

# Comonomer Enhancement Effect of 1-Hexene in Ethylene Copolymerization Catalyzed over $\text{MgCl}_2/\text{THF}/\text{TiCl}_4$ Catalysts

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## SYNOPSIS

Homo- and copolymerization of ethylene were performed by using a catalyst system composed of  $\text{TiCl}_4/\text{THF}/\text{MgCl}_2$  complex activated with  $\text{AlEt}_3$  at  $70^\circ\text{C}$  and 3 atm. To investigate the effect of the compositional difference of the catalyst on the rates of homo- and copolymerization and on the reactivity in ethylene-hexene copolymerization, a series of six catalysts with different compositions ( $\text{Mg}/\text{Ti} = 0.4\text{--}16.5$ ) were prepared by coprecipitation. The catalytic activity in ethylene polymerization increased sharply with the  $\text{Mg}/\text{Ti}$  ratio from 21 ( $\text{Mg}/\text{Ti} = 0.4$ ) to 1477 kg PE/g-Ti h ( $\text{Mg}/\text{Ti} = 16.5$ ). The activity in copolymerization with 1-hexene also increased with  $\text{Mg}/\text{Ti}$  ratio. The values of  $r_1$  were 120, regardless of  $\text{Mg}/\text{Ti}$  ratios within the experimental error range. Enhancement of the polymerization rate by the addition of 1-hexene in the reaction medium was observed only for the catalysts of low  $\text{Mg}/\text{Ti}$  ratio. This unusual effect of 1-hexene on the polymerization rate was explained by chemical and physical processes that occurred during polymerization.

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## INTRODUCTION

Since linear low-density polyethylene (LLDPE) appeared as an important product in the middle of the 1970s,<sup>1</sup> the copolymerization of ethylene with  $\alpha$ -olefins higher than propylene has aroused renewed interest, due mainly to the growing commercial significance of LLDPE.<sup>2,3</sup> The factors affecting the kinetics of olefin polymerization have been studied extensively.<sup>4-7</sup> Nevertheless, the factor controlling the copolymerization kinetics of a given catalyst system has not been completely understood. The kinetic behavior of Ziegler-Natta catalysts is known to be complicated and to be controlled by both chemical and physical processes.<sup>7</sup> A growing number of catalyst systems has exhibited significantly different kinetics for ethylene homopolymerization and its copolymerization with higher  $\alpha$ -olefins.<sup>6-8</sup> The

outstanding features of the  $\text{MgCl}_2$ -supported catalyst systems are the rate-enhancement effect and the kinetic changes in the copolymerization of ethylene with higher  $\alpha$ -olefins. Postulated explanations for these effects include increased ethylene solubility and diffusivity in the copolymer matrix,<sup>9</sup> the physical disintegration of the catalyst matrix particles thus exposing new potential active centers,<sup>10</sup> and the chemical effects of the comonomer on  $k_p$  or the rate of catalyst activation.<sup>6,7,11</sup>

This study presents a peculiar comonomer effect on the kinetics of ethylene polymerization catalyzed over a series of catalysts prepared by coprecipitating the solvated complex containing magnesium and titanium chloride, and tetrahydrofuran as a solvent. Unlike the typical  $\text{MgCl}_2$ -supported catalyst, this bimetallic complex is a well-defined compound of known structures.<sup>12-17</sup> These authors focused their attention on how the composition of the bimetallic complexes, the  $\text{Mg}/\text{Ti}$  ratio, influences catalytic activity in homo- and copolymerization and sensitivity to comonomer incorporation.

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## EXPERIMENTAL

### Materials

A polymerization grade of ethylene (Yukong Ltd., South Korea) and nitrogen of extrapure grade were further purified with the columns of Fisher RIDOX catalyst and molecular sieve 5Å/13X. 1-Hexene (Aldrich, U.S.A.) was passed through molecular sieves 5Å and 13X. *n*-Hexane of extrapure grade (Duksan, South Korea) was dried over sodium metal in a nitrogen atmosphere and passed through the columns of CaSO<sub>4</sub> and molecular sieve 5Å before use. An analytic grade of tetrahydrofuran (THF, J. T. Baker Chemical Co., U.S.A.) was purified by refluxing with LiAlH<sub>4</sub> for several hours. TiCl<sub>4</sub>, AlEt<sub>3</sub>, and anhydrous MgCl<sub>2</sub> (Aldrich) were used without further purification.

### Catalyst Preparation

In a 2 L round-bottom flask equipped with a stirrer, condenser, and inlet tube for N<sub>2</sub>, 120 mmol of MgCl<sub>2</sub> was mixed with 1 L of pure THF under nitrogen. The temperature of the reaction mixture was subsequently increased using a heating bath to the boiling point of THF while vigorously stirring. After MgCl<sub>2</sub> was completely dissolved, this homogeneous solution was divided into six identical portions. Prescribed amounts of TiCl<sub>4</sub> were added dropwise for 15 min to each portion at room temperature. Upon complete addition, the contents of the flask was refluxed for 2 h while stirring. After MgCl<sub>2</sub> and TiCl<sub>4</sub> were dissolved, the bimetallic MgCl<sub>2</sub>/THF/TiCl<sub>4</sub> complex composition was isolated by precipitation with *n*-hexane at room temperature. The supernatant liquid was decanted. The remaining yellow solid complex was washed with 100 mL of *n*-hexane three times. These solid complexes were dried at room temperature in vacuum and stored under inert atmosphere.

### Polymerization

Slurry polymerization was performed in a 1 L autoclave under a constant pressure of ethylene. A prescribed amount of AlEt<sub>3</sub> and 500 mL of *n*-hexane were introduced into the reactor in a nitrogen stream. 1-Hexene was also introduced in the case of copolymerization. After evacuation, ethylene was introduced at the polymerization temperature. Polymerization was started by breaking the glass ampule containing the prescribed amount of catalyst. The rate of polymerization was determined from the rate of ethylene consumption, measured by a hot-

wire flowmeter with a personal computer directly connected to it through an A/D converter. Ethylene concentrations in the liquid phase were calculated with a computer program for the gas-liquid phase equilibria based on Chao-Seader correlations.<sup>18</sup> Details on the polymerization setup were described elsewhere.<sup>10</sup>

### Copolymer Characterization

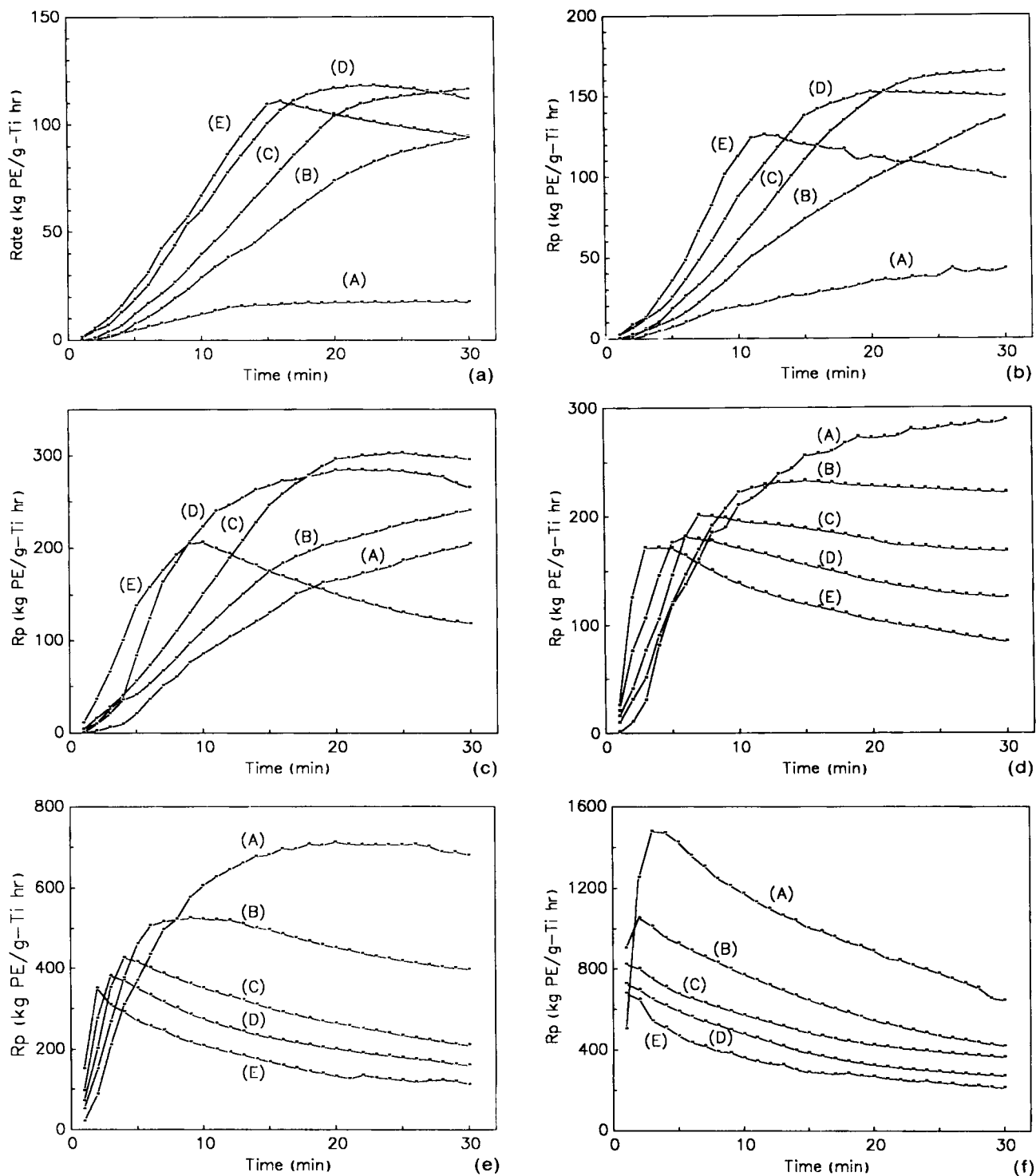
Copolymer compositions were measured by the IR method (with a Perkin-Elmer 130C infrared spectrophotometer) using the calibration curve reported by Nowlin et al.<sup>19</sup> based on an A<sub>1380</sub>/A<sub>1370</sub> absorbance ratio.

The morphology of catalysts and polymers was examined using a scanning electron microscope (SEM) technique at inert atmosphere. The average particle size and particle-size distribution of the polymer and catalyst were determined by a Malvern 2600C microphotosizer instrument. Ethylene-1-hexene copolymers were fractionated with boiling heptane in a Soxhlet apparatus to measure the amount of insoluble heptane.

## RESULTS AND DISCUSSION

Certain features of Ziegler-Natta catalysts have been described to allow classification to be made based on the operational methods used to prepare the catalysts.<sup>2,3,20</sup> One method of catalyst preparation is to dissolve the titanium and magnesium compound in an alcohol or an ether and then to evaporate the solvent so that the titanium compound can be precipitated onto the carrier.<sup>13,20</sup> In such preparations, the Ti and Mg components are not separated in the precipitation stage but, rather, produce Mg/Ti bimetallic complexes having different structures. These complexes were described in the literature.<sup>12,14-16</sup>

We have investigated a series of six catalysts prepared with MgCl<sub>2</sub>, THF, and TiCl<sub>4</sub> to evaluate their behavior in ethylene homo- and copolymerization. These catalysts prepared according to the different molar ratios of Mg/Ti were previously characterized by various methods.<sup>10,14,15</sup> During the dissolution of MgCl<sub>2</sub> and TiCl<sub>4</sub> in THF, MgCl<sub>2</sub>(THF)<sub>2</sub> and TiCl<sub>4</sub>(THF)<sub>2</sub> are formed. Reaction of these two complexes at various stoichiometric ratios, e.g., Mg/Ti = 1 or 2, yields several ionic complexes such as [TiCl<sub>5</sub>(THF)]<sup>-</sup> anion and [Mg(THF)<sub>*n*</sub>]<sup>2+</sup>, [MgCl(THF)<sub>*n*</sub>]<sup>+</sup>, and [Mg<sub>2</sub>(μ - Cl)<sub>3</sub>(THF)<sub>6</sub>]<sup>+</sup> cationic species.<sup>14,15</sup> A series of six catalysts prepared in this study, MT-1, MT-2, MT-3, MT-4, MT-5,



**Figure 1** The rate profiles of ethylene homo- and copolymerization catalyzed over (a) MT-1 catalyst, (b) MT-2, (c) MT-3, (d) MT-4, (e) MT-5, and (f) MT-6. Polymerization conditions:  $T = 70^{\circ}\text{C}$ ,  $P = 3 \text{ atm}$ ,  $[\text{AlEt}_3]/[\text{TiCl}_4] = 128$ . Caption (A) in each figure means homopolymerization; (B) means  $(C_{\text{H}}/C_{\text{E}})_{\text{mon}} = 1.16$ ; (C)  $(C_{\text{H}}/C_{\text{E}})_{\text{mon}} = 2.18$ ; (D)  $(C_{\text{H}}/C_{\text{E}})_{\text{mon}} = 3.64$ ; (E)  $(C_{\text{H}}/C_{\text{E}})_{\text{mon}} = 5.82$ .

and MT-6, have Mg/Ti molar ratios of 0.4, 1.0, 2.1, 3.1, 5.2, and 16.5, respectively.

Homo- and copolymerization of ethylene and 1-

hexene have been carried out with these catalysts at different feed ratios. Figure 1 shows the polymerization rates as a function of time for each cat-

alyst. The polymerization rates in the homopolymerization of ethylene increase sharply as the Mg/Ti ratio of the catalyst increases. MT-1, MT-2, MT-3, MT-4, and MT-5 exhibit an accelerating-type polymerization rate profile, whereas MT-6 exhibits a decaying type. The time to reach the maximum rate ( $R_{p,m}$ ) is reduced from 50 min (MT-1) to 3 min (MT-6). It is interesting to note the relationship between the catalytic activity and the Mg/Ti ratio of the catalyst. As the Mg/Ti ratio increases from 0.4 (MT-1) to 16.5 (MT-6) by about 41-fold, the  $R_{p,m}$  increases from 21 to 1477 kg PE/g-Ti h by about 70-fold. This result demonstrates that a better opportunity to expose and isolate the amount of Ti active species is provided at higher Mg/Ti ratio. In addition, the formation of discrete chemical complexes resulting from the reaction of a stoichiometric amount of Mg complexes and Ti complexes<sup>14,15</sup> is not a necessary condition to obtain a highly active catalyst.

The presence of 1-hexene as a comonomer caused major changes in the polymerization kinetics, as shown in Figure 1. When 1-hexene is present, the consumption rate of ethylene increased significantly compared to that for ethylene homopolymerization by MT-1, MT-2, and MT-3 catalysts, whereas ethylene consumption rates for MT-4, MT-5, and MT-6 catalysts are smaller than that in the ethylene homopolymerization. The homo- and copolymerization results obtained with six catalysts are summarized in Table I. The copolymerization data in Table I have been obtained in the case of the [1-hexene]/[ethylene] ratio of 2.18. The extent of the activity enhancement or decrease due to the presence of 1-hexene is shown as the ratio of the  $R_{p,m}$

value for each copolymerization to that of homopolymerization. The larger the extent of activity enhancement is, the lower the Mg/Ti ratio of the catalyst is. At the higher Mg/Ti ratio, catalytic activities in the copolymerization decreased significantly. It is also very interesting that the time required to reach  $R_{p,m}(t_{max})$  decreases as the Mg/Ti ratio and the 1-hexene concentration increase. The catalysts of low Mg/Ti ratio (MT-1 to MT-4) change their kinetic behavior from the acceleration type to the slightly decay type in the copolymerization (see Fig. 1), as the 1-hexene concentration increases.

The enhanced or decreased rates of copolymerization of ethylene and 1-hexene by Ziegler-Natta catalyst systems that are reported in this paper are not entirely new findings. However, it is unusual to observe the contrary comonomer effect in the copolymerization with a series of catalysts of the same type. There have been many reports<sup>6-8</sup> on the copolymerization of ethylene and  $\alpha$ -olefins with  $MgCl_2$ -supported catalysts. Rate enhancement has been observed in all  $MgCl_2$ -supported catalyst systems, even if the degree of rate enhancement depends on the types of catalyst system and comonomer. The physical effects of comonomer enhancement effect are due to the increased ethylene solubility and diffusivity in the copolymer matrix. The chemical effect of the comonomer on the propagation rate constant ( $k_p$ ) and the rate of catalyst activation are also reported.<sup>6-8</sup>

In explaining the complicated effects of the rate enhancement and decrease observed in the catalyst system of the present study, the dynamic nature during the disintegration of the catalyst matrix and the aggregation of polymer particles (physical pro-

**Table I** Homo- and Copolymerization of Ethylene and 1-Hexene with a Series of Six Catalysts

Catalyst	$\frac{Mg}{Ti}$	Polymerization	$R_{p,m}$ (kg PE/g-Ti h)	$t_{p,m}$ (min)	$\frac{R_{p,m}^{co}}{R_{p,m}^{homo}}$	$\bar{R}_{p,30\ min}$ (kg PE/g-Ti h)
MT-1	0.4	Homo-	21.0	50		13.2
		Co-	118.1	24	5.62	80.2
MT-2	1.0	Homo-	49.5	43		25.4
		Co-	164.8	29	3.33	96.1
MT-3	2.1	Homo-	220.9	37		118.3
		Co-	301.7	24	1.37	203.8
MT-4	3.1	Homo-	291.6	31		214.6
		Co-	200.8	8	0.69	164.4
MT-5	5.2	Homo-	712.2	20		580.6
		Co-	425.4	4	0.60	288.1
MT-6	16.5	Homo-	1477.0	3		1000.9
		Co-	820.1	1	0.55	518.3

cesses) should be considered as well as the chemical effect of comonomer on the propagation step. First of all, it can be speculated that 1-hexene facilitates the activation of additional sites. In this case, chemically different active sites can be generated by 1-hexene as proposed by many authors.<sup>6,21,22</sup> This explanation seems not to be supported by the copolymerization results obtained in the present study, because a series of six catalysts are assumed to have the identical catalytically active precursor: the  $[\text{TiCl}_5(\text{THF})]^-$  anion. If the rate was increased by the generation of additional sites, the rate enhancement must have been observed for all catalysts, not only for the catalysts of low Mg/Ti ratio.

Catalytically active sites can be characterized by investigation of the relative reactivity of ethylene and 1-hexene. Recent reports indicate that the distribution of titanium oxidation states may affect the copolymerization rate.<sup>23</sup> Table II summarizes the results of copolymerization experiments. The  $r_1$  values have been obtained based on the simplified equation of copolymer composition proposed by Kissin et al.<sup>19,24</sup> They proposed a simplified equation that can be applied when one comonomer exhibits

much higher reactivity than does the other comonomer, i.e.,  $r_1 \gg 1$  and  $r_2 \ll 1$ , as follows:

$$1/f = (1/r_1)F$$

where  $F = (C_E/C_H)_{\text{mon}}$  is the comonomer concentration ratio in the reaction medium,  $f = (C_E/C_H)_{\text{cop}}$  is the copolymer composition ratio, and  $r_1 = k_{EE}/k_{EH}$  is the reactivity ratio (subscripts  $E$  and  $H$  stand for ethylene and 1-hexene). The  $r_1$  values for all catalysts are about 120. The same  $r_1$  value for a series of catalysts indicates that the active sites of the catalyst are similar in spite of the difference in the composition and in the polymerization rate profile.

Soga and co-workers<sup>23</sup> found that titanium in the oxidation state of +3 is active for all  $\alpha$ -olefins, whereas titanium (+2) is active only for ethylene. If these findings are generally acceptable, it is reasonable to assume that titanium species of the catalyst matrix of the present study, supposed to be mainly  $[\text{TiCl}_5(\text{THF})]^-$  anion, are overreduced to Ti (+2) during the activation with  $\text{AlEt}_3$ . This explanation can be supported by the experimental finding that our catalysts have almost no activities

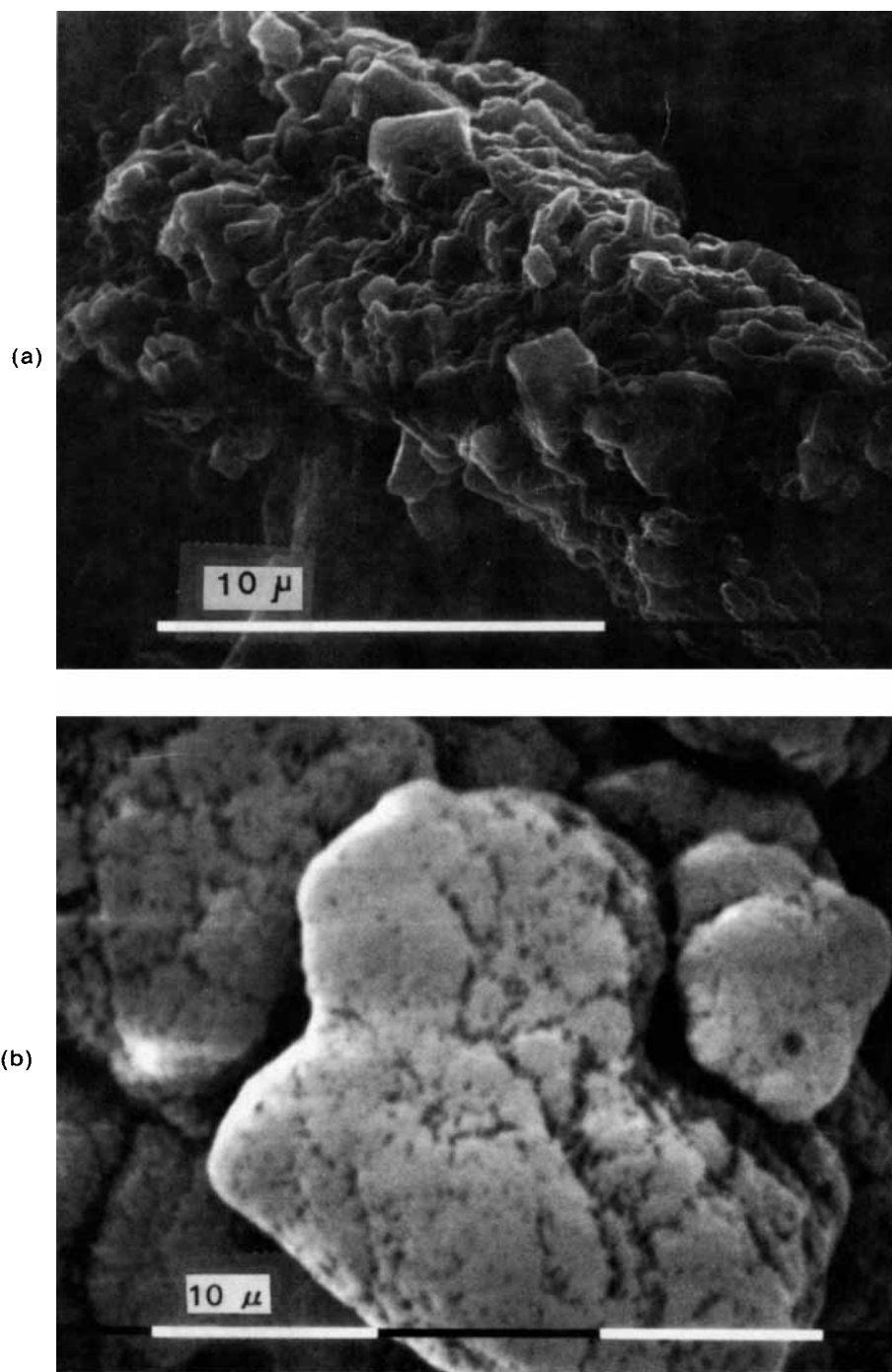
Table II Copolymerization of Ethylene and 1-Hexene with a Series of Six Catalysts

Catalyst	$1/F = (C_H/C_E)_{\text{mon}}$	$C_H$ (mol %)	$1/f = (C_H/C_E)_{\text{cop}}$	$r_1$	Heptane Soluble (%)
MT-1	1.16	1.2	0.012	120 ± 10	4.2
	2.18	2.0	0.020		6.0
	3.64	2.8	0.029		12.8
	5.82	4.8	0.050		20.9
MT-2	1.16	1.1	0.011	120 ± 10	—
	2.18	1.9	0.019		5.8
	3.64	3.0	0.031		—
	5.82	4.8	0.050		21.8
MT-3	1.16	1.0	0.010	120 ± 10	—
	2.18	1.8	0.018		—
	3.64	2.8	0.029		—
	5.82	4.6	0.048		20.2
MT-4	1.16	0.9	0.009	120 ± 10	—
	2.18	1.7	0.017		—
	3.64	3.0	0.031		—
	5.82	4.5	0.047		21.4
MT-5	1.16	—	—	120 ± 10	—
	2.18	1.8	0.018		—
	3.64	2.8	0.029		—
	5.82	4.6	0.048		20.8
MT-6	1.16	—	—	120 ± 10	—
	2.18	1.6	0.016		—
	3.64	2.6	0.027		12.0
	5.82	4.7	0.049		21.5

in propylene polymerization.<sup>16</sup> The complicated polymerization rate behavior observed in the presence of 1-hexene seems inappropriate to be explained by the chemical effects of 1-hexene on  $k_p$  or the rate of catalyst activation, since all catalysts have identical

active sites that are overreduced during the activation step.

Another proposal to explain the complicated kinetics of ethylene copolymerization is the dynamic physical effect occurring during polymerization. The



**Figure 2** SEM photographs of (a) MT-2 catalyst, (b) homopolymer [sample (A) in Fig. 1(b)], and (c) copolymer [sample (C) in Fig. 1(b)].

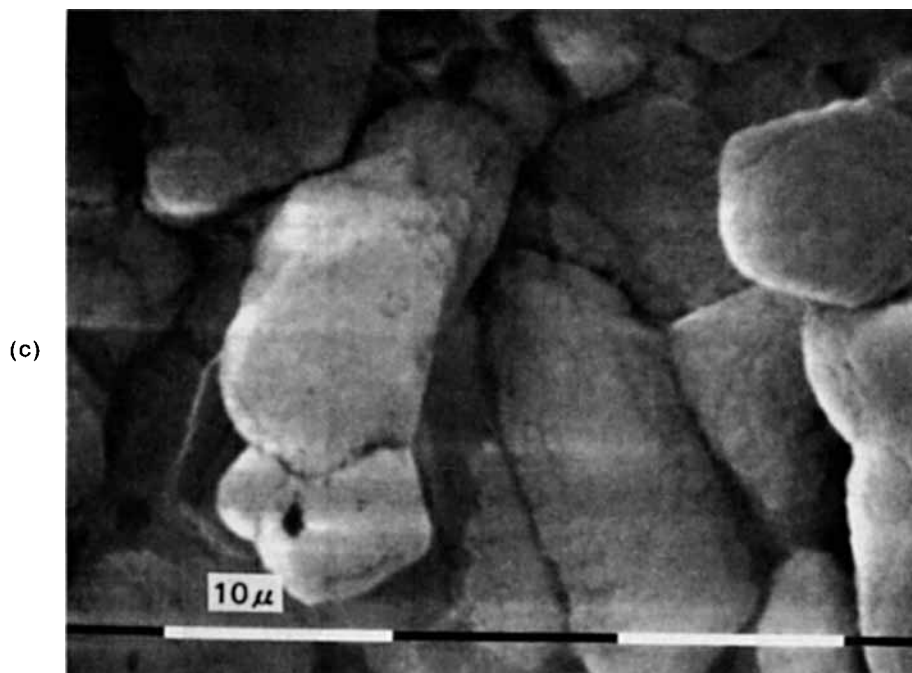


Figure 2 (Continued from the Previous Page)

catalysts of low Mg/Ti ratios, e.g., MT-1, MT-2, and MT-3, are formed by strong ionic interactions. According to the previous result,<sup>16</sup> the cationic Mg complex interacts with a stoichiometric amount of anionic Ti complex to form a cluster bound strongly to each other by the Coulombic interaction; thus, the particle size of the catalyst is large (100–500 μm). In these catalysts, most of titanium active species are occluded into the catalyst matrix, resulting in the low catalytic activity due to the lack of the utilization of active Ti sites. The physical disintegration of the catalyst matrix particles during polymerization may be slow due to the strong ionic coagulation; thus, it takes a long time to reach  $R_{p,m}$  in ethylene homopolymerization. However, the disintegration process can be facilitated by the presence of higher  $\alpha$ -olefins as originally proposed by Natta<sup>25</sup> and confirmed by many authors<sup>7,11</sup> in the copolymerization of ethylene. This may be the case in the copolymerization of ethylene and 1-hexene with MT-1, MT-2, and MT-3 catalyst. As shown in Figure 2, the subparticle size of copolymer obtained with the MT-2 catalyst is smaller than that of the ethylene homopolymer and the average particle size of the copolymer is also considerably smaller than that of the homopolymer in spite of much higher activity in the copolymerization (Fig. 3). Similar results have been obtained by using MT-1 and MT-3 catalysts, showing that the physical disintegration of

catalyst particles is activated by the presence of 1-hexene. Therefore, the enhancement of catalytic activities in the presence of 1-hexene can be explained by the proposal that the utilization of Ti species is enhanced by the physical disintegration of catalyst particles facilitated by 1-hexene, thus exposing new potential active sites to ethylene and 1-hexene.

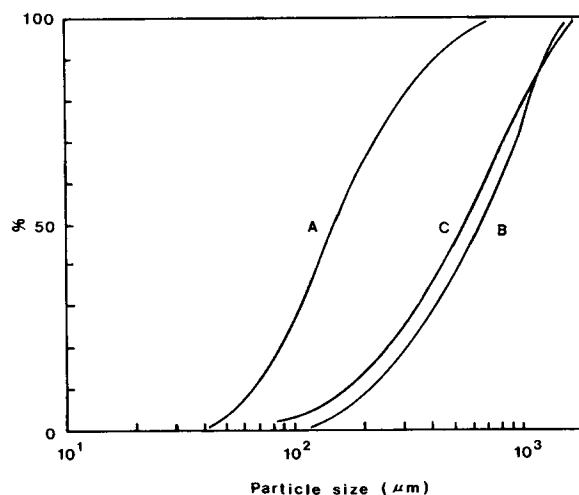
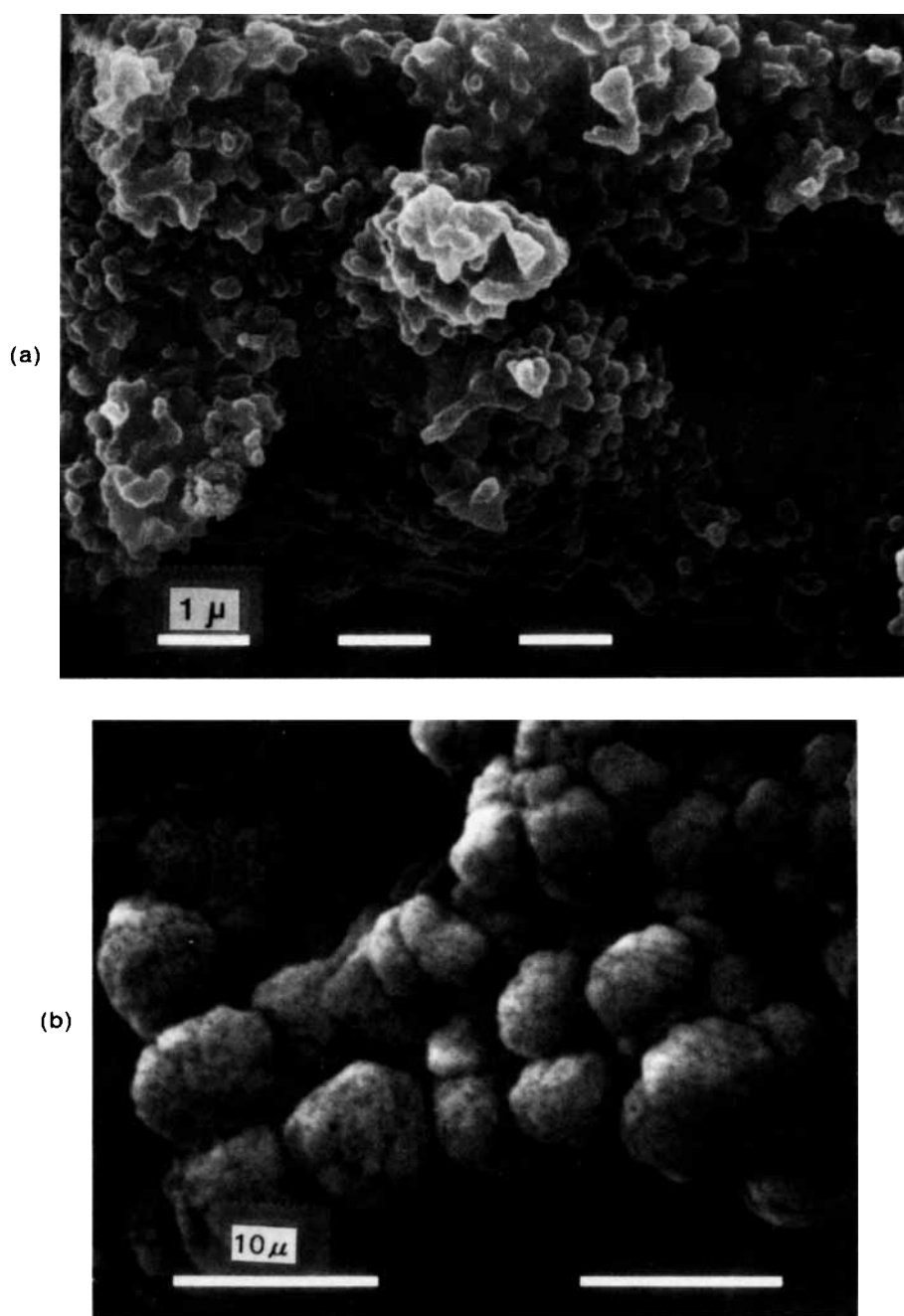


Figure 3 Particle-size distribution of (A) MT-2 catalyst, (B) as-nascent homopolymer [sample (A) in Fig. 1(b)], and (C) as-nascent copolymer [sample (C) in Fig. 1(b)].

As the Mg/Ti ratio of the catalyst increases, the ionic character of the complex is diminished, because Ti anionic species are diluted by the excess amount of nonionic Mg species such as  $\text{MgCl}_2(\text{THF})_2$ . Such weak ionic strength of the complex leads to small catalyst particles (50–200  $\mu\text{m}$ ). In this case, Ti active species are homogeneously distributed in the catalyst

matrix; thus, the catalytic activity is high. It seems that Ti species in MT-4, MT-5, and MT-6 catalysts are easily activated during both homo- and copolymerization since they are evenly distributed on the loosely bound catalyst matrix. Figure 4 shows the SEM photographs of the MT-6 catalyst and the resulting homo- and copolymer. Similar replication



**Figure 4** SEM photographs of (a) MT-6 catalyst, (b) homopolymer [sample (A) in Fig. 1(f)], and (c) copolymer [sample (C) in Fig. 1(f)].



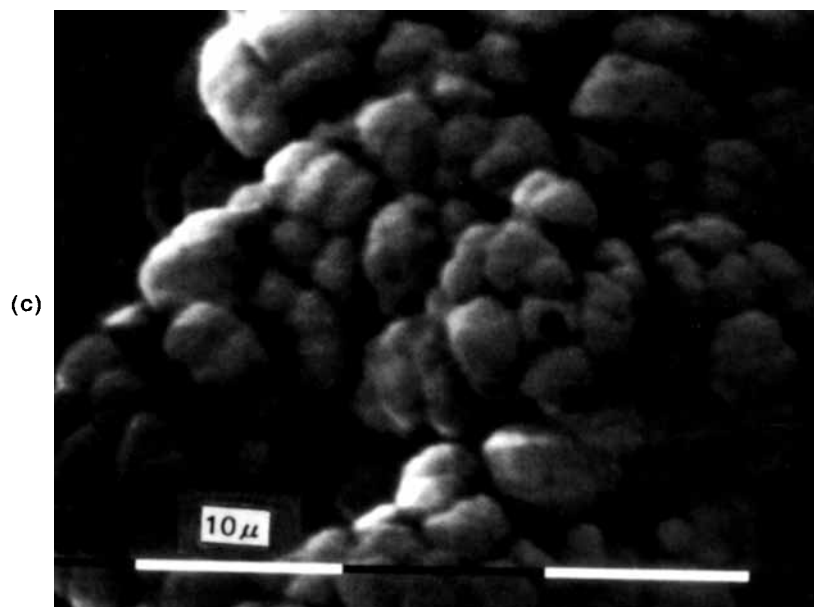
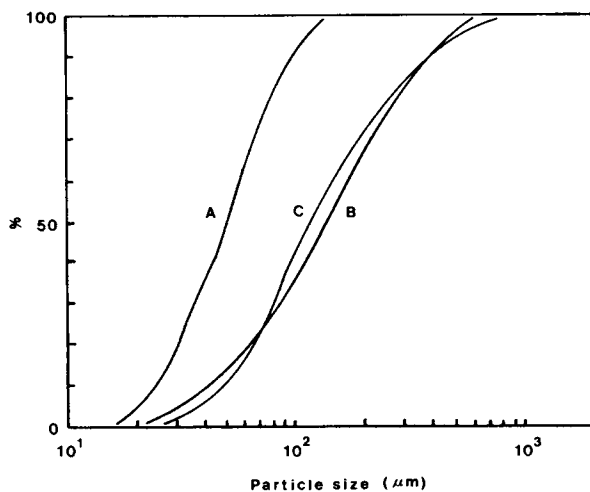


Figure 4 (Continued from the Previous Page)

phenomenon can be observed both in homo- and copolymerization. Contrary to the results obtained with the catalysts of low Mg/Ti ratio (e.g., Fig. 3), the average particle size of the copolymer obtained by the MT-6 catalyst is smaller than that of the homopolymer, as shown in Figure 5. The smaller size of the copolymer comes from the lower activity in the copolymerization. From these results, it can be speculated that any additional physical disinte-



**Figure 5** Particle-size distribution of (A) MT-6 catalyst, (B) as-nascent homopolymer [sample (A) in Fig. 1(f)], and (C) as-nascent copolymer [sample (C) in Fig. 1(f)].

gration by the help of 1-hexene has not occurred during copolymerization with the catalysts of high Mg/Ti ratios.

In conclusion, catalysts prepared by coprecipitating  $\text{TiCl}_4/\text{THF}/\text{MgCl}_2$  solvate by varying the ratio of Mg/Ti exhibited identical  $r_1$  value in ethylene-1-hexene copolymerization regardless of the differences in catalytic activity and kinetic behavior. These results indicate that similar active species are formed during preparation in spite of the compositional difference. The rate enhancement in copolymerization was observed in that the catalysts of low Mg/Ti ratio can be explained by the difference in the disintegration process that occurred during homo- and copolymerization.

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