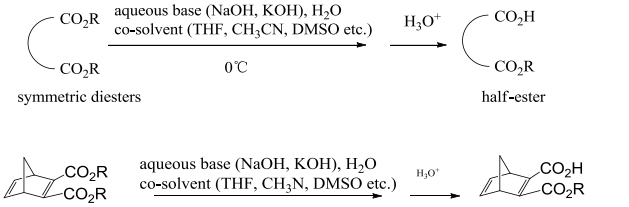
水溶媒中での非対称化反応を用いた高分子合成研究
Synthetic Studies of Polymers Applying Water-Mediated Desymmetrization Reactions

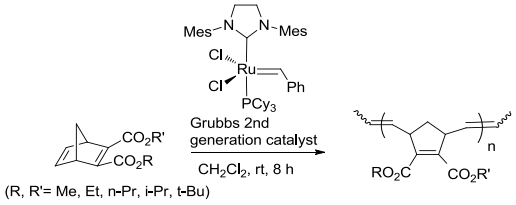
Jianjun Shi、Satomi Niwayama (Muroran Institute of Technology)

We have been developing highly efficient selective monohydrolysis reactions of symmetric diesters in the aqueous media (Scheme 1a). [1] Half-esters, produced by these reactions, are very versatile building blocks in organic synthesis, which are often applied to synthesis of polymers with a variety of physical and chemical properties. The half-esters with the norbornadiene skeleton are obtained rapidly in high yield with the use of this reaction, and the reaction mixtures were quite clean (Scheme 1b). As compounds having norbornene or norbornadiene skeletons are generally known to be efficient precursors for ring opening metathesis polymerization (ROMP) reactions due to their strained structures [2], we have been synthesizing a library of polymers with various physical and chemical properties applying these half-esters. Polymers thus produced will have cyclopentene backbones, which are expected to show stiffer properties than the linear backbones, and therefore are anticipated to expose the properties of the attached functional groups to the greater extent.

Scheme 1



Scheme 2



Various non-symmetric norbornadiene derivatives with two ester groups were prepared by esterification of the half-esters obtained above in the presence of the corresponding alcohols and various common Lewis acids, such as p-toluenesulfonamide and magnesiumchlord with good yields. [3] These doubly functionalized polar norbornadienes as well as the starting symmetric diesters were polymerized by ROMP with second generation Grubbs' catalyst in a living manner as in Scheme 2. In this way, a library of polymers having cyclopentene backbones has been synthesized. We are currently examining various physical and chemical properties of these polymers.

＜参考文献＞

1）Niwayama, S. *J. Org. Chem.*, 2000. 65, 5834-5836. 2） Nishihara, Y., et al. *Macromolecules*, 2006, 39, 7458-7460. 3）Bartoli, G.; Bosco, M., et al. *Synthesis*, 2007, 22, 3489-3496.

発表者紹介

氏名　　石 建軍（しー　じゃんじゅん）

所属　　室蘭工業大学 環境創生工学系専攻

学年　　D3

研究室　　有機化学 生物有機化学研究室