

고활성 염화마그네슘 담지 티탄촉매에 의한 에틸렌, 프로필렌, 1-부텐 및 스티렌 중합의 비교연구

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A Comparative Study on the Polymerization of Ethylene, Propylene, 1-Butene and Styrene over a Highly Active $MgCl_2$ -Supported $TiCl_4$ Catalyst

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요약 : $Mg(OEt)_2$ 를 $Ti(Obu)_4$, 무수프탈산 및 사염화티탄과 반응시켜 합성한 새로운 염화마그네슘 담지 염화티탄촉매를 $AlEt_3$ 혹은 $AlEt_3$ /삼에톡시페닐실란(PTES)으로 활성화시켜 에틸렌, 프로필렌, 1-부텐 및 스티렌 중합거동에 대한 비교연구를 행하였다. 또한 슬러리상 중합에서 더욱 정확하게 활성을 비교하고 성장속도 상수(k_p)를 계산하기 위하여 용매 (노르말헵탄)에 대한 단량체들의 용해도를 측정하였다. 올레핀중합에 대한 활성도는 노르말헵탄에 용해된 단량체농도에 입각하여 보정하기 전후에 그 순서가 달라졌다. 폴리프로필렌(PP)과 폴리(1-부텐) (PB)의 입체규칙도(I.I.)는 PTES의 첨가로 크게 개선되었고 프로필렌과 1-부텐중합에 대한 속도-시간 곡선의 유사함으로 미루어 보아 프로필렌과 1-부텐에 대한 활성점의 성질이 서로 비슷한 것으로 짐작되었다. 활성점 농도(C^*)의 측정결과 C^* 와 k_p 의 크기 순서는 에틸렌 > 프로필렌 > 1-부텐이었다. PTES의 첨가여부에 따른 스티렌중합의 거동 (활성도 및 입체규칙도)으로부터 스티렌에 대한 입체규칙중합은 프로필렌 중합에서의 입체규칙도와는 상관없이 비균질 지글러-나타 촉매의 반응기구에 의해 진행됨을 알 수 있었다.

Abstract : A comparative study has been made on the behaviors of ethylene, propylene, 1-butene and styrene polymerizations using a new $MgCl_2$ -supported $TiCl_4$ catalyst prepared by the reaction of $Mg(OEt)_2$ with $Ti(Obu)_4$, phthalic anhydride and $TiCl_4$, in conjunction with $AlEt_3$ or $AlEt_3$ and phenyltriethoxy silane (PTES). Solubilities of monomers to a solvent (n-heptane) were also measured with a view to comparing the productivity of catalyst for each monomer and calculating the propagation rate constant (k_p) more exactly in slurry-phase polymerizations. The order of activity for olefin polymerizations was changed before and after normalization based on the concentration of monomer in n-heptane. The isotacticity (I.I.) of polypropylene (PP) and poly(1-butene) (PB) was remarkably improved by PTES and similar rate-time profiles were observed for propylene and 1-butene polymeri-

zations, suggesting that the nature of active sites for both monomers is similar to each other. From the measurement of the number of active sites (C^*), it was clear that both C^* and k_p were in the order of ethylene > propylene > 1-butene. The results on styrene polymerizations (activity and isospecificity) in the absence and presence of PTES suggested that isotactic polymerization of styrene proceeds via heterogeneous Ziegler-Natta catalysts without regard to the I.I. in propylene polymerizations.

INTRODUCTION

It is generally accepted that the isotactic polymerization of olefins in the presence of heterogeneous Ziegler-Natta catalysts involves the stereospecific cis-insertion of the prochiral monomer at reactive metal-carbon bonds (active sites). Reported experimental evidence strongly suggests that the steric control is due to the asymmetric environment of the active sites.¹ In addition the similar general behavior of TiCl_3 -based and MgCl_2 -supported catalysts indicates that the nature of the active sites is the same.^{2,3} On the other hand, MgCl_2 supported catalysts usually combine one or two aromatic esters as Lewis bases with TiCl_4 and trialkylaluminum cocatalyst. A first aromatic ester is used in the solid component as internal electron donor, the second (possibly the same compound) is used complexed with trialkylaluminum as an external donor. Recent catalysts use a phthalate (diester) as an internal donor and a silane (with at least one alkoxy group in the molecule) as an external donor. The first family of supported catalysts has been reviewed in different papers, particularly by Pino et al.⁴ and Barbe et al.⁵ Scientific papers on the new systems were recently published in the literature.⁵⁻⁷

However, many academic studies are very restricted in the topic on the effect of internal and/or external Lewis bases on the isospecificity and the productivity of catalyst mainly in the propylene polymerization. Relatively little attention has been paid in the literature on olefin polymerization with such catalysts to the problem of relative reactivity of olefin. Considering the formation of a solid catalyst is a complex process depending on the chemical properties of the solid and on its porous and

crystal structure, the polymerization centers are expected not to be homogeneous, thus the productivity and/or the isospecificity of the catalyst might be diversified in the polymerization of various monomers.

In this study we compared the rate profiles of polymerization of different monomers including ethylene, propylene and 1-butene in the presence of a highly active and isospecific catalyst system using an alkoxy silane as an external donor. Styrene polymerization was also performed with the same catalyst system for comparison's sake. The concentration of active sites and the propagation rate constants were measured for each monomer.

EXPERIMENTAL

Materials

Polymerization grade of ethylene (from Yukong Ltd.), propylene, 1-butene (both from Korea Petrochem. Co.), and extra pure grade of CO (from Matheson Co.) were used after passing them through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Extra pure heptane (from Tedia Co., USA) was dried over sodium and fractionally distilled before use. Research grade of styrene obtained from Kanto Chemicals Co. was washed with an aqueous solution of sodium hydroxide and dried over calcium hydride for 12 hr. Phenyltriethoxy silane (PTES) and AlEt_3 purchased from Aldrich were used without further purification.

Catalyst

A highly active and isospecific catalyst with a diester as an internal donor was prepared from the reactions of $\text{Mg}(\text{OEt})_2$ with $\text{Ti}(\text{OBu})_4$, phthalic anhydride and TiCl_4 in a chlorobenzene medium.

The procedure for the preparation of the catalyst has been given previously.⁸

Polymerization

Ethylene, propylene and 1-Butene : Slurry-phase polymerizations in n-heptane were carried out in a 250 ml reaction flask at atmospheric pressure. The procedures were described in the previous paper.⁸

Styrene : In a 250ml reaction flask equipped with a stirrer, diluted styrene monomer by n-heptane was added, and then the prescribed amount of AlEt_3 , PTES and catalyst were added at 50°C in this order. Polymerization was performed under atmospheric pressure at 50°C for 6 hr and terminated by the addition of a small amount of methanol into the system. The whole product was precipitated with an excess amount of ethanol, collected by filtration and dried at 80°C under reduced pressure (10^{-3} torr).

Analysis of Polymer

Fractionation of PP by boiling n-heptane and PB by n-decane were carried out as the reported method.⁹ Isotactic indices were determined from the fraction which is insoluble in solvents. Extraction of one gram of polystyrene (PS) by boiling methyl ethyl ketone (MEK) was performed in a Soxhlet extractor for 5 hr. MEK insoluble polymer was dried under reduced pressure, while MEK soluble polymer was recovered by evaporating MEK from the extract. I.I. of polymer was defined as the weight fraction of MEK insoluble portion.¹⁰

Calorimetric examination of the homopolymer samples was carried out with a DSC (Du Pont 1090B), on polymer samples (c. a., 5mg) encapsulated in standard aluminum pans. All measurements were conducted at a scan rate of 20 K/min. Samples were held at 200°C for 5 min before conducting a cooling run.

RESULTS AND DISCUSSION

It has been generally accepted that the instantaneous rate of polymerization (R_p) at a given time is represented by the following relations for the

polymerization of gaseous monomers such as ethylene, propylene, and 1-butene, i.e.

$$R_p = k_p [M] C^*$$

where k_p is a rate constant of chain propagation, $[M]$ is a monomer concentration, and C^* is a concentration of active sites. Hence, k_p values are activities which are normalized with respect to monomer and active sites concentration, and these k_p values can be used to compare activities for different catalysts or for the same catalyst in different polymerization processes or at different monomer concentrations. For slurry phase polymerization, the concentration of monomer in the solvent should be used for calculation of k_p from a measured value of C^* . Monomer concentration in solvent in the case of ethylene, propylene and 1-butene polymerization in a hydrocarbon medium is usually calculated by application of the Henry equation :

$$[M] = K_H \exp(E/RT) P_M$$

where P_M is the monomer pressure (atm) over the solution. $K_H \exp(E/RT)$ is the Henry constant at temperature T (mol/l atm), and E is an empirical parameter (cal/mol) describing dependence of K_H on temperature.

In order to determine the value of K_H and E the solubilities of ethylene, propylene and 1-butene to solvent (n-heptane) were measured. A reaction flask of calibrated volume (250ml) was filled with monomer. The moles of monomer were calculated using a reference table.¹¹ Another calibrated flask (250ml) was filled with 100ml n-heptane and then the gas inside the flask was pumped out. Connecting the monomer flask with heptane containing flask, the equilibrium solubility of monomer at various temperatures were calculated by measuring the uptake of monomer using mass flow meter connected to personal computer. Monomer pressure was obtained by subtracting heptane pressure from total read pressure. The variation of monomer solubility with temperature is shown in Fig. 1 and the corresponding Arrhenius plots

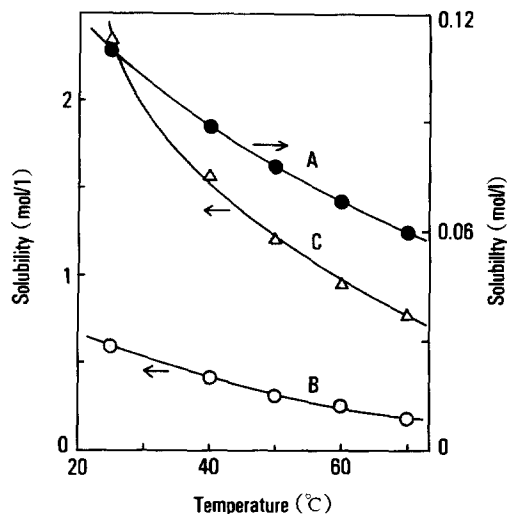


Fig. 1. Solubility of (A) ethylene, (B) propylene and (C) 1-butene in *n*-heptane at various temperature, under 1 atm. pressure.

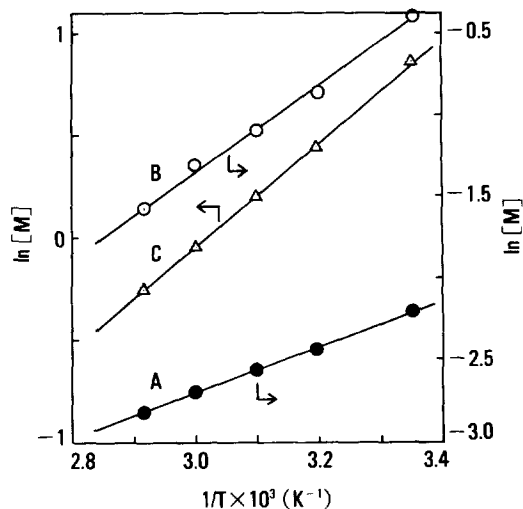


Fig. 2. Arrhenius plots ($\ln[M]$ vs. $1/T$) for (A) ethylene-heptane, (B) propylene-heptane and (C) 1-butene-heptane system.

are shown in Fig. 2. From the slope in Fig. 2 molar heat of solution was calculated to be -2730 , -4843 and -5046 cal/mol for ethylene-heptane, propylene-heptane, and 1-butene-heptane, respectively.

Homopolymerizations of ethylene, propylene and

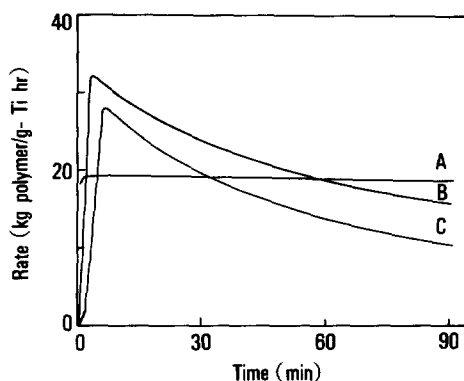


Fig. 3. Polymerization profiles at Temp.=50°C, $\text{Ti}=4.2 \times 10^{-4}$ g, $[\text{AlEt}_3]=8.9$ mmol/l and *n*-heptane=100 ml : (A) [ethylene]=0.1 mol/l ; (B) [propylene]=0.43 mol/l ; (C) [1-butene]=1.59 mol/l.

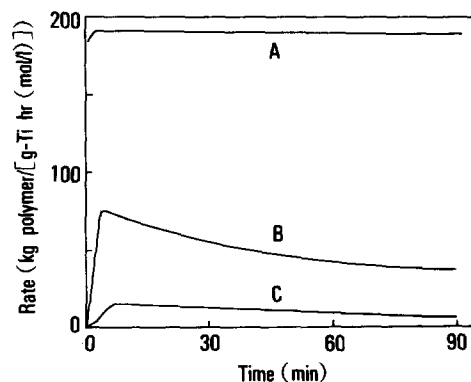


Fig. 4. Normalized rate profiles of those in Fig. 3 based on the concentration of monomer in heptane. Captions are the same as those in Fig. 3.

1-butene were carried out in a slurry-phase semi-batch reactor with a highly active and isospecific catalysts in conjunction with AlEt_3 or $\text{AlEt}_3/\text{PTES}$ at 50°C. Figure 3 shows the kinetic profiles of polymerization obtained in the absence of external donor (PTES) and Fig. 4 illustrates the normalized rate-time profiles based on the concentration of monomer in heptane. Before normalization the order of maximum rate ($R_{p,m}$) is :

Propylene > 1-butene > Ethylene

whereas the order is changed in the case of the

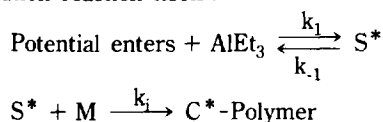
average polymerization rate (\bar{R}_p) over a 90 min of polymerization :

Propylene > Ethylene > 1-butene

Comparing the normalized activities based on the concentrations of each monomer in heptane presented in Fig. 4 the order of principal activities, both $R_{p,m}$ and \bar{R}_p , is clearly :

Ethylene > Propylene > 1-butene

and is usually explained as a manifestation of the coordination-anionic polymerization mechanism with the limiting step of the anionic center attack on the olefin double bond.¹² It is worth noting here that there is an initial build up of the rate of polymerization (R_p) to $R_{p,m}$ in about 3 min for propylene and in 6 min for 1-butene polymerization, whereas all the catalytic sites are activated immediately upon the introduction of alkylaluminum cocatalyst for ethylene polymerization. This difference of the polymerization kinetic curves suggests the existence of two consecutive reactions in the initial period : the reaction generating active centers (without monomer participation) and the initiation reaction itself :



where k_1 , k_{-1} and k_i are the rate constants, S^* and C^* -polymer are the active sites and the polymerization centers, respectively, and M is a monomer. Since the same catalyst was applied to the polymerization of monomer at the same conditions in the present study, the rate constants for the first reaction of above scheme should be same for all monomers. In this case, the initial reaction of chain initiation represented by the second reaction is the only initiation reaction inducing the difference of kinetic curves during initial period. Even if the concentration of 1-butene in a polymerization medium is higher than that of ethylene and propylene by about 16-fold and 4-fold, respectively, the time to reach $R_{p,m}$ is more delayed for 1-butene than for

propylene or ethylene. This implies that the value of k_i for 1-butene polymerization is much smaller than that for ethylene or propylene polymerization. According to the recent kinetic studies on the insertion of the first monomeric units into $\text{Ti-}^{13}\text{C}$ reactive bonds,¹³ the polymerization rate constant for ethylene was estimated at least 10 times higher than that for propylene.

Another fact to be pointed out from the rate-time profiles is the type of polymerization kinetic profiles. As shown in Fig. 2, when propylene and 1-butene are polymerized, the polymerization rates obey a first order deactivation, well fitted by the equation :

$$-dC^*/dt = kC^*$$

A sound experimental evidence exists¹⁴ that the rate decay is not due to the formation of a polymer layer enveloping the catalyst particles and slowing down the monomer diffusion to the active sites. The deactivation, indeed, occurs independently of the presence of the monomer, and is due exclusively to the interaction of the catalyst with the alkylaluminum cocatalyst. This reduces Ti(III) to lower oxidation states (mainly Ti(II)) ;¹⁸ it seems reasonable to associate such a reduction with the decay of polymerization rate. According to the previous results^{15(b), (d)} Ti(III) species are active for polymerization of various olefins, whereas Ti(II) species are active only for ethylene. Therefore, the decay of the polymerization rates in propylene and 1-butene polymerizations might be ascribed to the overreduction to the lower valence state of active Ti species. Since these Ti species remain active for ethylene polymerization, non-decay type rate profile is obtained for ethylene polymerization as shown in Fig. 2.

The complete differences in the rate-time profile of ethylene polymerization from that of propylene or 1-butene might be also explained by assuming that ethylene polymerization in the presence of highly active and stereospecific MgCl_2 -supported catalysts is controlled by monomer diffusion through the formed polymer. Considering the severe

differences in the rate constant of ethylene polymerization for the insertion of monomer into $\text{Ti}-^{13}\text{C}$ bonds (k_i) from that of propylene or 1-butene polymerization as discussed already, the potentiality of the catalyst is much higher for ethylene than for propylene or 1-butene, so that the monomer flux diffusing to the active sites through the polymer can be limiting only when polymerizing ethylene. If this is the case, intrinsic deactivation of polymerization centers found in propylene and 1-butene polymerizations would have no effects on the polymerization rate, unless the polymerization rate dropped below that allowed by monomer dif-

fusion.

The effect of external Lewis base on the polymerization of ethylene, propylene and 1-butene was also studied by the modification of catalyst with $\text{AlEt}_3/\text{PTES}$ ($[\text{AlEt}_3]/[\text{PTES}]=1/10$). Figure 5 shows the rate-time profiles. Similar curves are obtained compared with when polymerizing olefins in the absence of PTES. For propylene and 1-butene polymerizations, \bar{R}_p over a 90 min of polymerization is increased by the addition of PTES, but remains almost unchanged for ethylene polymerization (compare Fig. 3 with Fig. 5). The author previously showed⁸ that activation of the catalyst containing diester as an internal Lewis base with $\text{AlEt}_3/\text{PTES}$ induces not only to transform atactic sites to isospecific sites, but to stabilize the existing and the newly formed active sites. The slight increase in \bar{R}_p and the sharp increase in I.I. for propylene and 1-butene polymerization illustrated in Table 1 might be due to the specific role of PTES. In Table 1, C^* values for the polymerizations in the absence and presence of PTES are also given. We applied an inhibition method^{8, 14(b)} using carbon monoxide for the determination of C^* and the rate constants for chain propagation (k_p) are calculated based on the simplistic equation, $R_p = k_p C^* [\text{M}]$. The carbon monoxide was added when the polymerization rates reach maximum for all cases. From the results we can see that both C^* and k_p is the order of :

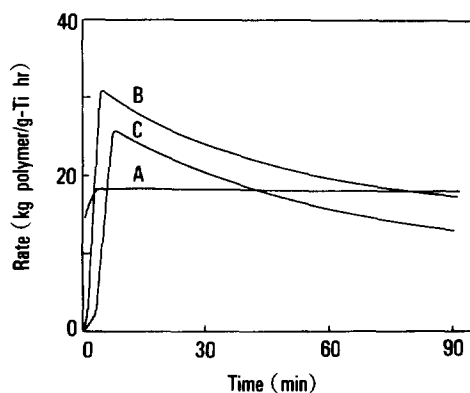


Fig. 5. Polymerization profiles of ethylene, propylene, and 1-butene. Polymerization conditions and captions are the same as those in Fig. 3 except the addition of PTES as a ratio of $[\text{AlEt}_3]/[\text{PTES}]=0.1$.

Table 1. Results on Olefin Polymerizations and on the Measurement of Active Site Concentration

Monomer	Cocatalyst Solution	I.I. (%)	\bar{R}_p^a	$C^* \times 10^2$ (mol/mol Ti)	k_p (1/mol s)	Melting Point(°C)
Ethylene	AlEt_3	82 ^b	183.2	31	276	136
	$\text{AlEt}_3/\text{PTES}$	84 ^b	176.4	29	288	138
Propylene	AlEt_3	73	46.5	17 ^c	143 ^c	—
	$\text{AlEt}_3/\text{PTES}$	97	51.2	16 ^c	143 ^c	169
1-Butene	AlEt_3	58	10.6	11	38	—
	$\text{AlEt}_3/\text{PTES}$	81	11.1	11	35	109

^a In kg polymer/(g-Ti hr (mol monomer/l)) over a 90 min polymerization.

^b The percentage crystallinity calculated from the relation : crystallinity(%) = $100 \Delta H_f / \Delta H_f^*$ (ΔH_f from DSC and ΔH_f^* taken as 66 cal/g).

^c From ref. 8.

Ethylene > Propylene > 1-butene

Even if we pointed out from the kinetic results that the nature of active sites for propylene and 1-butene monomers is more or less similar to each other, stereospecific sites for propylene is not always stereospecific for 1-butene. For PP, almost all atactic sites formed by the addition of AlEt_3 alone are transformed to isospecific sites by the modification with PTES. For PB, considerable amount (19%) of atactic sites remained unchanged as shown in Table 1.

The polymerization of styrene by heterogeneous Ziegler-Natta catalysts usually leads to crystalline or partly crystalline polystyrene.¹⁶ In order to check a relationship between the isotactic sites for propylene or 1-butene and those for styrene, polymerization of styrene was performed at 50°C for 6 hr in the absence and presence of PTES and the results are shown in Table 2. The activity is much lower than that of olefin polymerization (refer to Table 1). Surprisingly, highly isotactic PS is obtained without regard to the addition of PTES and the catalyst isospecificity for styrene polymerization is slightly increased by the modification with PTES. This result demonstrates that isotactic polymerization of styrene via reaction mechanism of heterogeneous Ziegler-Natta catalysts regardless of the catalyst isospecificity in propylene or 1-butene polymerizations. In the presence of heterogeneous Ziegler-Natta catalyst, the insertion of styrene monomer into the metal-carbon bond of the active sites is primary,^{16(c)} and the stereochemistry of the insertion is controlled by the chirality of the sites. However, considering this mechanism is analogous to that observed for polymerization of olefin in the presence of the same catalyst and the activity is much lower for styrene polymerization,

we may conclude that only part of the isospecific sites for propylene or 1-butene is also isospecific for styrene, and that atactic sites for olefins are not active for styrene. We can also speculate that various kinds of isospecific sites showing differences in propagation rate constant and acidity exist in the catalyst system of the present work.

The formation of atactic PS (5.2% and 2.8% in the absence and presence of PTES, respectively) can be explained by cationic polymerization, not by coordination polymerization. In heterogeneous Ziegler-Natta catalyst system like $\text{TiCl}_3\text{-AlEt}_3$, $\text{MgCl}_2\text{/EB/TiCl}_4\text{-AlEt}_3$, and a catalyst system of the present work, ligand exchange reactions take place between titanium chlorides and AlEt_3 to form mixed halides of organoaluminum during the formation process of active sites.⁸ These organoaluminum halides are reported to catalyze cationic polymerization.¹⁷ Accordingly, atactic polystyrene is considered to be produced by such cationic species. The formation of atactic PS by cationic polymerization has not been found in the special catalyst systems, in which no organoaluminum halides are formed.¹⁸ However, above proposals for the formation of isospecific and atactic PS become clear only after measuring active sites selectively by more precise experiments and correlating the activity of styrene polymerization with those of olefin polymerizations.

CONCLUSION

From a comparative study on the behaviors of ethylene, propylene, 1-butene and styrene polymerizations the following conclusions are drawn.

1. The molar heat of solution is -2730, -4843 and -5046 kcal/mol for ethylene-heptane, propylene-heptane and 1-butene-heptane systems, respectively.

2. Before normalization based on the monomer concentration in n-heptane, the order of $R_{p,m}$ and R_p over a 90 min of polymerization is :

$R_{p,m}$: propylene > 1-butene > ethylene
 $\bar{R}_{p,90\text{min}}$: propylene > ethylene > 1-butene

Table 2. Results of Styrene Polymerization

Cocatalyst Solution	Activity (kg PS/g-Ti hr)	I.I (%)	Melting Point(°C)
AlEt_3	0.72	94.8	214
$\text{AlEt}_3\text{/PTES}$	0.76	97.2	217

whereas both $R_{p,m}$ and R_p are in the order of ethylene > propylene > 1-butene after normalization. These orders do not change after modifying the catalyst with an external Lewis base (PTES).

3. The nature of active sites for propylene and 1-butene is more or less similar to each other, and an unexpected acceleration-type rate curve found in ethylene polymerization can be explained by monomer diffusion model as well as by active sites model.

4. The number of active sites and the propagation rate constant are in the order of ethylene > propylene > 1-butene

5. Even if the productivity for styrene polymerization is much lower than that for olefin polymerizations, highly isotactic PS has been obtained regardless to the presence of PTES.

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