Novel Elastomeric Polystyrene via Photopolymerization and Post-Functionalization of Durable Ultra-High Molecular Weight Perfluorostyrene Copolymer

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The development of durable and sustainable plastics is essential for the advancement of our society. Ultra-high Molecular Weight (UHMW) polymers are highly attractive due to the extreme durability and material properties granted by increased polymer entanglements. Previously, I conducted the first well-controlled, photoiniferter-mediated polymerization of UHMW polystyrene homopolymers up to 2.0 x 10^6 g/mol, and subsequently showed facile post-functionalization via nucleophilic aromatic substitution. In this project, I performed a quantitative modification of my polymer with dodecanethiol through a thiol-para-fluoro "click" reaction, yielding a rare and novel thermoplastic elastomer from a polystyrene homopolymer. Rheological analysis of this polymer showed properties unique to thermoset plastics, which are unrecyclable due to the covalent crosslinks between polymer chains. Despite the clear lack of covalent linking in my polymer, it exhibited similar behavior, suggesting that it could be used as a reprocessable alternative to these thermosets. Via aminolysis of RAFT-mediated poly(butyl acrylate) (pBA) and "grafting-to," I access ultra-long brush copolymers, which dramatically increase the viscoelasticity of the resulting pBA mixture. My findings illustrate my polymers viability as a template for further modifications to tune its physical properties in order to access advanced architectures and extremely desirable materials. Finally, I show that my initial polymerization can be extended to bio-based styrenic monomers for the production of more sustainable, bio-based UHMW polymers. These polymers show similar promise as recyclable alternatives to traditionally unrecyclable thermosets, along with remarkable properties such as room temperature shape memory.