Preparation and post-polymerization modification of iodo-ene and iodo-yne polymers

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The ability to adorn a polymer or material with additional functionality after polymerization, facilitates advanced, customized materials from common starting materials. An essential component to post-polymerization modification is a robust chemical handle which allows addition of multiple new functionalities. New polymerization methods with unique monomers offer opportunities to install versatile chemical handles into polymer backbones. Here we capitalize on the labile C-I bond of diiodoperfluoroalkanes which can undergo radical addition into dienes or diynes. Using a mild initiator in an acetonitrile/water solution, semi-fluorinated iodo-ene and iodo-yne polymers of notable molecular weight can be synthesized. When a diene is employed as a comonomer, the resulting iodo-ene polymers contain an alkyl iodide within the backbone. We have shown that the alkyl iodides can be can be eliminated or reduced, displaced with nucleophiles to provide click handles, or photochemically cleaved to cross-link the polymer into a fluoropolymer matrix. If the diene is replaced with a diyne, vinyl iodide is placed across the polymer which can be eliminated to form alkynes or diversified through cross-coupling chemistries . These methods can all be combined to provide a route to a library of polymers through simple polymerizations and modifications, setting the stage for the creation of novel advanced materials.