

Synthesis of Highly Improved Ziegler-Natta Catalyst

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ABSTRACT: The effects of media viscosity, mixing speed, and injection time on catalyst average particle size (APS), particle size distribution (PSD), and morphology in both conditions, with and without emulsifier, were investigated. Supports were prepared using a so-called recrystallization method; then they were catalyzed under the same condition. To show the effects of emulsifier on the final product's properties such as catalyst activity, polymer isotacticity, and so on, two types of catalysts were polymerized and finally their results were compared. Scanning electron microscopy micrographs were used for morphological study. Results show that by

increasing the media viscosity and injection time, APS of the catalyst support was decreased. But by increasing the mixing speed, APS was decreased and PSD was broadened. It was found that emulsifier reduces the sensitivity of APS and PSD of catalyst when the support preparation conditions are changed. Consequently, by employing emulsifier, highly improved catalyst was produced. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 3663–3668, 2009

Key words: Ziegler-Natta polymerization; catalyst activity; isotacticity; poly(propylene); morphology

INTRODUCTION

In the last decades, progresses in the technology of magnesium dichloride supported-Ziegler-Natta catalyst and the development of the slurry phase process have led to the production of different grades of propylene polymers. These polymers are proper for an unlimited number of applications because they can now be tailored for one determined specification. Despite the major technical investigation in the development of the products and process of propylene and ethylene polymerization, the catalyst is always the most important parameter both in the academic researches and industrial products.¹ In the last decades, magnesium chloride supported catalyst for propylene polymerization was produced using the so-called ball-milling method employing an internal donor (ID) and titanium tetrachloride (TiCl₄) as the active catalyst being. During last decade many techniques have been reported on producing spherical support such as spray drying, melt quenching, and recrystallization techniques.^{2–9} Among these methods recrystallization technique has an advantage of yielding a good morphology of catalyst support. These catalysts were cocatalyzed by alkyl aluminum plus an external donor (ED), usually

organic monoester such as ethyl benzoate (EB), or diisobutyl phthalate.¹⁰

Recently, many articles have focused on a new family of Ziegler-Natta catalysts with controlled morphology. According to replication phenomenon the size and morphology of the catalyst and catalyst support particles control the morphology of the resulting polymer particles.^{11,12} The most important step for the preparation of spherical catalyst particles is the support preparation step. This new generation of catalysts often utilizes organic diester as internal donor and silane as external donor.^{10,13} This research focuses on the preparation of MgCl₂.ID.TiCl₄.ED catalysts with controlled morphology from MgCl₂.*n*EtOH adducts, where DIBP and silane compound were used as internal electron donor and external electron donor, respectively. The performance of the catalyst was evaluated in slurry using triethylaluminum (AlEt₃) as a cocatalyst. Previously, some articles have been reported on the some effective parameters on the catalyst support morphology and polymerization conditions on the polymer morphology.^{13–20} In this article, the effects of media viscosity, mixing speed, and injection time on the morphology of the catalyst support in two different conditions (with emulsifier and without it) were investigated. Evidences show that catalyst with narrower particle size distribution (PSD) resulted in polymer with narrower PSD.

To show other advantages of catalysts containing emulsifier, the effects of some parameters such as:

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Al/Ti molar ratio, Al/Si molar ratio, and type of the catalyst on the polymer morphology and isotacticity, in two conditions were investigated. They show that catalysts produced by using emulsifier have higher performance than the others.

EXPERIMENTAL

Materials

Diisobutyl phthalate (DIBP, Merck, Germany) as internal electron donor (ID), ethanol (Merck, Germany), hexane and heptane (Navid Zar Chimi, Iran) were used after passing over molecular sieves (13XA/4°A) and Na before use. Anhydrous MgCl₂ (Merck), Span60 as an emulsifier (Fluka, Buchs, Switzerland), triethylaluminium (TEA) as cocatalyst (AKZO), TiCl₄ (Merck, Germany), silane compound (ED, cyclohexyl methyl dimethoxy silane) as external electron donor, paraffin oil (Merck), methyl siloxane and kerosene were used as received. All operations were performed under nitrogen atmosphere.

Preparation of spherical support

Catalyst support was prepared in a three-glass-reactors arranged in series.¹⁴ In the first reactor, magnesium dichloride was melted in ethanol as a solvent (EtOH/MgCl₂ = 3). The content of the first reactor was transferred via Teflon tube into the second reactor (equipped with stirrer model: Altra Turdax T25basic, IKA, 6500–25,400 rpm, Germany) under vigorous mixing speed, containing different hydrocarbon-based oils (paraffin oil, methyl siloxane, and kerosene) as a medium at 125°C and a proper quantity of emulsifier (span65) at 80°C for 1 h. After the formation of emulsion, the content of the second reactor was transferred into the third reactor containing hexane as a medium under vigorous mixing speed at –30°C for 15 min. After precipitation, the solid was washed out with hexane; then it was dried and collected under nitrogen atmosphere in a glove box for further use. Mixing speed of the third reactor was 1200 rpm and that of the second reactor was 6500 rpm.^{14,21}

Catalyst preparation

TiCl₄ (100 mL) at –20°C (the first curing step) and 7.5 g of the prepared spherical support were added to a 1.0-L glass reactor, equipped with an anchor agitator. The temperature of the reactor increased to 60°C in 3 h and then, 1.74 g of DIBP was added dropwise. The contents were kept at 100°C for 2 h; and then, the mixture was filtered out. The solid product was treated with 120 mL of TiCl₄ at 120°C for 2 h (the second curing step). Finally, the temper-

ature was cooled down to 70°C, and after the removal of the extra TiCl₄ with filtration, the solid catalyst was washed out three times with hexane and then it was dried and stored under N₂ atmosphere.¹⁴

Prepolymerization

Prepolymerization was carried out in a 1.8-L steel jacket Buchi reactor equipped with a mechanical seal stirrer (mixing speed was about 500 rpm, T-type) in slurry phase. After running out all moisture and air by nitrogen, 1 L of *n*-heptane was injected to the reactor. Triethylaluminium (TEA) as a cocatalyst was also injected to the reactor using a glass syringe. Then, silane compounds as an external electron donor (ED) was injected. After that, catalyst was injected to the reactor. Next, titration was performed to determine the ratio of Al/Ti. Then, to control the process of catalyst fragmentation at the beginning time of the reaction and also to prepare polymer with spherical morphology, the catalyst was subjected to prepolymerization condition, 25°C and 1 bar without hydrogen, in 30 min. Finally, the temperature was continually raised to the polymerization temperature.

Polymerization

After prepolymerization step, the polymerization conditions were changed to the polymerization conditions. Meanwhile, 0.3 bar hydrogen (H₂) as a chain transfer agent was used at the end of the prepolymerization step and then propylene was supplied continuously at 7.7 bar and 70°C for 1.5 h. After the polymerization, the untreated gases were slowly released and then the polymer particles were filtered out and dried in vacuum at 70°C overnight to a constant weight.

Polymer fractionation

The atactic and isotactic fractions of polymers were measured by extracting the insoluble fraction of polymers for 5 h with boiling *n*-heptane in a Soxhlet-type apparatus. The boiling-insoluble fraction is isotactic polypropylene, and the boiling-soluble fraction is atactic. The recovered fractions were dried in vacuum at 70°C to a constant weight. The weight percent of *n*-heptane-insoluble polymer in whole samples is referred to as an isotactic index (I.I.).^{22,23}

Characterization

Scanning electron microscopy (SEM) (Philips X130, The Netherlands) images were used for morphological study of polymer and catalyst. Average particles

size and particles size distribution of the catalysts were measured using mercury porosimetry (Thermo quest, Pascal 140, Italy); catalyst activity was calculated as the amount of produced polypropylene per gram of catalyst. Bulk density of polymers was measured using ASTM D1895-67 standard method.

Scanning electron microscopy

The morphologies of the samples were investigated using a Philips environmental scanning electron microscope X130 (Phillips, The Netherlands) equipped with energy dispersive X-ray spectrometer (EDX) for local and area distribution analyses of elements. Catalyst particles and polymer particles produced at different conditions were studied. Samples were mounted on aluminum sputter-coated with gold to make them conductive. Special care was taken during the sample preparation to study catalyst particles because of reactions of the catalyst with air, causing shape deformation.

RESULTS AND DISCUSSION

Effect of media viscosity on the catalyst average particles size and catalyst particle size distribution

Hydrocarbon oils are usually used as a dispersing medium at high temperature (80°C–120°C) in the second reactor for support preparation. Study on the type of the hydrocarbon oils used as the media (in the second reactor) shows that the media viscosity is an effective parameter on the catalyst support morphology. According to Table I, it was found that average particles size for catalyst produced by media with lower viscosity is larger. This behavior reflects that in lower media viscosity particles collided and agglomerated.

Effect of mixing speed

As shown in Table II, Figures 1(A,B) and 2, due to breaking down of the catalyst support at higher mixing speed, average particles size (APS) of the catalyst

TABLE I
Effect of Media Viscosity on APS of Based Catalyst

Catalyst	APS (μm)	Media (Type)	Viscosity
1	17	Paraffin oil	19.68
2	37	Paraffin Oil/siloxane	14.77
3	59	Paraffin oil/Kerosene	11.20

Viscosity order: Paraffin Oil > Siloxane > Kerosene

Paraffin/ Siloxane (v/v = 1), Paraffin/ Kerosene (v/v = 1).

Injection time (t_{inj} = 30 s) is the time of injection support adduct from first reactor into the second reactor.

N = 21,500 rpm, Et (OH)/MgCl₂ = 2.8 molar ratio, Emul/MgCl₂ = 0.16.

TABLE II
The Effect of Emulsifier and Mixing Speed on the Particles Size Distribution of Support Catalyst

N (rpm)	Span value ^a (μm)	
	Without emulsifier	With emulsifier
6500	1.12	1.08
9800	1.32	1.12
21,500	1.46	1.14
25,400	1.68	1.23

EtOH/MgCl₂ = 2.8; Media: Paraffin/Siloxane (v/v = 1).

^a Span value is the measure of the volume distribution relative to the median diameter; lower Span value means narrower PSD.

support decrease, but PSD is broadened (Span values were increased).²⁴

It is known that broad catalyst particle size distribution produced at higher mixing speed is the key problem for the polymerization process and extrusion. It will be discussed in the final section of this article.

Figures 1(A,B) and 2 and Table II show that by using emulsifier, the effects of mixing speed on the support morphology is far lower than another, samples without emulsifier.

Emulsifier prevents catalyst support from clustering and breaking, because it covers them with a thin layer. This method enables us to produce lower average particle size at higher mixing speeds besides sharper particles size distribution.

Effect of injection time

As shown in Table III, by decreasing the injection time, the time that is taken to inject adduct from first reactor to the second reactor, APS and PSD values increase in both containing emulsifier and without it, because support particles cluster. But the values belonged to the samples containing emulsifier are more acceptable.

The effect of polymerization condition on catalyst and polymer properties

Table IV shows that for the same catalyst, by increasing the Al/Ti molar ratio, the catalyst activity increases from 7.0 to 8.1 and then decreases to 7.80. The catalyst activity increases due to increase in the active center sites at higher Al/Ti molar ratio. The main reason for decreasing the catalyst activity at higher Al/Ti molar ratio is converting the Ti⁴⁺ valance to Ti³⁺, which leads the catalyst activity to reduce. Furthermore, it is observed that changing the activity in the first step, from 7.0 to 8.1 is more significant to the second step, 8.1 to 7.8. Because at Al/Ti = 100, the catalyst has the maximum number of active site; by increasing the Al/Ti molar ratio, no

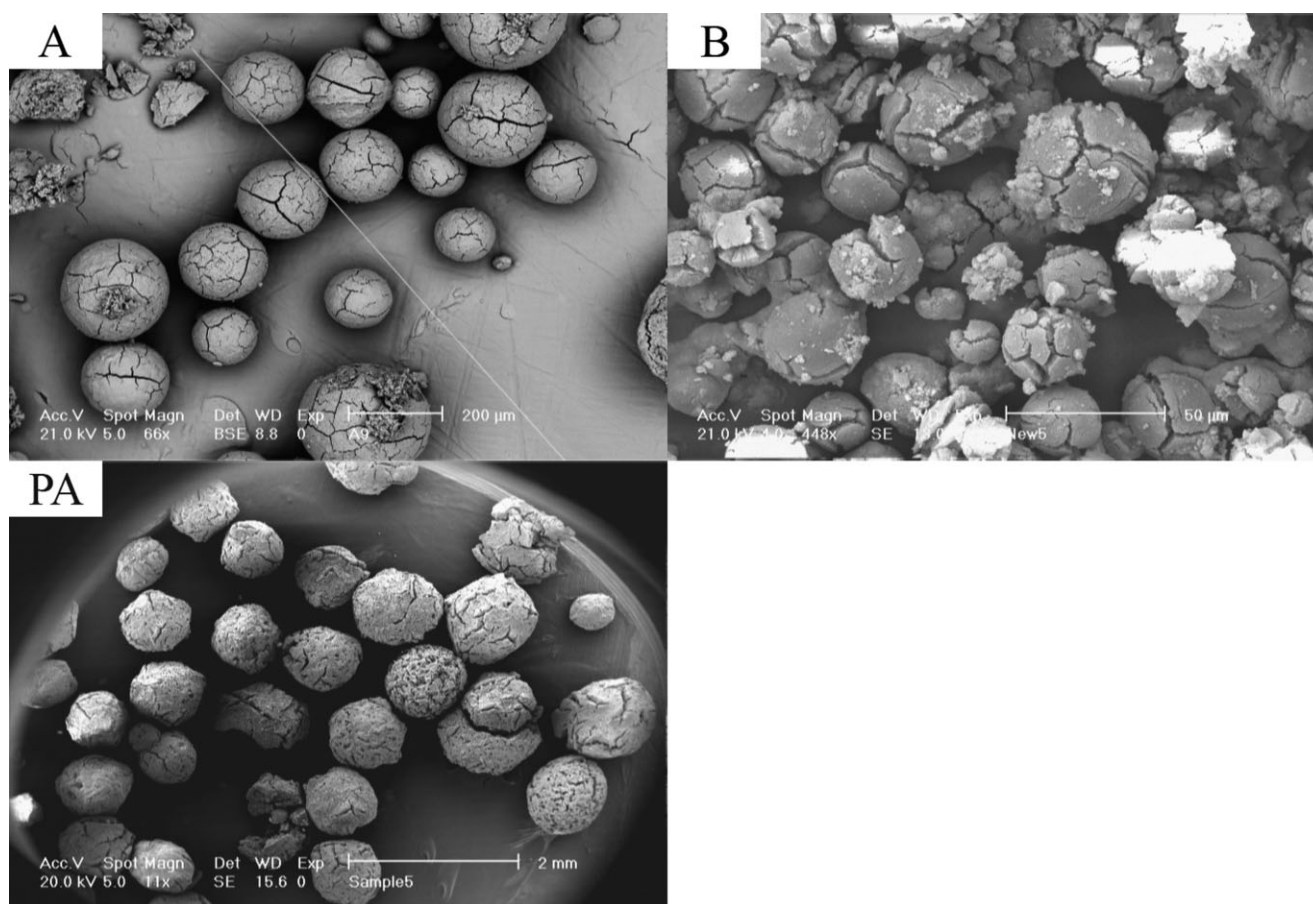


Figure 1 Scanning electron microscopy (SEM) images of catalyst and polymer. (A) Catalyst containing emulsifier; (PA) polymer produced with catalyst A; (B) catalyst without emulsifier; the other support preparation condition for two catalysts is alike.

more site is activated but the competition between monomer and Al in reaching the catalyst active sites increases. In this fact, few numbers of monomers are prohibited to reach the active site, and activity decreases in a limited range.

On the other hand, the extra Al/Ti molar ratio as though leads to titanium valence reduction from Ti^{3+} to Ti^{2+} , which is inactive to polymerization, and the catalyst activity decreases.²⁵ Generally, reduction in Ti concentration reduces the catalyst activity.²⁶ By increasing the Al/Ti molar ratio, this behavior reveals that polymer average particles size directly depends on the catalyst activity.

From Table IV it can be observed that by increasing the catalyst activity, bulk density of resulted polymers increases. The main reason for this behavior is that the number of catalysts is constant but the layer of polymer particles around the catalysts grows. This condition resulted in the increase of the bulk density. In this fact, the bulk density is parallel to catalyst activity by changing the Al/Ti molar ratios.

According to Table IV, for the same catalyst, by increasing the Al/Ti molar ratio, isotacticity index (I.I%) of the polymer gradually increases. Because

single metal active centers are converted to double metal active centers which lead to the reduction in atactic fraction and increasing the isotactic part.²⁷

Also, Table IV shows that the Si/Ti molar ratios have the major effect on the catalyst activity. For the

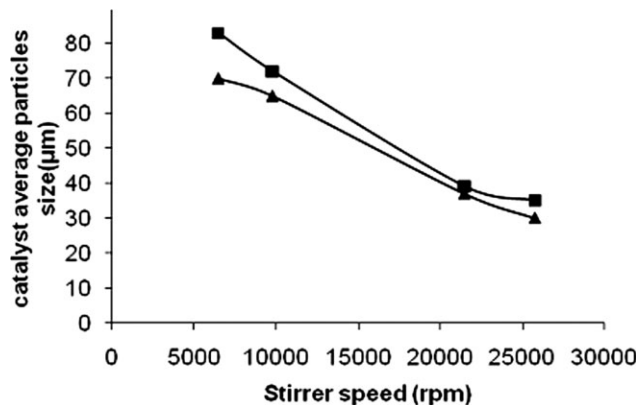


Figure 2 The effect of stirrer speed on the catalyst average particles size (APS) (μm), with emulsifier (■) and without emulsifier (▲). Preparation condition: Injection time = 30 s; media: Paraffin/siloxane (v/v = 1); EtOH/ MgCl_2 = 2.8.

TABLE III
The Effect of Emulsifier and Injection Time on the Average Particles Size and Particles Size Distribution of Support Catalyst

Injection time ^a (s)	APS1	APS2	Span value (μm)	
			Without emulsifier	With emulsifier
10	48	46	1.62	1.39
15	45	42	1.58	1.30
20	44	39	1.51	1.24
25	42	36	1.50	1.14
30	39	37	1.46	1.14

$N = 21,500$ rpm; EtOH/ $MgCl_2 = 2.8$; Media: Paraffin/Siloxane ($v/v = 1$).

^a Injection time is the time of injection support adduct from first reactor into the second reactor.

same catalysts, by increasing the Si/Ti molar ratio from 6.67 to 8.00, catalyst activity increases from 8.4 to 8.7; because the ratio of atactic center to isotactic center decreases. Although the number of atactic center for higher silane contents decreases, catalyst activity decreases from 8.7 to 6.5 because the large numbers of active centers are poisoned and occupied with the bulky silane groups.

The effects of catalyst type on catalyst activity and polymer properties

Catalyst activity and polymer isotacticity are strongly depended on the polymerization condition and catalyst type. Each catalyst combination has an optimum condition in which catalyst has a maximum activity, besides resulted polymer has a proper isotacticity

index. Different optimum conditions for each catalyst are related to their catalyst preparation condition and their elements. In the previous section, it was shown that each catalyst has a maximum catalyst activity in a certain Al/Ti molar ratio. On the other hand, by increasing the Si/Ti molar ratio, catalyst activity at first slowly increases and then suddenly decreases; but isotacticity index regularly increased. Since both catalysts activity and isotacticity index are very important parameters in industrial and academic researches, all catalysts were polymerized at condition in which they have the highest catalyst activity while isotacticity index is at least 95%. The various polymerization conditions for the first catalyst (M25400N35) are shown in Table I, but for other catalysts, the above-mentioned condition were applied. As a comparison, applying various polymerization conditions for different catalysts, reveal that it is not true to compare them at a constant condition. Because one specific condition may be optimum for one specific catalyst while for others is the worst condition.

Table IV shows, when comparing samples with emulsifier and without it, the higher catalyst activity and polymer isotacticity for the first samples can be observed. The reasons for improvement in catalyst activity are outlined as bellow:

1. As it is known, emulsifier tends to make the more spherical particles, because of decreasing the surface tension of the particles; as a result, highly regular catalyst particles with narrow PSD were produced. In the prepolymerization step, these regular particles have highly regular fragmentation. Narrow fragments tend to make a large number of active sites, during

TABLE IV
Catalyst $MgCl_2/DIBP/TiCl_4/TEA/EB$ Performance in Propylene Slurry Polymerization and Some Polymer Properties

Catalyst label	Catalyst D_{50} (μm)	Al/Ti (molar ratio)	Si/Ti (molar ratio)	Activity (kg. P/g.cat)	II (wt %)	Polymer D_{50} (μm)	Polymer bulk density (g/cc)
M25400N35A ^a	35	80	7.77	7.0	–	663	0.39
M25400N35B	35	100	7.77	8.1	90.1	715	0.40
M25400N35C	35	120	6.67	8.4	95.3	750	0.41
M25400N35D	35	140	7.77	7.8	96.0	680	0.40
M25400N35E	35	120	8.00	8.7	97.1	740	0.42
M25400N35F	35	120	12.0	6.5	98.4	550	0.38
M21500N39	39	100	5.00	8.2	–	–	–
M9800N72	72	140	5.60	8.0	97.2	–	0.40
M6500N83	83	120	6.67	7.5	96.0	–	–
M25400E36	36	170	11.3	8.6	97.4	790	0.42
M21500E37	37	120	8.00	8.7	95.7	–	–
M9800E65	65	100	6.67	8.6	98.4	–	–
M6500E70	70	120	8.00	8.0	98.0	722	–

The polymerization condition for each catalyst (M21500N39-M6500E70) was performed at its maximum catalyst activity when isotacticity above than 95% is considered.

Polymerization conditions: Catalyst 4cc (0.02 g cat/cc catalyst slurry), $T = 70^\circ C$; P (propylene) = 7.7 bar; $t = 1.5$ h; P (hydrogen) = 0.3 bar.

^a M(N/E)(b) = (Mixing speed, rpm)(no emulsifier/emulsifier)(catalyst D_{50}).

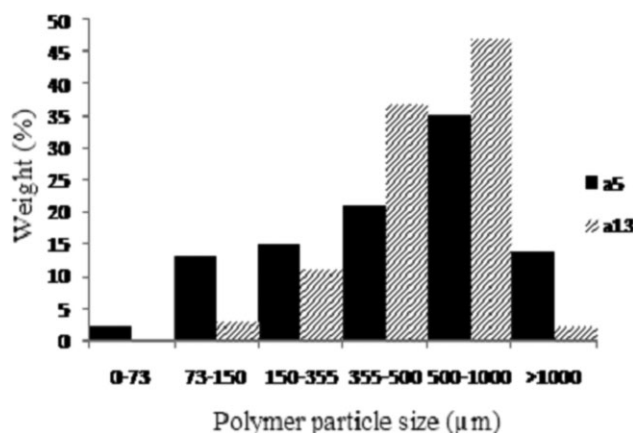


Figure 3 The effect of catalyst particles size distribution on the polymer particle size distribution. a5: polymer produced using catalyst A5 at vigorous mixing speed with no emulsifier, a13: polymer produced using catalyst A13 at lower mixing speed and using emulsifier all of the polymerization condition were described in Table 4.

prepolymerization and polymerization and then resulted in increasing the catalyst activity.

- ED plus emulsifier provide a unique ED which decreases the atactic sites; it resulted in more stable isotactic sites and improved catalyst activity. This behavior was discussed in the previous section. In addition, it behaves as a bridging during the support preparation step, because of its highly large groups; and it can also have the role of blend of two ID when adding to DIBP, which increases the activity of catalyst.
- According to Figure 1, having better mechanical properties of samples containing emulsifier (according to morphology) is another important reason for improving the catalyst activity, because the amount of fine formation gets its lowest value during the polymerization step.

The main reason for increasing the isotacticity is that as this material affects as a donor which increases the polymer isotacticity.

The effect of catalyst particle size distribution on the polymer particles size distribution

As shown in Figure 3, using catalyst with broader particle size distribution leads to production of polymers with broader particle size distribution. The reason is based on the replication phenomenon, in which polymer morphology replicates to catalyst morphology. Therefore, using emulsifier has an advantage of producing catalyst with narrower particles size distribution.

CONCLUSIONS

Highly active spherical Ziegler-Natta catalyst was synthesized using emulsifier as a surfactant agent.

According to experimental results, by increasing the mixing speed of homogenizer, average particles size of supports decreases and particles size distribution increases. By increasing the injection time from the second reactor to the third reactor and media viscosity, particles size of support decrease. In general, by using emulsifier, the effects of injection time and mixing speed on the support morphology decrease. It is possible to produce lower average particles size of catalyst and sharper particles size distribution by using emulsifier. It is observed that type and condition of support preparation affect the polymer isotacticity, the catalyst activity and particle size distribution. Finally, it can be concluded that polymer produced by catalysts containing emulsifier show a large fraction of isotacticity.

References

- Galli, P.; Simonazzi, T.; Del Duca, D. *Acta Polym* 1988, 39, 81.
- Iiskolan, E.; Koskinen, J. U.S. Pat. 4,829,034 (1989).
- Chung, J. S.; Song, I. K.; Lee, W. Y. *Macromol Chem Phys* 1995, 196, 1205.
- Sacchetti, M.; Govoni, G.; Fait, A. U.S. Pat. 6,407,028 (2000).
- Forte, M.; Coutinho, F. M. B. *Eur Polym J* 1996, 32, 223.
- Miya, S.; Tachibana, M.; Karasawa, Y. U.S. Pat. 5,100,849 (1992).
- Yu, H. J.; Wang, L.; Ye, Z. Y.; Ma, Z. L.; Jiang, S.; Wang, J.; Feng, L. F.; Gu, X. P. *Polym Plast Tech Eng* 2004, 43, 1115.
- Chung, J. S.; Han, J. H.; Cho, H. S.; Lee, W. Y.; Park, H. M. *Angew Makromol Chem* 1997, 253, 11.
- Wu, L.; Lynch, D. T.; Wanke, S. E. *Macromolecules* 1999, 32, 7990.
- Barbe, P. C.; Cecchin, G.; Noristi, L. *Adv Polym Sci* 1987, 81, 1.
- Galli, P.; Barbe, P. C.; Noristi, L. *Angew Makromol Chem* 1984, 120, 73.
- Galli, P.; Luciani, L.; Cecchin, G. *Angew Makromol Chem* 1981, 94, 63.
- Spitz, R.; Masson, P.; Bobichon, C.; Guyot, A. *Die Makromol Chem* 1989, 190, 717.
- Ye, Z.-Y.; Wang, L. *J Polym Sci Part A: Polym Chem* 2002, 40, 3112.
- Rubin, H.; Dongbing, L.; Shibo, W.; Bingquan, M. *Macromol Chem Phys* 2004, 205, 966.
- Abboud, M.; Peter, D.; Karl-Heinz, R. *J Appl Polym Sci* 2005, 98, 2191.
- Abedi, S.; Daftari-Besheli, M.; Shafiei, S. *J Appl Polym Sci* 2005, 97, 1744.
- Smit, M.; Severn, J. R.; Zheng, X.; Loos, J.; Chadwick, J. C. *J Appl Polym Sci* 2006, 99, 986.
- Jochem, T.; Pater, M.; Gunter, W.; Wim, P. M.; Van, S. *J Appl Polym Sci* 2003, 87, 1421.
- Tao, J.; Wei, C.; Feng, Z.; Yuexiang, L.; Ruen, W.; Hongbin, D.; Tianyi, Z. *J Appl Polym Sci* 2005, 98, 1296.
- Krystyna, C.; Bozena, K. *Macromol Chem Phys* 1998, 199, 451.
- Rob, R. C. (Shell Oil Co.). U.S. Pat. 4,525,065 (1985).
- Lee, D. H.; Jeong, Y.; Soga, K.; Shiono, T. *J Appl Polym Sci* 1993, 47, 1449.
- Jamjah, R.; Zohuri, G. H.; Vaezi, J.; Ahmadjo, S.; Nekomanesh, M.; Pouryari, M. *J Appl Polym Sci* 2006, 101, 3829.
- Ye, Z.; Wang, L.; Jiang, Sh. *J Appl Polym Sci* 2003, 90, 3737.
- Tait, P. J. T. *Catal Olef Polym* 1990, 56, 11.
- Busico, V.; Corradini, P.; De Biasio, R. T. *Macromol Chem Phys* 1992, 193, 1765.