

# Preparation of Ultra-High-Molecular-Weight Polyethylene and Its Morphological Study with a Heterogeneous Ziegler–Natta Catalyst

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**ABSTRACT:** Ultra-high-molecular-weight polyethylene (PE) with viscosity-average molecular weight ( $M_v$ ) of  $3.1 \times 10^6$  to  $5.2 \times 10^6$  was prepared with a heterogeneous Ziegler–Natta  $MgCl_2$  (ethoxide type)/ $TiCl_4$ /triethylaluminum catalyst system under controlled conditions. The optimum activity of the catalyst was obtained at a  $[Al]/[Ti]$  molar ratio of 61 : 1 and a polymerization temperature of 60°C, whereas the activity of the catalyst increased with monomer pressure and decreased with hydrogen concentration. The titanium content of the catalyst was 2.4 wt %. The rate/time profile of the catalyst was a decay type with a short acceleration period.  $M_w$  of the PE obtained decreased with increasing hydro-

gen concentration and polymerization temperature. The effect of stirrer speeds from 100 to 400 rpm did not so much affect the catalyst activity; however, dramatic effects were observed on the morphology of the polymer particles obtained. A stirrer speed of 200 rpm produced PE with a uniform globulelike morphological growth on the polymer particles. The particle size distributions of the polymer samples were determined and were between 14 and 67  $\mu m$ . © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3333–3339, 2010

**Key words:** morphology; polyethylene (PE); Ziegler–Natta polymerization

## INTRODUCTION

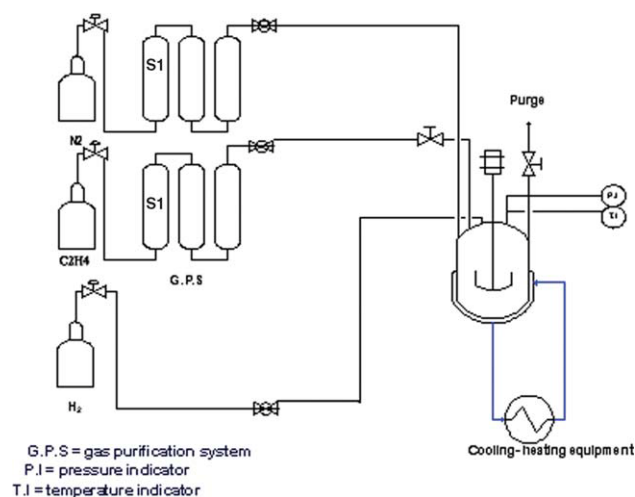
$MgCl_2$ - and  $SiO_2$ -supported Ziegler–Natta catalysts and also  $SiO_2$ -supported metallocene catalysts are typical examples of heterogeneous catalysts used in current industrial processes.<sup>1–3</sup> Heterogeneous systems supported on porous carriers are desirable, in that the final product replicates the support morphology, the so-called *replication phenomenon*.<sup>4,5</sup> These type of catalysts not only produce polyethylene (PE) and polypropylene with high activities and high stereospecificities but also control the morphology of the polymer particles obtained from their size and shape. Certainly, obtaining particles with good morphology is one of the most important goals in polymerization catalyst development.

Generally, researcher have used spherical  $MgCl_2$  adducted with alcohol to control the morphology of the catalyst replicated from its support to obtain polymers with suitable morphologies, mainly spherical particles with as little fine powder as possible to

prevent fouling of the polymerization reactor.<sup>6–10</sup> High polymer yields and good morphological properties can usually be obtained if catalyst fragmentation occurs in a proper and controlled way. However, if particle fragmentation is not controlled adequately, a considerable amount of dust polymer may produce fouling and undesirable fluidization through the reactor, pipe, and polymer processing equipment. Many researchers have studied polymer growth in the early stages of polymerization by monitoring catalyst fragmentation at this stage. Particles growth is believed to show the replication of the shape of the catalyst particles. However, there are some requirements with respect to the catalyst structure and polymerization conditions for obtaining uniform catalyst fragmentation. In addition to the morphology of the catalyst, the polymerization procedure and its conditions also affect the polymer morphology.<sup>2,4,11–13</sup> Process conditions determine the rate of the reaction with physical stress on the particles; for example, stirrer action can affect this morphology and the uniform growth of the polymer particles.<sup>4,14,15</sup> The effect of the relationships between the polymerization conditions, such as the temperature, effect of prepolymerization, hydrogen and monomer concentrations, and also external donors, on the morphology of PE powder produced with fourth-generation Ziegler–Natta catalysts have been investigated. Even for the growth of polymer

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**Scheme 1** Polymerization setup. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

particles, several models and mechanisms have been proposed.<sup>4,16–20</sup> The morphological development of the support, catalyst, and polymer are a major area of study nowadays.

In this study, a highly active Ziegler–Natta catalyst was prepared. The main feature of the study was the development of the morphology of ultra-high-molecular-weight PE. The effect of the polymerization conditions, such as the temperature, monomer pressure, hydrogen concentration, and stirrer speed, on the catalyst behavior and the polymer viscosity-average molecular weight ( $M_v$ ) were studied. Uniform growth of the polymerization on the particles was achieved by proper control of the reaction conditions.

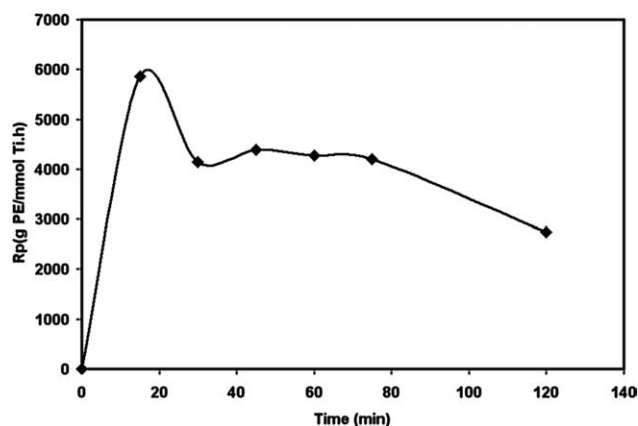
## EXPERIMENTAL

$\text{TiCl}_4$ ,  $\text{Mg}(\text{OEt})_2$ , and  $\text{AlEt}_3$  (Merck, Darmstadt, Germany) were used without any purification. Ethylene (Iran Petrochemicals Co, Arak, Iran, polymer grade) was used after it was passed through a column of activated 4 Å/13× molecular sieves (Scheme 1). Nitro-

**TABLE I**  
Effect of the TEA Concentration on the Polymerization Rate

$n$	TEA (mmol)	[Al]/[Ti] molar ratio	Yield [g of PE (mmol of Ti) <sup>-1</sup> h <sup>-1</sup> ]
1	2	24 : 1	3540
2	5	61 : 1	4270
3	6	73 : 1	2200
4	10	122 : 1	2070
5	16	195 : 1	2200

Polymerization conditions: temperature = 60°C, [Ti] = 0.2 mmol/L, time = 1 h, monomer pressure = 2 bar, hexane = 400 mL, and stirrer speed = 800 rpm.



**Figure 1** Plot of rate of polymerization ( $R_p$ ) versus time. Polymerization conditions: temperature = 60°C, [Ti] = 0.2 mmol/L, [Al] : [Ti] = 61 : 1, monomer pressure = 2 bar, hexane = 400 mL, and stirrer speed = 800 rpm.

gen (Roham Gas, Tehran, Iran) was used after it was passed through columns of silica gel, KOH, and 4 Å/13× molecular sieves. Heptane and hexane (Iran Petrochemical) were distilled over calcium hydride before use. Other chemicals, the structural studies of the catalyst, the polymer characterization, and the polymerization procedure were explained elsewhere.<sup>21,22</sup>

Fourier transform infrared (FTIR, Ettlingen-germany) spectroscopy (Bruker IF 548) and X-ray (Cu-Kα radiation, Siemens model U-500, Ettlingen-Germany) (Link Analytical XR300) were used to study of the catalyst structure. A morphological study of the support, catalyst, and polymer obtained was carried out with a Stereoscan 360 scanning electron microscopy (SEM, Würtemberg, Germany) instrument.  $M_v$  was determined according to refs. 23 and 24 with an Ubbelohde viscometer (Iran-tehran) with a heating jacket; the polymer was dissolved in decaline at 133°C. The  $M_v$  values of some of the polymer samples were obtained with the Mark–Houwink equation:

$$[\eta] = kM^\alpha$$

where  $k = 6.77 \times 10^{-4}$  and  $\alpha = 0.67$  are constants related to the polymer and measuring conditions.<sup>24</sup> The particle size distribution was determined by a laser diffraction method with a Master Size X long-bed version 2.15 instrument (Malvern,

**TABLE II**  
Effect of the Stirrer Speed on the Polymerization Rate

Stirrer speed (rpm)	100	200	400	800
Yield [g of PE (mmol of Ti) <sup>-1</sup> h <sup>-1</sup> ]	12.2	14.6	15.9	42.7

Polymerization conditions: temperature = 60°C, [Ti] = 0.2 mmol/L, [Al]/[Ti] = 61 : 1, monomer pressure = 2 bar, and hexane = 400 mL.

TABLE III  
Effect of the Polymerization Temperature on the Catalyst Behavior  
and Polymer Characteristics

Temperature (°C)	Yield [g of PE (mmol of Ti) <sup>-1</sup> h <sup>-1</sup> ]	Melting temperature (°C)	Crystallinity (%)	M <sub>v</sub> (g/mol)
50	2320	142.4	41.3	5.2 × 10 <sup>6</sup>
55	2200	—	—	3.8 × 10 <sup>6</sup>
60	4270	142.2	39.3	3.7 × 10 <sup>6</sup>
65	3290	142.2	40.0	3.5 × 10 <sup>6</sup>
70	1460	141.8	40.2	3.1 × 10 <sup>6</sup>

[Al]/[Ti] = 61 : 1. The other polymerization conditions were the same as those listed in Table I.

Worcestershire, UK). The crystallinity of the polymer was calculated according to ref. 25.

### Catalyst preparation

The MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub> catalyst was prepared under an atmosphere of nitrogen in a 0.5-L glass reactor containing a sinter glass filter in toluene. The preparation was started by the addition of TiCl<sub>4</sub> (50 mL) to predispersed Mg(OEt)<sub>2</sub> (7 g) at -10°C so that active MgCl<sub>2</sub> could be obtained from the reaction.<sup>21</sup> The reaction was carried out for a further 2–3 h at 80°C. The solution of the reactor was filtered out. Toluene (100 mL) and TiCl<sub>4</sub> (50 mL) were added. The temperature was raised to 105°C, and the mixture was stirred for another 2–3 h. The product was washed with *n*-heptane (10 × 100 mL) to remove unreacted TiCl<sub>4</sub>. The final catalyst was dried at 70°C.

## RESULTS AND DISCUSSION

The catalyst structure was studied with FTIR spectroscopy, X-ray fluorescence, and SEM. As we

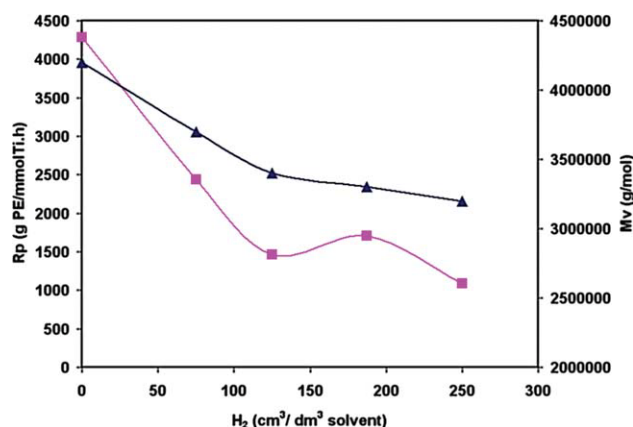


Figure 2 Effect of the hydrogen concentration on the polymerization activity: (—▲—) M<sub>v</sub> and (—■—) rate of polymerization (R<sub>p</sub>). The polymerization conditions were the same as listed in Figure 1. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

learned from the FTIR study, the Mg(OEt)<sub>2</sub> was converted to MgCl<sub>2</sub> as a result of the reaction with excess TiCl<sub>4</sub> during the catalyst preparation, as expected.<sup>21</sup> The content of titanium in the catalyst was 2.45 wt %. The polymerization of ethylene was carried out with the MgCl<sub>2</sub> (ethoxide type)/TiCl<sub>4</sub>/triethylaluminum (TEA) catalyst system under different conditions. The activity of the catalyst system increased with addition of TEA, the cocatalyst, to an optimum value of almost 4300 g of PE (mmol of Ti)<sup>-1</sup> h<sup>-1</sup> at a [Al]/[Ti] molar ratio of 61 : 1; it then decreased to a limiting value (Table I). The low ratio of [Al] to [Ti] obtained for the catalyst with a reasonable activity compared to this type of Ziegler–Natta catalyst could be an advantage of the catalyst.<sup>1,6</sup> However, the decrease in activity at higher TEA concentrations indicated instability in some of the active centers, which could have been due to an overreduction of Ti<sup>+4</sup> and Ti<sup>+3</sup> to Ti<sup>+2</sup>, which is less active than the former ions.<sup>26,27</sup>

The kinetic behavior of the polymerization is shown in Figure 1. The profile was a decay type, which is common for MgCl<sub>2</sub>-supported Ziegler–Natta catalysts.<sup>1,28</sup> The behavior also indicated instability in some of the active centers or a decrease in their activity with polymerization time.<sup>28–33</sup>

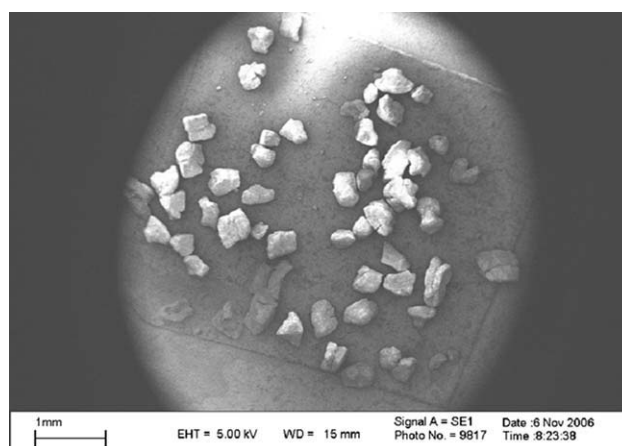
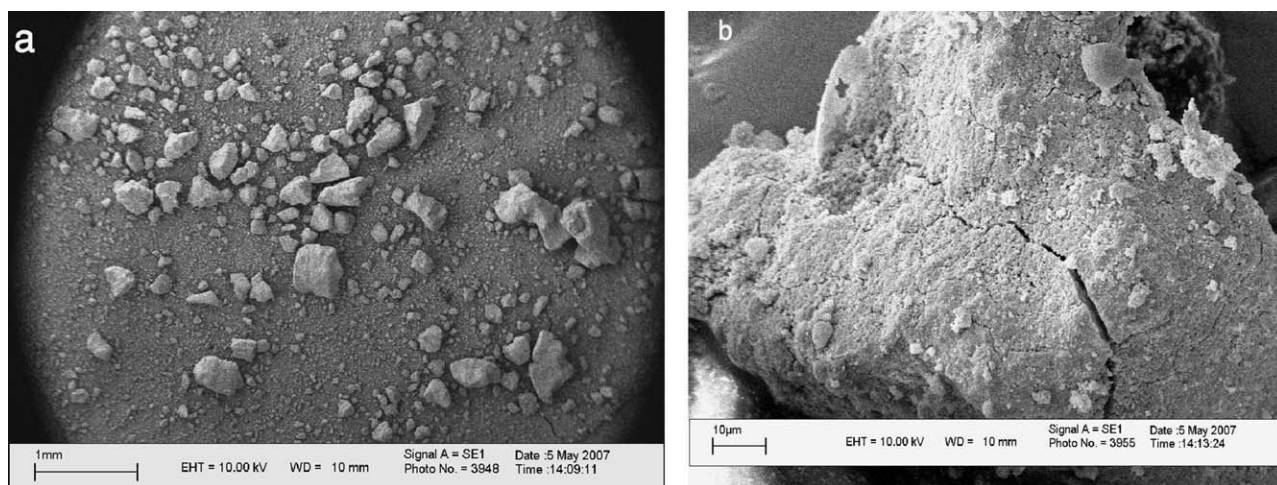


Figure 3 SEM micrograph of Mg(OEt)<sub>2</sub> (25× magnification).



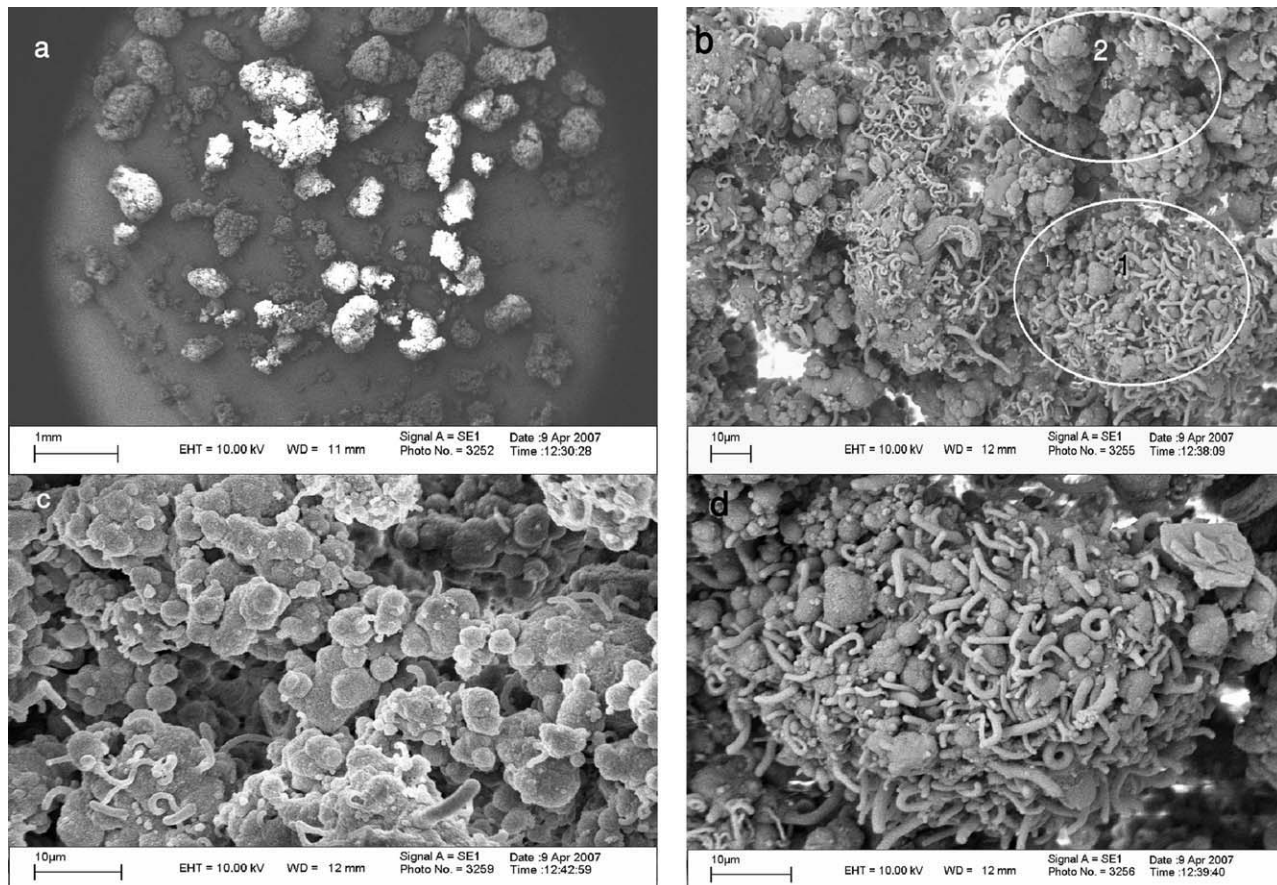


**Figure 4** Micrograph of the  $\text{MgCl}_2$  (ethoxide type)/ $\text{TiCl}_4$  catalyst at magnifications of (a) 25 and (b) 2000 $\times$

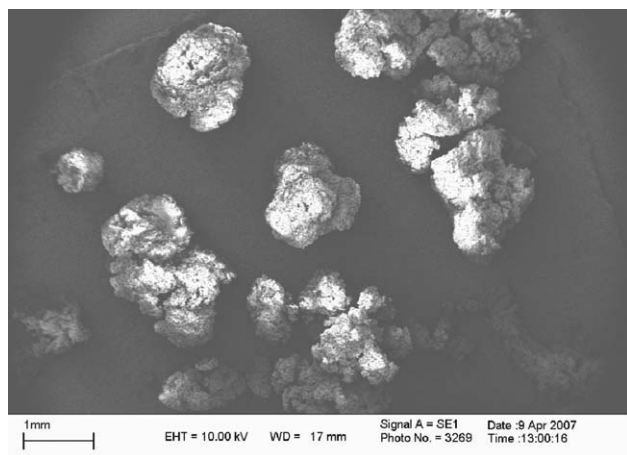
Monomer transfer to the catalyst active centers through the polymerization medium could have been a key point in the slurry polymerization with the heterogeneous catalyst system. A higher agitator speed may have facilitated the diffusion of monomer to the active centers. Table II shows the effect of agi-

tator speed on the polymerization behavior. A higher stirrer speed could have affected the yield and morphology of the polymer obtained.

The polymerization was carried out at temperatures between 50 and 70°C. The highest activity of the catalyst was obtained at about 60°C (Table III).



**Figure 5** SEM micrographs of PE obtained at 60°C with a monomer pressure of 2 bar and a stirrer speed of 800 rpm at magnifications of (a) 35, (b) 1500, and (c, d) 3000 $\times$ .



**Figure 6** SEM micrograph of PE obtained at 60°C with a monomer pressure of 2 bar, a stirrer speed of 200 rpm, and a magnification of 25 $\times$ .

The same behavior has been reported for this kind of catalyst.<sup>1,6,28</sup>

Hydrogen gas was used as chain-transfer agent. The polymerization was carried out at optimum conditions obtained previously. The polymerization behavior of the catalyst versus the hydrogen concentration is shown in Figure 2. The activity of the catalyst decreased with increasing hydrogen concentration in the range studied (50–250 cm<sup>3</sup>/dm<sup>3</sup> solvent). Hydrogen converted some of the active centers to Ti–H, which is less active than Ti–C, and also reduced the concentration of the monomer dissolved in the polymerization medium.<sup>29,34</sup>

#### Polymer characterization: $M_v$ measurement

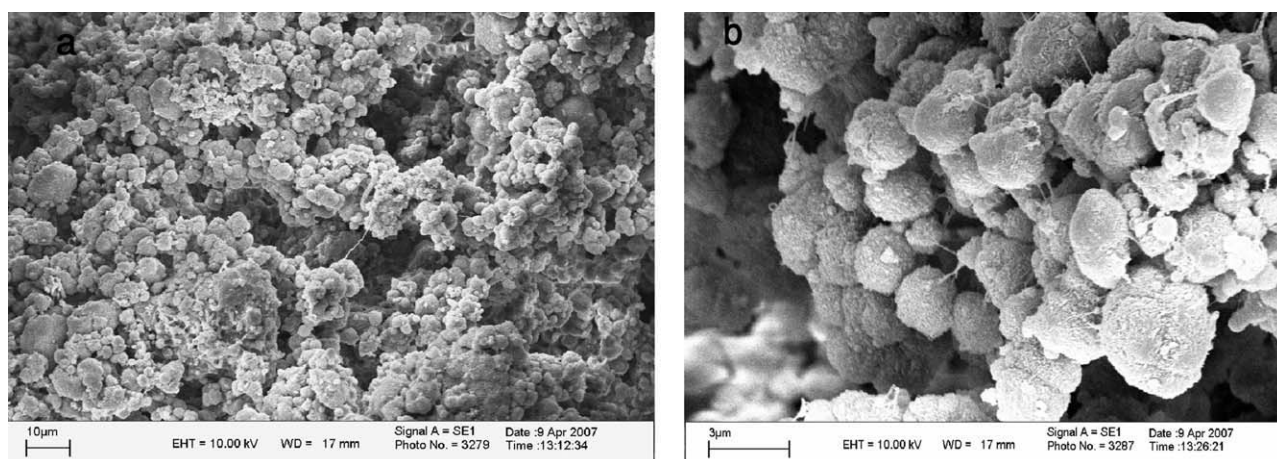
Ultra-high-molecular-weight PE with an  $M_v$  value of as high as  $5.2 \times 10^6$  was obtained with the MgCl<sub>2</sub>

(ethoxide type)/TiCl<sub>4</sub>/TEA catalyst system at 50°C. The molecular weight decreased with the addition of hydrogen and the polymerization temperature (Fig. 2 and Table III). The so-high molecular weight of PE produced indicated a low occurrence of the chain-transfer reaction compared to that of the propagation reaction for the catalyst system. Increasing the polymerization temperature facilitated the chain-transfer reaction, which lowered the  $M_v$  values.

Hydrogen is the best known chain-transfer agent for the catalyst polymerization of olefin. The higher the concentration of hydrogen is, the more chain transfer occurs.<sup>28,35</sup>  $M_v$  of the PE obtained at 250 mL of H<sub>2</sub>/L of solvent was even  $3.2 \times 10^6$ , which was still in the range of ultra-high-molecular-weight PE. The crystallinity of the polymer was about  $40 \pm 1\%$  and did not change with the polymerization temperature (Table III).

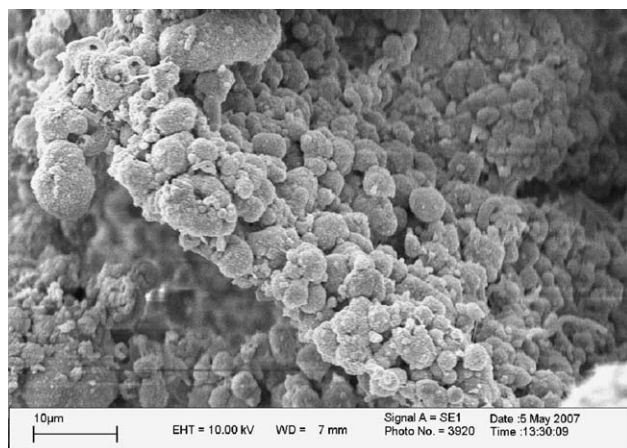
#### Morphological study

The SEM studies of Mg(OEt)<sub>2</sub>, the starting chemical for the preparation of MgCl<sub>2</sub>, the support, catalyst, and PE obtained under different conditions are shown in Figures 3–9, respectively. As shown in the SEM micrographs, the Mg(OEt)<sub>2</sub> particles had smooth surfaces without cavities and with very small amounts of fine particles (Fig. 3). Figure 4 shows the SEM micrographs of the catalyst particles; as shown, some of the particles were destroyed. High magnification of the catalyst surface showed that some pores with small cavities on some particles were formed because of the harsh chemical reaction of TiCl<sub>4</sub> with ethoxide during the catalyst preparation procedure. Although the catalyst preparation started at a low temperature, some of the particles were destroyed during the procedure. The SEM micrograph of PE obtained with the catalyst at



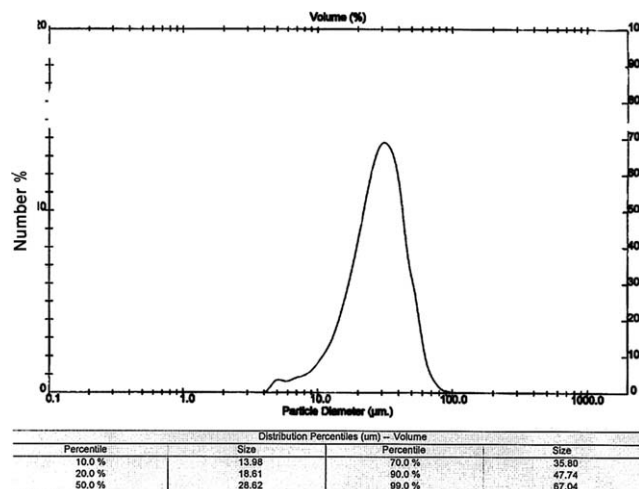
**Figure 7** High-magnification micrographs of PE at magnification of (a) 3000 and (b) 10000 $\times$ . The polymerization conditions were the same as those listed in Figure 6.





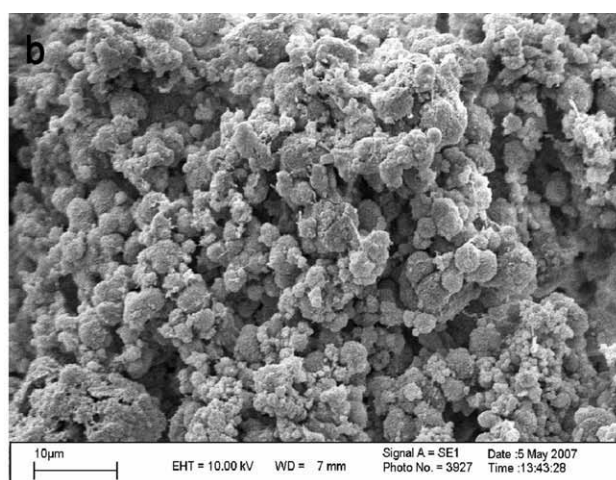
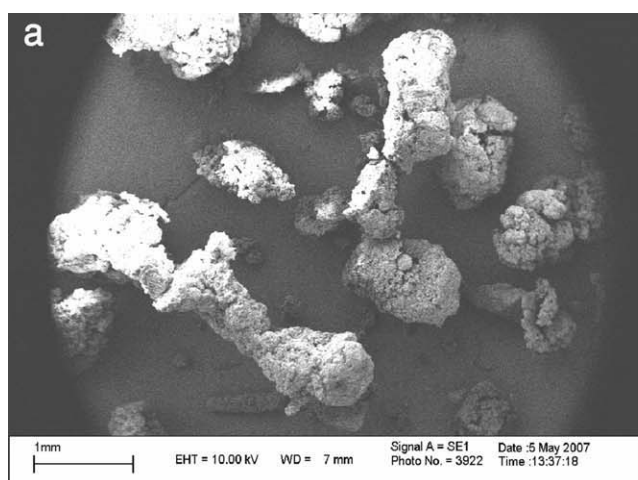
**Figure 8** High-magnification micrograph of PE obtained at 60°C with a monomer pressure of 5 bar, a stirrer speed of 200 rpm, and a magnification of 3000 $\times$ .

60°C with a stirrer speed of 800 rpm and a monomer pressure of 2 bar showed particles with no uniform shape and size (Fig. 5). The irregular surface of the PE particles indicated irregular growth of the polymer chain. Some of the polymer growth, like a filament, extruded through a pore during the polymerization. This extrusion may have taken place through the catalyst pore during the polymerization. Although the extruded particles showed irregular growth of the polymer, the prepared catalyst particles were mechanically strong enough and were not damaged during the polymerization. To study the effect of the stirrer speed on the morphology of the polymer particles, polymerization was further carried out at stirrer speeds of 100, 200, and 400 rpm. Polymer particles obtained at 100 rpm contained a broad distribution with fine dusty and very



**Figure 10** Particle size distribution pattern of the polymer obtained with an [Al] : [Ti] ratio of 61 : 1 and a temperature of 60°C.

large particles; this caused fouling of the reactor walls and were hard to remove from the reactor. PE particles produced at 60°C, a monomer pressure of 2 bar, and 200 rpm were more uniform in size (Fig. 6). High magnification of the particles showed an almost uniform growth of globulelike polymer particles compared to the particles obtained at 800 rpm (Fig. 7). Polymer particles obtained at 60°C, 200 rpm, and a monomer pressure of 5 bar were also uniform with globulelike particles on the surface of the polymer (Fig. 8). Polymer particles produced at a stirrer speed of 400 rpm are shown in Figure 9. Although high magnification of the particles showed uniform growth of the polymer with no extruded filament-like parts, the globulelike parts were a bit smaller than the ones obtained at a stirrer speed of 200 rpm.



**Figure 9** SEM micrographs of PE obtained at stirrer speed = 400 rpm at magnifications of (a) 35 and (b) 3000 $\times$ . The other conditions were the same as those listed in Figure 6.

The behavior indicated faster growth of the particles, which were still uniform. However, at a stirrer speed of 800 rpm, the polymerization was so fast; this caused irregular growth of the polymer. The particle size distributions of the polymer sample prepared with a [Al]/[Ti] molar ratio of 61 : 1 and a polymerization temperature of 60°C were between 14 and 67  $\mu\text{m}$ . The majority of the particles were in the range 35–66  $\mu\text{m}$ ; this was a reasonable distribution for the polymer (Fig. 10).

### CONCLUSIONS

Ultra-high-molecular-weight PE with  $M_v$  of  $3.1 \times 10^6$  to  $5.2 \times 10^6$  was produced with the  $\text{MgCl}_2$  (ethoxide type)/ $\text{TiCl}_4$ /TEA catalyst system. The so-high  $M_v$  produced could have been due to low [Al]/[Ti] molar ratio of 61 : 1 required to reach the optimum activity of the catalyst. The stirrer speed of the polymerization played a key role in obtaining a uniform morphology and a high polymerization activity. Polymerizations with stirrer speeds of 200 and 400 rpm produced polymers with uniform growth of globule-like particles, whereas a speed of 800 rpm produced a higher polymer yield. The polymerization with a stirrer speed of 200 rpm produced more uniform particles with globulelike growth of the polymer for monomer pressures of both 2 and 5 bar. Increasing both the polymerization temperature and hydrogen concentration decreased  $M_v$  of the obtained polymer. The crystallinity of the polymer was about  $40 \pm 1\%$ . The crystallinity was not affected by the polymerization temperature. The rate/time profile of the polymerization was a decay type.

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