Invited Paper

In-plane alignment of polymer semiconductors on electronic performance

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The long covalently bonded conjugated chains that define polymer semiconductors result in inherently anisotropic optoelectronic characteristics. In solution cast films, the semiconductor is typically semicrystalline with no preferential in-plane alignment of polymer chains. The in-plane isotropic distribution of crystallites embedded within an amorphous matrix not only limits the ability to develop detailed structure-property relationships, this microstructure also limits performance when applied to electronic devices. Developing processing strategies to align the polymer chains over macro-scales provides a significant opportunity to improve structure-property relationships in these materials and explore device limitations.[1] In this talk, we will discuss processing strategies for macroscale polymer alignment and how highly aligned films are able to provide insight into charge transport and optoelectronic characteristics in organic thin film transistors (OTFTs) and organic photovoltaics (OPVs).

Processing strategies that will be discussed include alignment during polymer solidification and alignment after film formation through physical deformation. More specifically, drop-casting polymer solutions onto tailored nanostructured substrates will be shown to be an effective polymer alignment strategy. In addition, the criteria for strain-aligned films will be discussed in terms of film ductility and crystallinity. The aligned films are characterized in detail using a combination of X-ray diffraction, UV-visible spectroscopy, and atomic force microscopy. The discussion will consider local microstructure features along with macroscale chain alignment that have a large effect on optoelectronic character.

In OPV devices, the alignment of poly(3-hexylthiophene) (P3HT) within a P3HT:PCBM (Phenyl-C61-butyric acid methyl ester) bulk heterojunction (BHJ) is demonstrated, resulting in a polarization sensitive device. The aggregate P3HT is shown to align to a much greater extent than the amorphous P3HT in these BHJ films, providing a unique opportunity to probe the energy conversion differences between aggregate and amorphous P3HT. By illuminating the OPV device under polarized light parallel and perpendicular to the direction of aggregate alignment, differences are observed in the internal quantum efficiency of the cell. The origin of these differences will be discussed in terms of the energy conversion process for light absorbed in the amorphous and crystalline P3HT.

In OTFTs, a discussion will focus on inter-aggregate molecular tie-chain coupling, charge percolation, and the limits of field effect mobility. Insights into charge transport is made possible by taking advantage of macroscale alignment of the conjugated backbone, where charge transport is believed to be significantly favored along the polymer backbone over intermolecular directions. The discussion will focus on the polymers P3HT and poly{[N,N′-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl]-alt-5,5′-(2,2′-bithiophene)} [Polyera Inc. (N2200)].[2] In the P3HT films, key differences are observed between local and macroscale charge transport anisotropy attributed to features of inter-aggregate molecular coupling. In N2200, processing methods that vary the level of order are shown to have a large effect on mobility anisotropy with implications on charge percolation processes. Generalizing these findings assist in determining processing strategies and microstructural features that maximize polymer based OTFT performance.

References

[1] O'Connor, B., Kline, R. J., Conrad, B. R., Richter, L. J., Gundlach, D., Toney, M. F., DeLongchamp, D. M., "Anisotropic structure and charge transport in highly strain-aligned regioregular poly(3-hexylthiophene)," *Advanced Functional Materials* **21**, 3697-3705, 2011.

[2] Yan, H., Chen, Z., Zheng, Y., Newman, C., Quinn, J.R., Dotz, F., Kastler, M. Facchetti, A., "A high-mobility electron-transporting polymer for printed transistors," *Nature* **457**, 679, 2009.