

Effect of Prepolymerization on Propylene Polymerization

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ABSTRACT: Polymerization of propylene was performed using MgCl₂. EtOH.TiCl₄.ID.TEA.ED catalyst system in hexane, where internal donor (ID) was an organic diester and external donor (ED) was a silane compound and also triethyl aluminum (TEA) as activator. A new method called isothermal/nonisothermal method (INM), a combination of isothermal and nonisothermal methods, was applied to produce the spherical polymer particles. The effects of the INM method and prepolymerization temperature on the final polymer morphology, M_w , and

catalyst activity were also investigated. The morphology of the polymers was evaluated through scanning electron microscopy (SEM) images. GPC results were used for molecular weight (M_w) evaluation. It was found that the polymers had a better morphology when they were prepared using INM method. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 1863–1867, 2009

Key words: Ziegler-Natta polymerization; poly(propylene); GPC; morphology

INTRODUCTION

Molecular weight, molecular weight distribution and morphology are the most effective parameters on the polymer properties. Because of having multisite, the polymers produced by Ziegler-Natta catalyst have broad MWD.^{1–4} At the beginning of the polymerization process, high catalyst activity may lead to a rapid temperature increase in the center of the catalyst. Because of low catalyst surface area and difficulty of the heat transfer at the initial time of polymerization, it is possible for the catalysts to be destroyed with increasing temperature.^{3–6} Using prepolymerization technique, catalyst surface area gradually increases at low reaction rate and also the fragmentation of the catalyst particles is controlled without fine formation.^{7,8} It is clear that many crystals agglomerate to form a catalyst particle.⁹ At the prepolymerization step, these crystal fragments are separated and covered with a thin layer of prepolymer formed at mild conditions. In fact, the mild conditions are responsible for the production of the regular fragments' size and better replication of the catalyst shape.¹⁰ Broad polymer particle size distribution and irregular morphology of polymer are the results of polymerization without using mild condi-

tions, because crystals are fragmented at very irregular shapes.^{8–11}

Totally, two main methods were reported in literature for the prepolymerization of olefins in Ziegler-Natta type polymerization systems: isothermal prepolymerization (IPP) and nonisothermal prepolymerization (NIPP). The isothermal method has an advantage of independency between the prepolymerization temperature and some polymer properties. The nonisothermal method has a disadvantage of shocking catalyst at the high conditions by the rapid rate of changing. As the nonisothermal method shocks the catalyst because of a sudden temperature increase, the polymers produced by this method do not show a very good behavior the same as the isothermal method. Some articles have been published on the effects of the prepolymerization conditions on the catalyst behavior and the produced polymer properties. The effects of polymerization time, Si/Mg molar ratio, hydrogen, temperature and type of catalyst on the catalyst and the produced polymers were also studied.^{12–16}

The present article reports on the prepolymerization methods and the effect of the prepolymerization temperature on the catalyst activity and M_w , morphology and isotacticity of the produced PP and finally, a novel technique for prepolymerization was suggested. This technique was a combination of IPP and NIPP methods. Because prepolymerization is widely used for the commercial production of PP and PE, such results can be of interest for PP and PE commercial producers and researchers in this field.

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EXPERIMENTAL

Materials

Diisobutyl phthalate (DIBP), ethanol, anhydrous MgCl_2 , TiCl_4 , silane compound, and paraffin oil were purchased from Merck. (Germany). Hexane and heptane were prepared from Navid Zar Chemical. (Iran). Span65 and TEA were purchased from Fluka. (Switzerland).

Preparation of spherical support

Catalyst support was prepared in three glass reactors arranged in series. In the first reactor, magnesium dichloride was melted in ethanol as a solvent ($\text{EtOH}/\text{MgCl}_2 = 3$). The content of the second reactor was transferred via Teflon tube into the second reactor (equipped with stirrer model: Altra Turdax T25basic, IKA, 6500-25400 rpm, Germany) under vigorous mixing, with hydrocarbon-based oil (paraffin oil) as a media 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 one contained hexane as the media under vigorous mixing at -30°C for 15 min. After precipitation, the solid was washed out with hexane for three times and then, 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 one was 6500 rpm.^{17,18}

Catalyst preparation

One hundred milliliter of TiCl_4 at -20°C (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 2 h and then, 1.74 g 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 TiCl_4 at 120°C for 2 h (second curing step). Finally, the temperature was cooled down to 70°C , and after the removal of the extra TiCl_4 with filtration, the solid (catalyst) was washed out three times with hexane and then, dried and stored under N_2 atmosphere.^{17,18}

Prepolymerization methods

Two different types of prepolymerization procedure are generally used in the Ziegler-Natta type polymerization. In the first case, a so-called isothermal prepolymerization (IPP) was used. Here, the reactor was prepared at 10°C and then, the components containing TEA, ED, catalyst and monomer were

injected. After 30 min, the reactor temperature was raised to the main polymerization temperature (70°C) as quickly as possible.

In the second case, a so-called nonisothermal prepolymerization (NIPP) was used. Here, the reactor was prepared at 10°C . The donor, TEA and catalyst were injected and then, the reactor temperature was raised to 70°C in 30 min. In this case, a short prepolymerization was resulted at a varying temperature (increasing from the injection temperature to the main polymerization temperature).^{12,13}

In the new case, at the first, the catalyst was subjected at the mild polymerization conditions similar to IPP in 20 min and then, the temperature steadily increased to the polymerization temperature in 10 min the same as NIPP. This method assembles the advantages of the two previous prepolymerization methods; In fact, INM is a combination of the IPP and NIPP methods.

Polymerization

Polymerization of propylene was performed in a 1.8 L steel jacket Buchi autoclave reactor equipped with a mechanical seal stirrer (mixing speed was around 500 rpm, anchor form) in the slurry phase.

After running out of all moisture and air by nitrogen, 1 L of *n*-hexane was added to the reactor. Adequate amounts of ED, TEA and 0.04 g of catalyst in hexane (0.02 gCat/mL hexane) were injected into the reactor. To control the catalyst morphology during the fragmentation process, the mild conditions were applied in the prepolymerization step. After the prepolymerization step, the polymerization conditions were changed to the main polymerization conditions. Meanwhile, 0.3 bar hydrogen as a chain transfer agent was used at the end of the prepolymerization step and then propylene was supplied continuously at 7.7 bars and 70°C for 1.5 h.

After the polymerization, the untreated gases were slowly released and the polymer was then filtered and dried in vacuum at 70°C overnight to a constant weight.

Polymer fractionation

The isotactic fraction of polymers was measured by extracting atactic fraction of polymers for 6 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 constant weight. The wt % of *n*-heptane-insoluble polymer in a whole sample is referred to as the isotactic index (I.I.).^{19,20}

TABLE I
Effect of the Prepolymerization Methods on the Catalyst Activity

Prepolymerization	Without prepolymerization	IPP	NIPP	INM
Catalyst activity (kgPP/gCat)	6.5	8.1	7.4	8.3

Polymerization conditions: $t = 90$ min, $T = 70^\circ\text{C}$, $\text{H}_2 = 0.3$ bar, $\text{Al/Ti} = 170$, $\text{Al/Si} = 20$, $P: 7.7$ bar prepolymerization method: INM.

Characterization

Scanning electron microscopy (SEM) (Philips XI30, Netherlands) photos were used for the morphological studies of the polymers. The activity of the catalyst was calculated as the amount of the produced polypropylene per gram of the used catalyst. The molecular weight of the polymers was measured using GPC (2000, WATERS USA).

RESULTS AND DISCUSSION

Catalyst behavior

MgCl_2 supported TiCl_4 catalysts are widely used in many commercial processes to produce the various grades of polypropylene. The $\text{MgCl}_2\cdot\text{EtOH}\cdot\text{TiCl}_4\cdot\text{ID}\cdot\text{TEA}\cdot\text{ED}$ catalyst system is one of the most important MgCl_2 Supported TiCl_4 catalyst systems that usually shows not only high activity and stereoselectivity but also good morphology in olefin polymerization.^{3,21,22}

The prepolymerization usually increases the rate of the regular polymerization and improves the resistance of the catalyst to deactivation and fragmentation that finally leads to better activity, stereoselectivity and morphology.^{12,13,23}

The effect of the prepolymerization on the catalyst activity in propylene polymerization using the above catalyst system was shown in Table I. As the table shows, the activity of the catalyst increases by carrying out prepolymerization. According to the table, the prepolymerization method had also influence on the catalyst activity so that about 10% increase in the catalyst activity was observed. Meanwhile, the INM had the best effect on the catalyst activity compared with the other methods; on the other hand, the isothermal prepolymerization method showed better activity than the nonisothermal prepolymerization method. In fact, sudden increasing the temperature caused a slight shock to the catalyst in NIPP method whereas there was not such a shock in IPP method. In INM method, the prepolymerization was performed at 10°C (the same as NIPP method) and

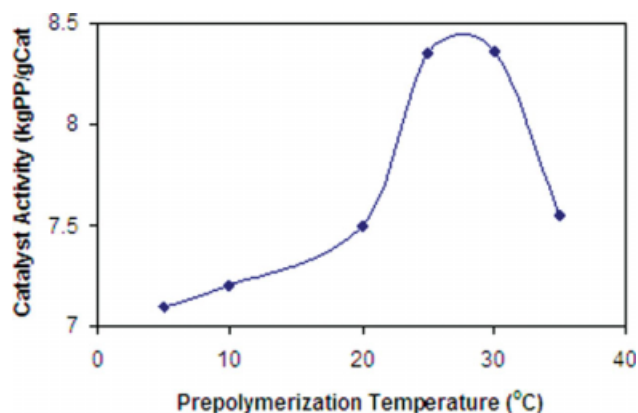


Figure 1 Effect of the prepolymerization temperature on the catalyst activity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

then, the temperature gradually increased to the main polymerization temperature (the same as IPP method). In that case, the influence of the sustained shock on the catalysts particles was minimum.

Figure 1 shows the effect of the prepolymerization temperature on the catalyst activity. As the figure shows, the activity of the catalyst increased by increasing the prepolymerization temperature and then decreased. The maximum activity was observed at $25\text{--}30^\circ\text{C}$. That result might be ascribed to the destruction of the active sites at the higher prepolymerization temperature.

POLYMER CHARACTERIZATION

Isotacticity

Figure 2 shows the effect of the prepolymerization temperature on the isotacticity of the produced polymers. According to the figure, the isotacticity of the produced polymers gradually increased by increasing in the prepolymerization temperature and then slightly felled down because of the destruction of the active sites at the higher prepolymerization temperature.

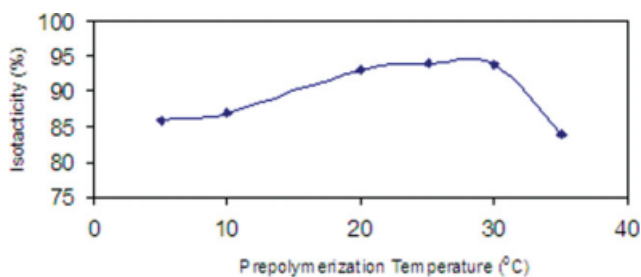


Figure 2 Effect of the prepolymerization temperature on the isotacticity of the produced polymers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com]

TABLE II
Effect of the Prepolymerization Temperature on the Molecular Weight of the Produced Polymers

Prepolymerization temperature (°C)	10	20	30	40
M_w	30,000	117,220	149,000	199,000

Molecular weight

The effect of the prepolymerization temperature on the molecular weight of the produced polymers has been shown in Table II. According to the table, the molecular weight of the produced polymers was

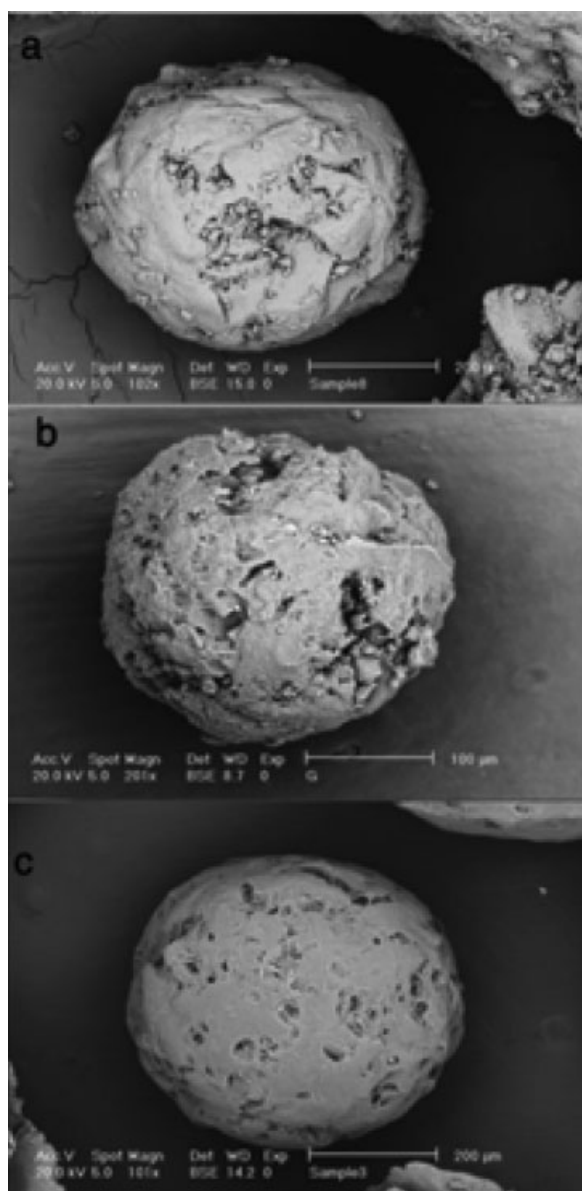


Figure 3 Effect of prepolymerization method on the polymer morphology: (a) isothermal (b) nonisothermal, and (c) INM.

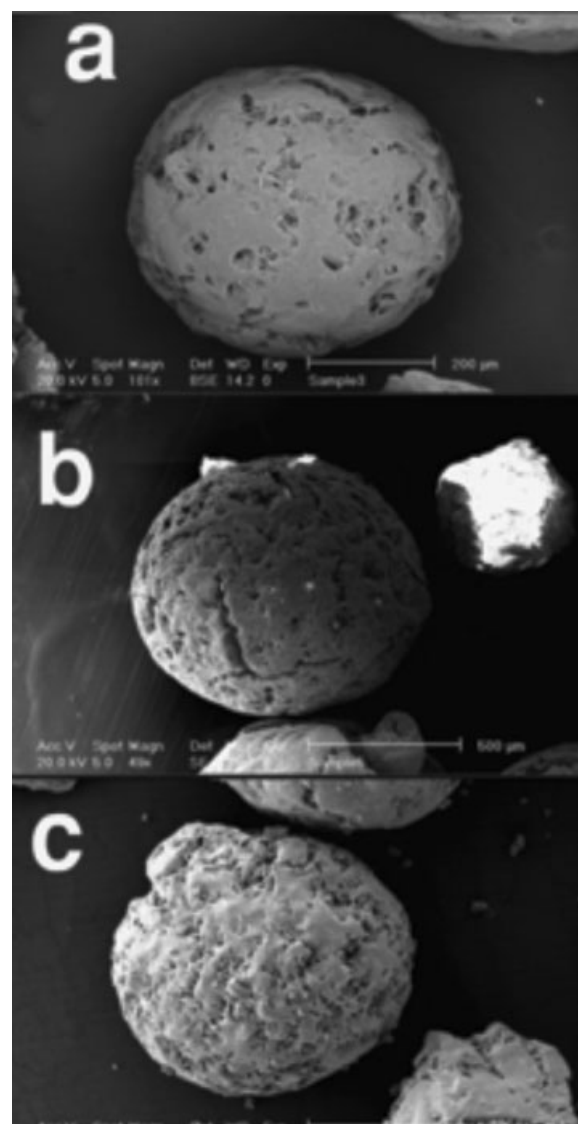


Figure 4 Effect of prepolymerization temperature on the polymer morphology: (a) 10°C (b) 20°C, and (c) 30°C.

noticeably sensitive to the prepolymerization temperature. In fact, it sharply increased with increase in the prepolymerization temperature; because the activity of the catalyst increased at the higher temperature. For example, the molecular weight was 30,000 at 10°C, whereas it increased to about 117,000 and 200,000 at 20 and 40°C, respectively.

SEM

Figure 3 shows the effect of the prepolymerization methods on the morphology of the produced polymers. Totally, prepolymerization improves the morphology of the polymers. The reason is that a thin layer of the polymer is formed on the catalyst that

protects it against the sustained shocks in the main polymerization conditions.

According to the figure, the polymer obtained from the INM showed better spherical shape than the other methods. Meanwhile, the morphology of the polymer produced by the isothermal method was slightly better than that of the produced polymer by the nonisothermal method. The SEM images also show that the porosity of the polymers produced by the INM was noticeably less than that of the other polymers. The main reason is that the minimum shock was sustained to the catalysts in the INM method compared with the two other methods.^{12,13}

In addition to the prepolymerization method, the temperature of the prepolymerization had a remarkable effect on the morphology of the produced polymers.^{12,13} Figure 4 shows the SEM images of the polymers obtained from various temperatures in INM prepolymerization method. According to the figure, the morphology of the polymers was gradually destroyed with increasing the polymerization temperature because the rate of the polymerization increased in the higher temperature. In fact, the amount of the produced heat increased when the polymerization rate went up. This heat increase led to the destruction of the polymer morphology at the higher temperature. Also, the polymers prepared at the high prepolymerization temperature showed more porosity.

CONCLUSIONS

The $\text{MgCl}_2\cdot\text{EtOH}\cdot\text{TiCl}_4\cdot\text{ID}\cdot\text{TEA}\cdot\text{ED}$ catalyst system has shown high stereoselectivity and activity in the polymerization of propylene in the slurry phase.

Markedly, the activity and stereoselectivity of the catalyst increased with prepolymerization. Meanwhile, the prepolymerization method and also polymerization temperature are effective on the catalyst behavior and the morphology of the produced polymers. SEM images show that the produced polymer with INM method had more spherical shape com-

pared with the IPP and NIPP methods. Totally, the hybrid system of the isothermal/nonisothermal prepolymerization method, especially in low temperature, is a suitable method for the prepolymerization of Ziegler-Natta catalysts. Also, the prepolymerization at low temperature led to a better morphology.

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