# Developing Structure-Property Relationships in Radical Polymers through Advanced Macromolecular Design

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Recently, there has been significant increase in research and development in the field of organic electronics. This is mainly because organic electronic devices can be flexible, lightweight, and processed from solution using low-cost manufacturing techniques. Typically, these devices have utilized conjugated polymers as their active layer components. This approach has been successful, but the use of conjugated polymers comes with limitations. To address these limitations and expand the field of organic electronics, this work studies a novel class of macromolecules, radical polymers. Unlike their conjugated polymer counterparts, radical polymers are comprised of a non-conjugated backbone with stable open-shell groups at their pendant sites.

First, radical polymer-based blends were evaluated for mixed electron and ion conduction purposes. Mixed electron- and ion-conducting polymers have received considerable interest due to their applicability in a variety of organic electronic devices. This work developed a novel radical polymer-based blend by combining poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO), poly(poly(ethylene oxide) methyl ether methacrylate) (PPEGMA), and lithium hexafluorophosphate ($LiPF_6$). PPEGMA with $LiPF_6$ had one of the highest polymer-based room temperature ionic conductivity of $10^{-4}$ S $cm^{-1}$. PTEO demonstrated an ability to conduct both charges and ions with an ionic conductivity of $10^{-6}$ S $cm^{-1}$. A blend of the two polymers at equal weight ratios had a room temperature ionic conductivity of $10^{-4}$ S $cm^{-1}$ and electronic conductivity of $10^{-2}$ S $cm^{-1}$ similar to pristine PPEGMA and PTEO thin films, respectively. This similarity resulted from the formation of distinct pathways of ion (i.e., through PPEGMA domains) and electron (i.e., through PTEO domains) conduction due to microscale phase separation between the two polymers with the lithium ions mainly incorporating in the PPEGMA domains. With the addition of lithium salt, the electronic conductivity of the blend increased by 1.7 times. However, at $[Li^+]$:[O] ratios higher than 0.08, the electronic conductivity suffered due to poor film quality.

Additionally, this work quantifies the electron exchange behavior of poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO). Due to the high number of pendant open-shell sites, PTEO displays strong paramagnetic behavior. Electron paramagnetic resonance spectroscopy revealed that 4-hydroxy-2,2,6,6-tetramethylpiperidin-N-oxy (TEMPO-OH), 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEO), and PTEO showed rapid electron exchange between the pendant radical groups. When compared to TEMPO-OH and TEO, there was more interaction between the unpaired electrons in PTEO due to their proximity along the polymer chain. This phenomenon was confirmed through magnetic susceptibility, $X_m$, measurements between 2 K and 300 K. At 2 K, TEMPO-OH and TEO had a $X_m$ of $1.8\times10^{-2}$ emu $mol^{-1}$ and $4.6\times10^{-2}$ emu $mol^{-1}$. PTEO on the other hand, had a $X_m$ of $1.3\times10^{-1}$ emu $mol^{-1}$. Due to its amorphous nature, PTEO had weak antiferromagnetic interactions. However, thin films of PTEO with TEMPO-OH additives showed increased antiferromagnetic interactions between the open-shell sites as well as stronger magnetoresistance effects of -0.88%

In conclusion, radical polymers offer researchers an opportunity to explore an underutilized class of macromolecules. By studying the structure-property relationships of these radical polymers, this work developed novel polymer systems for a variety of organic electronic applications. Furthermore, these studies can be applied to future radical polymer systems yet to be discovered. Ultimately, this work served as a template for expanding the field of organic electronics.