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Polysulfide Modification using Dynamic Sulfur Bonds

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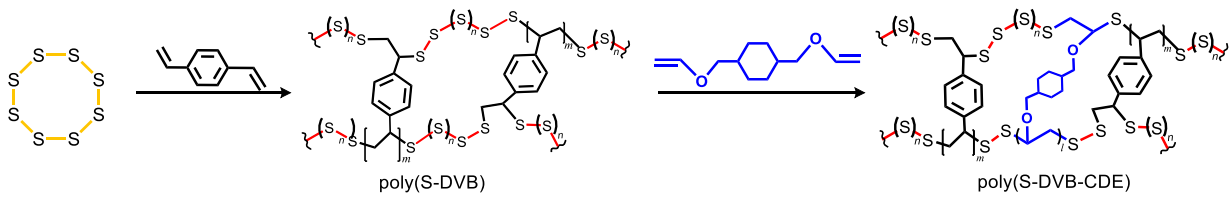
Abstract:

Sulfur containing compounds in crude oil are converted to elemental sulfur during petroleum refinement. Elemental sulfur has very limited applications leading to the accumulation of ~60 million tons of unused waste annually. Inverse vulcanization, developed by the Pyun group, repurposes this waste into polymers without the use of solvent. Heating sulfur above 159 °C generates free radicals that bind to monomers, creating high sulfur content polysulfides. These new materials have shown promise in the development of LiS batteries and infrared transparent lenses. Despite the many benefits of inverse vulcanization, high reaction temperatures and miscibility issues limit the use of many monomers. Polymers formed by inverse vulcanization, such as poly(S-divinylbenzene), contain sulfur chains in a linear arrangement. In this extended form sulfur radicals to form at much lower temperatures (80-100 °C). Polysulfides can then be used to initiate polymerization with a broader range of monomers with much lower boiling points. Terpolymers were formed by combining poly(S-divinylbenzene) and additional monomers with vinyl and allyl functional groups with boiling points as low as 95 °C. ^{1}H-NMR was used to confirm polymer formation and examine the terpolymer microstructure. Characterization by gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) generally revealed higher molecular weights and lower glass transition temperatures as more monomer was incorporated. Inverse vulcanization offers a solvent free method to create functional materials from the repurposed petroleum waste product, sulfur. Here that method has been expanded to incorporate a broader range of monomers at relatively mild temperatures.



Scheme: Polysulfide Initiated Terpolymer Synthesis. Elemental sulfur is combined with divinylbenzene to form poly(S-divinylbenzene) which can initiate the formation of terpolymers.