Precise evaluation of chain transfer rate constant for initial stage of propylene polymerization with TiCl$_4$/Diether/MgCl$_2$ catalyst

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ABSTRACT

In this study, 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 TiCl$_4$/MgCl$_2$ catalyst containing 2-isopentyl-2-isopropyl-1,3-dimethoxypropane 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. 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 ($[C^*]$). In spite of the expected heterogeneity of active sites, the time-M_n curve was accurately fit by a theoretical equation. Thus, we have revealed that the SF technique can be applied for the simultaneous determination of propagation and CT rate constants in heterogeneous ZN polymerization.

KEYWORDS: Ziegler-Natta polymerization, chain transfer rate constant, propagation rate constant, kinetic analysis, stopped-flow polymerization, internal donor

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1. INTRODUCTION

Heterogeneous-Natta (ZN) catalysts, composed by a solid pre-catalyst (TiCl$_4$/Internal donor/MgCl$_2$) and an activator system (alkylaluminum/external donor), account for the annual production of polypropylene (PP) more than 45 million tons over the world. In spite of substantial studies and developments contributed by many researchers, a lot of unclear issues still remain in the ZN catalysts and ZN olefin polymerization. One of the difficulties arises from the heterogeneity of Ti species and from their transient nature mainly caused by reactions with alkylaluminum, which makes it extremely challenging to perform spectroscopic analysis of the catalysts at a molecular level and to establish clear correlation between obtained polymer structures and the states of active site/structures.

The stopped-flow (SF) technique invented by Terano and Keii in 1987 has been regarded as one of the most powerful tools to study the polymerization mechanism and relationship between the states of active sites and polymer microstructures [1-5]. It minimizes the said difficulty based on time-resolved polymerization at a very early stage typically at the scale of seconds in contrast to minutes to hours for conventional polymerization. Especially, SF polymerization below the polymerization time of 0.2-0.3 s is almost free from transient behaviors of active sites and chain transfer (CT) reactions. Such advantages of quasi-living polymerization offer one-to-one

correspondence between growing polymer chains and active sites. Therefore most of the previous SF studies have been conducted in the quasi-living region, in order to obtain direct insights on active sites and polymerization mechanisms through structural characterization of the made PP. Terano *et al.* found that i) only active site concentration ([C*]) depended on the concentration of triethyl aluminum [6], ii) hydrogen did not act as a CT agent at an early stage of polymerization [7], iii) the propagation rate constant (k_p) was highly correlated with the stereospecificity of active sites [8], iv) longer pretreatment time of the contact of the catalysts with alkylaluminum before the polymerization led to higher H_2 response, suggesting that deactivation of active Ti species could be associated well with the formation of H_2 dissociation sites for CT reaction [9], v) the addition of poisoning materials such as methanol, acetone, and ethyl acetone decreased the activity through the reduction of the [C*] [10], vi) active site natures were independent of the kind and concentration of employed alkylaluminum as well as the catalyst preparation procedure [11], and so on.

As mentioned above, CT reactions, *i.e.* termination of the chain growth, are one of the most important reactions in olefin polymerization for controlling the melt and solid physical characteristics of the produced PP. Especially, the ratio between the propagation and CT rate constants, k_p/k_{tr}, and its distribution over different active sites are directly related to the polymer molecular weight and its distribution (MWD) [12, 13]. A chain end analysis of produced PP has been used by many researchers for the elucidation of the CT reactions mechanism. There are two types of preparation procedures of low molecular weight polymer for the increase in the chain end concentration. First procedure is hydro-oligomerization which can mainly produce an oligomer by large amounts of hydrogen. Busico *et al.* demonstrated that iso-butyl, *n*-butyl and unsaturated chain ends were also in the oligomer fraction when polymerization was carried out under high hydrogen concentration [14, 15]. Chadwick *et al.* showed that catalysts with diether as an internal donor increased the amount of *n*-butyl terminated chain ends which came from CT to hydrogen after regioirregular of 2,1 insertion [16, 17]. Vestberg *et al.* found that

$TiCl_4$/Diethylphthalate/$MgCl_2$ catalysts combined with cyclohexylmethyl dimethoxy silane induced more CT to hydrogen after regioirregular of 2,1 insertion, which exhibited the better hydrogen response of this catalyst/external donor combination [18]. Second procedure is a polymerization at high polymerization temperature. Kojoh *et al.* investigated the effects of external donors such as alkoxysilane on CT reactions with $TiCl_4$/Dioctylphthalate/ $MgCl_2$ catalysts at 100ºC [19]. They found that the addition of hydrogen led not only to the increase in the activity, but also to the decrease in the frequency of (2,1) insertion. Shiono *et al.* conducted propylene polymerization with $TiCl_4$/ Diisobutylphthalate/$MgCl_2$ catalysts combined with $AlEt_3$ and used oxygen gas as a quenching agent for the purpose of the detection of Al-terminated chain end [20]. They found that the rates of *ß*–hydrogen transfer and transfer of $AlEt_3$ should be affected by the stereospecificity of the active species as well as polymerization conditions. Sacchi *et al.* mentioned the chain end analysis with ^{13}C NMR using selectively ^{13}C enriched $AlEt_3$ as cocatalyst in order to evaluate the effect of internal and external donors [21, 22]. However, it is difficult to obtain the precise information of active site by primary-structure analysis with conventional polymerization system because the deactivation and transformation of active sites and CT reaction would occur during propylene polymerization with ZN catalysts.

Previous SF experiments in the quasi-living region succeeded to determine k_p for different types of active sites, while few researches have focused on the determination of k_{tr}. For that, it is required to extend the time of the SF polymerization beyond the quasi-living region. It is expected that the number-averaged molecular weight (M_n) starts to deviate from the linear behavior and level off due to an increasing contribution of CT reactions, while the active site nature and concentration are still kept constant and the polymerization yield linearly grows with time.

In the present paper, we have investigated the SF polymerization beyond the quasi-living region (up to 1.6 s) in order to enable the simultaneous determination of k_p and k_{tr} in heterogeneous ZN propylene polymerization. In this paper, k_p and k_{tr} were simultaneously evaluated for the first time

by using curve fitting of M_n of PP produced with ZN catalysts.

2. EXPERIMENTAL PART

Materials

Propylene of research grade (donated by JAPAN POLYPROPYLENE CORPORATION), nitrogen, TiCl$_4$, triisobutylaluminium (TiBA, donated by TOSOH FINECHEM CORPORATION), and anhydrous MgCl$_2$ (donated by TOHO TITANIUM CO., LTD.) were used without further purification. 2-isopentyl-2-isopropyl-1,3-dimethoxypropane (DE) as an internal donor and n-heptane were used after dehydration by passing through a column with the molecular sieve 4A.

Preparation of TiCl$_4$/DE/MgCl$_2$ catalyst

TiCl$_4$/DE/MgCl$_2$ catalyst was prepared by vibration milling based on a previous paper as follows [23]. MgCl$_2$ (36 g, 11m^2/g) and distilled DE (7.8 mL) were introduced into a 1.2 L stainless steel vibration mill pot with 55 stainless balls (25 mm diameter) under nitrogen atmosphere and ground for 30 h at room temperature. Then the ground product was treated with TiCl$_4$ (200 mL) in a 1 L three-necked flask equipped with a mechanical stirrer at 115°C for 2 h under nitrogen atmosphere. The catalysts were repeatedly washed with n-heptane, and stored in n-heptane. The Ti content of the catalyst was determined by titration as 2.6 wt-%.

Polymerization procedure

The SF apparatus used in this study was schematically illustrated in Figure 1. A solid catalyst slurry (containing 0.47 mmol of Ti in 100 mL of n-heptane) and an activator solution (containing 14 mmol of TiBA in 100 mL of n-heptane) were introduced in the Vessel A and B respectively under nitrogen atmosphere. The contents of each of the two vessels were then saturated with 1 atm of propylene at 30°C. The equilibrium concentration of propylene is 0.60 mol/L at 30°C. These solutions were simultaneously pushed out by nitrogen and were mixed at the T point to instantaneously start polymerization. The polymerization time was controlled to *ca.* 0.2-1.8 s by changing the length of the Teflon tube, and the polymerization is conducted in the tube and instantaneously terminated
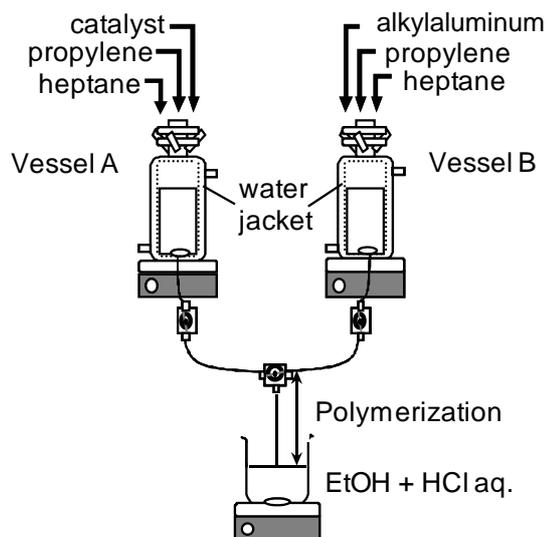

Figure 1. Schematic illustration of SF apparatus.

with acidic EtOH. The polymer obtained was washed with distilled water and dried in vacuo, followed by reprecipitation with xylene/EtOH.

Analytical procedures

The MWD of obtained polymer was measured by gel permeation chromatography (GPC, Waters ALS/GPC 150 C) with three polystyrene gel columns (Shodex AD806M/S) at 140°C using o-dichlorobenzene containing 0.5 mg/ml of 2,6-di-*tert*-butyl-p-cresol as a stabilizer.

Kinetic analysis

The propylene polymerization yield per Ti and M_n for PP are generally written below, Yield = $k_p M_0$[M][C*]t and $M_n = k_p M_0$[M][C*]t/([C*] + [C*]$k_{tr}t$), where M_0, [M], and t are the molecular weight, the propylene concentration and the polymerization time, respectively. k_{tr} is a lumped CT rate constant that collects all the rates from various CT reactions [24-26]. The equation was fit to experimental data for the time-dependence of M_n. In detail, the values of k_p and k_{tr} as fitting parameters were numerically optimized in a way to minimize a fitting error defined as $\Sigma\{M_{n,exp}^i (t_i) - M_{n,fit}^i (t_i)\}^2/N\{M_{n,exp}^i (t_i)\}^2$, where i and N correspond to the ith data set and the total number of the data, respectively. Note that the fitting error is normalized by $\{M_{n,exp}^i (t_i)\}^2$ to unify the weight of each data set in fitting. Even though the SF polymerization eliminates the expansion of the heterogeneity of active sites

caused by reactions with alkylaluminum, M_w/M_n values in the quasi-living polymerization are typically 2-3 in the case of heterogeneous ZN catalysts, contrary to unity in the case of single-site catalysts. Hence, ZN catalysts exhibit a multisite nature from a very early stage of polymerization. Accordingly, k_p and k_{tr} values determined in the present study correspond to the averages over different types of active sites.

3. RESULTS AND DISCUSSION

In order to evaluate the kinetic parameter such as the CT rate constant, SF polymerization method was selected because the SF polymerization for quite short polymerization time is free from various side reactions compared with slurry polymerization, and therefore the characterization of produced PP leads to direct insight on the active sites and polymerization mechanisms [1-5]. SF polymerization was conducted with DE-based catalysts due to higher initial activity and lower heterogeneity of active sites. Figure 2 and 3 showed the propylene polymerization yield and M_n of produced PP against polymerization time (about 0.2-1.8 s) using SF polymerization method with $TiCl_4/DE/MgCl_2$. Both the yield and M_n linearly
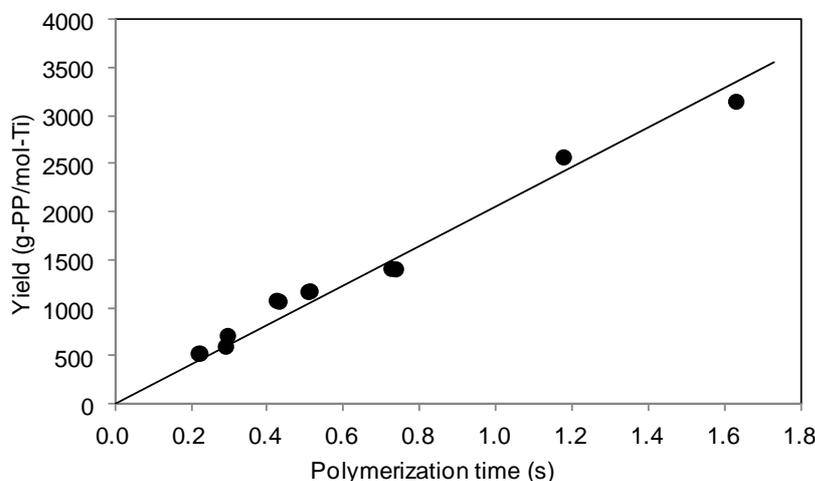
Figure 2. Time-yield curve of the SF polymerization results with $TiCl_4/DE/MgCl_2$.
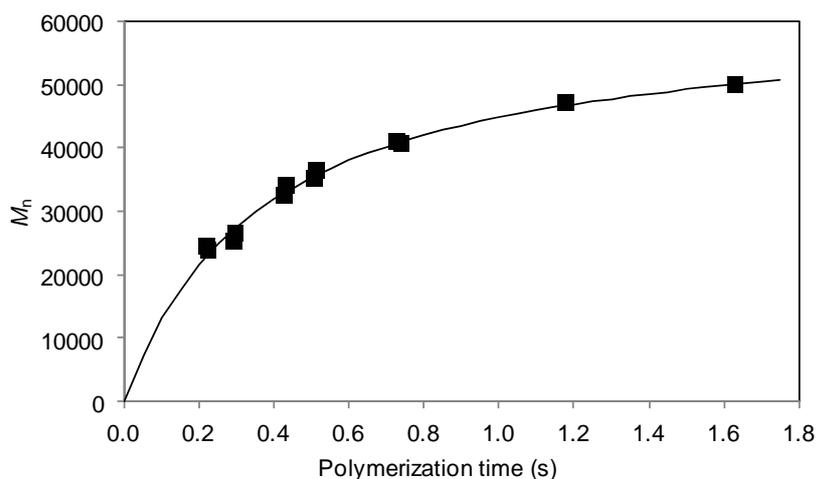
Figure 3. Time-M_n curve of the SF polymerization results with $TiCl_4/DE/MgCl_2$. Time-M_n curve was the best fit to the theoretical equation.

increased with polymerization time of the initial stage (bellow 0.3 s), which meant that only propagation reaction occurred with other side reactions ignorable. Moreover, the observed linearity clearly excluded not only the possibility of fragmentation-induced formation of active site but also the possibility of the increase in diffusion resistance by polymer at initial polymerization time, as we expected. Above 0.4 s, the relationship between yield and polymerization time was still linear, indicating that the nature and concentration of active site did not change, while M_n converged due to the CT reaction. We divided the curve shape of M_n into three region; linear (0-0.2 s), curve (0.2-0.8 s), and converge region (0.8-1.6 s). First,

linear region means that k_{tr} is extremely lower than 1 ($1 \gg k_{tr}$) by considering the equation of M_n. This indicates that the CT reaction could be negligible and that only propagation reaction occurs. Second, curve region means that k_{tr} is comparable to 1 ($1 \sim k_t$). This indicates that the CT reaction remarkably occurs. Finally, converge region means that k_{tr} is larger than 1 ($1 \ll k_{tr}$). This indicates that dead chain mainly produced by the CT reactions. Thus, it is better to obtain accurate value of k_{tr} by fitting of these three regions in order to estimate k_{tr} value precisely. These values of MWD of produced PP were increased gradually for longer polymerization time (Figure 4). However the values of MWD were low compared
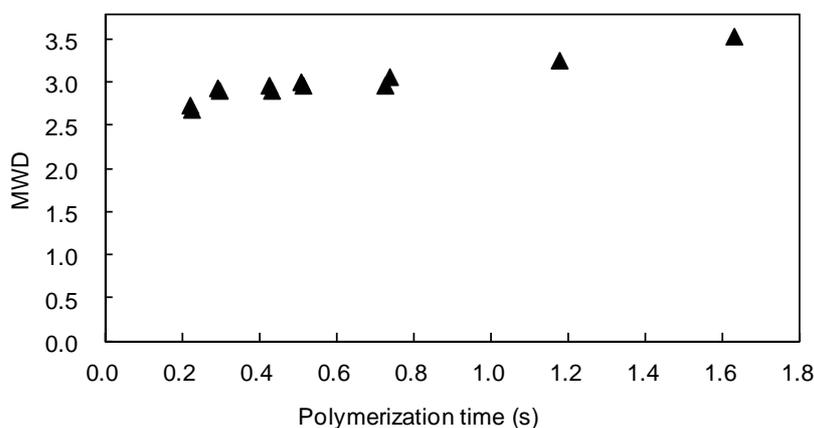

Figure 4. Time-MWD curve of SF results with TiCl$_4$/DE/MgCl$_2$.
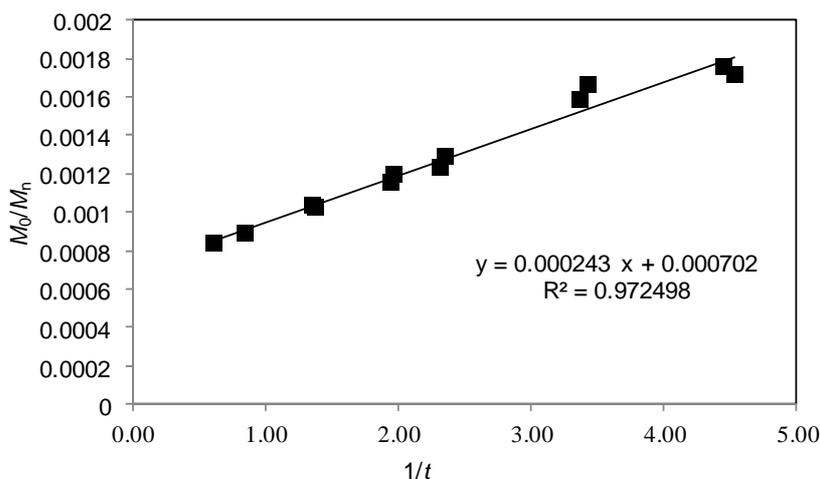

$$y = 0.000243\,x + 0.000702$$
$$R^2 = 0.972498$$

Figure 5. $1/t$-M_0/M_n curve of SF results with TiCl$_4$/DE/MgCl$_2$.

with the result of slurry polymerization (typically MWD = 4-5), indicating that heterogeneous nature of active sites were restrained.

Upon the evaluation of the kinetic parameters such as k_p and k_{tr} by using curve fitting, the linearity of the yield for the time must be assured for constant [C*]. In this polymerization, the [C*] showed almost constant value (1.31 mol%) for polymerization time and this value is typical on this catalyst. Thus it is possible to consider CT reaction without the active site transformation. In the previous kinetic analysis of SF polymerization, k_{tr} was forcibly evaluated from the reverse value of the average degree of polymerization (M_0/M_n) versus $1/t$ curve (Figure 5). However, this evaluation was not correct because CT reaction can be negligible in this time region. It is not suitable to apply this method to the SF result (0.2-1.8 s) because it is not able to approximate this time-M_n curve to linear. Hence, the curve fitting was adapted in this study. k_p and k_{tr} were decided in order to minimize MSE based on eq. (1) and (2). The experimental value of M_n was well fit to the theoretical equation (as shown in Figure 3), resulting in the first simultaneous determination of k_p and k_{tr}. In order to determine k_p and k_{tr} precisely, four calculations (Calc 1-4) were conducted. The Calc 1 was fitted using the data of samples (0.2-0.4 s), The Calc 2 was fitted using the data of samples (0.2-0.5 s), The Calc 3 was fitted using the data of samples (0.2-1.2 s) and The Calc 4 was fitted using the data of samples (0.2-1.8 s) (Figure 6). Table 1 showed the
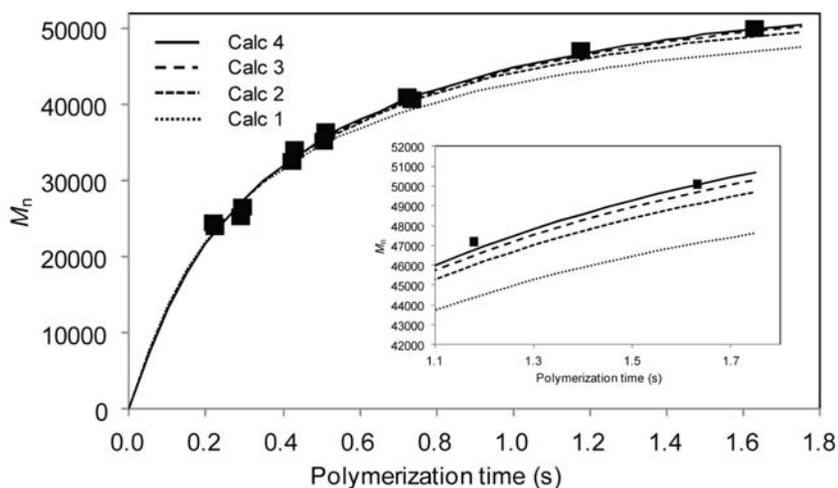
Figure 6. Comparison between curve fitting results corresponds to Calc 1, Calc 2, Calc 3 and Calc 4, respectively.

Table 1. Kinetic analysis of obtained polymer measured by curve fitting.

Run	Number of DATA set	k_p (l·mol^{-1}·s^{-1})	k_{tr} (s^{-1})	MSE×1000[a]
Calc 1[b]	6	7.15 x 10^3	3.22	1.89
Calc 2[c]	8	6.81 x 10^3	2.88	1.55
Calc 3[d]	10	6.71 x 10^3	2.79	1.26
Calc 4[e]	12	6.65 x 10^3	2.73	1.06

[a]MSE×1000 represented fitting error.
[b]Selected polymerization time was 0-0.4 s.
[c]Selected polymerization time was 0-0.5 s.
[d]Selected polymerization time was 0-1.2 s.
[e]Selected polymerization time was 0-1.6 s.

kinetic analysis of obtained polymer using curve fitting. At least 10 plots are necessary for the precise evaluation of k_{tr} value.

Table 1 shows a comparison between linear and curve fitting results of obtained polymer. In the conventional SF polymerization for quite short polymerization time (0.2 s <), k_p is able to be obtained by using linear fitting between 1/polymerization degree (P_n) and $1/t$. However, it is difficult to estimate k_{tr} precisely by linear fitting because CT reaction is negligible on quasi-living region. Full fitting resulted in $k_p = 6.7$ x 10^3 (l·mol^{-1}·s^{-1}) and $k_{tr} = 2.7$ (s^{-1}) (Calc 4 in Table 1). The obtained k_{tr} value was comparable with previously reported values ($k_{tr} = 1.0$ (s^{-1}) [6] and $k_{tr} = 2.3$ (s^{-1}) [2]). This indicated that it was better to increase the number of plots over 0.2 s for the estimation of k_{tr} value and that the curve fitting seems to be better than the linear fitting because curve fitting corresponds to the curvature of M_n. According to these results, the first attempt to investigate the CT rate constant was achieved.

4. CONCLUSION

SF propylene polymerization (0.2-1.8 s) was conducted using TiCl$_4$/DE/MgCl$_2$ catalysts in order to evaluate k_{tr} value. The first simultaneous determination of k_p and k_{tr} was achieved from curve fitting. It became clear that at least 10 plots were needed for the precise evaluation of k_{tr} value. These insights on the CT reactions are valid for the future developments aiming at more precise control of the molecular weight and its distribution.

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