Synthesis and Characterization of Radical Polymers in Organic Electronic Applications

Lizbeth Rostro
Major Professor: Bryan W. Boudouris

Abstract:

Organic electronics have become of great interest due to the potential for lightweight, flexible, and even transparent electronic devices. Specifically, they can be incorporated into organic field effect transistors (OFETs), organic photovoltaic (OPV) devices, and organic light emitting diodes (OLEDs). The majority of the focus for the molecular design and synthesis has focused on π-conjugated small molecules and polymeric systems. However, concerns regarding the controlled synthesis of these materials and limited lifetimes has significantly hindered the commercialization of many of these technologies. As such, the focus in this work is to demonstrate that π-conjugated is not a requirement for efficient charge transport in the effort to establish more synthetic flexibility for next-generation organic electronic materials. Specifically, this work has focused on a completely amorphous class of electrically-active polymers comprised of stabilized radical moieties, which can transport charge efficiently through an oxidation-reduction (redox) reaction.

Moreover, the model radical polymer poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA) was synthesized in a facile manner utilizing a controlled radical polymerization (reversible addition-fragmentation chain transfer [RAFT]) to obtain polymers of controlled molecular weights. Furthermore, the electronic properties of these macromolecules was established to be on par with commonly used π-conjugated polymer systems (*e.g.*, poly(3-hexylthiophene) [P3HT]). In addition, utilizing facile chemistry the pendant group chemistry is optimized to attain polymers with even higher electronic properties. Importantly, the stability of thin films of PTMA was investigated and no degradation was observed for a range of bias stressing and exposure to environmental conditions. These results demonstrate the high stability of radical polymers once incorporated into organic electronic applications. Furthermore, the radical polymer, PTMA, was successfully incorporated into OPV devices to serve as interfacial layer between the evaporated metal and the photoactive layer. In this manner, the radical polymer serves to enhance the charge collection at the anode. Furthermore, the incorporation of the PTMA layer resulted in stable device performance for the OPVs after 5 days of exposure to ambient conditions.

Finally, in the efforts develop a system with even higher performing electronic properties the self-assembly of radical containing block copolymers was investigated. Specifically, utilizing polydimethylsiloxane as a macroinitiator the radical polymer PTMA was chemical grown to obtain a diblock copolymer system of polydimethylsiloxane-*b*-poly(2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PDMS-PTMA). Importantly, thin films of PDMS-PTMA demonstrated self-assembly for moderated block sizes of PTMA (*i.e.*, 10-36 kg mol^{-1}). Importantly, these results establish the viability to fabricate nanosize devices incorporating radical polymers.