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Design and Synthesis of Stereoregular and Optically Active Poly(carbosiloxane)s and Poly(silyl ether)s

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Abstract

In this work, stereoregular and optically active polymers containing silicon-oxygen bond in the main chain were synthesized for the first time by two ways: (1) from the optically active organosilicon monomers and (2) stereoselective polymerization of racemic or prochiral organosilicon compounds.

A highly stereoregular (isotacticity $>$ 99 %) and optically active ($>$ 99 % ee) poly(carbosiloxane), poly[{(1*S*)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyl}ethylene], was prepared via the polyaddition (hydrosilylation) and the ring-opening polymerization of an optically active bifunctional disiloxane and an optically active cyclic disiloxane, respectively.

The ring-opening polymerization of racemic 2-(1-naphthyl)-2-phenyl-5,5-dimethyl-1-oxa-2,5-disilacyclopentane using PhLi showed a stereoselective feature, affording polymers with enhanced syndiotacticity (r / m dyad ratio = 62.9 / 37.1 at -20 °C). Although the mechanism for the stereoselectivity is still not clear, it is tentatively considered that the propagating chain end and the approaching monomer may form diastereomeric intermediates via lithium cation, which contribute to the above outcome.

The catalytic cross-dehydrocoupling polymerization of organosilanes, a novel route to polymers containing Si-O bond in the main chain such as poly(carbosiloxane)s, poly(silyl ether)s, poly(silyl ester)s, was developed. This polymerization possess many attractive features, e.g., the very mild conditions (room temperature to 100 °C), less by-products (only hydrogen), and readily available monomers.

The asymmetric synthesis of stereoregular and optically active poly(silyl ether)s having asymmetric silicon atoms in the main chain was attempted for the first time via the stereoselective cross-dehydrocoupling polymerization of bis(organosilane)s with diols. The best result was observed in the cross-dehydrocoupling polymerization of 1,2-bis(phenyldihydridosilyl)ethane with 1,4-cyclohexanediol in the presence of RhCl[(*R*)-BINAP)] in benzene, which afforded a poly(silyl ether) with an optical purity of 39.8 % e.e. of silicon atoms.

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[3] **Yuning Li** and Yusuke Kawakami "Synthesis and Polymerization of an Optically Active Bifunctional Disiloxane. 1. Preparation of Optically Active and Highly Stereoregular Poly[(1S)-1-(1-naphthyl)-1-phenyl-3,3-dimethyldisiloxane-1,3-diyle thylene] by Polyaddi-tion via Hydrosilylation" *Macromolecules* **1998**, *31*, 5592.

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[10] **Yuning Li** and Yusuke Kawakami "Asymmetric Synthesis of Reactive Optically Active and Stereoregular Poly(silyl ether)s" submitted.

Note: the thesis is written in English.

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