ABSTRACT

Baradwaj, Aditya G. Ph.D., Purdue University, August 2016. Solid State Charge Transport in Radical Polymers. Major Professor: Bryan Boudouris.

Organic materials have been gaining visibility for the last 25 years for the design and fabrication of electronics. The basis of these electronic applications has been the use of conjugated small molecule and polymeric semiconductors and conductors that can transport charge efficiently. However, with the exception of light emitting diodes, widespread commercialization of organic electronics has been limited by poor device performance. This is a result of the poor charge transport ability and lack of air stability of the current subset of organic semiconductors relative to their inorganic counterparts. Thus, in order to make organic electronics a viable part of the technological future, novel classes of organic semiconductors must be developed and probed. One such class of polymers, radical polymers, are non-conjugated, redox-active macromolecules that have shown immense potential in electrolyte-supported applications. Unlike traditional organic semiconductors which rely on conjugation to govern charge transport, radical polymers transport charge utilizing a reversible oxidation-reduction mechanism. However, only a minimal amount of solid-state charge transport characterization of these polymers has occurred.

Here, we present a quantification of the charge transport ability of a model radical polymer, poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA). We demonstrate that charge transport in PTMA occurs across a singularly occupied molecular orbital (SOMO) level, and that this level is 5.2 eV removed from vacuum. We have fabricated hole-only devices through which we have quantified a space charge limited (SCL) hole mobility of 10^{-4} cm^2 V^{-1} s^{-1}, on par with pristine π-conjugated polymers such as poly(3-hexylthiophene) (P3HT). We illustrate that the SCL carrier mobility is only a weak function of temperature. This implies that the charge transport is

limited not by the reversible oxidation-reduction charge transfer step between neighboring radical sites, but rather by the spatial proximity of these sites.

Furthermore, we investigate the electrical and chemical stability of radical polymer thin films. We demonstrate that PTMA thin films show excellent charge transport characteristics when repeatedly electrically biased across a wide voltage range. Additionally, these films remain stable when exposed to electrical biasing for over 20 hours. Similarly fabricated PTMA thin films exhibit consistent electronic performance when exposed to varying amounts of moisture and solar light. These key results illustrate the stability and chemical reversibility of the oxidation-reduction reaction dictating charge transport. Furthermore, the robustness of the PTMA thin films when environmentally stressed show the potential for radical polymers to be utilized in electronic applications.

Finally, we probe the effect of molecular dopants on the electrical performance of radical polymer thin films. We demonstrate that the addition of a redox-active cation salt to PTMA thin films at an optimal doping level results in a five times increase in electrical conductivity relative to that of a pristine PTMA thin film. Furthermore, we illustrate that while the addition of the cation salt does alter the electrochemical environment of the thin films, it does not diminish the stability or presence of the redox-active sites on the PTMA. Larger increases in electrical performance are not observed due to poor film quality at higher doping levels of cation salt. These results establish a mechanism of doping redox-active macromolecules and provide a template for future studies into improving the electronic performance of radical polymers. As such, we anticipate that these findings will contribute towards the continued implementation of radical polymers in flexible electronic applications.