

Title	大容量ストップフロー法を用いたチーグラマー・ナックタ触媒における様々なドナーの影響の速度論的評価
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# Kinetic Evaluation of Various Donor Effects on Ziegler-Natta Catalysis with Large-Scale Stopped-Flow Technique

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## 1. Background

Heterogeneous Ziegler-Natta (ZN) catalysts nowadays produce polypropylene (PP) more than 50 million tons per year over the world, which is one of the most popular and important plastic materials and still has much room for development. The ZN catalysts are generally composed by a solid catalyst ( $\text{TiCl}_4$ /internal donor/ $\text{MgCl}_2$ ) and an activator system (alkyl-aluminium/external donor/hydrogen). Lewis base compounds called as donors play an important role in the modification of catalytic properties, especially for the improvement of the stereoregularity of PP. Catalytic properties of ZN catalysts are largely influenced by the combination of different internal and external donors, making the discovery of new donors as a key to the development of catalyst. The present focus to find new donors is to offer added-values in addition to high isospecificity, especially for broader MWD and chain transfer properties.<sup>1</sup> However, it is generally thought that broad MWD and chain transfer properties are incompatible.

There are four kinds of basic reactions in ZN propylene polymerization ; activation and propagation and chain transfer, and termination reaction. The chain transfer reaction is the termination reaction of the propagation, which accompany the transfer reaction of the growing chain to some agent such as monomer, alkyl-aluminium, and hydrogen. Additionally, chain transfer reaction is more important for the control of molecular weight as most important first order structure. However, there is no evidence on effects of donors for the chain transfer reaction. For achieving the above-mentioned requirement for donors, it is essential to understand how a donor affects MWD and chain transfer properties through the interaction with Ti species. Generally, a broad MWD is believed to originate from the heterogeneity of the active sites nature, more precisely, the distribution of the ratio between the propagation and chain transfer rate constants ( $k_p/k_{tr}$ ). Since it was previously found that the distribution of  $k_p$  is rather narrow for isospecific catalysts.<sup>2</sup> Therefore, the distribution of  $k_{tr}$  is the key for broader MWD. In detail, to expand the distribution of  $k_{tr}$  with a donor is required for the expansion of MWD. Consequently, the understanding of the acting mechanism of a donor on MWD is will be firstly achieved by uncovering the acting mechanism of a donor on chain transfer properties, especially on  $k_{tr}$ .

## 2. Objective

The objective of this dissertation is to investigate the influences of donors on the chain transfer properties of initially formed active sites using the Large-Scale Stopped-Flow (LSF) method. For this purpose, SF method was selected with various internal donor based grinding catalysts (Cat-G). Because LSF polymerization method is free from various side reactions during polymerization and therefore the characterization of produced PP leads to direct insights for active sites and polymerization mechanisms.

### 3. Results and discussion

The stopped-flow (SF) technique was extended for Ziegler-Natta polymerization over a quasi-living period in order to obtain deeper insights into chain transfer (CT) reactions. Propylene polymerization with a  $\text{TiCl}_4/\text{MgCl}_2$  catalyst containing 2-isopentyl-2-isopropyl-1,3-dimethoxypropane (DE) as an internal donor exhibited a linear growth of  $M_n$  for the polymerization time below 0.3 s, indicating quasi-living polymerization. Over 0.4 s,  $M_n$  deviates from the linearity in a convergent manner due to the increasing contribution of CT reactions (Figure 1). On the other hand, the polymerization yield evolved completely proportionally to the polymerization time even up to 1.6 s, which enabled us to presume a constant active site concentration ( $[C^*]$ ).  $k_p$  and  $k_{tr}$  were evaluated according to theoretical equation:  $M_n(t) = k_p M_0 [M] t / (1 + k_{tr} t)$ . In spite of the expected heterogeneity of active sites, the time- $M_n$  curve was accurately fit by a theoretical equation. Thus, it is revealed that the SF technique can be applied for the simultaneous determination of propagation and CT rate constants in heterogeneous ZN polymerization.

More recently, a large-scale SF (LSF) polymerization apparatus was developed, which enables highly reproducible and scalable polymerization over wider polymerization time without changing any polymerization conditions (figure 2).<sup>3</sup> The LSF polymerization was conducted for three catalysts with ethyl benzoate (EB) and DE, and dibutylphthalate (DBP) as an internal donor to examine the effects of the internal

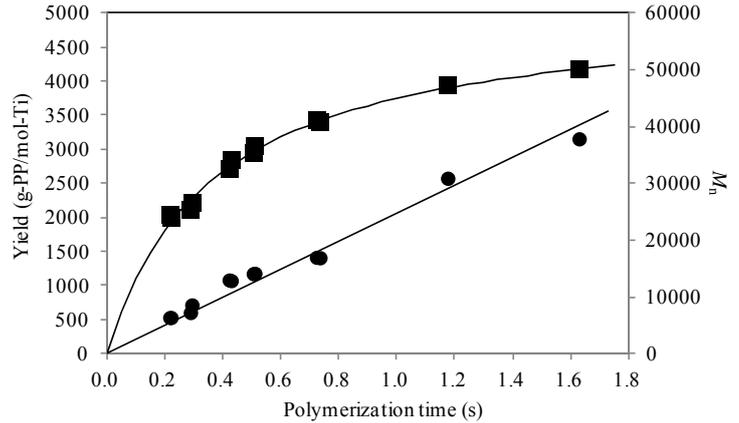


Figure 1. Time-dependence of Yield (circle) and  $M_n$  (square) of the conventional Stopped-Flow polymerization results with Cat-G(DE). Time-dependence of  $M_n$  (solid line) was the best fit to the theoretical equation.

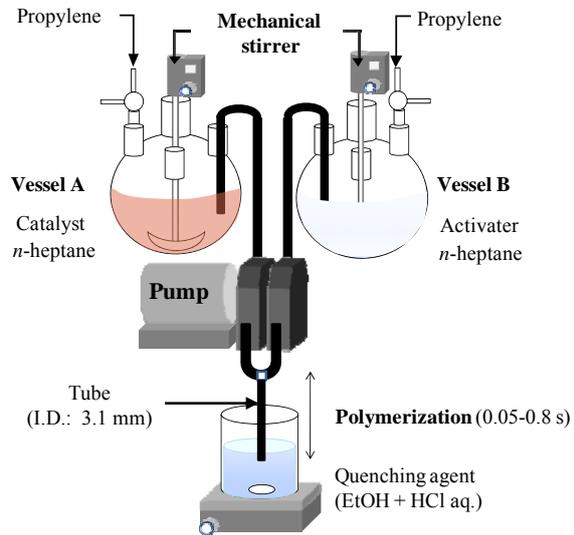


Figure 2. Schematic illustration of Large-Scale Stopped-Flow apparatus.

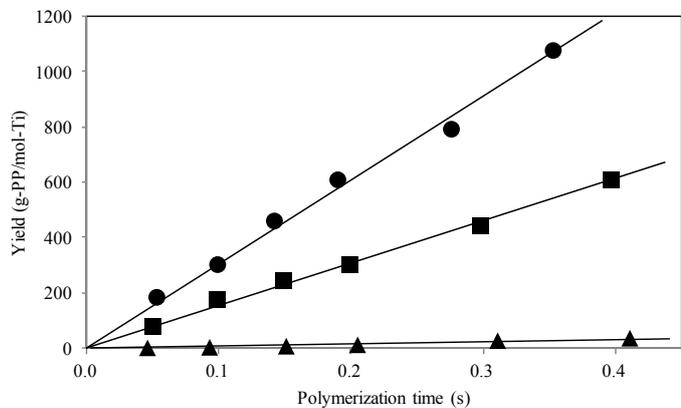


Figure 3. Comparison of yields of polypropylene obtained with the LSF polymerization: (●) Cat-G(EB), (■) Cat-G(DE), (▲) Cat-G(DBP).

donor. The yield linearly increased with time for all of the catalysts, indicating that the nature and the number of active sites were kept constant.  $M_n$  linearly increased at the beginning, then started to converge because of the increasing contribution of chain transfer reactions (Figure 3, 4). The  $k_p$  and the  $k_{tr}$  were evaluated according to the theoretical equation. Since the  $k_p$  values are known to correlate with  $mmmm$ , the improvement of the stereospecificity followed the order of Cat-G(DE) > Cat-G(EB) > Cat-G(DBP). On the contrary,  $k_{tr}$  values did not largely change despite of the electronic and structural differences of donors (Table 1).

Finally, the effects of donors on the chain transfer properties to hydrogen were examined. In the above result, first of all, the effects of donors on the chain transfer properties to both alkylaluminum and monomer were examined. And then, it is acceptable to investigate the effects of donors on the chain transfer properties to hydrogen in order to add the hydrogen which has high chain transfer ability. The differences of hydrogen response on the different catalyst system were observed with LSF polymerization technique on 0.15 s and 0.3 s in a different hydrogen volume. Two polymerization time, i.e. 0.15s and 0.3 s, were selected as the polymerization time in order to evaluate chain transfer properties because 0.15 s is included in quasi-living region and 0.3 s is included in the time region that chain transfer reaction apparently occurs. Figure 5 showed  $M_n$  using LSF polymerization technique with Cat-G(EB) and Cat-G(DE) in the presence and absence of hydrogen. Hydrogen has almost no effects on both yield and  $M_n$  for 0.15 s with both Cat-G(EB) and Cat-G(DE) regardless of hydrogen volume. This result has good agreement with our previous research.<sup>4</sup> On the other hand, hydrogen has almost no effects on yield for 0.3 s with both Cat-G(EB) and Cat-G(DE), however  $M_n$  slightly increased with Cat-G(EB) and clearly decreased with Cat-G(DE)

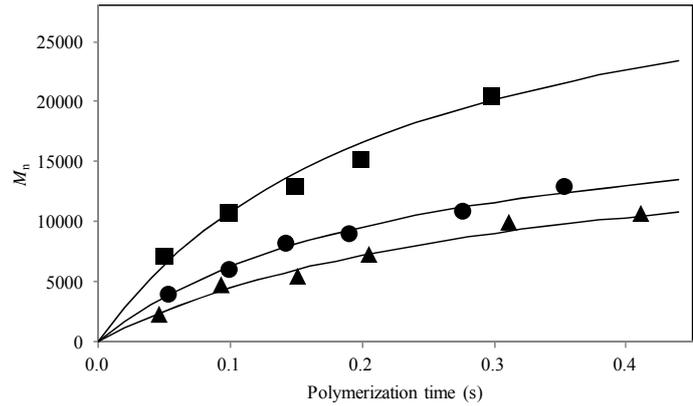


Figure 4. Comparison of  $M_n$  of polypropylene obtained with the LSF polymerization: (●) Cat-G(EB), (■) Cat-G(DE), and (▲) Cat-G(DBP). Solid line is the best fit to the theoretical equation.

**Table 1.** Results of kinetic analysis in various catalysts system

	Cat-G(EB)	Cat-G(DE)	Cat-G(DBP)
$k_p$ ( $\text{l}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$ )	$3.6\times 10^3$	$6.2\times 10^3$	$2.4\times 10^3$
$k_{tr,lump}$ ( $\text{s}^{-1}$ )	4.5	4.4	3.3
$[C^*]$ (mol%)	3.5	1.0	0.1
MSE $\times 1000$ <sup>a</sup>	1.1	6.3	4.5

<sup>a</sup> MSE $\times 1000$  represented fitting error

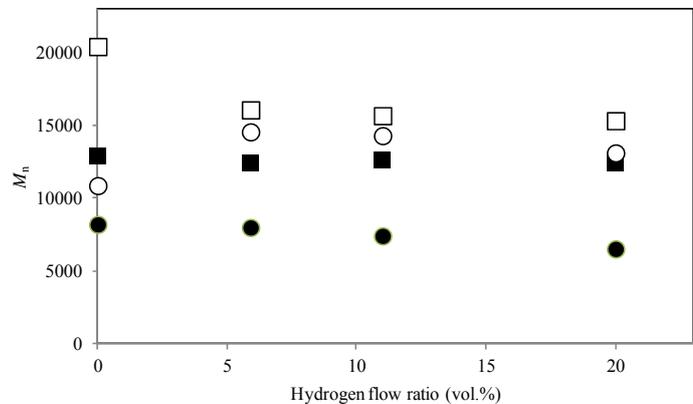


Figure 5.  $M_n$  of the LSF polymerization results in different hydrogen volume ratio: Cat-G(EB) at 0.15 s (●), Cat-G(EB) at 0.3 s (○), Cat-G(DE) at 0.15 s (■), and Cat-G(DE) at 0.3 s (□).

for 0.3 s. These results might indicate that activation effect and/or time-difference of chain transfer reaction to hydrogen seems to be affected on the catalyst system.

Thus obtained discussion in this work suggests for finer design of ZN catalysts to control a MW, MWD in PP. The results and discussion in this dissertation will be helpful in improvement and in development for the ZN catalyst having more superior catalytic properties.

#### 4. Reference

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- (2) H. Matsuoka, B. Liu, H. Nakatani, M. Terano, *Macromol. Rapid. Commun.* **2001**, 22, 326.
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- (4) For example, H. Mori, K. Tashino, M. Terano, *Macromol Rapid Common.* **1995**, 16, 651.

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#### Achievements

##### Original Articles

Precise Evaluation of Chain Transfer Rate Constant for Initial Stage of Propylene Polymerization with TiCl<sub>4</sub>/Diether/MgCl<sub>2</sub> Catalyst

**Ikeya, M.**; Hiraoka, Y; Taniike, T; Terano, M.

*Current Trends in Polymer Science*, 2013, accepted.

Kinetic Evaluation of Chain Transfer Properties in Propylene Polymerization for Precise Molecular-Level Structure Design

**Ikeya, M.**; Taniike, T; Terano, M.

*Journal of Materials Life Society*, 2013, submitted.

##### Others

Development of Large-Scale Stopped-Flow System for Heterogeneous Olefin Polymerization Kinetics

Sano, S.; **Ikeya, M.**; Thang, V, Q.; Taniike, T; Terano, M.

*Macromol. React. Eng.* **2012**, 6, 275.