CHAPTER VI

POISONING OF ACTIVE SITES ON ZIEGLER-NATTA CATALYST

6.1 Introduction

Electron donor is a crucial component in the Ziegler-Natta heterogeneous catalytic system to achieve polymer with high activity and isotacticity [9]. The function of such donors in the $MgCl_2$-supported catalysts has been known to provide electronic and steric effects on active species. Its coordination on the catalyst surface in the surrounding of the active sites leads to a dramatic increase of the catalyst stereospecificity. A selective poisoning of nonstereospecific sites or transformation of aspecific sites to isospecific ones have been proposed by several authors [207-210]. In general, the former leads to a lowering in the number of active centers while the latter can improve the propagation rate constant. Terano et al. [113,167] also have reported that this kinetic parameter of isospecific sites was several times higher than that of aspecific sites. Thus, the coordination of the electron donors can be regarded to influence the catalyst activity on both the directions of activation and deactivation but the addition of electron donor often causes a decrease in overall productivity rather than provide the activity enhancement. However, up to now, these fundamental matters concerning the activation/deactivation behaviors of the active sites have not yet been fully elucidated and still open for discussion as a consequence of the complexities of the catalytic system. No detailed studies have so far been carried out to investigate the precise kinetic parameters relating to the number of the active sites and their chain propagation rate constants.

Recently, the stopped-flow technique has turned out to be one of the most powerful methods for studying the kinetic and stereospecific natures of the active sites on the heterogeneous Ziegler-Natta catalysts for propylene polymerization [129]. Interestingly, polymerization reaction proceeded within an extremely short period (*ca.* 0.2s) exhibits a quasi-living characteristic, where the states of the active sites are kept constant without time-dependent changes, and any side reactions including chain

transfer and deactivation after the initiation of polymerization are negligible. Because of this outstanding advantage, direct information corresponding to the nature of active sites and polymerization mechanism can be obtained [154,167,211,212].

In the present chapter, a catalyst of type $TiCl_4$/ethylbenzoate/$MgCl_2$ was prepared via a chemical route by using magnesiumethoxide as a support precursor. The catalyst was pretreated with several chemically different poisoning materials such as alcohol, ketone and ester with the aim at deactivating active Ti species. In fact, some compound, i.e., oxygen, carbon monoxide or carbon dioxide are often used to poison olefin catalyst or even count the number of active sites [213,214] but they possess too high mobility which can not be used to poison only a small fraction of active sites. Poisoning compounds with simple structure and small molecules were instead selected in order to directly clarify the mechanism of the site deactivation and in the mean time avoiding their steric effect, which may have a beneficial influence on generating isospecific sites or even transforming aspecific sites into isospecific ones. A precise kinetic study for the effect of the poisoning materials was conducted using the stopped-flow polymerization combined with gel permeation chromatography (GPC) analysis.

6.2 Materials

Chemical 2 were used in these experiments. Catalyst 2 was prepared and used. Two series of polymerization were carried out using reactor 2 and 3, respectively. Polymer characteristics were done on ^{13}C NMR 2 and GPC 2. More experimental details are described in Chapter III.

6.3 Results and Discussion

6.3.1 Slurry Polymerization

In the first series of polymerization, different poisoning compounds such as methanol, acetone and ethyl acetate as a representative of alcohol, ketone and ester, respectively, were used to study the poisoning impact on catalyst performance and polymerization behavior. Due to their low steric hindrance structure, the consideration

of the steric effect of such components to the coordination of the catalyst is minimized. That is to say, the influence of the poisoning materials on the improvement of catalyst stereospecificity somehow by generating isospecific site or even transforming apecific site to higher isospecific one would be negligible. Propylene polymerizations were conducted with a pretreatment of catalyst for 1 min in order to partially destroy the catalytic active centers. The polymer obtained were characterized and the results are illustrated in Table 6.1, consisting of activity, *mmmm* pentad, number-average molecular weight ($\overline{M}_n$) and molecular weight distribution (MWD). It was observed that at a Poisoning materials/Ti molar ratio of 0.1 (entries 1-4), the catalyst activity decreased substantially in the following order: none > ethylacetate > acetone > methanol, while there was no significantly change in *mmmm* pentad, $\overline{M}_n$ and MWD. The results obviously demonstrated that the catalytic activity was greatly influenced by the nature of poisoning materials, and that all the materials poisoned the active sites independently of their stereospecificity.

Table 6.1 Characterization of polypropylene obtained with different poison pretreatment[a]

Entry	Poisoning materials	Poison/Ti mole ratio	Yield (kg/mmole-Ti)	*mmmm*[b]	$\overline{M}_n$[c] ($\times 10^{-4}$)	MWD[c]
1	None	-	95.3	83.1	6.0	9.5
2	Methanol	0.1	58.9	82.6	5.1	11.6
3	Acetone	0.1	73.9	82.0	5.6	12.0
4	Ethylacetate	0.1	91.0	82.1	6.2	10.9
5	Acetone	10	2.1	76.4	-[d]	-[d]
6	Ethylacetate	10	9.6	86.2	-[d]	-[d]

[a]Slurry propylene polymerization was carried out with TIBA (Al/Ti = 30) in heptane 200 ml at 30°C after the pretreatment of catalyst with poisoning materials for 1 min.
[b]Determined by ^{13}C NMR.
[c]Determined by GPC.
[d]Not determined.

In the case of methanol, it is generally accepted that $TiCl_4$ is readily reacted with alcohol to produce alkoxide complex which is inactive for propylene polymerization [215] and HCl. In addition, HCl must react with TIBA to reduce its activation power and the titanium chloride alkoxides produced on the catalyst surface

might have some negative effects on the catalyst activity. In the case of ethyl acetate, it might trend to coordinate on the $MgCl_2$ support though their oxygen atom since there is no experimental evidence of the direct interaction between the electron donors and the titanium center [216]. Their structure could be moreover small enough to place adjacent to the catalyst. In this sense, the electron density of oxygen atom could be considered to responsible for the stability of the complex structure. Accordingly, ethylacetate, ethyl benzoate (EB) like structure, could give rise to the electron density of cationic metal center and make the catalytic sites kinetically more stable and active comparing to acetone. As opposed to ethylacetate, acetone might interact with the catalyst surface in a similar fashion while it could moreover react with the Ti-alkyl or Ti-polymer to form bulky alkoxy-Ti chlorides [217] resulted in an apparent decrease in catalytic activity. To implement the oversimplified view, the interaction mechanism of poisons on the catalyst surface is shown in Figure 6.1.

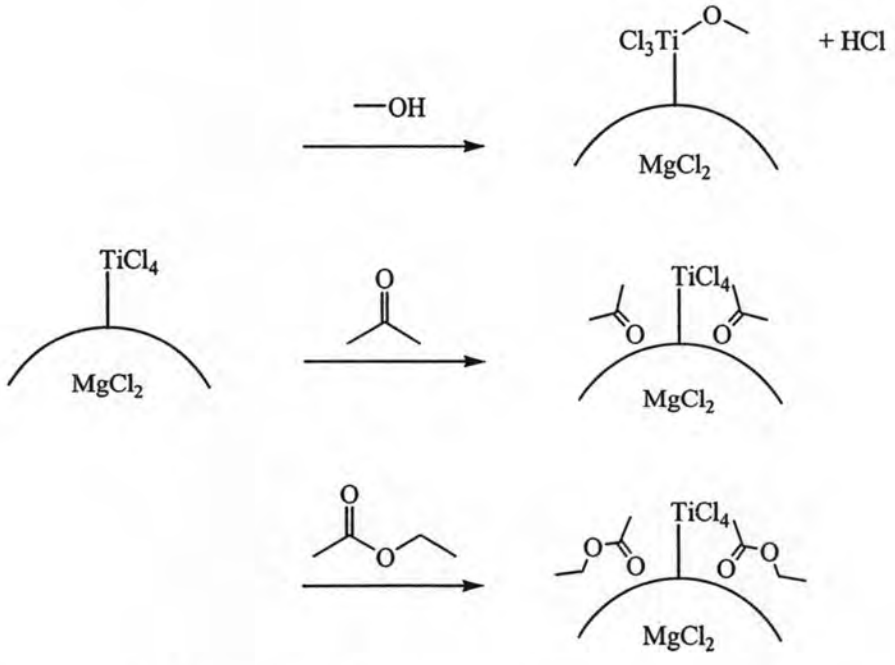

Figure 6.1 Purposed mechanism of the interaction between solid catalyst and poisons.

The study has also been extended for evaluation of these two poisons by increasing the addition of donor to a Poison/Ti mole fraction of 10 (entries 5-6). Based on the reference polymerization result, a remarkable reduction of catalytic activity of both compounds was represented. As would be expected, acetone produced a stronger evident deactivation effect which was substantially in line with the previous

results. However, ethyl acetate revealed interestingly some typical features of donor-like structure which was able to improve stereospecificity of catalyst to some extent while acetone brought about lowering in polymer stereoregularity. Unstable reaction sites resulted in less active and less selective would be preferred for the latter compound. Nevertheless, it was unclear that how ethyl acetate can result in increased tacticity of the polymer due to the fact that when the catalyst is brought into contact with the co-catalyst, a large proportion of the internal donor is lost as a result of alkylation and complexation reactions as already reported by some researchers [57,106]. Moreover, it has long been known that EB as internal donor coordinates much more weakly with the catalyst surface and reacts more easily with TEA, thus it is more easily extracted by the cocatalyst during the polymerization process. On the basis of this consideration, even ketone or ester could bond to the Ti coordination site. This type of interaction was supposed to be relatively weak and would be lost during the activation process. Therefore, one possible explanation is that large amount of ethyl acetate addition resulted in some remained coordinated to the coordination sites or even the extracted one could also act as external donor to replace the internal donor in the course of polymerization.

6.3.2 Stopped-flow Polymerization

In the second series of polymerization, kinetic studies were carried out using a combination of stopped-flow technique and GPC method with the aim to verify the effect of poisoning materials in terms of the number of the active sites and the propagation rate constant. In the similar way as slurry polymerization, the catalysts were pretreated with various alcohols for 1 min before starting polymerization because such compound showed the most prominent deactivation effect. Figure 6.2 represents the dependence of polymer yield on polymerization time with the addition of methanol, ethanol and 1-butanol. The linear correlation of which was observed within 0.2 s in all experiments indicating that the catalyst possessed a constant activity without deactivation and late activation even after adding alcohols, suggesting that the reaction of the compounds with the catalyst completed within the 1 min pretreatment. It was apparent that alcohol compounds caused an unfavorable effect on the polymerization reaction by reducing the catalyst activity. The poisoning effects essentially increased with increasing the steric bulkiness of the alcohol. In fact, in

these series methanol is the smallest alcohol having highest reactivity to remove Cl ligand from the Ti species forming titanium chloride alkoxide which was inactive for propylene polymerization. These results are in good agreement with the observation of Garoff *et al.* [215] which have stated that the appearance of $TiCl_3(OR)$ has a strong tendency to deactivate the active centers in the activated support material. It could moreover strongly bind to the magnesium atom surface to form a stable complex as a result of hydrogen bonding between the complexes alcohol and a chloride ion of the surface [218,219]. However, it should be emphasized that the alcohol compound has the ability to dissolve $MgCl_2$ and such capability can typically enhance by an increase in its steric hindrance. That is to say even though 1-butanol have the lower reactivity towards the displacement of chlorides attached to titanium, the pronounced effect of 1-butanol on the activity reduction might be mainly attributed to the destruction of support surface by alcoholysis of the $MgCl_2$. Additionally in the presence of the coordination of 1-butanol and Ti-Cl species, the larger hindrance of exchanged Ti-alkoxide may have a favorable on hindering the neighboring active sites resulted in the lowering of catalyst productivity while the exchange reaction products containing small alkoxy group (Ti-OMe, Ti-OEt) would be easily realkylated by the trialkylaluminium as reported by Albizzati *et al.* [70].

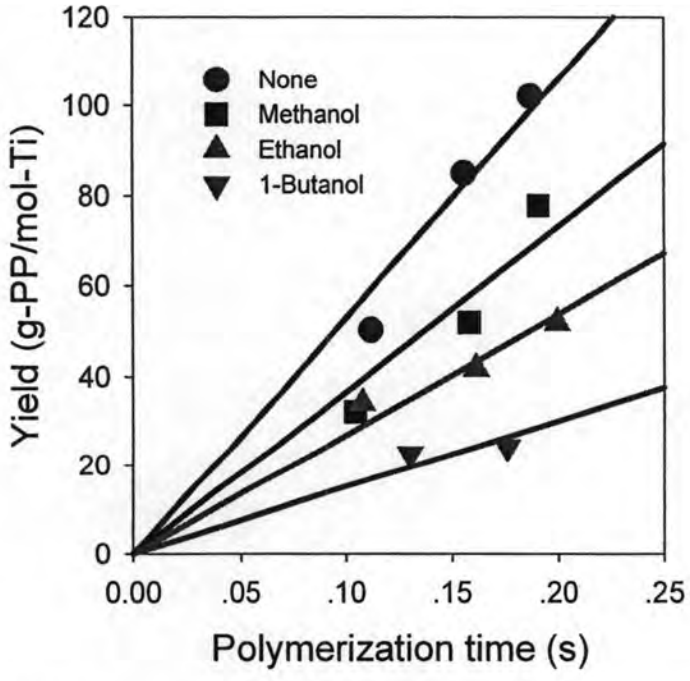

Figure 6.2 Dependence on polymerization time of polymer yield of the PP obtained with the monoester-type supported catalyst.

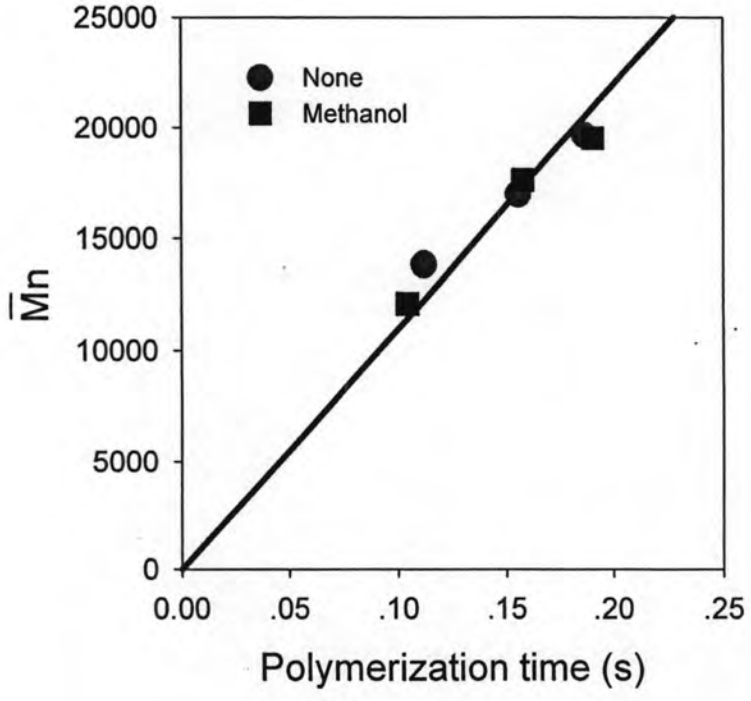

Figure 6.3 Dependence on polymerization time of number-average molecular weight ($\overline{M}_n$) of the PP obtained with the monoester-type supported catalyst.

For further study, the experiment concerning the methanol as poisoning material was chosen to determine the kinetic parameters. From Figures 6.2 and 6.3, the polymer yield and molecular weight were obviously proportional to the polymerization time, which confirmed a quasi-living nature of the polymerization. It could be also noticed from the figures that there were no effect existed on molecular weight both in the presence and absence of methanol.

Table 6.2 Kinetic parameters for propylene polymerization[a]

Entry	Poisoning materials	k_p (L/mol·s)[b]	[C*] (mol%)[b]
1	None	4,700	0.40
2	Methanol	4,500	0.28

[a]Stopped-flow propylene polymerization was performed with the TIBA (Al/Ti = 30) in heptane at 30°C after the pretreatment of catalyst with poison for 1 min (Poison/Ti = 0.1).
[b][C*] and k_p were estimated by Eqs. (1) and (2).

From the kinetic parameters as reported in Table 6.2, the value of k_p was hardly changed while the number of [C*] decreased from 0.40 to 0.28 mol% which was accounted for 30% reduction in relation to the reference polymerization. The findings herein proved that the active site concentration was quite sensitive to the external agents and it was the key factor in determining the performance of catalyst owning to the evidence of deactivation effect. On consideration of k_p, it is well recognized that heterogeneous Ziegler-Natta catalysts contain a great variety of active sites and the propagation rate constant of different types of active sites significantly increases as the isospecificity of the active sites increases. In other word, higher k_p originated from higher isospecific site [113,206]. In this regard, the value of k_p could be changed only in the case that there are some selective poisonings on the different types of the active sites which could be aspecific sites or isospecific sites. Therefore, the altering will cause effect on the variation of *mmmm* pentad, for example, a selective poisoning of aspecific sites or isospecific sites must lead to higher or lower k_p, respectively. In this way, the constant k_p was indicative of a non-selective poisoning, which was supported by the nearly constant *mmmm* pentad in the slurry polymerization in Table 6.1. With the stopped-flow polymerization, we could attribute the poisoning effect of methanol on the catalyst performance only to the decrease of the number of the active centers.

Finally, the stopped-flow result suggested that the active site concentration was quite sensitive to the methanol. The reaction taking place at methanol/Ti molar ratio of 0.1 would result in the reduction of the activity by 10% if the reaction had undergone stoichiometrically ($CH_3OH + TiCl_4 \rightarrow$ *inert* $TiCl_3OCH_3 + HCl$). However, the actually observed decrease of the activity reached as large as 30%. This might be explained by the spatial distribution of the $TiCl_4$ species. It is well known that the heterogeneous Ziegler-Natta catalyst particles correspond to aggregates of primary particles (5-8 μm) [220]. In the pretreatment, $TiCl_4$ species exposed on the outermost surface of the secondary particles should be easily accessed and therefore dominantly killed by methanol, compared with the $TiCl_4$ species hidden inside the secondary particles. Namely, the deactivated $TiCl_4$ species on the outermost surface of the secondary particles must largely exceed 10%. Further, the polymers synthesized by the stopped-flow method should come from such the outermost $TiCl_4$ species, since such the short-time polymerization hardly causes the breakage of the secondary

particles as was evidenced by the absence of any later activation. In this regard, the number of the active centers derived by the stopped-flow method is directly related to the activated outermost $TiCl_4$ on the surface of the secondary particles, which were dominantly damaged by the methanol pretreatment.

6.4 Summary

Poisoning materials showed a remarkably effect on the lowering of catalytic activity without improving in catalyst stereospecificity. Methanol exhibited the strongest deactivation power comparing to acetone and ethyl acetate due to its high reactivity to form titanium chloride alkoxide which was inactive in polymerization. In alcohol series, 1-butanol clearly provided stronger poison ability as a consequence of the higher dissolve capability to the catalyst support and high steric complex formation presented beside the active site. The interaction of acetone and ethyl acetate might obstruct or impose some restrictions on the Ti coordination leading to active site destruction. A precise kinetic study with the stopped-flow method for the effect of the methanol pretreatment revealed that the catalytic reduction came mainly from the decrease of the active site concentration. The constant of the propagation rate constant along with consistency in the degree of isotacticity reflected the unselective poisoning on the catalytic sites.