# ABSTRACT

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Title: Influence of Radical Proximity on the Charge Transport of Nitroxide-Based Electronics.
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As the societal dependence upon electronics continues to expand, consumer demand dictates the development of new materials to further augment both device performance and the user experience. Organic electronic materials enable unique features and applications due to the synthetic tunability of their optoelectronic properties, light weight, compatibility with flexible substrates, and biocompatibility. Radical polymers, macromolecules bearing pendant stable radical sites, have emerged as a new class of conducting polymers. These materials have demonstrated charge storage and transport capabilities in electrolyte-supported systems (e.g., secondary batteries) and have since been a source of inquiry for solid-state applications. Initial studies of their solid-state properties have established the conductivity of these amorphous materials to be on par with undoped conjugated polymers [e.g., poly(3-hexylthiophene) (P3HT)]. This warranted further investigation into developing design rules such that next-generation radical polymer materials could be realized. Herein, we investigate the pendant radicals of poly(2,3-bis(2’,2’,6’,6’-tetramethylpiperidinyl-N-oxyl-4’-oxycarbonyl)-5-norbornene) (PTNB) as a handle in electrical performance. Specifically, we create polymer blend solutions of the electrically-active PTNB homopolymer and a quenched insulating polymer poly(2,3-*bis*(2’,2’,6’,6’-tetramethylpiperidinyl-N-hydroxyl-4’-oxycarbonyl)-5-norbornene) (PTNB-OH). Through the use of electron paramagnetic resonance (EPR) spectroscopy, we confirm that hydrogen atom transfer occurs between active and quenched pendant sites to yield a copolymer system. This blending method is used to control the proximity of radicals in thin films, and we establish that electrical conductivity increases exponentially as radical sites are brought into closer proximity with each other. In conjunction with observed temperature-independent electronic performance, this exponential relationship suggests a tunneling mechanism governing charge transport in solid-state radical polymer systems. This confirms a different operating paradigm for solid-state charge transport of these redox-active materials, as compared with their conjugated counterpart. Additionally, we

present this redox capability as a handle by which we can induce swelling in grafted radical polymer brushes for stimuli-responsive applications.