

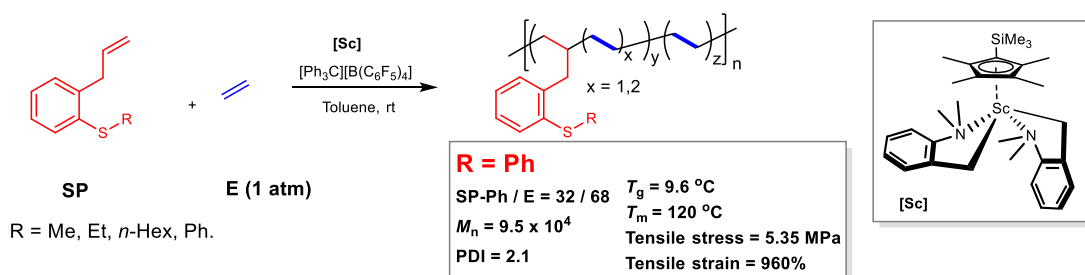
Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Copolymerization of Ethylene with Thioether-Substituted Propylenes

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The copolymerization of nonpolar and polar olefins in a controlled fashion is of great interest and importance. We recently reported the sequence-controlled copolymerization of ethylene (**E**) and anisyl-substituted propylenes (**AP**) by a half-sandwich scandium catalyst, which afforded unique multiblock copolymers composed of relatively long **E-alt-AP** sequences and short **E-E** sequences.^{1,2} Such microstructure-regulated polymers exhibited excellent elasticity and self-healing properties because of the microphase separation of nanodomains of the crystalline **E-E** segments from a flexible **E-alt-AP** matrix. To further investigate the influences of heteroatom functional groups on the copolymerization and the mechanical and self-healing properties of the resulting copolymers, we then examined the analogous copolymerizations by using various heteroatom-functionalized propylenes.

Herein we report the scandium-catalyzed copolymerization of ethylene (**E**) with thioether-substituted propylenes (**SP**) having different substituents (Me, Et, *n*-Hex, Ph) at the sulfur atom. The copolymerization afforded unique multi-block copolymers with relatively long alternating **E-alt-SP** and **E-E-SP** sequences and short **E-E** blocks. The copolymers with phenylthio substituent (**SP-Ph**) exhibited excellent elasticity and remarkable self-healing property, because of the microphase separation of nanodomains of the crystalline **E-E** segments from very flexible **E-alt-SP-Ph** and **E-E-SP-Ph** matrices.



1) Wang, H.; Yang, Y.; Nishiura, M.; Higaki, Y.; Takahara, A.; Hou, Z. *J. Am. Chem. Soc.* **2019**, *141*, 3249.

2) Yang, Y.; Wang, H.; Huang, L.; Nishiura, M.; Higaki, Y.; Hou, Z. *Angew. Chem. Int. Ed.* **2021**, *60*, 26192.