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Department of Chemistry



2:30 p.m. Monday, March 10 • 117/119 Smith Hall



Assistant Professor
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Molecular Design of Novel Polymeric Chiral Catalysts for Asymmetric Reaction

Research interests include polymer-supported chiral catalyst, catalytic asymmetric reaction, noncovalent immobilization, polymer microsphere, anionic polymerization, end-functionalized polymer, and branched polymer. Website:

http://www.tutms.tut.ac.jp/STAFF/HARAGUCHI/index.html.en

Abstract

Polymeric chiral catalysts have attracted much interest in the aspect of facile isolation of the product and reuse of the recovered catalyst.1 Even though the catalytic activity of polymeric chiral catalysts was influenced on the property of support polymer, some conventional support polymers such as Merrifield resin and poly(ethylene glycol) have been used and little attention has been paid to the design of support polymer. To date, most immobilization of chiral organocatalyst onto polymer was achieved by covalent bond to support polymer. However, these polymeric chiral organocatalysts have some drawbacks, including multistep preparations and loss of catalytic activity due to the modifications of chiral organocatalysts. In this study, novel polymeric chiral organocatalysts by a facile immobilization method and main-chain polymers of chiral organocatalyst have been developed.

Novel immobilization method of chiral organocatalyst comprising quaternary ammonium salts onto support polymers was achieved by ion exchange reaction of chiral organocatalyst with sulfonated polymer or polymerization of functional monomer bearing chiral organocatalyst. Both ion exchange reaction and polymerization proceeded smoothly to afford ionically polymer-supported chiral organocatalyst.2 Non-covalently interaction has certain advantages since commercially available organocatalysts are directly used for the immobilization and the reaction via ion exchange reaction between sulfonated polymer and quaternary ammonium salt proceeded under mild condition without any side reaction.

The ionic bond formation reaction can be applied to the synthesis of novel main-chain polymer of chiral organocatalyst. For example, the reaction between chiral imidazolidinone dimer and disulfonic acid occurs readily to afford main-chain polymer of chiral imidazolidinone.3 The resulting polymers were employed as polymeric organocatalysts in asymmetric reaction such as asymmetric Diels-Alder reaction and asymmetric benzylation of glycine Schiff base.

- 1. N. Haraguchi, S. Itsuno, Polymer-immobilized chiral Organocatalyst. *In Polymeric chiral catalyst design and chiral polymer synthesis*, Itsuno, S., Ed.; Wiley: Singapore, 2011; p 17-61.
- 2. (a) N. Haraguchi, H. Kiyono, Y. Takemura, S. Itsuno, Tetrahedron Lett. 2010, 51, 1205-1208.
- (b) Y. Arakawa, N. Haraguchi, S. Itsuno, Angew. Chem. Int. Ed. 2008, 47, 8232-8235.
- 3. (a) N. Haraguchi, H. Kiyono, Y. Takemura, S. Itsuno, *Chem. Commun.* 2012, *48*, 4011-4013.
 (b) S. Itsuno, D. K. Paul, M. A. Salam, N. Haraguchi, *J. Am. Chem. Soc.* 2010, *132*, 2864-2865.

Host: Professor Thomas Hoye