Kinetic Investigation of Propene Polymerization with Stopped-flow Method

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SUMMARY: The stopped-flow technique, by which a quasi-living polymerization process can be performed within an extremely short period (ca. 0.2s), is a powerful method for kinetic investigation in Ziegler catalysis. Significant understanding of many controversial problems was achieved, such as arguments concerning the nonuniformity of the active sites, the accurate kinetic parameters, the active sites formed in the different stages, the role of cocatalyst, the effects of hydrogen and electron donors, etc..

Introduction

Kinetic investigation is a useful and powerful approach for the further development of the scientific aspects in Ziegler catalysis. Information can be obtained on the nature of the active sites and also the polymerization mechanism. The stopped-flow method was first developed by Keii and Terano in 1987 to evaluate specific kinetic parameters in the polymerization of propene with a $MgCl_2$-supported Ziegler catalyst[1-5]. In industrial processes or conventional experimental methods of kinetic study, polymerization is normally performed for 1-3 h, accompanied with catalyst deactivation as well as various types of chain-transfer reactions. In contrast, in the stopped-flow method polymerization is conducted within an extremely short period of time (ca.0.2s) using the stopped-flow technique. In the case of the latter the states of the active sites are constant, without time-dependent changes, and chain-transfer reactions can be negligible, indicating that a quasi-living polymerization can be performed. Therefore, the information from the polymer produced in the initial polymerization stage corresponded to the nature of the active sites just after their formation. In this decade, the technique has been extensively applied to various kinds of investigations for olefin polymerization with $MgCl_2$-supported Ziegler catalysts. The objective of this paper is to summarize some results of these studies and to demonstrate the advantages of using the technique for the kinetic investigation of Ziegler catalysts for propene polymerization.

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Stopped-flow Method

The basic stopped-flow system is shown schematically in Fig.1 and the typical procedure is described. A and B are special glass vessels equipped with water jackets. The catalyst slurry and cocatalyst solution saturated with propene were placed in vessels A and B, respectively. After the slurry and the solution had attained stationary conditions, they were forced to flow simultaneously through a Teflon tube from vessels A and B into flask C under a small pressure of nitrogen. The polymerization occurred in the Teflon tube from point X to Y. C is a flask containing ethanol/HCl solution, which is agitated vigorously to quench the polymerization at point Y. The polymer obtained was washed and dried in vacuum, prior to characterization.

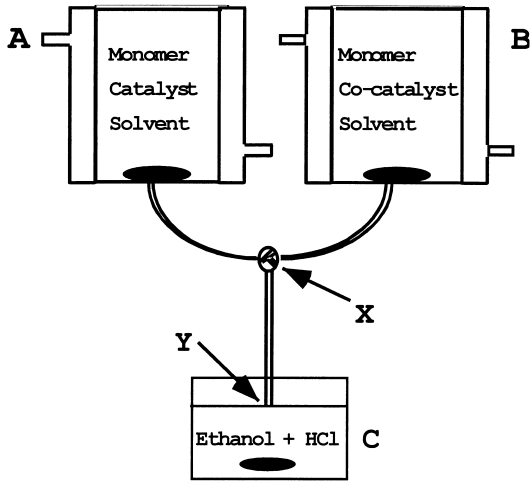

Fig.1: Schematic illustration of the stopped-flow polymerization apparatus.

Insight into the Broad Molecular Weight Distribution

There have been three suggested explanations for the broad molecular weight distribution for polyolefins produced with heterogeneous Ziegler catalysts: variations of rate constants for propagation and transfer reactions with polymer chain lengths; the existence of monomer diffusion limitation due to polymer layers; and the non-uniformity of active sites. From stopped-flow polymerization analysis with a $MgCl_2$-supported Ziegler catalyst[1)], in which the transfer reaction is negligible and the polymer layer can be ignored, molecular weight

distributions of the polypropenes obtained at the initial polymerization stage showed similar values (M_w/M_n=3.2-4.3, determined by GPC) of up to 0.2 s and even remained constant up to 10s (M_w/M_n=3.6), at which point the chain-transfer reaction had already started in competition with the propagation reaction. Hence, the only feasible reason for the broad molecular weight distribution is due to the existence of nonuniform active sites in the system.

Determination of Kinetic Parameters

The stopped-flow method, due to its excellent features, seems to be the most reliable and useful method by which to obtain kinetic parameters in olefin polymerization using Ziegler catalysts. The details of determining rate constants of propagation (k_p), transfer (k_{tr}) and the concentration of the polymerization centers ([C*]) were described by Keii et al. [2-4]. Generally, the stopped-flow technique gives lower values for [C*] and higher values for k_p compared with other methods. The [C*] and k_p values from the stopped-flow technique can precisely reflect the state of the active sites just after their formation, whereas, those determined by other methods can only describe the average state of active sites during a long polymerization stage with many varying and superimposing factors generated from propagation, transfer, deactivation reactions as well as diffusion.

Active Sites Formed in the Different Stages

In propene polymerization with $MgCl_2$-supported Ziegler catalysts, it was reported that the original catalyst cluster broke into small particles which dispersed throughout the resulting polymer, thus inducing the generation of new active sites in the course of polymerization[6]. Here, a question may be what is the difference in the active sites formed during the different stages of polymerization. To answer this, a $MgCl_2$-supported catalyst was ground by a ball-milling method prior to polymerization. The pre-treated, fine-grain catalyst, with an average particle size ranging from one-half to one-third of the original value, was taken as a model of catalyst fragmentation in the course of polymerization. The results show that the activity of the fine-grain catalyst was higher than the original catalyst. No difference in the molecular weight of the resulting polymer was observed in the initial stage of the propene polymerization. Table1 shows that the [C*] value increased and the k_p value was constant for the fine-grain catalyst. Thus the active sites produced in the later stage of polymerization by the catalyst fragmentation had the same properties as those produced in the initial stage.

Table 1. Characterization of catalyst and kinetic parameters for polymerization and the meso pentad fraction of resulting polymer.

Catalyst	Ti content [a] (wt%)	Average particle size (μ m)	[C*] (mol%)	k_p (L/mol·s)	*mmmm* [b] (mol%)
$MgCl_2$-supported	1.8	6.3	5.2	2850	93
Fine-grain	1.8	2.7	7.5	2750	92

a) Determined by titration
b) Determined by ^{13}C NMR

Effect of Cocatalyst

To obtain a clearer insight into the cocatalyst effect in Ziegler catalysis, the stopped-flow technique was applied to the investigation of the influence of different alkylaluminiums on the kinetic parameters obtained in the initial stage of propene polymerization. When varying the types of alkylaluminums, the value of [C*] decreased drastically with an increase in bulkiness of the alkyl group of the aluminum compound [7]. The change in the value of k_p was rather small and was proportional to the meso pentad fraction of the resulting polypropene, suggesting that the order of the k_p corresponded to the ratio of isotactic polypropene to total polypropene. The kinetic parameters, $k_{p,insol}$ and [C*$_{insol}$] which can be regarded as those of isospecific active sites, were calculated from the yield and molecular weight of the fraction insoluble in boiling heptane.

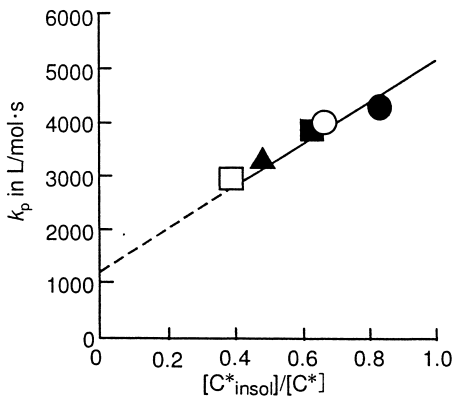

Fig.2: The relationship between k_p and [C*$_{insol}$]/[C*] TEA:○,TNBA:●,TNHA:■,THOA:▲, TIBA:□.

The values of $k_{p,insol}$ were observed to be almost the same regardless of the cocatalyst, while the overall values of k_p were dependent on the ratio of [C*$_{insol}$] to overall [C*] as shown in Fig. 2. The results suggested that the nature of isospecific active sites produced by various alkylaluminums was essentially the same, but the ratio of the different active sites as well as the whole active sites formed with a variety of alkylaluminums were different. This difference was further confirmed to be related to the variation in the titanium species arising from the use of various alkylaluminiums [8].

Effect of Hydrogen

Although numerous reports have been published on the effect of hydrogen in the polymerization of olefins, the mechanism of the chain-transfer reaction with hydrogen has not yet been clarified. Thus, the stopped-flow polymerization method was used for the study of the chain-transfer reaction by hydrogen in the initial stage of propene polymerization[9].

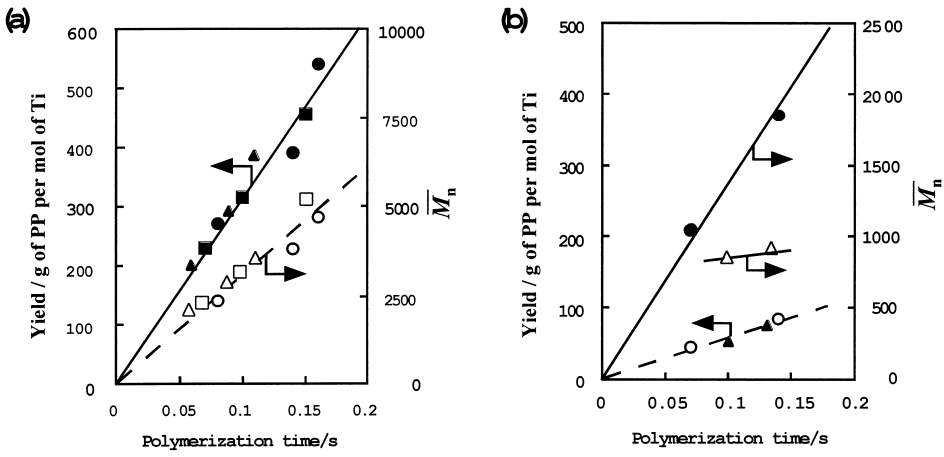

Fig.3: Dependence of polymer yield (●,▲,■) and M_n (○,△,□) on polymerization time. (a) The polymerization was carried out with an $MgCl_2$-supported Ziegler catalyst in the presence (▲,△ 1 atm; ■,□ 4atm) or absence (●,○) of hydrogen. (b) The polymerization was performed with a pre-treated $MgCl_2$-supported Ziegler catalyst in the presence (▲,△1atm) or absence (●,○) of hydrogen.

As shown in Fig. 3a, the hydrogen has no effect on the molecular weight nor the polymer yield of polypropene produced with $MgCl_2$-supported Ziegler catalyst. Whereas, when the catalyst was pre-treated with TEA before polymerization, the molecular weight of the produced polymer was decreased by using hydrogen (Fig. 3b), indicating that hydrogen acted as a chain-transfer agent for the catalyst that was modified by the pre-treatment with a cocatalyst. These results indicate that the effect of hydrogen in the initial stage of propene polymerization appeared with the existence of the different states of the active sites, where the reduction of titanium species is considered to occur to give lower oxidation state species by the pre-treatment with TEA.

Variation of Isospecific Active Sites

Variation of the isospecificity of active sites on a $MgCl_2$-supported Ziegler catalyst was investigated for a better understanding of the nature of the active sites. Polypropene was prepared by the stopped-flow method in the absence or presence of an electron donor and its isospecificity distribution was analyzed by the TREF method. Thus, the variation of isospecific active sites formed on the catalyst can be detected. Fig. 4 shows the TREF diagrams of each polymer, and Table 2 shows the characterization of the highest isotactic fraction (elution temperature by TREF is over 112°C) of resulting polymer and kinetic parameters. It can be seen that highly isospecific active sites derived from the highest isotactic fraction also exist in the electron donor-free catalyst system. From the increase of the $\overline{M}_n$, meso pentad fraction and k_p of overall polymers, it can be deduced that some aspecific active sites were converted to isospecific active sites by the addition of electron donors. However, all the values of the highest isotactic fraction (elution temperature by TREF is over 112°C), such as Yield, $\overline{M}_n$, $\overline{M}_w$ over $\overline{M}_n$, meso pentad fraction, k_p and [C*], are constant (Table 2) showing no effect on the highest isospecific active sites by the addition of electron donor.

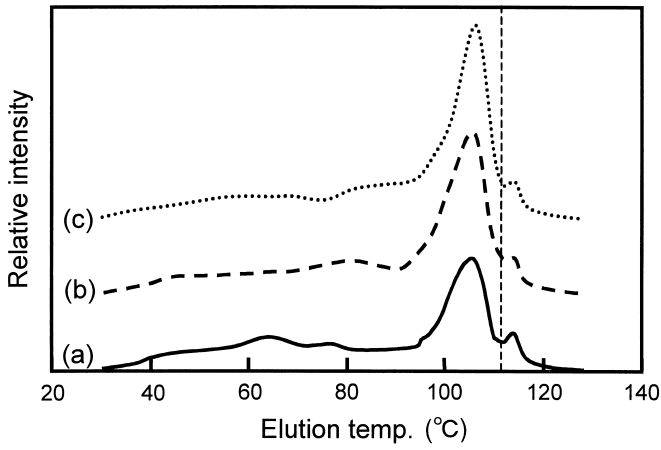

Fig.4: TREF diagrams of PPs (a)The polymerization was carried out in the absence electron of an electron donor. The polymerization was carried out in the presence of ethylbenzoate [EB] (b) and cyclohexylmethyldimethixasilane [CMDMS] (c) as external electron donors.

Table 2. Characterization of the highest isotactic fraction of PPs[a] and kinetic parameters.

External Donor	Yield (g/mol-Ti)	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	*mmmm*[c] (mol%)	$k_{p,iso}$ (L/mol·s)	[C*$_{iso}$] (mol%)
-	16.7	41600	1.8	98.5	9300	0.041
EB	16.4	41700	1.7	98.4	9300	0.039
CMDMS	16.2	41500	1.7	98.6	9270	0.038

a) High isotactic fraction (>112ž) of PP was obtained by TREF analysis system.
b) Determined by GPC
c) Determined by ^{13}C NMR

Based on the above results it can be postulated that there exist mainly three kinds of active sites in the $MgCl_2$-supported Ziegler catalyst: the first is an isospecific titanium species which produces isotactic polypropene, the second is an aspecific titanium species which is not affected by its local circumstances and creates atactic polypropene; the third is a sterically hindered aspecific titanium species due to the strong interaction with its surroundings and preferably make polymer with moderate isotacticity. The effect of the electron donor is to occupy one of the vacancies of the aspecific titanium species by coordination and consequently the latter is transferred to be an isospecific active site.

Conclusion

Based on results of kinetic investigations in Ziegler catalysis with the stopped-flow method, several aspects concerning the nature of the active site and its polymerization mechanism have been clarified. These include: the reason for the broad molecular weight distribution of the polymer, the difference in the active sites formed at different stages of the reaction, the cocatalyst effect on the active sites, the conditions for chain transfer by hydrogen and the variation of isospecific active sites induced by the addition of electron donor, etc.. Further development in this field can eb expected by extensive application of the stopped-flow method.

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