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Title	Ziegler-Natta触媒上の水素解離サイト形成と連鎖移動反応についての助触媒及びドナーの役割に関するストップフロー法を用いた研究
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Roles of Alkylaluminum and Electron Donor for Chain Transfer Reactions related to Formation of Hydrogen Dissociation sites with Stopped-Flow Method on Ziegler-Natta catalysts

Namiko MURAYAMA
School of Materials Science,
Japan Advanced Institute of Science and Technology
(Supervised by Prof. Dr. M. Terano)

Ziegler-Natta catalyst is one of the most important discoveries of the last century for polymer chemistry and the chemical industries, and has been widely studied because of its commercial and academic importance. However, there are still many unsolved problems relating to the mechanism of heterogeneous Ziegler-Natta catalysis due to its complexity of active sites structures. As one of the important reaction mechanisms for olefin polymerization, chain transfer reaction by hydrogen and alkylaluminum is also far a way from perfect understanding.

The objective of this dissertation is elucidation of chain transfer reaction mechanisms on Ziegler-Natta catalysts by concerning role of alkylaluminum and electron donors using stopped-flow polymerization method.

The kinetic investigation by stopped-flow method is useful and powerful approach for the further development of Ziegler-Natta catalyst in the scientific aspects. In industrial processes or conventional methods, it is very difficult to obtain the specific results for deactivation reaction and also various chain transfer reactions occurred during the polymerization. In contrast, in the stopped-flow method, which is developed, by Keii and Terano in 1987 is conducted within an extremely short period. In this period, the states of the active sites are constant without time-dependent changes, and chain transfer reactions mainly by alkylaluminum can be negligible, indicating that a quasi-living polymerization can be performed. Therefore, the kinetic information from the polymer produced in the initial polymerization stage corresponded to the nature of the active sites just after their formation.

On Ziegler-Natta catalysis, alkylaluminum has the important roles for deactivation of active sites and also chain transfer reaction to alkylalminum itself and hydrogen. However, the specific mechanism on how alkylalminum affects these process and physicochemical feature of stereospecific active sites has remained ambiguous. The aging process of the catalyst by alkylaluminum cocatalyst with stopped-flow method in short period, which is called “pretreatment” is most effective way to obtain the certain information of alkylalminum especially for deactivation of active sites.

The stopped-flow method (Fig.1) could be very useful tool by modification for investigating the mechanism of these chain transfer reactions especially for chain transfer reaction by hydrogen. In the quasi-living state, no other chain transfer reactions and deactivation were conducted without hydrogen. However, with short-period-pretreatment, the hydrogen reduced the molecular weight of obtained polypropylene. The hydrogen has been widely used in all polyolefin plants to control the molecular weight. The enhancement of hydrogen response of the catalyst has been one of the important targets for industrial polyolefin manufacturing because it is a crucial factor for determining the character of the catalyst. Based on the previous results by Terano et al, hydrogen atom acts as a chain transfer agent for propylene polymerization with Ziegler-Natta catalysts. Moreover, the hydrogen response of the catalyst might be differed from existing electron donor. However, its mechanism had not been clarified yet completely. Therefore, it was specifically investigated the formation of hydrogen dissociation sites relate to deactivation of active sites in this dissertation.

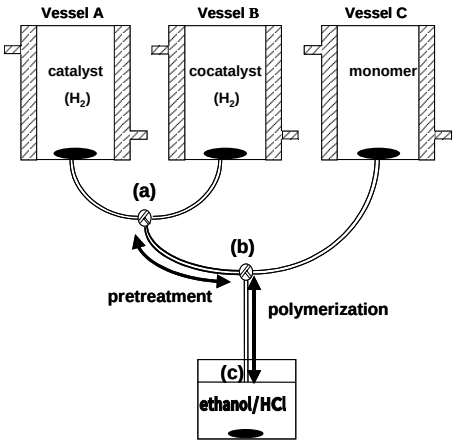

Fig. 1 Modified stopped-flow method.

This dissertation consists of the following six chapters: The first chapter is consisted by general introduction to lead the objective of this research. The guard effect on the active sites in the initial stage of propylene polymerization is in chapter 2, The kinetic investigation of chain transfer reaction by alkyl-Al on Ziegler-Natta catalysis is in chapter 3, The relationship between deactivation of active sites and formation of hydrogen dissociation sites on Ziegler-Natta catalysts is in chapter 4, the formation of hydrogen dissociation sites on olefin polymerization catalysts is in chapter 5, and finally general conclusion is shown in chapter 6.

From the results obtained by these approaches, achieving additional insight into the chain transfer mechanisms was attempted, which could not be obtained from the conventional experimental method so far. The findings obtained form this dissertation will be useful in developing the novel catalyst which can produce the new generation polyolefin materials in the future.

Key words: Ziegler-Natta catalyst, chain transfer reaction, electron donor, hydrogen, alkylaluminum, propylene polymerization