Influence of temperature on ethylene octene-1 copolymerization catalyzed by supported metallocene catalyst

Wang Dengfei1,2*, Wang Jian1, He Shuyan2, Yan Yibin3, Yang Guoxing2, Zhao Xinglong2, Guo Feng2

1Provincial Key Laboratory of Oil & Gas Chemical Technology, College of Chemistry & Chemical Engineering, Northeast Petroleum University, Daqing 163318, China
2Daqing Petrochemical Research Center, Petrochemical Research Institute of PetroChina, Daqing City, Heilongjiang Province, 163714, China
3Shantou High-tech Industrial Development Zone Industry and Technology Service Center, Shantou City, Guangdong Province, 515051, China

*Corresponding author: Wang Dengfei, email: wdf459@petrochina.com.cn

Abstract: A supported (nBuCp)2ZrCl2 metallocene catalyst was prepared and used in the slurry copolymerization of ethylene/octene-1 with triethylaluminium (TEAL) as co-catalyst. The effects of polymerization temperature on the properties of both the catalyst and resulted copolymers were investigated. The results show that the yield of supported metallocene catalyst reaches 4.3 kgPE/gcat and the bulk density of PE is higher than 0.4 g/cm3, the fines content of the polymer is less than 12.0 wt%, and the molecular weight distribution (MWD) of products ranges from 2.9 to 4.0 within the polymerization temperature range of 73~88 ℃. These results are beneficial for large-scale industrialization of supported metallocene catalysts, and also provide a reference for academic research.

1. Introduction
As one of the most common polyolefin, polyethylene is the largest thermoplastic polymer in the world. Due to its excellent strength, temperature performance range and fatigue resistance, the global demand for polyethylene materials from the end user industries such as automotive, construction and packaging is expected to rise dramatically[1-3]. With the rapid growth of polyethylene production capacity, the competition of traditional polyethylene market is increasingly fierce[4]. Therefore, it is urgent to develop high-end products with high added-value.

Metallocene catalysts are famous for their versatility and flexibility in the synthesis of polyolefins with controllable microstructures[5-11]. Due to their high insertion ability of alpha-olefin such as butene-1 and hexene-1 into copolymer chains, copolymerization technology has always been one of the most active research directions of metallocene[12]. By changing the combination catalyst structure and monomers modifications, copolymers with different physical properties can be obtained, which is of great significance for the development of high-end PE products. At present, all the industrial polyethylene processes including solution processes, gas processes, high-pressure processes and slurry processes have adopted metallocene catalysts to produce versatile polyethylenes that are used in various fields[13-16].

Metallocene catalysts can be divided into homogeneous and heterogeneous types[17]. In order to be directly used in the current gas phase or slurry processes, many metallocene catalysts are supported on
inorganic carriers, typically silica, to form a heterogeneous catalyst\textsuperscript{[1,5-6,12-19]}. The catalyst-supporting technology is always one of the hottest research fields because the supported metallocene catalysts have boasted many advantages such as enhancing the catalyst’s performance, reducing catalyst cost, preventing reactor-fouling, generating of uniform particles with narrow size distribution and high bulk density et al. Several papers have reviewed the advance on supporting metallocene catalysts in detail\textsuperscript{[13,14,20]}. The vigorous development of supported metallocene catalysts, especially commercial catalysts “drop-in” large-scale gas-phase and slurry-phase units, has greatly promoted the prosperity of PE industry. The major metallocene polyethylene players around the world such as Exxon-Mobile, Dow, Mitsui, Borealis, Chevron-Phillips, LyondellBasell, Sinopec and Petrochina involved in this technology race are establishing competitive advantages.

Bis(\textit{n}-butylcyclopentadienyl)zirconiumdichloride, (\textit{n}BuCp)\textsubscript{2}ZrCl\textsubscript{2}, is the most promising metallocene catalysts for large-scale industrialization because of its stability, commercial availability at a reasonable price, capability of polymerizing ethylene with high activity and considerable use by researchers in the synthesis of supported metallocene catalysts\textsuperscript{[21-23]}. What’s more, (\textit{n}BuCp)\textsubscript{2}ZrCl\textsubscript{2} complex is famous, an approach of supported catalyst preparation is similar to well-known. Nowadays, three olefins are commonly used in industry to manufacture high performance PE: butene-1, hexene-1, and octene-1\textsuperscript{[24-26]}. Due to its longer side-chain branching, ethylene-octene-1 copolymers exhibit properties which are superior to those of ethylene-butene-1 and ethylene-hexene-1 copolymer. However, previous literatures mainly focused on the copolymerization of butene-1 or hexene-1 catalyzed by supported metallocene, and the copolymerization of octene-1 in gas and slurry polymerization processes is rarely involved. The investigation of polymerization temperature mostly focused on the activity and copolymerization performance of catalyst and little pay attention to the study of polymer particle morphology and its bulk density. In this paper, the effect of polymerization temperature on ethylene/octene-1 copolymerization catalyzed by supported (\textit{n}BuCp)\textsubscript{2}ZrCl\textsubscript{2} metallocene catalyst was systematically investigated from an industrial viewpoint, which is important for the industrialization of ethylene-octene-1 copolymer.

2. Experimental Section

2.1. Materials.

The main metallocene compound, (\textit{n}BuCp)\textsubscript{2}ZrCl\textsubscript{2}, 98\%, Aldrich. Methyl aluminoxane (MAO), 10\% in toluene solution, TIBAL, 2.0M in toluene solution, TEAL, 1.0M in hexane solution, Beijing J&K Chemical Co., Ltd, were used as received. SiO\textsubscript{2} (grade 955, surface area 270.4 m\textsuperscript{2}/g, pore volume 1.65 cm\textsuperscript{3}/g, and average pore diameter 22.6 nm) was obtained from W. R. Grace & Co., USA. Toluene, analytical purity, J&K Chemical; ethylene, nitrogen, octene-1, n-hexane, Daqing Petrochemical Company. Ethylene, toluene, octene-1 and hexane were deoxygenated and dried by passage through columns of Cu catalyst (PPP, Dalian shengmai technology Co. Ltd) and activated molecular sieves (13X, Dalian shengmai technology Co. Ltd), respectively. All manipulations involving air-sensitive compounds were performed inside an inert atmosphere glovebox continuously purged with high purity N\textsubscript{2} (moisture content of < 1 ppm).

2.2 Synthesis of supported metallocene catalyst

80g silica was activated under Nitrogen (0.1 bar) for 20 h at 600 \textdegree{}C and cooled to room temperature, then added into a 200ml 2.0M MAO toluene solution. (\textit{n}BuCp)\textsubscript{2}ZrCl\textsubscript{2} toluene solution was premixed with 2.0M TIBAL for 30 min at room temperature, then the mixture was added into the activated silica, corresponding to a 0.25 wt\% Zr/SiO\textsubscript{2} and stirred for 4 h. After this procedure, zirconocene and silica were placed still for 30 min. In the end, the solution was removed by filtration and the solid supported catalyst dried in vacuum. The Zr and Al content were determined by ICP AES and 0.12wt\% Zr, 7.53wt\% Al of the end-catalyst was reported respectively.
2.3 Polymerization
About 0.04g of the supported catalyst was weighed in the nitrogen glove box and added into a glass sample-bottle, and then 10ml hexane was also added into the sample-bottle to disperse the catalyst. Polymerization was carried out in a 2 L autoclave. The autoclave was purged with dry nitrogen for five times and ethylene once. Then 1L solvent hexane, 20mL octene-1, co-catalyst TEAL and supported catalyst (the mole ratio of Al/Zr = 200) were introduced successively into the reactor under nitrogen atmosphere. After that, the autoclave was heated to given reaction temperature within a few minutes and the reaction pressure was increased up to 1.6 MPa. The polymerization proceeds for a predetermined time (2 h). 2 hour later, the ethylene pressure was vented and the reaction quenched with a large excess of ethanol. The precipitated polymer was filtered and dried under vacuum at 60 °C until the weight of the polymer was constant. Catalyst activity was determined in terms of the amount of produced polymer (g) per the amount of applied catalyst (g).

2.4 Characterization and Analysis

2.4.1 Inductively Coupled Plasma (ICP)
The Zirconium and aluminum contents were estimated by Inductively Coupled Plasma (Avio 220 Max ICP Optical Emission Spectrometer, Perkinelmer) taking standard solution of zirconium and aluminum salt (Aldrich, USA). The samples were digested in 5 mL of aqua regia and heated to near dryness. About 30 mL of distilled water was added to the sample, which was then mixed, heated and filtered. The volume of the final sample solution was adjusted to 20 mL for ICP spectral analysis.

2.4.2 Scanning Electron Microscopy (SEM)
The morphology of the obtained polyethylenes and catalysts samples were studied using JEOL JSM-6360LA model at 10 kV. The samples were deposited on doublesided carbon tape in a glove box under N2 atmosphere, then fixed onto an SEM stub and coated with gold.

2.4.3 Bulk Density (BD) Measurement
The bulk density of the polyethylene powder was calculated according to the ASTM-D 1895B method, weighting the polymer in a graduated cylinder (without compacting the sample). The weight of polymer by a given volume was registered as a result.

2.4.4 Fines Content Analysis
The fines content of PE samples was determined using a standard 100 mesh sieve to separate the fractions. Then the mass fraction of each fraction was collected and weighed. The fines content was calculated as the proportion of the mass fraction of higher than 100 mesh.

2.4.5 High Temperature Gel Permeation Chromatography (HT-GPC)
The molecular weight distributions (MWD, Mw/Mn) of polyethylene samples were measured by high-temperature Gel-Permeation Chromatography instrument (Waters 150-C ALC/GPC) at 160°C in trichlorobenzene solvent. μ-Styragel columns (10^5, 10^4, 10^3, 500A) were used and the peaks were calibrated using standard polystyrene.

2.4.6 Differential Scanning Calorimetry (DSC)
The thermal properties were determined on an updated computer interfaced Perkin-Elmer DSC-7 instrument. The DSC was calibrated for static temperature and thermal lag effects with indium and connected to an intra-cooler to maximize heat transfer and to allow sub-ambient temperature control. The heating cycle was performed twice, but only the results of the second scan are reported, because the first scan could be influenced by polymer mechanical and thermal history. Measurements of the melting points were performed at a heating rate of 10 °C/min with a typical sample weight of 5±0.1 mg under nitrogen to prevent thermal degradation of the sample. The melting peaks and the
corresponding areas were determined to obtain the temperature ($T_m$) and enthalpy ($\Delta H_m$) of fusion. The degree of crystallinity ($X_c$) was calculated using the following relationship with the melting enthalpy for 100% crystalline PE ($\Delta H_{m100}$) of 293 J/g.

$$X_c = \frac{\Delta H_m}{\Delta H_{m100}} \times 100\%$$

3. Results & Discussion

The scanning electron microscope (SEM) images of supported catalyst were shown in Fig.1. It clearly showed that the resulting supported metallocene catalysts kept the morphology of the support, which was round and oval with some particle size variation. The largest particle size is 55.1 μm. Fig.2 showed SEM result of the resulted polyethylene particle morphology. As is seen, all the polyethylene particles remain in good sphere shape, which is beneficial to improve the bulk density and fluidity of the polymer.

Fig.1 SEM micrographs (scale bar 50 and 10 μm) of the supported catalyst

Fig.2 SEM micrographs (scale bar 500 and 100 μm) of the resulted polyethylene

Fig.3 shows the effects of reaction temperature on catalyst activity. It is speculated that the activity of catalyst increases with reaction temperature. After an initial quick increase of activity, the curves became parallel as reaction temperature extending to 85 °C. According to literature [27], the propagation rate constant K of the active centers in supported catalyst increases with the polymerization temperature, which means the polymerization rate is accelerated and the percentage of active molecules is increased. Besides, the reactivity of alkyl aluminum also increases. On the one hand, more active centers are activated resulting in quick increase of catalyst activity, but on the other hand, the solubility of ethylene decreases with temperature, which restricts the catalyst to access the monomer. When the polymerization temperature reached to 85 °C, the activity of the catalyst reached 4312 gPE/gcat; when the polymerization temperature was above 85 °C, the activity of the catalyst increased slowly.
Fig. 3 Effect of reaction temperature on activity of the catalyst

Fig. 4 Effect of reaction temperature on bulk density of polymer particles

Bulk density is one of the most important factors for controlling a polyethylene factory. Ideally, the morphology of catalyst particle is replicated by polymer particle. Polymerization mainly occurs on the surfaces and pores of catalyst particles, resulting in the formation of dense particles with stable skin formation, and this skin holds the sub-grains together. One polymer particle results from one catalyst particle [28,29]. The relationship between reaction temperature and BD of resulted polyethylene was shown in Fig. 4. It can be seen that BD firstly increases with reaction temperature and reaches maximum (>0.42 g/cm³) at 82 °C and then decreases fast. However, all of the BDs of resulted polyethylenes in the experimental range were above 0.40 g/cm³. As mentioned above, the activity of catalyst is low at lower temperature. During the first seconds of polymerization, polymer generated at the surface of catalyst particles. Due to its low activity, the new active center is embedded in the polymer formed earlier, which hinders the diffusion of ethylene monomer into the particles and results in a not-dense polymer [22]. So the bulk density of polymer is low. With the increase of polymerization temperature, the activity of catalyst increases. Rapid polymerization makes the surface of particles form a gap. Ethylene enters into the particles through the gap and acts with the internal active center to form dense polyethylene particles, which improves the bulk density. However, when the polymerization temperature is too high, the solubility of ethylene in hexane is low, and the concentration of polymerization monomer decreases. Moreover, the initial activity of catalyst is too high, and the local heat is too high, which affects the regularity of the particles, resulting in the formation of voids in the particles and reducing the apparent density of the polymer.

Generation of fines has been a major problem in ethylene polymerizations since its large-scale commercial production. Fines (the particle diameter is less than 150 μm) in industrial reactors leads to a multitude of problems like-wall sheeting, bad heat-transfer characteristics, non-homogeneous polymerization, off-spec products, disturbances in downstream processes, shutdown units and so on and so forth [30]. It can be seen from Fig. 5 that the fines content of resulted polymer is tolerable at different polymerization temperatures, and all of the test samples are less than 12.0 wt%. With the increase of polymerization temperature, the fines content first increases and then decreases; when the reaction temperature is 82–85 °C, the fines content is less than 5 wt%. As is well-known, ethylene polymerization is an exothermic process. The temperature gap between inside and outside of supported catalysts particles lead to the resulted polymer breakage. When the polymerization temperature is low, the polymerization heat on the surface of the particles is quickly removed by the solvent. Due to the transfer resistance, the heat of inner particles is not easy to be removed resulting in excessive temperature difference between the inside and outside of resulted polyethylene particle. This phenomenon is also aggravated by the low activity of the catalyst. As the polymerization temperature increases, a certain amount of crevices are formed on the surface of polyethylene particles, which is beneficial for the removal of internal reaction heat. The temperature difference between internal and external of polyethylene particles is gradually eliminated, so the particle breakage is not easy to occur. However, when the polymerization temperature is too high, more pores and voids were occupied in the polymer particles due to the high activity of catalyst. The particles are easy to disengage and lead to relatively high level of fines. The results were in agreement with the findings of Jiang B. B. [30].
Fig. 5 Effect of reaction temperature on fines content of polymer particle

Fig. 6 Effect of reaction temperature on crystallinities of polymer particles

Fig. 6 shows the effect of polymerization temperature on the crystallinity of ethylene/octene-1 copolymer. As mentioned above, all of experiments were operated in batch mode and comonomer octene-1 was added completely to the reactor before polymerization. It is known that the crystallinity of polyethylene is usually determined by the incorporation content of comonomer. The higher comonomer, the lower the crystallinity \[3,24-26\]. In addition, small molecule polymers are easy to crystallize. At lower polymerization temperature, the solubility of ethylene in hexane is better, so the ratio of octene-1/ethylene near the active center of catalyst is lower than that in high temperature polymerization environment. What’s more, the polymerization activity of the catalyst is mild at low polymerization temperature. Lower molecular weight polyethylene is produced comparing with high temperature polymerization environment, so the crystallinity of the polymer is improved and the molecular weight distribution is broadened, which is also verified by GPC results.

It can be seen from Fig. 7 that the MWD of the polymer decreases continuously with increasing of polymerization temperature. The homogeneous metallocene catalysts are generally recognized as single-site catalysts that allow the synthesis of polymers with a narrow MWD (Mw/Mn=2) \[31,32\]. In this study, The MWD of the prepared polymer is 2.9~4.0 in the range of 73~88 °C and 2.9~3.2 in the range of 82~85 °C. That is, there are many active centers in the supported metallocene catalyst system. The different responses of the multiple active centers to polymerization temperature bring in broadened MWD. The wide distribution of metallocene polyethylene is beneficial for polyethylene processing and application. Broadening of the MWD of the obtained polyethylene can be attributed to the mass-transfer resistance during early stages of ethylene polymerization. Active sites near surface of supported catalyst available for more monomer and easier heat removal from the growing particles, and thus produce longer chains (in the absence of significant transfer reactions). By comparison, the impact of mass-transfer resistance and heat removal on the inner of supported catalyst cannot be negligible, which produce more low-molecular weight polyethylenes. These findings were consistent with Muhammad Ahsan Bashir’s research \[22\].

Fig. 7 Effect of reaction temperature on MWD of polymer
4. Conclusions
Polymerization temperature is an important means to maneuver the performance of supported \((nBuCp)_2ZrCl_2\) metallocene catalyst and tailor the microstructure of resulted polymers. The effects of polymerization temperature on the activity of catalyst, bulk density, fines content, crystallinity and molecular weight distribution of the resulted polymers were summarized. The experimental results showed that the supported metallocene catalyst is a multi-site catalyst and the polymerization performance of the catalyst is stable in the range of 73~88 °C. Based on the activity of the catalyst and the performance of the polymer, the optimal polymerization temperature of supported metallocene catalyst is 82~85 °C. At this range, the activity of the catalyst reached 4312 gPE/gcat, the apparent density of the resulted polymer is greater than 0.4 g/cm³, and the fines content is less than 5.0 wt%. The MWD of polyethylene prepared tends to narrow with the increase of temperature. The results from this study offer the possibility of choosing the optimum polymerization reaction temperature range to run a polyethylene unit using supported \((nBuCp)_2ZrCl_2\) metallocene catalyst smoothly and steadily.

References
[1] Antonio F, Persi P, Lars van T, Mitch S, Klein A, Schmitz S, Rastogi S, Blom B, Romano D. (2020) Ind. Eng. Chem. Res., 59(28): 12710-12718.
[2] Yuan S F, Yan Y, Solan G A, Ma Y P, Sun W H. (2020) Coord. Chem. Rev., 411: 213254.
[3] Ray Hoff. (2018) Handbook of Transition Metal Polymerization Catalysts, Second Edition [M]. Wiley, New York.
[4] Wang D F, Yang G X, Guo F, Wang J, Jiang Y F. (2018) Pet. Chem., 58(3): 264-273.
[5] Muhammad A, Siripon A, Abdul-Hamid M E, Mamdouh A Al-H, Hussain I, Anwar Ul-Hamid Anwar Hossaen,(2014) Polym. Int. 63: 955-972.
[6] Entezami A, Moghadam P N. Polym. Int., 54: 1326-1329.
[7] Zijlstra H S, Sjoerd Harder. Eur. J. (2015) Inorg. Chem., 1: 19-43.
[8] Kaminsky W. (2016) Macromol. Symp., 360(1): 10-22.
[9] McNight A L, Waymouth R M. (1998) Chem. Rev., 98(7): 2587-2598.
[10] Gibson Vernon C., Spitzmesser Stefan K. (2003) Chem. Rev., 103(1): 283-315.
[11] Kaminsky W, Sinn H. (2013) Adv. Polym. Sci., 258(5): 1-28.
[12] B. Jongssomjit, S. Ngamposri, P. Praserthdan. (2005) Molecules., 10(6): 672-678.
[13] Hlatky G G. (2000) Chem. Rev. 100(4): 1347-1376.
[14] Severn J R., Chadwick J C., Duchateau R, Friederichs N. (2005) Chem. Rev., 105(11): 4073-4147.
[15] Qiao J L, Guo M F, Wang L S, Liu D B, Zhang X F, Yu L Q, Song W B, Liu Y Q. (2011) Polym. Chem., 2(8): 1611-1623.
[16] Muhammad A B, Vincent M, Christophe B, Timothy F.L. McKenna. (2016) Macromol. Symp., 360: 61-68.
[17] Marjolein E.Z. Velthoën, Jelle M. Boereboom, Rosa E. Bulo, Bert M. Weckhuysen. (2019) Catal. Today, 334: 223-230.
[18] Duarte M. Cecílio, Auguste Fernandes, João Paulo Lourenço, M. Rosário Ribeiro. Chem. Cat. Chem., 2018, vol. 10, no. 17, pp. 3761-3769.
[19] Bernardes A A, Zarth C S P, Gossler F S, Netto A M, Brambilla R. (2021) J. Appl. Polym. Sci., 138(10): 49961.
[20] Pauer W. (2018) Polymer Reaction Engineering of Dispersed Systems[M]. Springer, Cham.
[21] Víctor E. Comparán-Padilla, Catalina M. Pérez-Berúmen, Gregorio Cadenas-Pliego, María T. Rodríguez-Hernández, Collins S, Odilia Pérez-Camacho. (2017) Can. J. Chem. Eng.,95(6): 1124-1132.
[22] Muhammad A B, Vincent M, Christophe B, Timothy F. L. McKenna. (2017) AIChE. J., 2017, 63(10): 4476-4490.
[23] Alba Nidia Estrada-Ramirez, Carolina Ventura-Hunter, Jürgen Vitz, Enrique Diaz-Barriga Castro,
René D. Peralta-Rodriguez, Ulrich S. Schubert, Carlos Guerrero-Sánchez, Odilia Pérez-Camacho. (2019) Macromol. Chem. Phys., 220(19): 1900259.

[24] Muhammad Atiqullah, Sagir Adamu, Zuhair O. Malaibari, Mamdouh A. Al-Harthi. (2016) AIChE. J., 62(5): 1688-1706.

[25] Gao Y S, Christianson Matthew D., Wang Y, Chen J Z, Marshall Steve, Klosin Jerzy, Tracy L. Lohr, Marks Tobin J. (2019) J. Am. Chem. Soc., 141(19): 7822-7830.

[26] Colin Li Pi Shan, João B. P. Soares, Alexander Penlidis. (2002) J Polym Sci A Polym Chem, 40: 4426-4451.

[27] Chung J.S., Hsu J.C. (2002) Polymer, 43(4): 1307-1311.

[28] Gerhard Fink, Bernd Tesche, Frank Korber, Stefan Knoke. (2001) Macromol. Symp., 173: 77-87.

[29] Wang X, Xu R W, Zhu B C, Li Y F, Han X Y. (2016) RSC Adv., 6: 52464–52474.

[30] Jiang B B, Ye J, Liao Z W, Shi X M, Huang Z L, Wang J D, Yang Y R. (2018) J. Appl. Polym. Sci., 135: 46589.

[31] I. V. Sedov, V. D. Makhaev, P. E. Matkovskii. (2012) Catal Ind, 4(2): 129-140.

[32] Eliana G B, Fernanda C. S, Rodrigo B, João H.Z. dos S. (2017) Appl. Surf. Sci., 393: 357-363.