

고활성, 고입체규칙성 촉매에 의한 슬러리상 및 기상 프로필렌 중합의 비교연구

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A Comparative Study of Slurry and Gas Phase Polymerization of Propylene Using a Highly Active and Isospecific Catalyst

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요 약 : 이에톡시 마그네슘을 사부톡시 티탄, 무수프탈산 및 사염화 티탄과 반응시켜 합성한 새로운 염화마그네슘 담지 염화티탄촉매를 이용하여 슬러리상 및 기상 프로필렌중합의 비교연구를 행하였다. 25~60°C의 온도범위에서 삼에틸알루미늄/삼에톡시페닐 실란(PTES)를 첨가하여 수행한 프로필렌중합의 중합속도는 슬러리상에서보다 기상에서 더 낮았으나 중합속도-시간곡선은 60°C에서 행한 기상중합을 제외하고는 공히 일차로 비활성화 되었다. 이와같은 중합매체의 변화에 따른 중합속도의 변화는 특수하게 설계한 중합실험으로 확인할 수 있었다. 슬러리상 중합의 겔보기활성화에너지(25~60°C의 온도범위에서 10.3 kcal/mol)는 기상중합의 겔보기활성화에너지(25~50°C의 온도범위에서 4.3 kcal/mol)보다 훨씬 컸는데 이와같은 차이는 중합활성점의 형성과정의 차이로 설명할 수 있었다. 고분자의 입체규칙도(II)의 변화는 활성의 변화와 비교하여 볼 때 중합공정이나 온도에 상관없이 무시할 수 있을 정도였다.

Abstract : A comparative study has been made for propylene polymerization in gas phase and slurry phase reactors using a new $MgCl_2$ -supported $TiCl_4$ catalyst prepared by the reaction of $Mg(OEt)_2$ with $Ti(OBu)_4$, phthalic anhydride, and $TiCl_4$. The experimental results obtained from polymerizations combined with $AlEt_3$ /phenyltriethoxy silane (PTES) showed that the rate of polymerization was lower for gas phase than for slurry phase within an experimental temperature range (25-60°C), even if rate-time profiles obeyed first-order deactivation for both cases except the gas phase polymerization at 60°C. The change of polymerization rate according to the variation of polymerization medium could be confirmed by a specially designed polymerization. The apparent activation energy of slurry phase polymerization (10.3 kcal/mol over a temperature of 25-60°C) was much larger than that of gas phase (4.3 kcal/mol over a temperature range of 25-50°C), and the differences could be explained by referring the formation process of polymerization centers. The change of isotacticity(II) of polymer was ne-

gligible without regard to the process and temperature of polymerization compared with the large differences of activity.

INTRODUCTION

Recent progress in propylene polymerization reactor technology has made it possible to produce polypropylene(PP) with desired properties by liquid slurry, bulk, and gas phase processes using various types of Ziegler-Natta catalysts.¹ Among current industrial propylene polymerization processes, the liquid slurry process is still the most widely used. In the latter process propylene is polymerized to maintain the propylene in the liquid phase. While this process has some advantages such as good temperature control, flexibility of reactor operation, and high content of solids in the slurry, redundant step to recover inert solvent is needed. Gas phase polymerization of monomer in which gaseous monomer is polymerized over solid catalyst in the presence of aluminum alkyl cocatalyst is a rather recently-developed economic process. In this process, polymer separation, diluent recovery, and polymer drying steps may be eliminated. This process has been extensively commercialized for polyethylene. For PP, it is far less available in industry than either liquid slurry process or liquid propylene bulk process.² However, commercial importance of gas phase polymerization of propylene is increasing due to the various advantages over slurry and bulk processes.³

In laboratory studies semi-batch slurry reactors are most commonly used since they are much easier to operate than semi-batch gas phase polymerization reactors. There are two reasons which delayed the use of propylene gas phase polymerization reactor. Firstly, the dead spots in gas phase reactor causing agglomeration cannot be completely avoided. Secondly, a significant temperature gradient inside catalyst particles can be present due to the poor heat transfer between gas phase and catalyst particles.

In the present study, polymerization of propy-

lene was carried out in a slurry reactor and a gas phase reactor with a highly active and isospecific catalyst. The objective of the study was to directly compare the polymerization rate profiles and isospecificity obtained in slurry phase polymerization of propylene with those obtained in gas phase.

EXPERIMENTAL

Materials

Polymerization grade of propylene(Korea Petrochem. Co.) was used after passing it through columns of Fisher RIDOX catalyst and molecular sieve 5A/13X. Extra pure heptane (Tedia Co., USA) was dried over sodium drops and fractionally distilled before use. Triethyl aluminum (TEA, Aldrich Chemicals, USA) was used without further purification. Reagent grade of sodium chloride with a diameter of about 0.5 mm was dried at 500 °C for 10 hr, then for 3 hr at 200 °C under vacuum (10^{-3} torr) before use.

Catalyst

A highly active and isospecific catalyst with a diester as an internal donor [$\text{MgCl}_2/\text{dibutyl phthalate}(\text{DBP})/\text{TiCl}_4$] was prepared from the reactions of $\text{Mg}(\text{OEt})_2$ with $\text{Ti}(\text{OBu})_4$, phthalic anhydride, and TiCl_4 . The procedure for the preparation of the catalyst has been given previously.⁴

Polymerization

Slurry phase polymerization of propylene in n-heptane was carried out in a 250 ml reaction bottle. The procedures are the same as those reported previously.⁴ Gas phase polymerization of propylene was performed using a 250 ml reactor. In order to improve the control of polymerization temperature and prevent the coalescence of dry catalyst particles 10 ml of sodium chloride particle was added to the reactor. The reaction mixture was agitated by a magnetic stirrer having two blades at both ends. A given amount of catalyst slurry

and cocatalyst (15wt% n-hexane solution) was introduced into the reactor with a PTES, which was then evacuated at 50 °C for 15 min in order to remove the solvent completely. Propylene was admitted into the reactor quickly at a polymerization temperature and then the polymerization was started with a vigorous stirring (500 rpm). The instantaneous rates of polymerization were measured according to the previous method.⁴

Isotactic index(II) was determined from the fraction which is insoluble in boiling heptane using a Soxhlet extractor. The morphology of polypropylene was observed with a SEM (JEOL JSM-T20), using a gold sputtering techniques.

RESULTS AND DISCUSSION

The effect of temperature on the rate of slurry phase polymerization of propylene is shown in Fig. 1. At 60 °C the maximum rate of polymerization ($R_{p,m}$) was occurred within a couple of minutes followed by a first-order deactivation. At lower temperature (25 °C) it took 15 min to reach $R_{p,m}$. At 25 °C the value of $R_{p,m}$ is less than half of that at 60 °C. The difference of $R_{p,m}$ values is actually more conspicuous when considering the monomer

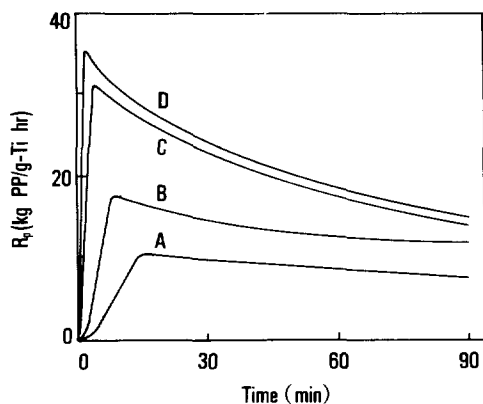


Fig. 1. Kinetic curves of slurry phase polymerization of propylene obtained at $[Ti] = 4.24 \times 10^{-4}$ g, n-heptane = 100 ml, $[propylene] = 0.43$ mol/l, $[AlEt_3] = 8.9$ mol/l, $[PTES]/[AlEt_3] = 0.1$ and various temperatures of : (A) 25 °C, (B) 40 °C, (C) 50 °C, and (D) 60 °C.

concentration in solvent at 25 °C is about twice as large as that at 60 °C, since the polymerization rate is generally proportional to monomer concentration. The maximum yield over a 90 min of polymerization is recorded at 60 °C.

The situation was somewhat different in the case of gas phase polymerization. Figure 2 represents the rate-time profiles for the gas phase polymerization. The concave dot profiles at the beginning of polymerization appear since the polymerization starts by the introduction of propylene. The type of kinetic profiles, a few minute of acceleration followed by a first-order deactivation, is corresponding to that found during slurry phase polymerization, though the maximum is less pronounced. Similar result was reported for the propylene polymerization with a first generation catalyst.⁵ The maximum productivity was appeared at 50 °C. At 60 °C the $R_{p,m}$ is significantly lowered compared with that obtained in slurry phase, from 35 to 23 kg pp/g-Ti hr. Comparing the average rates of 90 min of polymerization the difference becomes more conspicuous since the rate at 60 °C in the gas phase polymerization deactivates by a second-order.

The depression of the rate observed in the gas

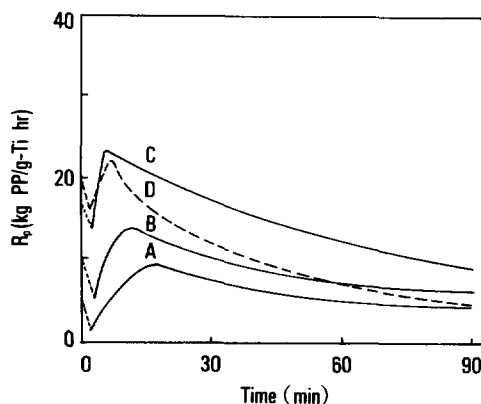


Fig. 2. Kinetic curves of gas phase polymerization of propylene obtained at $[Ti] = 4.24 \times 10^{-4}$ g, $P = 1$ atm, $[AlEt_3] = 8.9$ mmol/l, $[PTES]/[AlEt_3] = 0.1$ and various temperatures of : (A) 25 °C, (B) 40 °C, (C) 50 °C, and (D) 60 °C.

phase polymerization is caused by the decrease in the monomer concentration at the surface of catalyst. Even if it is difficult to measure the actual monomer concentration at the catalyst surface, the monomer concentration of slurry phase polymerization is thought to be much higher than that of gas phase polymerization, since the monomer concentration in solvent (slurry phase) is about 30-fold higher than that of gas phase at the same monomer pressure. As mostly admitted, R_p is proportional to the monomer concentration. The decrease of R_p may also be partly due to the blocking of active sites caused by the agglomeration due to the poor heat transfer. In slurry phase polymerization, a build-up by agglomeration of subparticles (about $0.3\ \mu\text{m}$ in diameter), is disintegrated easily. Thus the mass and heat transfer from the catalytically active sites in the core of the growing polymer particles is dependent on how effectively the surrounding gas phase, which is a very poor heat transfer agent, can remove the heat of polymerization outside of the reactor.⁶ As a result, the temperature of the growing polymer particles can be much higher than that measured by temperature probes in the reactor of gas phase polymerization. Especially the initial temperature rise for highly active catalyst may be above the melting point of polypropylene. This is likely to be the cause of sticking and agglomeration problems so that only part the catalytically active sites is effectively used. Heat transfer limitations are not an only factor to reduce the productivity of the catalyst and induce the abnormal second order deactivation [see Fig. 2(D)]. The poor thermal stability of catalytically active species in the gas phase polymerization is one of the reasons why the polymerization rate is small in the gas phase reaction.

In order to get a better understanding on the productivity a specially designed polymerization was performed and the result is shown in Fig. 3. After 30 min of usual gas phase polymerization at 50°C (stage A), 30 ml of *n*-heptane was introduced into the reactor, then recorded the instantaneous rate for 30 min (stage B). The increase of the rate

can be observed by the addition of solvent. The increase of monomer concentration by the addition of solvent must be a main reason for the sharp increase in R_p . This may also be partly due to removal of agglomerated polymers which cause heat transfer limitations and block active sites. The agglomeration of polymer at initial stage of gas phase polymerization can be observed from a SEM photograph of nascent polymer taken at $t=10$ min in Fig. 3 [see Fig. 4(A)]. Shapeless and bulky polymer particles, on which numerous sticky fibrills are grown, are formed due to the meting of the polymer. However, polymer morphology is considerably changed by the addition of solvent. It leads to an increase in the monomer concentration on the surface of catalyst and in the rate of formation of polymerization centers from the active centers which are ineffective in gas phase polymerization due to the blocking caused by a poor heat transfer. Figure 4(B) shows SEM photograph of polymer taken at $t=45$ min in Fig. 3. It can be seen that many globular particles which are generally observed from the polypropylene polymerized with a

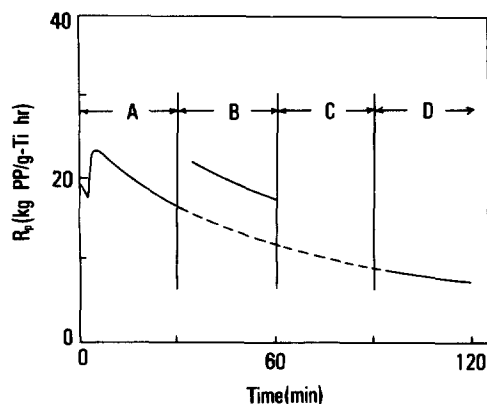


Fig. 3. Effect of solvent on gas phase polymerization of propylene. Gas phase polymerization is performed at $[\text{Ti}] = 4.24 \times 10^{-4}\ \text{g}$, $P = 1\ \text{atm}$, $[\text{AlEt}_3] = 8.9\ \text{mmol/l}$, $[\text{PTES}]/[\text{AlEt}_3] = 0.1$ (stage A), 30 ml of *n*-heptane is injected (stage B), all gases and liquid are pumped out under vacuum (10^{-3} torr) (stage C), and gas phase polymerization is again carried out (stage D).

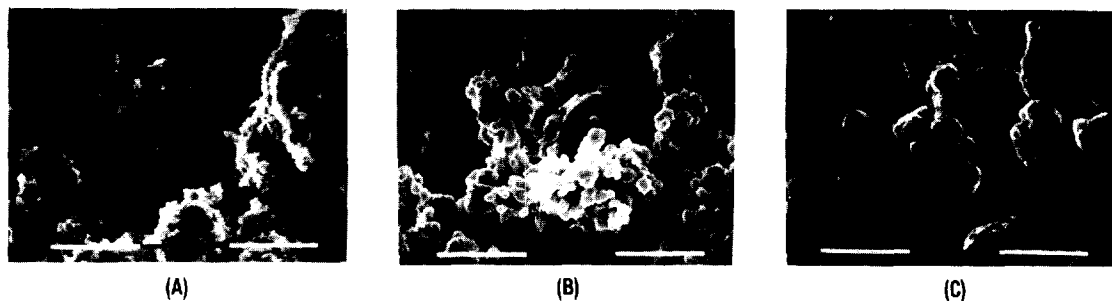


Fig. 4. SEM photographs($\times 3,000$) of as-polymerization polypropylenes (A) after 10 min polymerization time (stage A in Fig. 3), (B) after 45 min(stage B in Fig. 3), and (C) after 110 min(stage D in Fig. 3).

highly active supported catalyst appear, and that the sticky fibrils as shown in Fig. 4(A) disappear.

After pumping out the solvent including propylene (stage C in Fig. 3), gas phase polymerization was performed over again (stage D). The rate is decreased to coincide with original rate profile, due to the decrease in monomer concentration at catalyst surface. It is interesting to follow up the variation in the polymer morphology at this stage. SEM photograph of polymer taken at $t = 110$ min (Fig. 4(C)) shows that the blocking of active sites is recurred. The subparticle size of polymer taken at $t = 110$ min is much larger than that taken at $t = 45$ min due to the agglomeration of neighboring particles.

It has been generally accepted that the overall polymerization rate (R_p) is first order with respect to monomer concentration in the olefin polymerization with Ziegler-Natta catalysts. Therefore,

$$R_p = k_p [M]_b$$

$$k_p = k_0 \exp(-E_{app}/RT)$$

$$\ln(R_p/[M]_b) = -E_{app}/RT + \text{constant}$$

where $[M]_b$ is the bulk monomer concentration and E_{app} is the apparent activation energy. Figure 5 shows the Arrhenius plots based on average polymerization rate in the range of temperature between 25°C and 60°C . Linear relations are obtained from overall experimental temperature range for slurry phase, while from 25°C to 50°C for gas phase polymerization. These results demon-

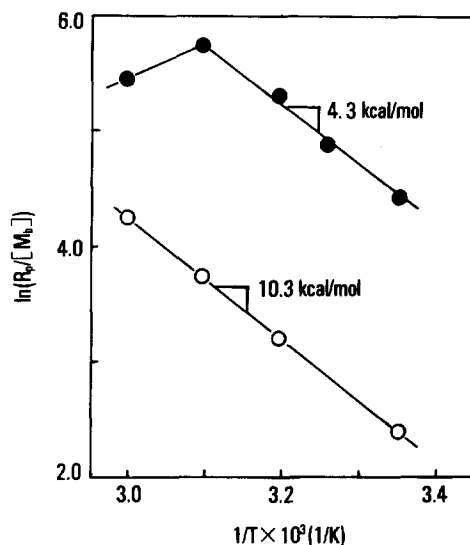


Fig. 5. Arrhenius plots of (A) gas phase and (B) slurry phase polymerization over 90 min.

strate that the thermal stability of catalyst active sites is better in slurry phase polymerization than in gas phase one. The apparent activation energies calculated from the slopes of plots are listed in Table 1 with reference data. It appears that the activation energy in the gas phase polymerization is always smaller than that in the slurry phase polymerization. The intrinsic solvent effects on the catalyst matrix during the formation process of polymerization centers might be a factor for this result.¹³

Chemical aspects of the interaction between

Slurry and Gas Phase Polymerization of Propylene

Table 1. The Apparent Activation Energy in Propylene Polymerization

Catalyst System	Temperature Range (°C)	E _{app} (kcal/mol)	Polymerization Process	Reference
This work	25-60	10.3	Slurry	
	25-50	4.3	Gas	
TiCl ₃ -AlEt ₃ Cl	40-60	11.3	Slurry	12
		5.5	Gas	
MgCl ₂ /TiCl ₄ /EB-AlEt ₃	1-41	11.9	Slurry	13
	1-41	5.3	Gas	14
Mg(OEt) ₂ /BzCOCl/TiCl ₄ -AlEt ₃	25-42	8.5	Slurry	15

TiCl₃ and organometallic compounds have been studied by many authors.⁷⁻¹¹ The following qualitative picture of the interaction between transition metal halides (TMH) and organometallic compounds can be envisaged in the presence or absence of solvent. Transition metal halides when mixed with solution of AlEt₃ or AlEt₂Cl under conditions typical for olefin polymerization (0-80 °C) undergo reaction that is restricted mostly to their surface. This interaction includes three main reactions : (a) substitution of chlorine atoms on the TMH surface by alkyl groups, i. e., the formation of organic derivatives of the transition metals ; (b) partial destruction of these organometallic compounds resulting in the liberation of gaseous products and transition metal reduction ; and (c) complexation between the remaining surface alkyl derivatives of the transition metals and the organoaluminum compounds present in solution. These three reactions are competitively occurred during the formation process of polymerization centers with are capable of polymerizing propylene. It is safe to say that uniform dispersion of TMH (typical of the current catalyst systems including the catalyst system of the present study) influences the catalytic activity in two ways. The presence of numerous defects in the high-surface-area solids induces easy cleavage of the crystals with the formation of fresh surfaces and an increase in the catalytic activity. One the other hand, the increase in the rate of the reduction results in instability of the centers. Apparently this phenomenon is the principal

reason for the decay-type polymerization kinetics that are characteristic of the current highly active catalyst systems. However, it is pertinent to say here that abundant complexation and substantial transition metal reduction (at high temperature) can dramatically reduce the catalytic activity regardless of the type of catalyst.

The extent of the three main reactions between TMH and AlEt₃ that lead to form polymerization centers might be dependent on the conditions of polymerization as well as the type of catalyst. Burfield⁹ studied the formation of organic derivatives of the transition metals from the TiCl₃-AlEt₃ interaction and showed that only 33% of all surface Cl is removed from the TiCl₃ in gas phase systems (dry interaction between TiCl₃ and AlEt₃) and that the efficiency of conversion does not change so much according to the reaction temperature. However, the extent of the reaction was reported to be significantly dependent on the temperature of contact in the slurry phase polymerization. Even if all the surface chlorine atoms are released in solution even at 10-30 °C, the conversion of the reaction to form AlEt₂Cl by the interaction of AlEt₃ with TiCl₃ is highly dependent on the temperature, i. e., low at lower temperature and vice versa.⁹⁻¹¹ This inherent discrepancies in the activation of transition metals to form polymerization centers lead to the difference in the activation energy of slurry phase polymerization from gas phase, even if a more complicated situation is expected in the case of the current highly active catalysts based on

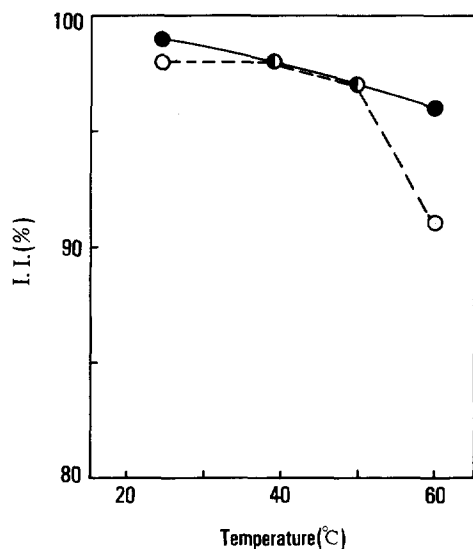


Fig. 6. Variation of isotactic index with polymerization temperature : (A) slurry phase, (B) gas phase.

MgCl₂, internal and external donor in addition to TMH and AlEt₃. High temperature will be a necessary condition for the achievement of sufficient concentration of polymerization centers in slurry phase, but the temperature effect on the formation of polymerization centers will be alleviated in gas phase.

The peculiar differences in the activation process of polymerization centers are also expected to lead to the variation of isotacticity of the polymer. However, both polymers, either those from slurry phase polymerization or those from gas phase, show similar isotacticity except polymer obtained at 60 °C by gas phase polymerization (see Fig. 6). Even if this result is difficult to explain without considering the complicated interactions among TMH, AlEt₃, MgCl₂, internal donor and external donor,⁴ it can be assumed that the process of catalyst activation, disintegration into subparticles followed by the formation of organic derivatives of TMH, is not a vital part of isospecific center formation, and that effective utilization of catalyst subparticles effects an increase in the number of active centers but does not influence their structure. Isospecificity of polymer obtained at 60 °C from the

gas phase is unexpectedly lower than others. High temperature in the core of the catalyst caused by heat transfer limitations caused the structure of isospecific active sites to be changed, which leads to a decline of isotacticity.

CONCLUSION

From a direct comparison of productivity for gas and slurry phase polymerization of propylene with a highly active and isospecific catalyst system, following conclusions are drawn :

1. The rates observed in gas phase polymerization were lower than those in slurry phase one because the blocking of active sites caused by heat transfer limitations is distinctive for the former case.
2. A specially designed experiment showed that polymers blocking the polymerization centers are removed by the addition of small amount of solvent.
3. The apparent activation energy for gas phase was smaller than that for slurry phase polymerization by about two-fold due to the differences in the formation process of polymerization centers.
4. There was no considerable difference in isotacticity between gas and slurry phase unless the crystal structure is changed during polymerization.

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