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題目(和文)	スカンジウム触媒による官能化プロピレン と非極性オレフィンの共重合による自己修復エラストマーの合成
Title(English)	Synthesis of Self-Healing Elastomers by Scandium-Catalyzed Copolymerization of Functionalized Propylene and Non-polar Olefins
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論 文 要 約

THESIS OUTLINE

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要約
Thesis Outline

The copolymerization of non-polar olefins with heteroatom-functionalized polar olefins is the most efficient and practical approach for the synthesis of functionalized polyolefins and has recently received significant attention. However, the controlled copolymerization of non-polar olefins and polar functional olefins remains a great challenge because of the difference in reactivity between the two different types of olefin monomers. Therefore, developing efficient and selective copolymerization reactions of non-polar and polar olefin monomers is of great interest and importance. Recently, Hou group in RIKEN found that half-sandwich rare-earth catalysts can show unique activity and selectivity in the copolymerization of non-polar and polar olefins due in part to the relatively strong affinity of rare earth metal ion with heteroatom. In particular, the copolymerization of ethylene and anisyl-substituted propylenes using a sterically demanding half-sandwich scandium catalyst afforded unique multiblock copolymers composed of relatively long ethylene-*alt*-anisylpropylene sequences and short ethylene-ethylene blocks. Such sequence-regulated copolymers showed autonomous self-healing property under various chemical environments through microphase separation of crystalline ethylene-ethylene nanodomains from a flexible ethylene-*alt*-anisylpropylene matrix via van der Waals interactions. During these studies, I became interested in copolymerization of non-polar olefins with heteroatom-functionalized polar olefins for synthesis of self-healing polymers by using scandium catalyst.

In this thesis, I introduced general background of copolymerization of polar with non-polar olefins and intrinsic self-healing polymers, especially the rare-earth metal catalyzed copolymerization of polar with non-polar olefins and the self-healing polymers with microphase separation structures.

By using a sterically demanding scandium catalyst, I have achieved for the first time the efficient and controllable copolymerization of ethylene and *N,N*-dimethylaminophenyl-substituted propylene (**AMP**), offering a series of aniline-functionalized copolymers with tunable polar monomer incorporation ratio (up to 26 mol%). The dimethylamino group in **AMP** showed significant impact on the copolymerization process, leading to formation of the unique microstructure composed of **AMP-E-E** sequence and short **E-E** segments. Continuous **AMP**–**AMP** units and **AMP**–*alt*–**E**

units were not observed probably owing to the steric hindrance of the NMe_2 group in **AMP**. The **E-AMP** copolymer behaved like soft viscoelastic material without visible self-healing behavior. This is in sharp contrast with the analogous **AP-E** copolymers, which exhibited excellent elasticity, high toughness and excellent self-healing property, demonstrating significant influences of heteroatom functional group on the comonomer sequence and the physical and mechanical properties of the resulting copolymers.

For the first time, I have successfully achieved the terpolymerization of two different non-polar olefins (ethylene and styrene) and dimethylaminophenyl-functionalized propylene (**AMP**) using a sterically demanding half-sandwich scandium catalyst. This process resulted in a unique multi-block terpolymer composed of relatively long **AMP-E-E** sequences, short **St-St** segments, and short crystalline **E-E** segments. Continuous **AMP**–**AMP** units, **AMP**–*alt*–*E* units, and **AMP**–*alt*–**St** units were not observed, likely due to the steric hindrance of the NMe_2 group in **AMP**. The terpolymers exhibited excellent elasticity and unprecedented self-healing properties, attributed to the nanophase separation of the crystalline **E-E** segments and the hard amorphous **St-St** segments within a very flexible **AMP-E-E** segment matrix. These findings were confirmed by X-ray diffraction analyses and scanning transmission electron microscopy (STEM) images. Notably, none of the respective two-component copolymers, such as **E-AMP** copolymer and **E-St** copolymer, demonstrated significant elasticity or self-healability. The exceptional elasticity and self-healability of the **E**–**St**–**AMP** terpolymers can be ascribed to the synergistic effects of the three different components. Additionally, significant influences of the styrene substituents on the mechanical properties were observed. Terpolymers with tert-butyl-substituted styrene exhibited stronger tensile strength and faster self-healing properties.

These findings demonstrate that sequence-regulated copolymerization of multiple olefins with different properties may serve as an efficient route for synthesizing novel self-healing polymers with potential applications in various fields. Further studies on the creation of self-healing polymers through catalyst-controlled olefin polymerization are currently in progress.