



Preparation of Ultra High Molecular Weight Polyethylene Using Bi-supported $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4 Catalyst: A Morphological Study

Gholamhossein Zohuri^{1*}, Mahbobeh Ahmadi Bonakdar¹, Saman Damavandi¹
Melika Eftekhari¹, Mahdiah Askari¹, and Saeid Ahmadjo²

(1) Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad,
P.O. Box: 1436, Mashhad, Iran

(2) Iran Polymer and Petrochemical Institute, P.O. Box: 14965/115, Tehran, Iran

Received 7 March 2009; accepted 17 June 2009

ABSTRACT

Polyethylene with a viscosity average molecular weight (\bar{M}_v) as high as 3.42×10^6 was synthesized. The \bar{M}_v increased with monomer pressure, while higher polymerization temperature decreased the molecular weight of the resulting polymer. The method of polymerization involved slurry using morphologically improved bi-supported catalyst of spherical $\text{SiO}_2/\text{MgCl}_2/\text{TiCl}_4$. Triethylaluminum (TEA) was used as a cocatalyst, and hydrogen served as the chain transfer agent. The crystallinity of the obtained polymer was between 50% and 60%, indicating semicrystalline polyethylene. Morphological study reveals that the main damage suffered by the catalyst particles was due to chemical interactions with the cocatalyst at the early stages of the polymerization. The rate/time profile of the polymerization decayed with the highest activity at the beginning of the polymerization. The behaviour also affected the morphology of the polymer particles which could be due to the sudden fragmentation that resulted from fast-growing polymer particles. The optimal activity was obtained at $[\text{A}]:[\text{Ti}] = 770:1$ molar ratio at 60°C . The polymerization was first order with respect to the monomer concentration. Polymerization activity was stable between 55°C and 70°C .

Key Words:

polyethylene;
ultra high molecular weight;
Ziegler-Natta catalyst;
bi-supported catalyst;
morphology.

INTRODUCTION

High molecular weight polymers and their morphological development are the most important achievements of heterogeneous catalyst polymerization of the Ziegler-Natta type [1-6]. MgCl_2 and SiO_2 are the most common bi-supports used to heterogenize olefin polymerization catalysts [7-10], and SiO_2 is also used to support metallocene and late transition metal catalysts [11,12]. The morphological development of the catalyst originally obtained from its support could replicate the

polymer in controlled conditions.

Heterogeneous catalyst particles break up during the early stages of the polymerization, possibly due to the chemical reaction of the catalyst component, mechanical stress and also polymer growth, respectively [11,13,14]. In Ziegler-Natta polymerization, the rate/time profiles are mainly a decay type with very high polymerization activity at the early stage of the reaction. Therefore, the fast growth of the polymer into the pore and channel of the catalyst could

* To whom correspondence to be addressed.

fragmentate the catalyst particles. To achieve a reasonable morphology, the fragmentation must be controlled, since uncontrolled fragmentation may produce fine particles. Using SiO_2 and MgCl_2 components of a solid support not only raised the activity of the catalyst but also improved its morphology. SiO_2 also improved the mechanical and thermal stability of the catalyst [9,15-17]. Morphological development of support, catalyst and polymer is the major area of study nowadays.

Ultra high molecular weight polyethylene (UHMWPE) has many desirable physical and mechanical characteristics comparable to some engineering plastics [1,18-21].

In the present work, spherical MgCl_2 and morphologically improved SiO_2 were used as two components of a solid support for the preparation of the heterogeneous catalyst. The main feature of the article is some development in morphology of UHMWPE. UHMWPE was prepared, while its morphology was studied at different conditions. The catalyst showed high activity, good morphology of spherical particles and also thermal stability of ethylene polymerization leading to UHMWPE.

EXPERIMENTAL

SiO_2 (PQ3050) was acquired from PQ Corporation (USA). The compound was calcinated at about 400°C for nearly 5 h before use [22]. Spherical adducted $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$ were prepared according to literature [6]. Slurry polymerization of ethylene was carried out in a 1-L stainless-steel reactor of Buchi (bds300), a semibatch type, equipped with a stirrer speed control, temperature and pressure control. The reactor was purged with nitrogen. A volume of 400 mL heptane was charged into the reactor and degassed at least three times. When the polymerization temperature reached the required temperature, the catalyst components were added in the following order; TEA, the solid catalyst, and hydrogen (if any). All the reagents were added as a slurry in *n*-heptane or a gas. The pressure inside the reactor was maintained constant with the monomer gas. Therefore, the required amount of the monomer to feed into the reactor is equal to the consumption of the monomer.

At the end of the reaction time, mainly one hour, the monomer feed was stopped. The polymerization was terminated by draining the slurry polymer into a small volume of acidified methanol. The polymer obtained was filtered and dried at 70°C for overnight.

The viscosity average molecular weight (\overline{M}_v) of the polymer was obtained using Ubbelohde suspended level dilution viscometer. The temperature of the viscometry was maintained at $133 \pm 1^\circ\text{C}$ by boiling chlorobenzene in the vapour jacket of the viscometer. The \overline{M}_v was calculated from the intrinsic viscosity using the Mark-Howink Sakurada equation.

$$[\eta] = K\overline{M}_v^\alpha$$

where K and α are 6.77×10^{-4} and 0.67, respectively [23,24].

Other chemicals, polymerization procedure, and characterizations were also taken from the literatures [7,16,17,23].

Catalyst Preparation

The $\text{SiO}_2/\text{MgCl}_2/\text{TiCl}_4$ catalyst was prepared using the adducted spherical $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$. The ethanol was chemically removed during the catalyst preparation procedure. The calcinated SiO_2 (2.5 g) and $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$ (2.5 g) were added to a catalyst preparation reactor containing a sinter glass heated with a jacket. The chemicals were suspended in toluene (100 mL), and then TiCl_4 (40 mL) was added dropwise, while, the contents of the reactor were stirred at 5°C . The temperature was raised to 115°C in increments of 20°C , while stirring at each step for at least one hour. The product was filtered, and washed with *n*-heptane (100 mL). Toluene (100 mL) and TiCl_4 (40 mL) were added at 40°C . The temperature was raised to 115°C incrementally, as before. The final catalyst was filtered, washed with *n*-heptane to completely remove unreacted TiCl_4 , and dried. All the steps were carried out under an atmosphere of dried N_2 .

RESULTS AND DISCUSSION

Polymerization of ethylene using the bi-supported $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4 /TEA catalyst system

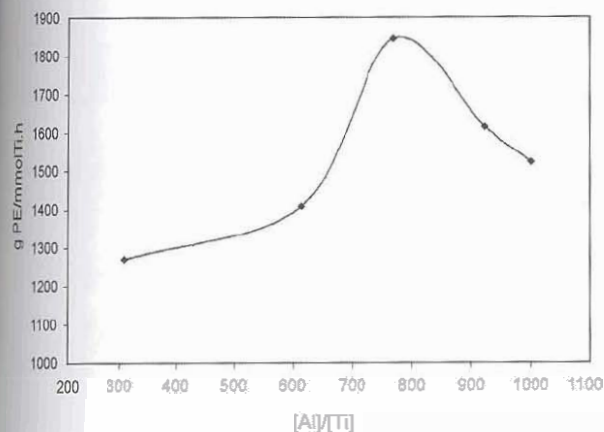


Figure 1. Effect of [Al]:[Ti] molar ratio on average rate of polymerization, temperature 60°C.

shows the optimum activity at [TEA]:[Ti] = 770:1 molar ratio (Figure 1) and reaction temperature of 60°C (Figure 2). At low concentration of TEA it is possible that the impurity of the system has affected the results and not all active centres being activated, whilst at higher concentration than the optimum value the over reduction of Ti^{+4} to Ti^{+2} occurred which is less active for the polymerization. H_2 was used as chain transfer agents. Addition of H_2 decreased productivity of the catalyst. H_2 competes with monomer in adsorption on active centres, which decreases the productivity of the catalyst. This behaviour could be due to increasing concentration of the monomer close to the active centres and probably fragmentation of the catalyst particles during polymerization [5,10,11,17,23].

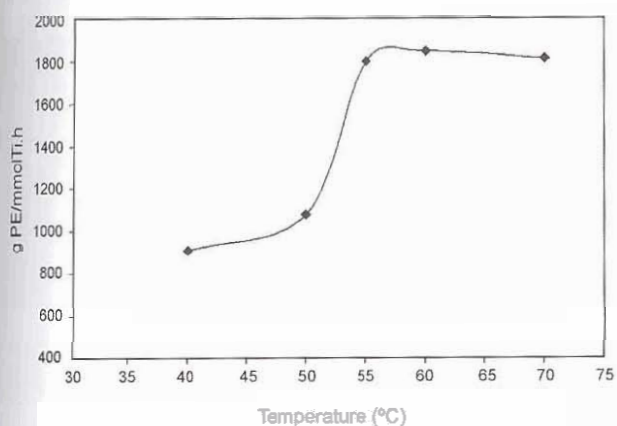


Figure 2. Effect of temperature on polymerization behaviour, [Al]:[Ti] = 770:1.

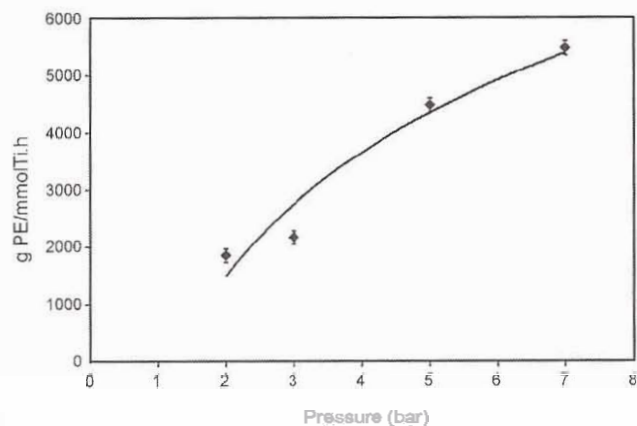


Figure 3. Effect of monomer pressure on polymerization behaviour. [Al]:[Ti] = 770:1, other conditions as in Table 1.

The polymerization activity increases with monomer pressure and decreases with H_2 concentration (Figures 3 and 4). The rate/time profile of the polymerization is a decay type without an induction period (Figure 5). The behaviours are reported and described in references [23,25-28]. The productivity of the catalyst has been almost stable with temperature between 55°C and 70°C (Figure 2). The thermal stability of the catalyst could be affected by presence of SiO_2 supported in the catalyst system [9,15-17], as an advantage of the prepared catalyst.

Variation of $\log(R_p)$ (average rate of polymerization) against $\log[M]$ reveals that the polymerization is almost first order with respect to the monomer concentration (Figure 6).

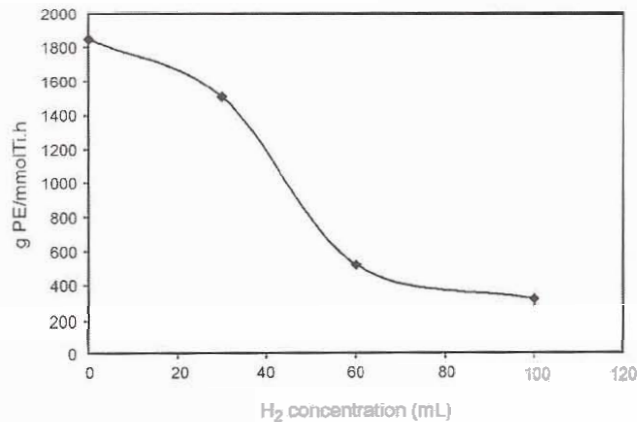
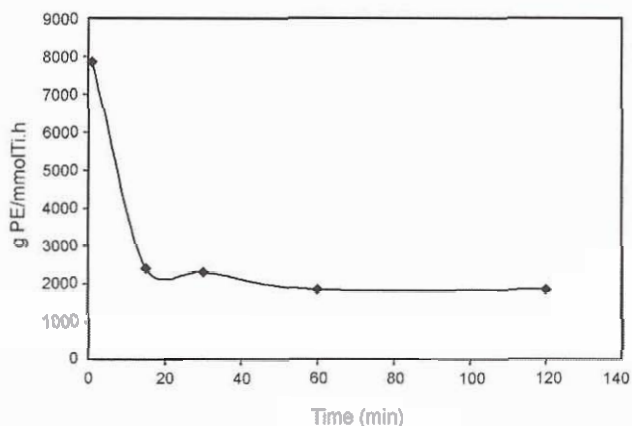


Figure 4. Effect of H_2 concentration on polymerization, [Al]:[Ti] = 770:1, temperature = 60°C.

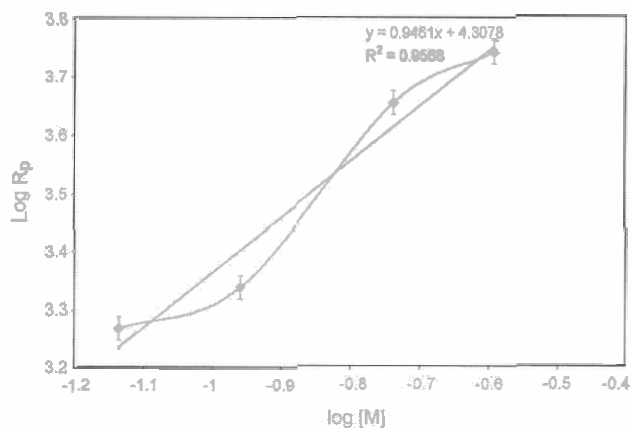
Table 1. Effect of temperature and monomer pressure on polymerization behaviour.

Temperature (°C)	40	50	55	60	70	60	60
Monomer pressure (bar)	2	2	2	2	2	3	7
\bar{M}_v	3.38×10^6	3.42×10^6	2.79×10^6	1.70×10^6	1.14×10^6	2.47×10^6	3.3×10^6
T_m (°C)	145	144	144	135	142	-	-
Crystallinity (%)	52.2	60.9	52.3	51.1	49.4	-	-

**Figure 5.** Rate/time profile of the polymerization behaviour, $[A]_0:[Ti] = 770:1$, temperature = 60°C.

Characterization

A viscosity average molecular weight \bar{M}_v as high as 3.42×10^6 was obtained; the value decreased with increasing temperature, while, a higher pressure of the monomer led to higher values of \bar{M}_v (Table 1). The molecular weight of the polymer was not significantly affected by the polymerization time (Table 2). The crystallinity of the obtained polymer was in the range of 50% to 61% indicating the

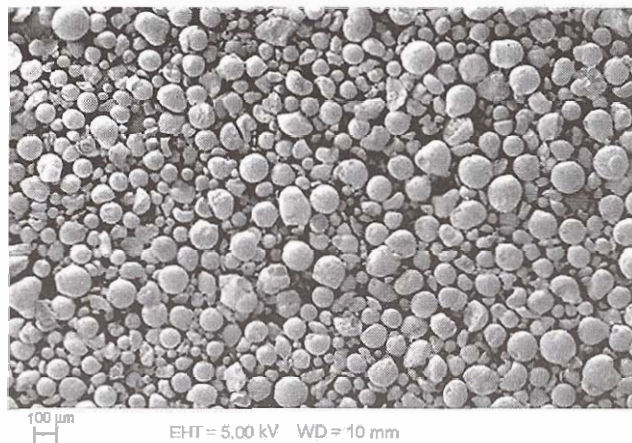
**Figure 6.** Variation of $\log R_p$ versus $\log [M]$.**Table 2.** Effect of polymerization time on the \bar{M}_v .

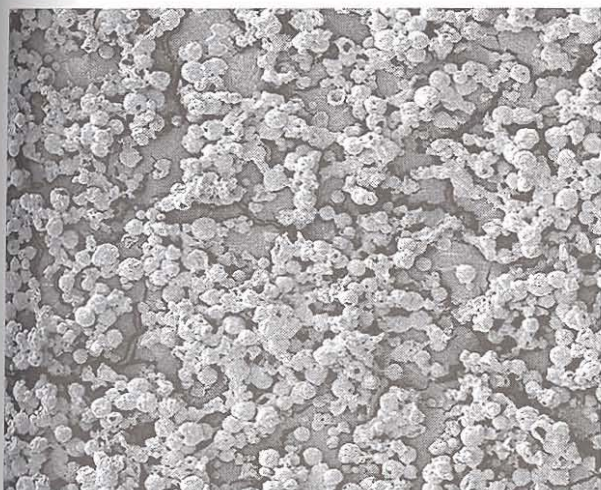
Polymerization time (min)	15	30	60	120
\bar{M}_v	1.74×10^6	1.68×10^6	1.70×10^6	1.70×10^6

production of a semicrystalline polymer. Due to very high molecular weight polyethylene samples, lower percentage of the crystallinity was obtained in comparison with normal HDPE. No regular behaviour of the crystallinity was observed with reaction temperature. The melting point of the polymer was between 135°C and 145°C (Table 1). The characteristics are comparable with high density polyethylene (HDPE) [1].

Morphological Study

Scanning electron microscopy (SEM) of SiO_2 shows mainly spherical particles with some distribution in size; however, some of the particles are broken (Figure 7). The prepared spherical form of $MgCl_2 \cdot nC_2H_5OH$ contained smaller particles than SiO_2 (Figure 8). The prepared catalyst shows more

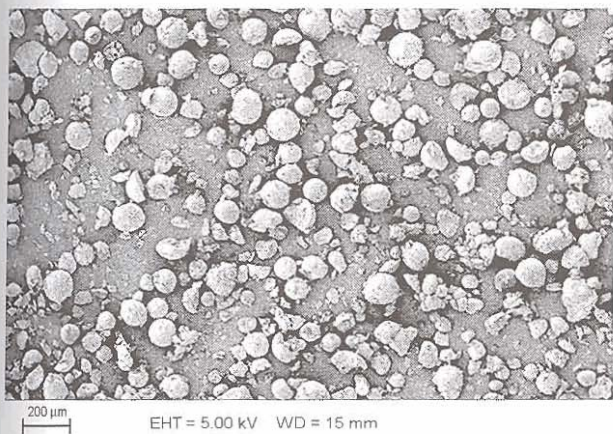
**Figure 7.** SEM micrograph of the SiO_2 (PQ3050), magnification 100x.



EHT = 5.00 kV WD = 15 mm

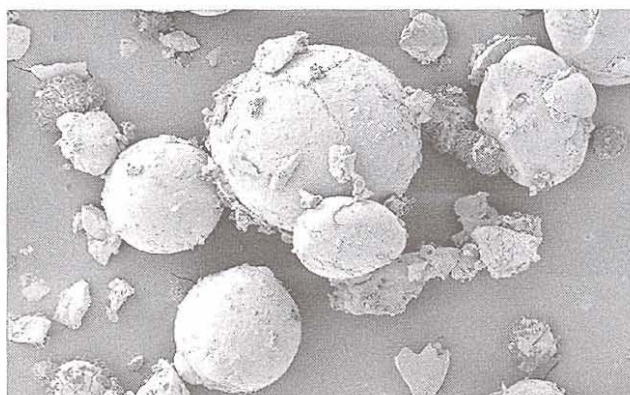
Figure 8. SEM micrograph of $\text{MgCl}_2 \cdot n\text{C}_2\text{H}_5\text{OH}$, magnification 100x.

broken particles than the supports used (Figure 9). The spherical morphology of the support was damaged during the catalyst preparation, indicating a strenuous reaction between the supports and TiCl_4 . SEM micrograph of the catalyst treated with TEA for one minute without using monomer shows many broken particles. The result indicates a harsh reaction between the catalyst and TEA. The reaction is mainly responsible for losing the spherical morphology of the catalyst particles at an early stage of the reaction, affecting the morphology of the obtained polymer particles via a replication phenomenon (Figure 10). The polymer particles obtained after just one minute of polymerization show very few spherical particles



EHT = 5.00 kV WD = 15 mm

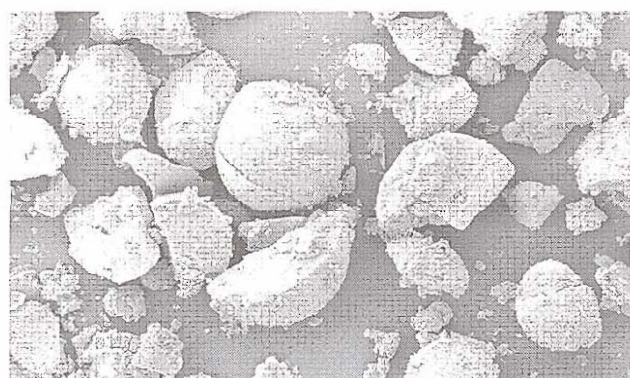
Figure 9. SEM micrograph of $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4 catalyst, magnification 100x.



20 μm

EHT = 5.00 kV WD = 15 mm

(a)



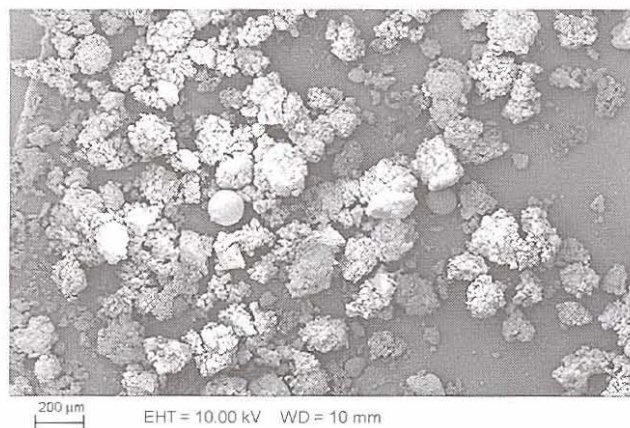
20 μm

EHT = 10.00 kV WD = 10 mm

(b)

Figure 10. SEM micrographs of: (a) $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4 and (b) $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4/TEA , magnification 100x.

as well. A general view of the polymer particles is more likely to the particles of the catalyst treated with



200 μm

EHT = 10.00 kV WD = 10 mm

Figure 11. SEM micrograph of the polyethylene obtained using $\text{SiO}_2/\text{MgCl}_2$ (spherical)/ TiCl_4/TEA catalyst system, polymerization time = 1 min, magnification 100x.

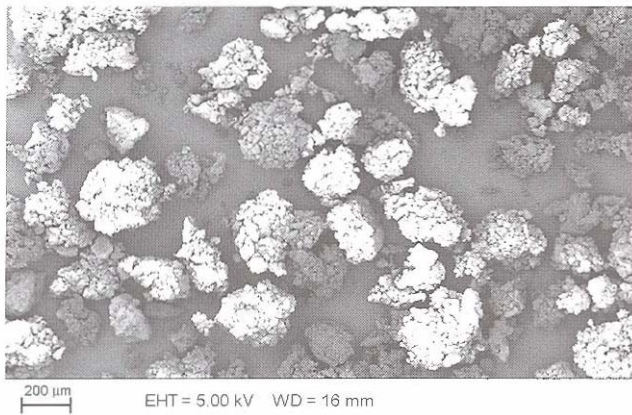
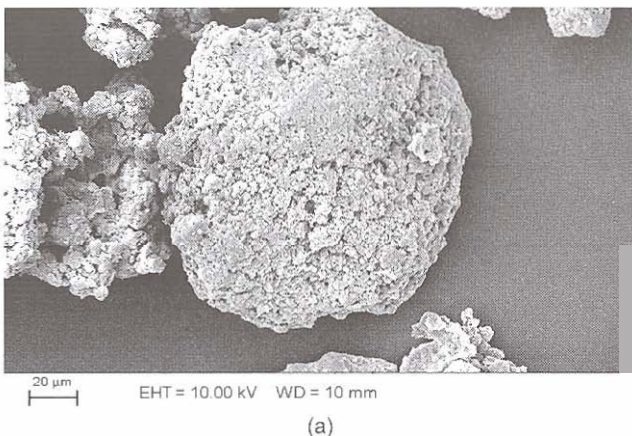
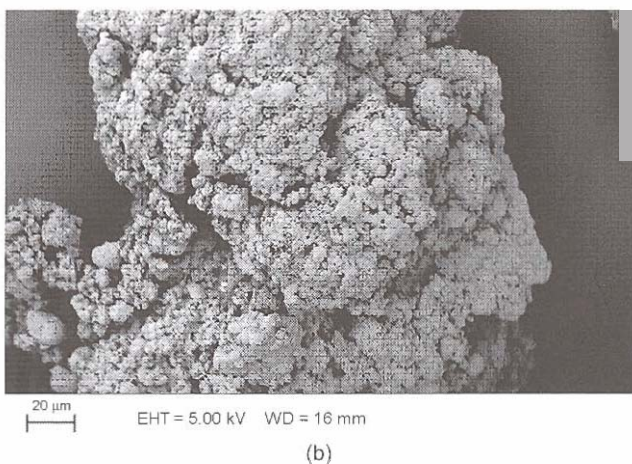


Figure 12. SEM micrograph of polyethylene, polymerization at 60°C, monomer pressure = 2 bars, polymerization time = 1 h, magnification 100x.

TEA than the original particles of the catalyst (Figure 11). SEM micrograph of the polymer particles

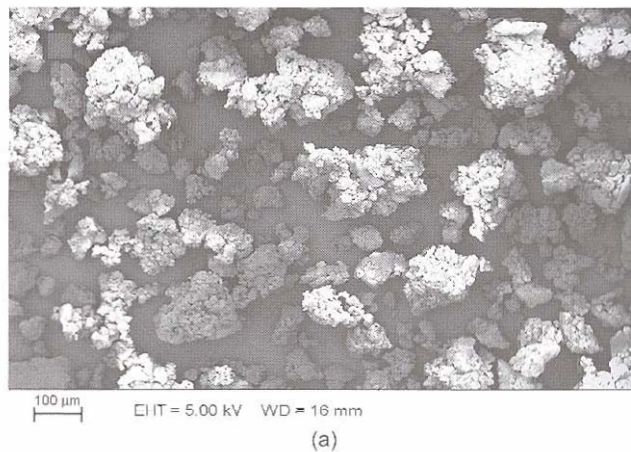


(a)

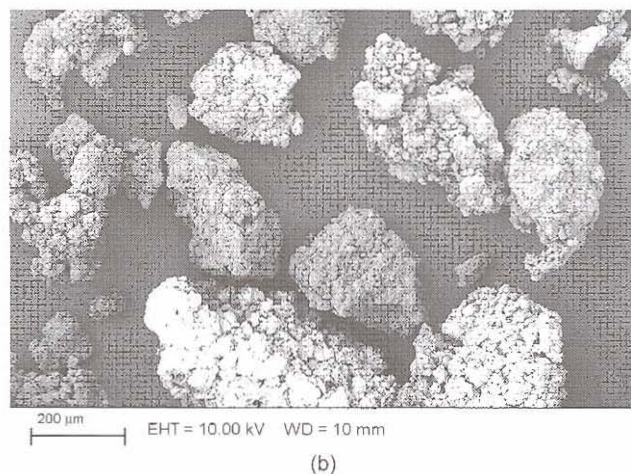


(b)

Figure 13. SEM micrographs of high magnification of two different views (a and b) of the polyethylene, polymerization conditions as in Figure 12, magnification 200x.



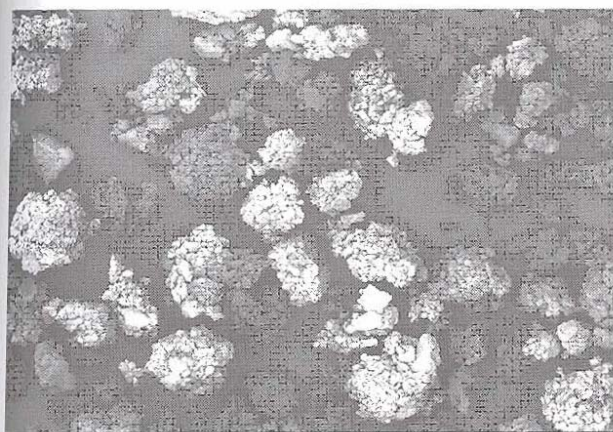
(a)



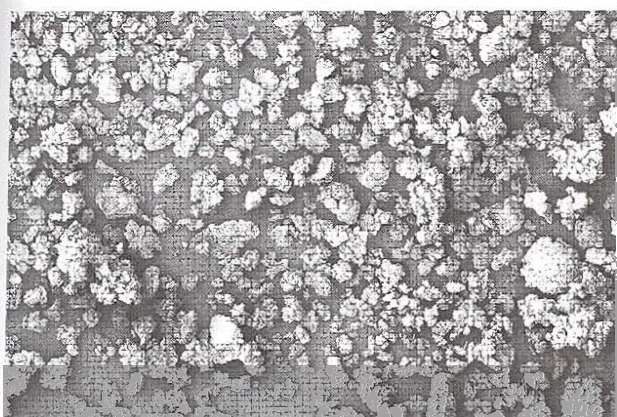
(b)

Figure 14. SEM micrographs of the polyethylene produced at monomer pressure of: (a) 2 bars and (b) 7 bars magnification 200x.

obtained at 60°C and at a monomer pressure of 2 bars shows large particles without any fine dusty polymer, but mainly with irregular shape and a small number of spherical forms (Figure 12). High magnification of the polymer particles shows porous particles (Figure 13). The polymers obtained at monomer pressures of 2 and 7 bars are shown in Figure 14. The particles obtained under a monomer pressure of 7 bars were larger than those obtained at 2 bars. The particles polymerized for 2 h were also larger than the particles obtained after 30 min of the polymerization (Figure 15). The behaviour indicates polymer growth with time. The study indicates that there are many factors that control the morphology of the polymers. The factors include using support(s) with adequate morphological and mechanical stability, catalyst preparation method, polymerization procedure, and reaction conditions. It is unsurprising that the



EHT = 5.00 kV WD = 16 mm
(a)



200 μm
EHT = 10.00 kV WD = 9 mm
(b)

Figure 15. SEM micrographs of polyethylene for polymerization time of: (a) 2 h and (b) 30 min, magnification 100x

morphology was strongly influenced by the initial reaction conditions [5,11].

CONCLUSION

Ultra high molecular weight polyethylene was prepared using a morphologically improved catalyst system of $\text{SiO}_2/\text{MgCl}_2(\text{spherical})/\text{TiCl}_4$. The bi-supported catalyst showed a stable polymerization profile within a temperature range of 55°C to 70°C . The rate/time profile of the polymerization was a decay type. Polymerization activity of the catalyst was increased with increasing the monomer pressure, while increasing hydrogen concentration decreases the activity of the catalyst. Rate of the polymerization was found to be first order with respect to the monomer concentration. The initial stage of the poly-

merization, including the reaction of the catalyst with the cocatalyst and the high polymerization activity, broke up the catalyst particles into smaller particles of irregular shape and size. The morphology of the polymer particles was almost the same as that of the catalyst, which reacted with the cocatalyst at the early stage of the polymerization. In addition, the morphology of the particles may be affected by polymerization conditions, such as temperature and monomer pressure. However, the parameters of the initial stages may also be critical.

ACKNOWLEDGEMENT

The authors wish to thank Mr G. Asghari of DSC Lab of Iran Polymer and Petrochemical Institute and Mrs M. Houshyar Sadeghian of the SEM Lab of Ferdowsi University of Mashhad for their kind help.

REFERENCES

1. Peacock AJ, *Handbook of Polyethylene*, Marcel & Dekker, New York, 2000.
2. Jamjah R, Zohuri GH, Nekomanesh M, Javaheri M, Ahmadjo S, Farhadi A, Synthesizing UHMWPE by a Ziegler-Natta catalyst based on $\text{MgCl}_2(\text{ethoxide type})/\text{TiCl}_4/\text{tri-isobutylaluminum}$, *Macromol Symp*, **274**, 48-153, 2008.
3. Dasilva JC, Defigueiredo GMO, Spherical catalyst, process for preparing a spherical polyethylene of ultra-high molecular weight, *US Patent 6,384,163* (May 7, 2002).
4. Shiraishi T, Uchida W, Matsuura K, Process for preparing ultra-high molecular weight polyethylene, *US Patent 4,962,164* (Oct 9, 1990).
5. Pater JTM, Weickert G, Van Swaaij WPM, Polymerization of liquid propylene with a fourth-generation Ziegler-Natta catalyst: influence of temperature, hydrogen, monomer concentration, and prepolymerization method on powder morphology, *J Appl Polym Sci*, **87**, 1421-1435, 2003.
6. Jamjah R, Zohuri GH, Vaezi J, Ahmadjo S, Nekoomanesh M, Pouryari M, Morphological study of spherical $\text{MgCl}_2 \cdot n\text{EtOH}$ supported TiCl_4 Ziegler-Natta catalyst for polymerization of ethyl-

- ene, *J Appl Polym Sci*, **101**, 3829-3834, 2006.
7. Zohuri GH, Jamjah R, Ahmadjo S, Comparative study of propylene polymerization using monosupported and bisupported titanium-based Ziegler-Natta catalysts, *J Appl Polym Sci*, **100**, 2220-2226, 2006.
 8. Moore EP, *Polypropylene Handbook*, Hanser, Munich, 2005.
 9. Galli P, Vecellio G, Polyolefins: the most promising large-volume materials for the 21st century, *J Polym Sci Part A: Polym Chem*, **42**, 396-415, 2004.
 10. Barbe PC, Cecchin G, Noristi L, The catalytic system Ti-complex/MgCl₂, *Adv Polym Sci*, **81**, 1-81, 1986.
 11. Silva FM, Broyer JP, Novat C, Lima EL, Pints JC, Mckenna TF, Investigation of catalyst fragmentation in gas-phase olefin polymerisation: a novel short stop reactor, *Macromol Rapid Commun*, **20**, 1846-1853, 2005.
 12. Shaotian W, Liu JC, Make MP, Lee CC, Ethylene polymerization process, *US Patent 625,541,5* (Jul 3, 2001).
 13. Kono H, Mori H, Terano M, Novel olefin block copolymer, polypropene-block-poly(methylene-1,3-cyclopentane-co-propene), synthesized from propene and 1,5-hexadiene by a modified stopped-flow method, *Macromol Chem Phys*, **202**, 1319-1326, 2001.
 14. Yamahiro M, Mori H, Nitta KH, Terano M, Synthesis and basic characteristics of polypropene-block-poly(ethene-co-propene) by modified stopped-flow polymerization with an MgCl₂-supported Ziegler catalyst, *Macromol Chem Phys*, **200**, 134-141, 1999.
 15. Fukuda K, Liu B, Nakatani H, Nishiyama I, Yamahiro M, Terano M, Significant variation of molecular weight distribution (MWD) of polyethylene induced by different alkyl-Al co-catalysts using a novel surface functionalized SiO₂-supported Ziegler-Natta catalyst, *Catal Commun*, **4**, 657-662, 2003.
 16. Zohuri GH, Azimfar F, Jamjah R, Ahmadjo S, Polymerization of propylene using the high-activity Ziegler-Natta catalyst system SiO₂/MgCl₂ (ethoxide type)/TiCl₄/Di-*n*-butylphthalate/triethylaluminum/dimethoxy methyl cyclohexyl silane, *J Appl Polym Sci*, **89**, 1177-1181, 2003.
 17. Zohuri GH, Ahmadjo S, Jamjah R, Nekoomanesh M, Structural study of mono- and bi-supported Ziegler-Natta catalysts of MgCl₂/SiO₂/TiCl₄/donor systems, *Iran Polym J*, **10**, 149-155, 2001.
 18. Kissin YN, *Encyclopedia of Polymer Science and Engineering*, Mark HF, Bikales NM, Overberger CG (Eds), 2nd ed, Wiley, New York, **6**, 384, 454, 490, 1986.
 19. Xiao CF, Zhang YF, An SL, Jia GX, Structural changes of gel drawn, ultra-high molecular weight polyethylene fibers with kerosene as a solvent, *Polym Eng Sci*, **40**, 238-246, 2000.
 20. Smith P, Lemstra, PJ, Booij HC, Ultra drawing of high-molecular-weight polyethylene cast from solution. II. Influence of initial polymer concentration, *J Polym Sci Polym Phys Ed*, **19**, 877-888, 1981.
 21. Xiao CF, Zhang YF, An SL, Jia G, Investigation on the thermal behaviors and mechanical properties of ultra high molecular weight polyethylene (UHMWPE) fibers, *J Appl Polym Sci*, **59**, 931-935, 1996.
 22. Ma Z, Sun W H, Zhu N, Li Z, Shao Ch, Hu Y, Preparation of silica supported late transition metal catalyst and ethylene polymerization, *Polym Int*, **51**, 349-352, 2002.
 23. Zohuri GH, Jamjah R, Mehtarani R, Ahmadjo S, Nekoomanesh M, Slurry polymerization of ethylene using bisupported Ziegler-Natta catalyst of SiO₂/MgCl₂(ethoxide type) TiCl₄/TEA system, *Iran Polym J*, **12**, 32-36, 2003.
 24. Brandrup J, Immergut EH, *Polymer Handbook*, 3rd ed, Wiley, New York, Sec VII, 1989.
 25. Zheng X, Loos J, Morphology evolution in the early stages of olefin polymerization, *Macromol Symp*, **236**, 249-258, 2006.
 26. Pater, JTM, Weickert G, Loos J, Van Swaaij WPM, High precision prepolymerization of propylene at extremely low reaction rates-kinetics and morphology, *Chem Eng Sci*, **56**, 4107-4120, 2001.
 27. Abboud M, Deni P, Reichert KH, Fragmentation of Ziegler-Natta catalyst particles during propylene polymerization, *Macromol Mater Eng*, **290**, 558-564, 2005.
 28. Keii T, Suzuki E, Tamura M, Murta M, Doi Y, Propene polymerization with a magnesium chloride-supported Ziegler catalyst. 1. Principal kinetics, *Makromol Chem*, **183**, 2285-2304, 1982.