608c Effect of Chemically Modified Dielectric Interfaces on Semiconducting Polymer Chain Orientation

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Conjugated organic semiconductors such as poly(3-hexylthiophene) (P3HT) have shown promise for use in applications such as flexible display technology and radio frequency identification tags. Unlike inorganic materials, organic device performance is strongly dependent on the structure and properties of the interfaces between materials. Previous research has shown that P3HT films spin-coated onto modified dielectric interfaces can show an increase in the charge carrier mobility presumably due to changes in microstructure that result in improved ƒàƒ{ƒnƒà interactions in the plane of charge transport. A clear understanding of the effect of interfacial properties on the structure and electrical characteristics of the polymer, however, remains incomplete. Here, we systematically investigate the influence of interfacial chemistries on the microstructure of conjugated semiconducting polymers. Specifically, we use two strategies to vary the interfacial chemistry to clarify the influence of either surface energy or chemical functionality on the chain orientation of P3HT. First, linear surface energy gradients were prepared by systematically oxidizing several aliphatic silane chemically modified surfaces with a UV ozone lamp. P3HT was spin coated on top of these substrates and the polymer axis tilt was determined using Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy. We find a weak dependence of chain orientation on substrate surface energy and some dependence on the aliphatic surface functionality. Second, the chemical functionality at the polymer monolayer-interface was modified using a versatile monolayer chemistry based on isocyanate-amine chemistry. This strategy allows the production of monolayers with aromatic functionality such as thiophene, fluorine, and pyridine surfaces. We quantify the relative surface coverage of the reactive units using NEXAFS and characterize the monolayer before coating with polymer. P3HT exhibited varying levels of orientation depending upon the monolayer chemistry and the solvent from which the polymer was spin coated, even for surfaces with the same water contact angle. These results suggest that specific interfacial chemical interactions as well as the film formation variables (casting solvent) can strongly influence the polymer conjugated plane tilt.