

# Discrimination of Cryptochirality in Isotactic Polystyrene Oligomer in Conjunction with Asymmetric Autocatalysis

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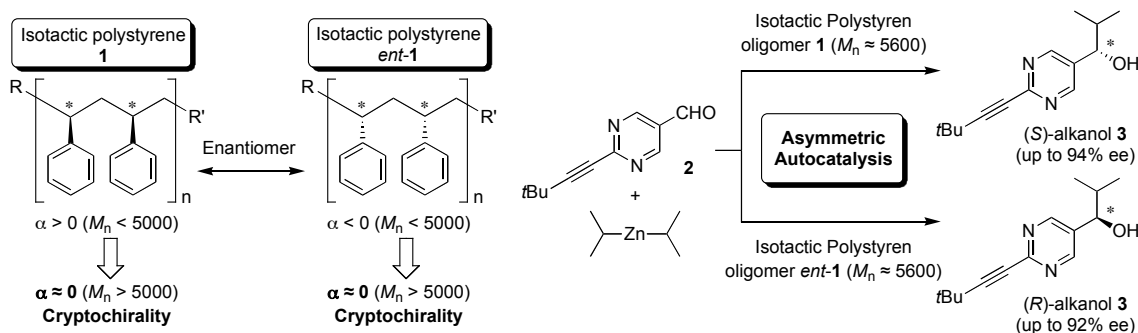
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Chirality plays a key role in many interesting aspects of current chemistry. The development of the method for discriminating the enantiomeric forms is the essential prerequisite to study on the chirality. Although significant progress has been achieved, there remains a class of compounds whose chiral discrimination has been very difficult or even impossible [1].

In recent years, one of us reported the asymmetric synthesis of isotactic polystyrene oligomers, which are optically active with very low value when molecular weight is under 5,000, but when molecular weight is over 5,000, optically inactive [2]. Isotactic polystyrenes have a pseudo-mirror plane because they don't possess the secondary helical structure, and the relative difference between the terminal groups is becoming smaller in the polymers with much longer chain. Thus the isotactic polystyrene oligomers with much larger molecular weight possess the cryptochirality.

We report here the highly sensitive chiral recognition reaction of cryptochiral polystyrene oligomer **1** ( $M_n = 5,600$ ) in conjunction with asymmetric autocatalysis. The addition reaction of *i*-Pr<sub>2</sub>Zn to pyrimidine-5-carbaldehyde **2** was performed in the presence of isotactic polystyrene oligomer **1** and *ent*-**1**. Then, the subsequent asymmetric autocatalysis with an amplification of the ee afforded 5-pyrimidylalkanol **3** with high ee, which showed the absolute configuration corresponding to the cryptochirality of the polystyrene oligomer **1**. These results show that the asymmetric autocatalysis has the enormous power to discriminate the tiny chirality (cryptochirality) due to the small difference between two remote chain ends of isotactic polystyrene oligomers.



[1] Kawasaki, T.; Tanaka, H.; Tsutsumi, T.; Kasahara, T.; Sato, I.; Soai, K. *J. Am. Chem. Soc.* **2006**, *128*, 6032–6033.

[2] Beckerle, K.; Manivannan, R.; Lian, B.; Meppelder, G.-J. M.; Raabe, G.; Spaniol, T. P.; Ebeling, H.; Pelascini, F.; Ihaupt, R. M.; Okuda, J. *Angew. Chem. Int. Ed.* **2007**, *46*, 4790–4793.