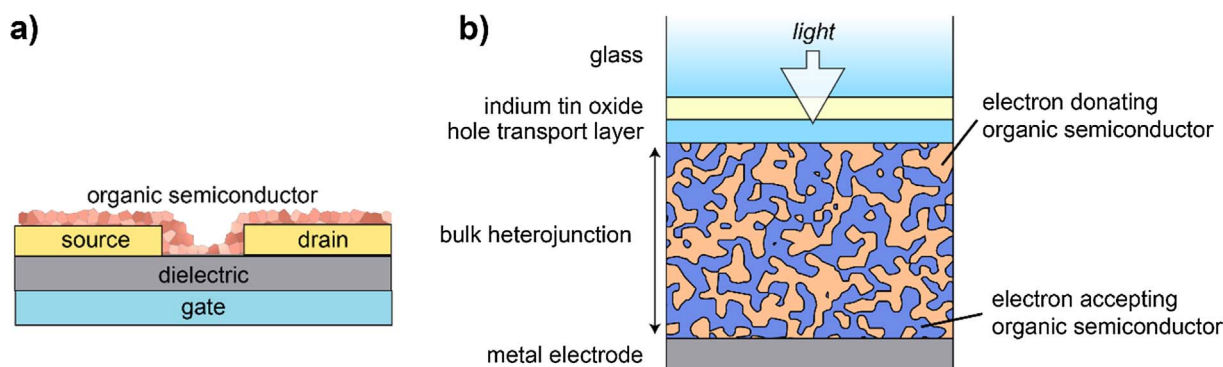
Fig. 1. Schematic of (a) a bottom-gate/bottom-contact organic thin-film transistor (OTFT) and (b) a bulk heterojunction (BHJ) organic photovoltaic (OPV) device in what is called the "conventional" geometry (contrasted by a now-common "inverted" geometry with electron extraction on the glass side).

In this perspective, we will examine some connections between glassy phases and the processing, structure, and device considerations of organic semiconductors. We believe that understanding the physics of glassy materials can accelerate the development of organic semiconducting materials with superior properties, and it is essential for the optimization of organic semiconductor processing. We will primarily focus on organic thin film transistor (OTFT) and organic photovoltaic (OPV) devices (see Fig. 1). Although it is true that in organic light emitting devices (OLEDs) [8] the behavior of glassy phases is of paramount importance, it is most relevant in OLEDs to long-term device stability. This is because OLED devices are generally processed to ensure that the materials remain homogeneous glasses, as aggregates will induce quenching that dramatically degrades device performance [9]. Contrarily, in OTFT and OPV applications some extent of crystallinity is thought to be advantageous, so controlling glassy phases and understanding their interactions with more ordered phases becomes more important. The focus of this perspective is on the broad category of organic semiconductors, which includes both small molecule and polymeric semiconductors. However, because of the unique aspects of polymeric materials, such as chain entanglement, additional emphasis will be placed on semiconducting polymers.

First, in this perspective, we will begin by considering the different types of glassy states that can exist in materials and their respective levels of order, the challenges associated with discerning between these different types of glassy states due to semiconductor backbone rigidity, and the connection between types of order and charge carrier mobility. Secondly, the added complications that arise in multicomponent systems, either during processing from solution or in mixed-glass phases such as in a BHJ, and the effect of phase purity on charge transport in BHJ's will be discussed. Thirdly, the impact of confinement and interfaces on ordering/vitrification and the resultant effect on charge transport will be examined. Finally, we will explore the challenges associated with measuring the glass transition temperature of organic semiconductors.

2. Glassiness and charge transport

Before discussing the connections between glassy phases and other aspects of organic semiconductors, we feel it necessary to define what we mean by a glassy phase. At its simplest, a glassy phase forms by a transformation from a state with molecular mobility to an immobilized state, relative to the experimental timescale, with the same or similar structure due to, for example, a decrease in temperature or removal of solvent [10]. Because this transition into a glass occurs when large-scale cooperative molecular or segmental rearrangements (dynamics) are arrested [11], it is not limited to a transition from an amorphous state, i.e., amorphous melt, but also includes transitions of mesophases (such as liquid crystals, plastic crystals, and conformationally disordered (CONDIS) crystals, as well as possibly in fully crystalline materials) into

their associated glassy phase, such as a liquid crystalline glass [12]. For example, at temperatures significantly below the glass transition temperatures (T_g) of their mesophases, a nematic liquid crystalline (LC) glass will no longer have translational motion and a plastic crystal glass will no longer have rotational motion [13]. Therefore, as we continue our discussion into the glassy phase of organic semiconductors, there will always be two underlying concerns related to the device performance: (1) the nature and composition of the glassy phase, which govern its underlying order, and (2) the underlying molecular dynamics related to where the system is relative to its T_g, which will influence what phases can form in both neat and blended systems as well as the thermal stability of the nanostructures and the mechanical properties of the device [14].

One metric for determining the nature of glassy state present in the system, i.e., amorphous or mesophase, is through Hosemann's paracrystalline disorder parameter g [15,16]. At the simplest level, the parameter is a measure of the relative cumulative statistical fluctuations across all crystallographic planes, with the higher g values pointing to higher levels of disorder. Rivnay and coworkers discussed methods for accurately determining g for semiconducting polymers; however, it is often challenging due to the frequently limited number of crystalline reflections in organic semiconductors [5]. g values have been attributed to various phases and mesophases with extreme limits of $g = 0$ for a perfect crystal and $g = 100\%$ for a Boltzmann gas. Real materials fall more broadly into the following ranges for g: $< 1\%$ for highly crystalline samples, $\approx (10\text{–}15)\%$ for amorphous materials, and therefore $\approx (1\text{–}10)\%$ for the remaining imperfect crystals and mesophases [5,16,17]. Using this range to strictly identify mesophases in polymers can be problematic, however, because it has been shown, in some cases, that as the degree of crystallinity of a polymer increases, g decreases [16]. Thus, it can be challenging to discriminate between a low crystallinity, nearly amorphous material and a 100% liquid crystalline material [13,18]. As pointed out elsewhere [19], this difference makes a huge impact on semiconducting polymer post-processing and annealing schemes, and this will be one of the challenges we return to repeatedly throughout this perspective. With effort, however, the thermodynamics and kinetics of the phase transitions of these systems can be used to properly classify these two separate cases, but a discussion of those methods is beyond the scope of this perspective [19].

If we, for the moment, limit ourselves to amorphous glasses, it must be emphasized that not all amorphous glasses are the same because their thermal processing history determines their packing (volume). Subsequent aging below their T_g can, through structural recovery, help them approach their equilibrium state (as shown in Fig. 2). With increased aging time, the observed T_g on heating (known as the fictive temperature) decreases as the packing density increases. However, the lower the annealing temperature, the exponentially longer it will take to reach the equilibrium line [20]. This packing density will influence the "structure" of the underlying semiconducting organic glass and