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Elucidating the Charge Transfer Mechanism in Radical Polymer Thin Films SANJOY MUKHERJEE, BRYAN BOUDOURIS, Purdue Univ — The active role of polymers in organic electronics has attracted significant attention in recent decades. Beyond conventional conjugated polymers, recently radical polymers have received a great deal of consideration by the community. Radical polymers are redox-active macromolecules with non-conjugated backbones functionalized with persistent radical sites. Because of their nascent nature, many open questions regarding the physics of their solid-state charge transfer mechanism still exist. In order to address these questions, well-defined radical polymers were synthesized and blended in a manner such that there was tight control over the radical density within the conducting thin films. We demonstrate that the systematic manipulation of the radical-to-radical spacing in open-shell macromolecules leads to exponential changes in the macroscopic electrical conductivity, and temperature-independent charge transport behaviour. Thus, a clear picture emerges that charge transfer in radical polymers is dictated by a tunnelling mechanism between proximal sites. This behavior is consistent with a distinct mechanism similar to redox reactions in biological media, but is unique relative to transport in common conjugated polymers. These results constitute the first experimental insight into the mechanism of solid-state electrical conduction in radical polymers.

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