

## 모노 및 디에스테르 루이스염기를 함유한 고효율 촉매에 의한 에틸렌 중합 : 활성점 농도의 측정

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### Polymerization of Ethylene over Highly Active Catalysts Containing Mono- and Di-ester Lewis Base : Determination of Active Site Concentration

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**요 약 :** 고효율을 나타내는  $\text{Mg}(\text{OEt})_2/\text{benzoyl chloride}(\text{PhCOCl})/\text{TiCl}_4$  (모노에스테르함유) 촉매 또는  $\text{MgCl}_2/\text{butanol/phthaloyl chloride} [\text{Ph}(\text{COCl})_2]/\text{TiCl}_4$  (디에스테르 함유) 촉매를  $\text{AlEt}_3$ 로 활성화시켜 에틸렌중합에 대한 활성점농도 ( $\text{C}^*$ )를 측정하여 프로필렌중합에서 얻은 활성점농도와 비교하였다. 활성점농도의 측정은 중합시에 일산화탄소를 흡착시키는 방법을 사용하였다. 촉매의 티탄종과 내부 루이스염기의 상호작용의 세기에 따라 에틸렌중합과 프로필렌중합에 대한 활성점농도는 큰 차이를 보였다. 즉, 프로필렌중합의 경우 최대중합속도 ( $R_{p,m}$ )에서 측정한 활성점농도 ( $\text{C}^*$ )는  $0.17 \sim 0.33 \text{ mol/mol Ti}$ 이었으나, 에틸렌중합에 대한 활성점농도는  $0.28 \sim 0.45 \text{ mol/mol Ti}$ 이었다. 중합이 진행되는 동안의 활성점의 안정도를 조사하기 위하여 여러가지 중합시간에서의 활성점농도를 아울러 비교하였다. 에틸렌중합에 대한 활성점농도는 중합시간에 따라 변함이 없거나 늘어났고, 이 결과는 프로필렌중합시의 활성점농도의 변화와는 완전히 다른 경향이었다.

**Abstract :** The concentration of active sites ( $\text{C}^*$ ) for the polymerization of propylene has been compared with that for the polymerization of ethylene using highly active  $\text{Mg}(\text{OEt})_2/\text{benzoyl chloride}(\text{PhCOCl})/\text{TiCl}_4$  catalysts (containing monoester) or  $\text{MgCl}_2/\text{butanol/phthaloyl chloride} [\text{Ph}(\text{COCl})_2]/\text{TiCl}_4$  catalyst (containing diester) activated with  $\text{AlEt}_3$ . The method used to measure a concentration of active sites is based on the inhibiting effect of carbon monoxide on polymerization. Depending on the strength of interaction between catalytic species and internal Lewis base anchored onto catalyst matrix, there was much difference between the  $\text{C}^*$ -values for propylene polymerization and those for ethylene polymerization. While the  $\text{C}^*$ -values for propylene polymerization measured at the maximum

polymerization rate ( $R_{p,m}$ ) were in the range between 0.17 and 0.33 mol/mol Ti, the  $C^*$ -values for ethylene polymerization were in the range between 0.28 and 0.45 mol/mol Ti. In order to investigate the stability of active sites during polymerization the  $C^*$  values have been compared at various polymerization times of determination. The  $C^*$ -values were constant or increased for ethylene polymerizations, which was completely different trend for propylene polymerizations.

## INTRODUCTION

$MgCl_2$  supported  $TiCl_4$  catalysts have been prepared by using various kinds of monoester and/or diester as internal donors. The effect of such Lewis base in enhancing catalyst stereospecificity have been discussed in some detail by many authors.<sup>1,2</sup> Busico et al. have reported that internal monoester is readily removed by aluminum alkyl cocatalyst when polymerization is carried out in the absence of external donor.<sup>3</sup> Soga and Shiono have published that the active Ti species in the monoester system have a strong interaction with the neighboring Ti species, whereas those in the diester system do not have such an interaction.<sup>4</sup> As a result, the kinetic behavior of the mono- and di-ester systems are completely different.

In the previous papers we studied a series of highly active and stereospecific catalysts obtained by chlorinating  $Mg(OEt)_2$  with  $TiCl_4$  and benzoyl chloride ( $PhCOCl$ ) which reacted with ethoxide group of  $Mg(OEt)_2$  to form ethyl benzoate (EB) in situ.<sup>5,6</sup> Similar catalytic system has been extensively studied by Jeong and Lee.<sup>8</sup> Depending on the repeated treatments of catalyst with  $TiCl_4$  in the presence of  $PhCOCl$ , the strength of the coordination of EB to the catalyst matrix was varied according to the simple differences in the operational procedure employed during catalyst preparation.<sup>5</sup> Accordingly the kinetic behaviors of the catalysts containing monoester (EB) as internal donor were completely different from each other, even if they were composed of similar chemical composition, in the polymerization of propylene.<sup>5-7</sup>

In this paper we have studied the polymerization of ethylene with the same catalysts and different type of catalyst containing dibutyl phthalate

(DBP, diester) which is generated from the reaction of phthaloyl chloride [ $Ph(COCl)_2$ ] and butanol in the presence of  $Ti(OBu)_4$  and  $TiCl_4$ , and the results are compared with those of propylene polymerization for the better understanding on the interaction between internal Lewis base and catalytic active species.

## EXPERIMENTAL

### Materials

Polymerization grade of ethylene (from Yukong Ltd., Korea) 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) and hexane (from Duksan Pharmaceutical Co., Korea) were dried over Na and fractionally distilled before use.  $Ph(COCl)_2$  (from Aldrich), chlorobenzene (from Kanto Chemical Co.) and  $PhCOCl$  (from Kanto Chemical Co.) were purified according to previous method.<sup>5</sup> Magnesium diethoxide (from Strem Chem. Co.), magnesium chloride (from Toho Titanium Co.),  $AlEt_3$  (from Aldrich), and  $TiCl_4$  (from Kanto Chemical Co.) were used without further purification.

### Preparation of Catalysts

Catalysts containing monoester (EB) were prepared and named according to the previous method.<sup>5</sup> Fig. 1 shows a schematic diagram for the procedure of preparing solid product and catalysts.

For the preparation of catalyst of diester system  $MgCl_2$  was used as a starting material instead of  $Mg(OEt)_2$  which was used for monoester system. Five grams (52.5 mmol) of powder  $MgCl_2$ , 5 ml (14.7 mmol) of  $Ti(OBu)_4$  and 50 ml of n-heptane were reacted at 70°C for an hour under inert atmo-

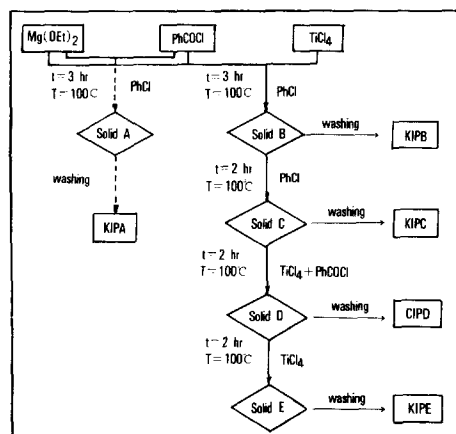


Fig. 1. Schematic diagram for the procedure of preparing solid product and catalysts.

sphere. And then 3.4 ml (37.2 mmol) of butanol containing 20 ml of heptane was added dropwise to the above mixture over 30 min and reacted at 70°C for an hour. A solution of 0.87 ml (6.0 mmol)  $\text{Ph}(\text{COCl})_2$  and 25 ml heptane was added at 70°C over 30 min, and mixed at 90°C for an hour. After washing the resulting solid with heptane, 75 ml of  $\text{TiCl}_4$  was added dropwise over 30 min and reacted at 110°C for 3 hours. Hot-filtered solid obtained from above was washed with 150 ml of boiling hexane 7 times (called KIPF).

### Polymerization

Details of polymerization process has been given elsewhere.<sup>5</sup>

For the determination of the concentration of active centers the prescribed amounts of carbon monoxide were added during polymerization by means of a gas-tight syringe and a decrease in the overall rate of polymerization was measured simultaneously in order to determine the number of active centers.<sup>5~7</sup>

## RESULTS AND DISCUSSION

According to the investigation of the effect of Lewis base modifiers on the productivity of stereoregular polyolefin, it has been postulated that atactic active sites can be totally or partially inacti-

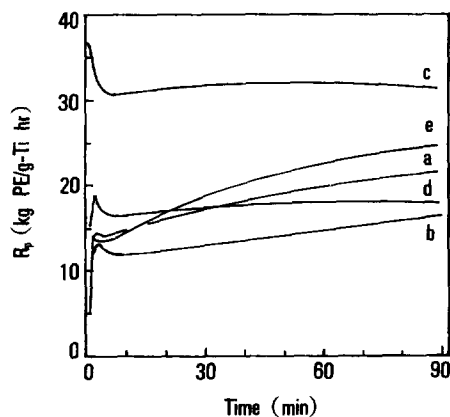


Fig. 2. The rate profiles of ethylene polymerization at  $\text{Ti}=0.41$  mg,  $[\text{M}]=0.1$  M,  $\text{Al/Ti}=47$ , and  $T=50^\circ\text{C}$ : (a) KIPB, (b) KIPC, (c) KIPD, (d) KIPE, and (e) KIPF.

vated by the Lewis base.<sup>2,9</sup> It seems that this mode of action may be differentiated by checking the effect of Lewis base on the ethylene polymerization in which the stereospecificity of the active sites is not a dominant factor.

The profiles of ethylene polymerization are illustrated in Fig. 2. There are no observable initial build-up periods of the polymerization rate for all catalysts. KIPD and KIPE catalyst exhibit the constant-rate-type kinetics, while KIPB, KIPC and KIPF catalyst show the increasing-rate-type kinetics. These types of rate profiles demonstrate that the active centers are uniformly distributed throughout the entire catalyst particles and are not all active at the same time. The formation of active sites may be continuously driven by the complicated chemical composition of these catalysts together with a progressive and controlled break-up of the catalyst into subparticles on which the growth of the polymer takes place.

The kinetic behavior of these catalysts for the polymerization of ethylene are completely different from that for the polymerization of propylene. For the polymerization of propylene two sets of different rate profiles were obtained;<sup>5,7</sup> KIPB and KIPC catalyst showed the constant-rate-type profile for 90 min of polymerization period while

KIPD, KIFE and KIPF catalyst the decay type so that KIPD obeyed the second order deactivation, and KIFE and KIPF the first order. These interesting kinetic features for the polymerization of propylene have been interpreted based on the strength of interaction between EB generated in situ by the chemical reactions of  $\text{PhCOCl}$  with ethoxide group of  $\text{Mg}(\text{OEt})_2$  and catalytic species.<sup>5</sup> The interaction between EB and catalytic species in KIPB and KIPC catalyst was so strong that EB was not removed from the catalyst surface by the interaction with  $\text{AlEt}_3$  during polymerization, resulting in the relatively constant  $C^*$ -value. On the other hand, there was sharp decrease in the  $C^*$ -values during propylene polymerization with KIPD catalyst, because the weak interaction of EB with KIPD catalyst matrix led to an easy removal of EB by  $\text{AlEt}_3$  during polymerization. The resulting donor-free catalytic species may easily interact with the neighboring donor-free catalytic species to deactivate according to the second order kinetics.<sup>4</sup> The interaction strength of EB in KIFE catalyst was intermediate between KIPB or KIPC catalyst and

KIPD catalyst so that KIFE catalyst obeys a first-order deactivation. Relatively slow decrease in the rate of propylene polymerization with KIPF catalyst was also resulted from the strong interaction between DBP which might be formed from the reaction of  $\text{Ph}(\text{COCl})_2$  with butoxide groups of  $\text{Ti}(\text{OBu})_4$  and butanol in the presence of  $\text{TiCl}_4$ .

For the better understanding of the effect of the interaction between internal Lewis base (LB) and catalytic species on the concentration of active sites, we measured the  $C^*$ -values for ethylene polymerizations by CO inhibition method. In this method a prescribed quantity of CO is injected into a polymerization medium and simultaneous measurements carried out on the drop in the overall rate of polymerization and the amount of CO adsorbed. The dependences of the residual rates on the amounts of CO observed at 10 min and 60 min of polymerization time for KIPB through KIPF catalysts are shown in Fig. 3. It can be seen that the amounts of CO required for zero residual rate do not change so much at 10 min and 60 min of polymerization times for all catalysts. On the assump-

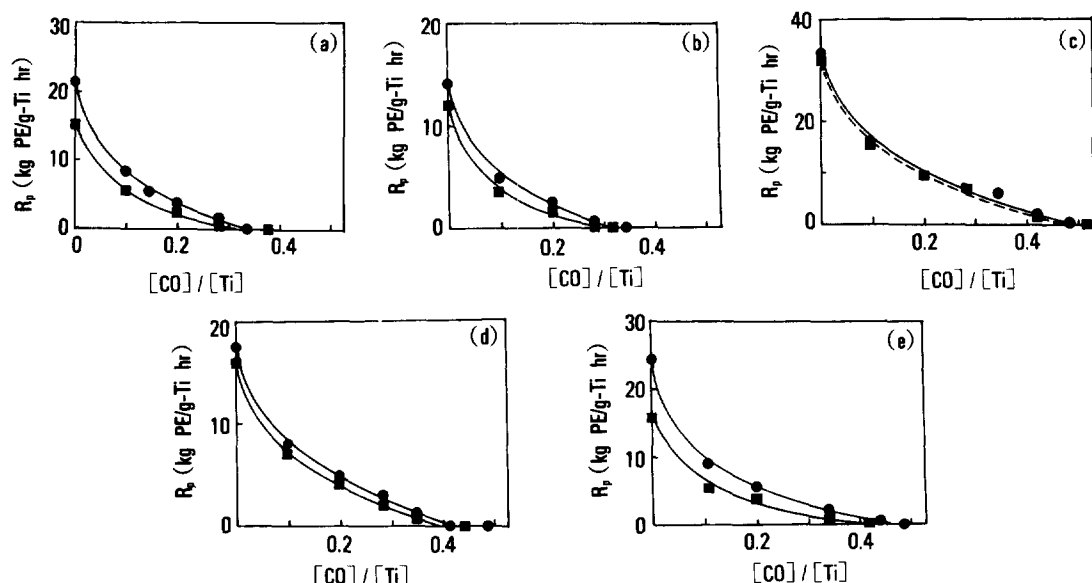


Fig. 3. Relation between the polymerization rate and the amount of CO added: (■) at 10 min; (●) at 60 min. Polymerization conditions are the same as those indicated in Fig. 2. (a) KIPB/ $\text{AlEt}_3$ , (b) KIPC/ $\text{AlEt}_3$ , (c) KIPD/ $\text{AlEt}_3$ , (d) KIFE/ $\text{AlEt}_3$ , and (e) KIPF/ $\text{AlEt}_3$  catalyst systems.

tion that one molecule of CO is adsorbed on each active site, the  $C^*$ -value may then be evaluated by extrapolation of the plots of percent drop in rate versus amount of CO adsorbed to 100% drop in rate at different polymerization times. The results are summarized in Table 1, together with the rate constant for chain propagation,  $k_p$ , calculated from the relation  $R_p = k_p C^* [M]$ , with the observed values of  $C^*$ , and the data for propylene polymerization obtained from the previous paper.<sup>5</sup>

As to the methods for the determination of active site concentration based on the assumption that a molecule of CO reacts with active centers quantitatively, the following remarks should be made. Considering a high extent of side reactions involved in the CO inhibited polymerization, the assurance that all CO has been used up is not a proof that the agent reacts with active sites selectively.<sup>10(a)-10(d)</sup> The  $C^*$ -values thus obtained should be considered as their upper limit.<sup>5,10</sup>

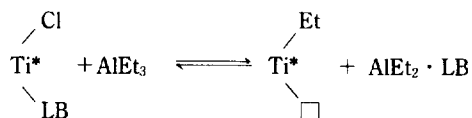
**Table 1.** The Number of Active Sites and the Propagation Rate Constant in the Propylene and Ethylene Polymerization with Various Catalyst Systems

Catalyst System (References)	Monomer	Temp. (°C)	Time (min)	$10^2 \times C^*$ (mol/mol Ti)	$k_p$ (l/mol s)
TiCl <sub>4</sub> /MgCl <sub>2</sub> /EB/AlEt <sub>3</sub> [9(e)]	Propylene	38	10	1.6	320
		38	30	1.0	320
		38	60	0.6	360
TiCl <sub>4</sub> /MgCl <sub>2</sub> /AlEt <sub>3</sub> [9(c)]	Propylene	70	—	0.7	800
TiCl <sub>4</sub> /MgCl <sub>2</sub> /AlEt <sub>3</sub> [9(c)]	Ethylene	75	—	36	13000
TiCl <sub>3</sub> /AlEt <sub>2</sub> Cl [9(f)]	Propylene	41	80	0.8	32
TiCl <sub>3</sub> /AlEt <sub>2</sub> Cl [9(f)]	Ethylene	60	—	0.7	78
TiCl <sub>3</sub> /AlEt <sub>3</sub> [9(e)]	Propylene	40	—	1.5	31
TiCl <sub>3</sub> /Al( <i>i</i> -Bu) <sub>3</sub> [9(g)]	Ethylene	75	—	0.6	14000
KIPB/AlEt <sub>3</sub> (5)	Propylene	50	10	19.0	120
		50	30	21.0	126
		50	60	21.0	122
KIPB/AlEt <sub>3</sub>	Ethylene	50	10	31.4	226
		50	60	33.7	267
KIPC/AlEt <sub>3</sub> (5)	Propylene	50	10	17.0	104
		50	30		
		50	60		
KIPC/AlEt <sub>3</sub>	Ethylene	50	10	28.4	209
		50	60	30.2	220
KIPD/AlEt <sub>3</sub> (5)	Propylene	50	5	26.0	221
		50	15	8.4	230
		50	30	5.7	234
		50	60	3.8	215
KIPD/AlEt <sub>3</sub>	Ethylene	50	10	47.0	313
		50	60	49.4	307
KIPE/AlEt <sub>3</sub> (5)	Propylene	50	5	33.0	149
		50	15	22.0	156
		50	30	17.0	153
		50	60	11.0	165
KIPE/AlEt <sub>3</sub>	Ethylene	50	10	39.0	207
		50	60	41.0	254
KIPF/AlEt <sub>3</sub>	Ethylene	50	10	40.1	177
		50	60	45.3	241

Table 1 shows that the number of active sites for the ethylene polymerization is higher than that for the propylene polymerization for all catalysts. For KIPB and KIPC catalysts, the  $C^*$ -values for ethylene polymerization are higher than that for propylene polymerization by 1.5 times without regard to polymerization time, and  $k_p$ -values are about 2-fold larger for the ethylene polymerization. On the other hand,  $C^*$ -values show large difference according to polymerization time for KIPD catalyst. At the early period of polymerization the  $C^*$ -values for ethylene polymerization are higher than those for propylene polymerization by 1.8 times, while the  $C^*$ -values are higher than by 13 times at 60 min of polymerization. The variation in the  $C^*$ -values with polymerization time for KIPE is also conspicuous. The  $C^*$ -values for ethylene polymerization are higher than that for propylene polymerization by 1.2 times at the early period of polymerization and by 3.7 times at 60 min. The  $k_p$ -values for the ethylene polymerization are always larger than those for the propylene polymerization, so that the overall activity should be much greater for ethylene polymerization than for propylene polymerization, if the rates are normalized based on the concentrations of monomer in solvent.

The  $C^*$ -values for the ethylene polymerization with KIPF catalyst in which DBP is assumed to be strongly coordinated to catalytic species increases from 0.401 mol/mol Ti at 10 min to 0.453 mol/mol Ti at 60 min.

Chien<sup>11</sup> studied the effect of external Lewis base on the polymerization of ethylene by the  $MgCl_2/EB/p\text{-cresol}/AlEt_3/TiCl_4$  catalyst activated with  $AlEt_3$ . They postulated two other functions for the Lewis base. The internal Lewis base complexes with those strongly acidic Ti sites, while the external one assures that these sites remain coordinatively saturated. In the absence of external Lewis base, the internal Lewis base ligands are dissociated,



Where LB is an internal Lewis base, and  $\square$  represents a vacant coordination position and the resulting Lewis acidic Ti sites can polymerize ethylene, but in the case of propylene these sites either produce stereoirregular polymers or are inactive possibly due to the over-reduction of Ti sites.

For the catalyst systems of the present work it may be seen that the readiness of dissociation is different from each other depending on the strength of interaction between catalytic species and the internal Lewis base. Chien neglected this specific point of view. The difference of the strength of interaction can be caused by the difference of the delicate operational procedures employed during catalyst preparation, even if the composition of the prepared catalyst is similar. The type of LB, mono- or di-ester, must be another factor determining the strength of interaction.

The dissociation to coordinatively unsaturated Ti sites is more active in KIPD catalyst than in KIPB or KIPC catalyst, because  $Ti^*\text{-LB}$  bond in KIPD catalyst was not so strong that a large amount of LB is removed from the catalyst surface forming a complex with  $AlEt_3$ . Comparing the results in the change of the number of active sites during ethylene and propylene polymerization for KIPD catalyst (Table 1), almost all dissociated Lewis acidic Ti sites are not active for the propylene polymerization but active for the ethylene polymerization. As a result, the active sites for the propylene polymerization with KIPD are deactivated by a second-order while those for ethylene polymerization are almost constant over a polymerization period. On the other hand, relatively small amount of coordinatively unsaturated Ti species which is active only for ethylene and is responsible for the slight increase in the  $C^*$ -values at the later stage of ethylene polymerization is assumed to be formed with KIPB, KIPC and KIPF catalyst during polymerization, because of the strong  $Ti^*\text{-LB}$  bond. It may be noted from Table 1 that the concentration of active sites active only for ethylene polymerization is 0.114-0.21 mol/mol Ti at the early period of polymerization.

Table 1 also shows that the  $C^*$ -values for the propylene polymerization with KIPB through KIPF catalyst are higher than that of  $TiCl_3$  and  $TiCl_4/MgCl_2/EB/AlEt_3$ , Montedison-Mitsui type catalyst, by one order of magnitude, and that the  $k_p$ -values of the KIPB through KIPE catalyst are the same order with magnesium chloride-supported catalyst and are higher than that of  $TiCl_3/AlEt_3$  by one order of magnitude. Accordingly the superior activity of the present catalyst systems to that of magnesium chloride-supported catalyst or  $TiCl_3$  is due to the higher  $k_p$ -values as well as to the higher  $C^*$ -values.

When comparing  $C^*$ -values for the propylene polymerization with different catalyst systems, it is important to state the appropriate time of determination. This is of considerable importance when dealing with the catalyst systems whose polymerization rates change sharply as a function of time. As shown in Table 1, the decreases of the  $C^*$ -values during propylene polymerization with Montedison-Mitsui type catalyst, KIPD, KIPE and KIPF are the first or second order with respect to the polymerization time and the  $k_p$ -values are almost constant throughout the decay of  $C^*$ . However, it seems that the time of determination of  $C^*$ -values is insignificant for ethylene polymerization with KIPB through KIPF catalyst, because both  $C^*$ -values and  $k_p$ -values do not change so much according to polymerization time without regard to the strength of interaction between catalytic species and LB. In this case only the initial  $C^*$ -values are thought to be a principal factor in determining the activity of catalyst since the values are constant within an experimental error or slightly increased during the long period of polymerization.

It is interesting to note from Fig. 2 and Table 1 that the catalysts characterized by the weak interaction between Ti species and LB, e. g., KIPD and KIPE, show higher concentration of active sites for ethylene polymerization than those characterized by strong interaction, e. g., KIPB and KIPF. This unexpected result might be due to the fact that considerable amounts of active sites which are

active only for ethylene polymerization are newly generated by the removal of LB from the catalyst matrix. The  $C^*$ -value of KIPD at the early period of polymerization (5 min) of propylene is much higher than that of KIPB at 10 min. The consideration of this difference of active sites between ethylene and propylene polymerization might be practically useful in developing the catalysts of good performance.

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## REFERENCES

1. F. J. Karol, *Catal. Rev. -Sci. Eng.*, **26**, 557 (1984).
2. P. C. Barbe, G. Cecchin, and L. Noristi, *Adv. Polym. Sci.*, **81**, 1 (1987).
3. V. Busico and P. Corradini, "Transition Metal Catalyzed Polymerizations", R. P. Quirk, Ed., Cambridge Univ. Press, New York, p. 551 (1988).
4. K. Soga, T. Shiono, and Y. Doi, *Makromol. Chem.*, **189**, 1531 (1988).
5. I. Kim and S. I. Woo, *Polym. Bull.*, **23**, 35 (1990); *J. Polym. Chem. Sci., Polym. Chem. Ed.*, submitted.
6. I. Kim and S. I. Woo, *Polymer (Korea)*, **16**(3), in press.
7. I. Kim, Ph. D. Dissertation, KAIST, Seoul, 1990.
8. Y. T. Jeong and D. H. Lee, *Makromol. Chem.*, **191**, 1487 (1990); Y. T. Jeong, D. H. Lee, and K. Soga, *Makromol. Chem., Rapid Commun.*, **12**, 5 (1991).
9. For example :
  - (a) P. Pino and R. Müllhaupt, *Angew. Chem. Int. Ed. Engl.*, **19**, 857 (1980).
  - (b) K. Soga, T. Shiono, and K. Yamamoto, *Chem. Lett.*, 425 (1982).
  - (c) Y. Hu and J. C. W. Chien, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 2003 (1988).
  - (d) Y. V. Kissin and A. J. Sivak, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3747 (1984).
  - (e) V. Busico, P. Corradini, A. Proto, and V. Savino, *Makromol. Chem.*, **186**, 1279 (1985).
10. For example :

- (a) A. D. Caunt, *Br. Polym. J.*, **13**, 22 (1981).
- (b) A. D. Caunt, *Catalysis (London)*, **1**, 234 (1977).
- (c) J. Mejzlik, M. Lesna, and J. Kratochvila, *Adv. Polym. Sci.*, **81**, 83 (1987).
- (d) A. D. Caunt, S. Davies, and P. J. T. Tait, "Transition Metal Catalyzed Polymerization", R. P. Quirk, Ed., Cambridge Univ. Press, New York, p. 105 (1988).
- (e) T. Keii, E. Suzuki, M. Tamura, M. Murata, and Y. Doi, *Makromol. Chem.*, **185**, 2285 (1982).
- (f) H. Schnecko, K. A. Jung, and W. Kern, "Coordination Polymerization", J. C. W. Chien, Ed., Academic Press, New York, p. 73 (1975).
- (g) N. B. Chumaevskii, *Makromol. Chem.*, **177**, 747 (1976).
- 11. J. C. W. Chien, "Transition Metal Catalyzed Polymerization", R. P. Quirk, Ed., Cambridge Univ. Press, New York, p. 55 (1988).