Polymerization Kinetics of Propylene with the MgCl$_2$-Supported Ziegler-Natta Catalysts—Active Centers with Different Tacticity and Fragmentation of the Catalyst

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Abstract The catalytic activity and stereospecificity of olefin polymerization by using heterogeneous TiCl$_4$/MgCl$_2$ Ziegler-Natta (Z-N) catalysts are determined by the structure and nature of active centers, which are mysterious and fairly controversial. In this work, the propylene polymerization kinetics under different polymerization temperatures by using Z-N catalysts were investigated through monitoring the concentration of active centers [C*] with different tacticity. SEM was applied to characterize the catalyst morphologies and growing polymer/catalyst particles. The lamellar thickness and crystallizability of PP obtained under different polymerization conditions were analyzed by DSC and SAXS. The PP fractions and active centers with different tacticity were obtained with solvent extraction fractionation method. The catalytic activity, active centers with different tacticity and propagation rate constant $k_p$, fragmentation of the catalyst, crystalline structure of PP are correlated with temperature and time for propylene polymerizations. The polymerization temperature and time show complex influences on the propylene polymerization. The higher polymerization temperature (60 °C) resulted higher activity, $k_p$, and lower [C*], and the isotactic active centers C$_i^*$ as the majority ones producing the highest isotactic polypropylene (iPP) components showed much higher $k_p$ when compared with the active centers with lower stereoselectivity. Appropriate polymerization time provided full fragmentation of the catalyst and minimum diffusion limitation. This work aims to elucidate the formation and evolution of active centers with different tacticity under different polymerization temperature and time and its relations with the fragmentation of the PP/catalyst particles, and provide the solutions to the improvement of catalyst activity and isotacticity of PP.

Keywords Polypropylene; Catalytic activity; Active center; Catalyst fragmentation

INTRODUCTION

Since the discovery of Z-N catalysts in the 1950s, iPP catalyzed with MgCl$_2$-supported Z-N catalyst has become the second largest volume commercial polymer with more than 50 million tons output yearly.[1,2] Although fundamental studies on the catalytic behaviors of propylene polymerizations including catalytic activity and stereoregularity have attracted lots of attention,[3,4] the catalytic mechanism for propylene polymerization by using Z-N catalysts is still mysterious and controversial.[5-7]

Many efforts have been made to give insight into the fragmentation of catalyst and the growing of polymer particles in propylene polymerization.[8-16] Theoretical studies proved that the structures of the catalysts affect the catalyst fragmentation and then the propylene polymerization activity.[8-14] Especially, the porosity of the catalyst greatly influenced the way that catalyst fragmented in the early stage of polymerization.[1,13] In addition, factors such as size of the catalytic nucleus, the catalyst support and the spatial distribution of macropores in the catalyst were recognized to influence the catalyst fragmentation.[5,11,14] Chiovetta et al. reported that the crystallinity of the produced polymers affected the rate of catalyst fragmentation.[15] Fan et al. pointed out that the comparable lamellar thickness (<20 nm) of iPP with the nanopores (15–25 nm) in the catalyst was essential in propylene polymerization by the growing of the iPP lamellae inside the nanopores of the catalysts to break up the catalyst particles.[16]

![Image](https://example.com/image.png)

$$R_p = k_p[C^*][M]$$

(1)

According to the polymerization rate equation (1),[17] the polymerization rate $R_p$ is influenced by the concentration of active center [C*], the propagation rate constant $k_p$ and monomer concentration [M]. Actually, the [M] changes gradually from the surface to the core of polymer/catalyst particles due to the increasing diffusion resistance inside the particles.
the polymer/catalyst particles, and the [M] at active sites cannot be accurately measured. Therefore, the [M] is frequently assumed to be the same as in the whole polymerization medium even though its real value is a little smaller, while the $k_p$ is strongly dependent on the stereospecificity of active centers. Based on the determinations of the $\left[ C^* \right]$ with kinetic method and chemical quenching method, and chemical quenching method, the catalytic mechanism and catalytic behaviors of the Z-N catalysts have been discussed. Terano et al. proposed the modified three-site model mechanism to explain the formation of active centers with different stereoselectivity. Chadwick et al. found that an increased $\left[ C^* \right]$, instead of $k_p$, could lead to the high activity of the Z-N catalysts in propylene polymerization. Bukatov et al. pointed out that the diffusion limitations could be neglected by decreasing $\left[ C^* \right]$ to improve catalytic activity of the Z-N catalyst.

Polymerization temperature affects not only the polymerization activity, but also the formation and distribution of high stereoregular active centers in propylene polymerization. Rishina et al. and Chadwick et al. found that the polymerization activity and stereoregularity of PP increased with the increase in temperature in the range of 30–120 °C, and the polymerization temperature affected the formation of isotactic and syndiotactic centers, and thus the polymerization rate constant. Bresadola et al. pointed out that the increase in polymerization temperature affected the oxidation-reduction degree of TiCl4 and then the valent state distribution of the active centers.

In this work, the propylene polymerization kinetics under different polymerization temperatures with MgCl2-supported Z-N catalyst were studied. 2-Thiophencarbonyl chloride (TPCC) quenching method, solvent extraction, DSC, SAXS, SEM were used to analyze the number and distribution of active centers with different tacticity, crystalline structure of PP and morphology of the PP/catalyst particles under different polymerization conditions. The formation and evolution of active centers with different tacticity and its relations with the fragmentation of the PP/catalyst particles under different polymerization temperature and time are elucidated for deeper understanding of the factors beneficial to the improvement of catalyst activity and isotactity of PP.

**EXPERIMENTAL**

**Chemical**

The TiCl4/MgCl2 Z-N catalyst (Ti content=2.1 wt%, provided by Shandong Orient Hongye Chemical Co., Ltd.) was used as catalyst in the polymerization. TEA (provided by Yanshan Petrochemical Co.) diluted in n-hexane was used as co-catalyst. Propylene (purity ≥99.6%, supplied by Shandong Chambroad Petrochemical Co., Ltd.) was used as polymerization monomer. TPCC (purity 298%, supplied by Alfa Aesar Co.) was used to quench the active propagation chains. The n-heptane (C7) was purified through distillation over Na for 24 h. All other solvents including n-octane (C8) were received and used without further treatment.

**Polymerization and Sample Purification**

Firstly, 100 mL of purified n-heptane, precise amounts of TEA, electron donor, appropriate amount of hydrogen, and continuous propylene gas (0.4 MPa) controlled by solenoid valve were put into the reactor, successively. Subsequently, the catalyst powders were introduced to initiate the polymerization of propylene. After a certain polymerization time, TPCC with three times as much as the content of TEA was quickly injected into the reactor to quench the growing PP chains with stirring at the constant temperature for 5 min, ensuring the completion of the quenching reactions with the lowest interferences from side reactions. Then the quenched PP was purified with excess alcohol, filtered, and overnight treatment in a vacuum drying oven at 40 °C.

According to the references, the purification of the TPCC quenched PP samples was carried out as the following process. Firstly, 200 mg of polymer and 150 mL of ethanol were added into a 250 mL flask with stirring at 80 °C for 60 min. Then the above suspension was separated by filtering and the insoluted PP was washed with ethanol for three times. Secondly, the dried polymer was dissolved in 100 mL of n-octane by stirring at 100 °C for 30 min. Then the above solution was introduced into a beaker filled with sufficient ethanol, precipitated, and filtered. Finally, the isolated polymers were eluted with boiling ethanol for 24 h and overnight treatment in a vacuum drying oven at 40 °C.

**Polymer Fractionation**

Firstly, about 100 mL of n-octane was heated to 100 °C to dissolve 1 g of TPCC quenched PP, and then the mixture was cooled to 20 °C. Subsequently, the PP was allowed to crystallize and precipitate completely from the solution after sufficient time of standing. The suspension was separated into n-octane insoluble fraction (C8-ins) and soluble fraction (C8-sol) by centrifuging and filtering. After drying in vacuum at 40 °C for 12 h, the C8-sol was extracted with n-heptane at 100 °C for 24 h in the Soxhlet extractor, and the n-heptane soluble fraction (C7-sol) was collected by rotational evaporation and then precipitation with plenty of ethanol. Finally, the C8-sol, C7-sol, and C7-ins (n-heptane insoluble fraction) were obtained after drying at 40 °C for 12 h in a vacuum drying oven.

**Characterization**

The sulfur content in the TPCC quenched PP was determined by an ultraviolet fluorescence detector (REK-205, Taizhou Ruikle Instrument Co.). Three parallel measurements of the samples with the weight of 3–4 mg were carried out and the average value was taken as the final result. The $\left[ C^* \right]$ was determined by the molar concentration of sulfur.

The morphologies of the catalyst particle and PP particles synthesized at different polymerization conditions was characterized by scanning electron microscopy (SEM) on a JEOL-
7500F instrument, whose acceleration voltage was 3 kV.

Differential scanning calorimetry (DSC) thermograms were recorded using PerkinElmer DSC8500. 4–6 mg of PP was first heated from 25 °C to 200 °C with a rate of 10 °C/min, kept at constant temperature for 5 min to eliminate thermal history. Then, the sample was cooled to 25 °C with a rate of −10 °C/min. Finally, the sample was reheated to 200 °C with a rate of 10 °C/min. The first heating step was used to study the lamellar structures of PP synthesized from the polymerization reactor. The second heating step was recorded for the melting point of the PP fractions without residual thermal history. The crystallinity ($X_c$) of the PP was determined according to the Eq. (2).

$$X_c (%) = \frac{\Delta H_m}{\Delta H^0_m} \times 100\% \ (2)$$

where $\Delta H_m$ is the melting enthalpy tested from the second DSC heat flow and $\Delta H^0_m$ is the melting enthalpy of completely crystalline PP (165.5 J/g). [48]

The molecular weight of PP was investigated by the PL 220 gel permeation chromatography (GPC) analyzer at 150 °C with 1,2,4-trichlorobenzene containing 5% antioxidant as eluant, and calibrated by polystyrenes standards.

The long spacing ($d_{ac}$), the thickness of amorphous layer ($d_p$) and crystalline lamellae (d$_c$), of the original PP particle crystals without any thermal treatments were measured with the small-angle X-ray scattering (SAXS) on a Xenoecs 2.0 7500F instrument, whose acceleration voltage was 3 kV. The distance between the detector and samples was 2.470 m, and the instrumental with wavelength of X-ray 0.15418 nm. The distance between the detector and samples was 2.470 m, and the instrument with wavelength of X-ray 0.15418 nm. The fitted electron density correlation function ($K(q)$) was obtained from the experimental intensity distribution ($I(q)$) and the inverse Fourier transformation, determined according to Eq. (3):[49,50]

$$K(q) = \int_0^\infty \frac{I(q) \frac{\cos(qz)}{q^2} dq}{\int_0^\infty \frac{I(q) dq}{q^2}} \ (3)$$

RESULTS AND DISCUSSION

Polymerization Kinetics of Propylene

A series of propylene polymerizations were conducted under different polymerization temperatures with gradually extended polymerization time by using TiCl$_4$/MgCl$_2$ Z-N catalyst, and all the polymerization runs were quenched by adding TPCC at the end of the polymerizations. The concentration of active center ([C*]) was determined based on the sulfur content,[41] and $k_p$ could be calculated according to the Eq. (1). The relevant synthesis and characterization results are shown in Table 1 and the catalytic activity, the number of active centers ([C*]/[Ti]) and $k_p$ under different polymerization conditions are shown in Fig. 1.

Firstly, the activity of the propylene polymerization under all the polymerization temperature increased rapidly during the first 3 min to reach a maximum value, and then decreased obviously at high temperature, but gently at low temperature (Fig. 1a). The rapid growth of the activity at the initial stage of polymerization was due to the producing of large number of active centers by the fragmentation of the catalyst (Fig. 1b) as well as the highest propagation rate constant, although [C*]/[Ti] still showed a trend of growth (Figs. 1b and 1c). As shown in Fig. 1(b), the value of [C*]/[Ti] had an increasing trend with the increase

| Table 1 | Kinetic parameters and polymer properties of propylene polymerizations. |
|---------|-------------------------------------------------|
| Run     | $T^*$ (°C) | $t^*$ (min) | CE $^*$ | CA $^*$ | $R_p \times 10^3$ (kg/g-poly) | $k_p \times 10^{-4}$ (L/mol·s) | $M_w$ (g·mol$^{-1}$) | $D^0$ | $d_{ac}$ (nm) | $d_p$ (nm) | $d_{cr}$ (nm) | $T_m$ (°C) | $X_c$ (%) |
| PP1     | 15 | 3 | 20 | 20.0 | 1.32 | 89 | 13.8 | 4.72 | 163.2 | 31.5 |
| PP2     | 15 | 6 | 33 | 16.0 | 1.06 | 64 | 15.3 | 5.74 | 162.7 | 38.7 |
| PP3     | 15 | 10 | 63 | 18.0 | 1.23 | 74 | 15.4 | 5.56 | 164.5 | 38.4 |
| PP4     | 15 | 30 | 120 | 11.4 | 0.78 | 39 | 18.6 | 5.13 | 162.6 | 38.9 |
| PP5     | 30 | 3 | 39 | 36.0 | 2.51 | 228 | 15.6 | 5.74 | 163.6 | 33.1 |
| PP6     | 30 | 6 | 67 | 32.0 | 2.12 | 181 | 16.7 | 5.78 | 163.8 | 33.8 |
| PP7     | 30 | 10 | 116 | 33.0 | 2.26 | 169 | 19.0 | 5.74 | 163.2 | 37.3 |
| PP8     | 30 | 30 | 347 | 33.0 | 2.25 | 186 | 17.1 | 5.68 | 165.2 | 49.7 |
| PP9     | 45 | 3 | 100 | 96.0 | 6.48 | 763 | 15.8 | 5.85 | 163.8 | 38.5 |
| PP10    | 45 | 6 | 159 | 76.0 | 5.03 | 521 | 18.5 | 5.99 | 164.7 | 38.4 |
| PP11    | 45 | 10 | 265 | 75.6 | 5.16 | 514 | 18.8 | 6.12 | 164.7 | 40.4 |
| PP12    | 45 | 30 | 580 | 56.8 | 3.76 | $-$ $f$ | $-$ $f$ | 21.3 | 6.38 | 164.9 | 43.4 |
| PP13    | 60 | 3 | 149 | 142.0 | 9.66 | 2420 | 10.4 | 13.3 | 5.18 | 164.5 | 47.2 |
| PP14    | 60 | 6 | 304 | 145.0 | 9.59 | 2232 | 11.2 | 15.5 | 5.64 | 164.7 | 44.5 |
| PP15    | 60 | 10 | 463 | 132.6 | 9.01 | 2030 | 11.6 | 15.2 | 5.63 | 164.6 | 43.5 |
| PP16    | 60 | 30 | 1167 | 111.2 | 7.57 | $-$ $f$ | $-$ $f$ | 18.6 | 5.50 | 164.7 | 47.9 |

$^a$ Propylene polymerization condition: [Ti]=0.215 mmol/L; [Al]/[Ti]=300 (mol/mol); [Si]/[Ti]=10 (mol/mol); pressure of hydrogen=0.03 MPa. $^b$ Polymer-ization temperature. $^c$ Polymerization time. $^d$ Catalytic efficiency. $^e$ Catalytic activity. Not determined because of the low sulfur content in the PP. $^f$ Weight-average molecular weight ($M_w$) and molecular weight distribution ($D$). $^g$ Crystal structural parameters measured with SAXS. $^h$ Melting point ($T_m$) and crystallinity ($X_c$).
in polymerization time under the constant polymerization temperature. This was because the PP/catalyst particles were gradually broken and the inside active centers were released with the growth of PP particles. In addition, the [C*/Ti] increased with the increase in polymerization temperature until the temperature exceeded 45 °C. The high polymerization temperature (60 °C) resulted in the lower [C*/Ti], but the higher $k_p$ in propylene polymerization with Z-N catalyst. It was obvious that the $k_p$ was the key factor affecting the $R_p$ and increased with the increase in temperature according to the Arrhenius equation. However, the $k_p$ undergoes a decrease with the increase in polymerization time due to the gradual increase in the monomer’s diffusion resistance in the growing particles (Fig. 1c).

The changes of [C*/[Ti]] with the PP/catalyst mass ratio ($m_{PP}/m_{cat}$) in Fig. 2 show clearly that [C*/[Ti]] and $m_{PP}/m_{cat}$ kept increasing within 10 min under the applied polymerization temperature, due to the continuous fragmenting of catalyst and the growing of the PP particles with polymerization time prolonging. Importantly, the highest [C*/[Ti]] was achieved at 30 °C, 10 min, while highest $m_{PP}/m_{cat}$ with relatively low [C*/[Ti]] was achieved at 60 °C,10 min (Fig. 2). These reflected that [C*/[Ti]] was not only influenced by the catalyst fragmentation reflected by $m_{PP}/m_{cat}$, but also the polymerization temperature. As Fig. 2(b) shows, with the same polymerization time, the [C*/[Ti]] increased first and then decreased with the increasing in polymerization temperature. When comparing Fig. 2(a) with Fig. 2(b), a conclusion could be drawn that the polymerization temperature was the key factor determining the [C*/[Ti]].

**Fig. 1** (a) The catalytic activity, (b) [C*/[Ti]], and (c) $k_p$ in the propylene polymerization under different polymerization temperatures and time.

Morphology of PP

The catalyst in this study presented spherical particle morphology with the diameter of about 70 μm (Fig. 3a). The enlarged SEM images show many small pores with pore sizes in the range

https://doi.org/10.1007/s10118-020-2473-z
of hundred nanometers on the rough surface of the catalyst, which could ensure the propylene to diffuse into the inside section of the catalyst for further polymerization easily (Fig. 3b).

Importantly, lots of primary particles with globate morphology in the size of about 50 nm could be found on the surface of the catalyst (Fig. 3c). These primary particles initiate propylene...
polymerization to form the microglobule particles in a spherical PP granule, as observed in Figs. 4(i)−4(l) and Figs. 5(g) and 5(h).

The particle morphologies and the surface morphologies of the growing PP particles obtained at 30 °C with different polymerization time are shown in Fig. 4. PP particles with size in the range of 100−800 μm completely replicated the morphology of the catalyst. The PP particles grew gradually with time prolonging as shown in Figs. 4(a)−4(d). It is assumed that in the initial stage of polymerization (Figs. 4a−4c), catalyst particles were broken into subparticles which can be separated into some primary particles further. The primary catalyst particles initiated propylene polymerization to form the PP primary particles with size in the range of 0.1−0.5 μm (Figs. 4i−4l). With the extension of polymerization time (30 min), PP subglobule particles composed by the primary PP particles are observed (Fig. 4l). It could be inferred that the fragmentation of catalyst and PP occurs mainly in the first 10 min of the polymerization, which contribute to the increased \([C^*/[Ti]\) as shown in Fig. 1(b). With the extension of polymerization time, the accumulation degree of PP primary particles becomes more and more dense (Figs. 4i−4l), which can lead to the increase in diffusion resistance to propylene, and eventually the decrease in \(k_{p}\) (Fig. 1c).

After \(n\)-heptanes extraction, the PP particles composed by the PP subglobule particles are shown in Figs. 5(a) and 5(b). The surface of the PP7 (Table 1) with 10 min polymerization (Fig. 5g) was more porous than PP8 with 30 min polymerization time (Fig. 5h), which can explain higher \([C^*/[Ti]\) in PP7 than that in PP8 (Fig. 1b). In addition, in the enlarged SEM images of PP8, the primary PP particles in the surface (about 500 nm) are larger than that in the inner section (about 100 nm) (Figs. 5h and 5i). When the polymerization time was long enough, the PP primary particles were piled up very closely, and little space was left for the monomer to diffuse into the inner sections of the particles, resulting in the embedding of the internal active center and smaller primary PP particles (Fig. 5i), which account for the lower \([C^*/[Ti]\) with 30 min polymerization time at 30 °C than that with 10 min polymerization time at 30 °C.

**Aggregation Structure of the PP**

In order to study the relations between fragmentation of the catalyst and the matching requirements between lamellar thickness of PP and the pore size in the catalyst, the achieved PP without any other thermal pretreatment was analyzed by DSC and SAXS. As shown in Fig. 6(a), the melting temperature of PP obtained at higher temperature is higher than that of PP synthesized at lower temperature. The lamellar thickness in the PP was calculated according to the Thomson-Gibbs Eq. (4):

https://doi.org/10.1007/s10118-020-2473-z
where $T_m^0$, $\sigma_e$, $L$, $\Delta H_f^0$ are equilibrium melting temperature, free surface energy of the end faces at which the chains fold, lamellar thickness and melting enthalpy of the perfect crystal, respectively. For calculation of $L$ in PP samples, the following parameters were adopted: $T_m^0$=208 °C, $\sigma_e$=70×10$^{-7}$ J/cm$^2$, and $\Delta H_f^0$=165.5 J/cm$^3$.

According to Eq. (4), the lamellar thickness $d_{ac}$ of PP calculated through the DSC is in the range of 9.1–9.4 nm (Fig. 6b), which is similar to that calculated through the SAXS (8.94–9.39 nm) (Fig. 7). The polymerization temperature had little effect on the lamellar thickness of nascent PP (Figs. 6 and 7). The pore size distribution of the catalyst as shown in Fig. 8 is mainly in the range of 1.4–57.8 nm, indicating the PP crystals can generate inside most pores of Z-N catalyst to fragment the catalyst.

**The Fractionation of PP**

To better understand the evolution of active centers with different tacticity under different polymerization conditions, solvent fractionation of PP was conducted. The PP was fractionated into fractions including C8-sol, C7-sol, and C7-ins, which were assigned to atactic PP (aPP) with no obvious melting temperature ($T_m$), medium-isotactic PP (miPP) with $T_m$, and =165.5 J/cm$^3$..

As shown in Table 2 and Fig. 10, iPP components increased gradually while the miPP and aPP components decreased with the increase in polymerization temperature (Fig. 10a). The isotactic active centers (C*) producing iPP as the majority ones reached the highest at 30 °C and then declined with the further increase in the polymerization temperature, the active centers producing miPP (C$m$*) and aPP (C$a$*) occupied

**Fig. 6** (a) The first heating curves of PP synthesized at different polymerization temperatures for 10 min. (b) Lamellar thickness of PP synthesized at different polymerization temperatures for 10 min.

**Fig. 7** (a) Evolution of one-dimensional SAXS scattering intensity distributions, (b) the $K(z)$ curves, and (c) crystal structural parameters of PP synthesized at different polymerization temperatures for 10 min.

at 126.3–143.8 °C, and iPP with $T_m$ at 161.6–167.1 °C (Fig. 9), respectively [42,43].

As shown in Table 2 and Fig. 10, iPP components increased gradually while the miPP and aPP components decreased with the increase in polymerization temperature (Fig. 10a). The isotactic active centers (C*) producing iPP as the majority ones reached the highest at 30 °C and then declined with the further increase in the polymerization temperature, the active centers producing miPP (C$m$*) and aPP (C$a$*) occupied
less than 3.4% among the total titanium and reached the highest at 45 °C and then declined with the further increase in the polymerization temperature (Fig. 10b). Comparing the results from Figs. 1 and 10, it can be deduced that the C\textsuperscript{*} as the majority ones were sensitive to the temperature and a higher temperature (more than 30 °C) resulted in the inactivation of some C\textsuperscript{*}. While Fig. 10c shows that the extremely high k\textsubscript{p} at 60 °C contributed to the highest iPP component at 60 °C.

Considering the effect of polymerization time, the mass percentage of the iPP, mIPP, and dPP fractions showed little change in the initial 10 min, while iPP component increased from about 87 wt% to 93.7 wt% when the polymerization time reached 30 min (Fig. 10d). The [C\textsuperscript{*}]/[Ti] producing iPP, mIPP and dPP fractions increased while k\textsubscript{p} decreased with the polymerization time increasing in the initial 10 min (Figs. 10e and 10f). The above results showed that, a large number of active centers especially ones producing iPP fractions were released through the fragmentation of the catalyst during the polymerization process in the first 10 min in the studied time scope. It is generally accepted that the molecular weight of PP from C\textsuperscript{*} was significantly higher than that from active centers with lower stereoregularity.\textsuperscript{64,65} The increase in the M\textsubscript{w} of PP with the increase in polymerization time further proved the increase in the C\textsuperscript{*}, as shown in Table 1. The isotactic active centers showed higher k\textsubscript{p} than active centers with lower stereoselective (Fig. 10c).\textsuperscript{64,65,66}

![Fig. 8](image)

**Fig. 8** Pore size distributions of the catalyst and its enlarged composite figure with the lamellar thickness distribution of PP synthesized at different temperature for 10 min.

![Fig. 9](image)

**Fig. 9** DSC curves of PP fractions. (a) C8-sol (aPP), (b) C7-sol (mIPP), (c) C7-ins (iPP).

### Table 2: Fractionation and characterization results of the PP.

| Run | Polymerization conditions | Atactic PP | Medium-Isotactic PP | Isotactic PP |
|-----|--------------------------|------------|---------------------|-------------|
|     | Temperature (°C) | time (min) | [C\textsuperscript{*}]/[Ti] (mol%) | k\textsubscript{p} (L/mol·s) | Content (wt%) | [C\textsuperscript{*}]/[Ti] (mol%) | k\textsubscript{pm} (L/mol·s) | Content (wt%) | [C\textsuperscript{*}]/[Ti] (mol%) | k\textsubscript{pi} (L/mol·s) |
| PP3 | 15 | 10 | 2.3 | 0.63 | 42 | 11.8 | 2.32 | 58 | 85.9 | 12.45 | 79 |
| PP5 | 30 | 3 | 2.0 | 0.33 | 216 | 11.0 | 1.79 | 219 | 87.0 | 13.48 | 230 |
| PP6 | 30 | 6 | 2.6 | 0.47 | 171 | 9.7 | 2.08 | 145 | 87.7 | 14.15 | 192 |
| PP7 | 30 | 10 | 2.2 | 0.51 | 139 | 10.6 | 2.47 | 138 | 87.2 | 16.02 | 174 |
| PP8 | 30 | 30 | 2.2 | 0.45 | 155 | 3.9 | 1.08 | 115 | 93.9 | 15.57 | 192 |
| PP11| 45 | 10 | 1.4 | 0.70 | 193 | 8.3 | 3.44 | 232 | 90.3 | 14.66 | 593 |
| PP15| 60 | 10 | 0.8 | 0.70 | 268 | 6.9 | 1.73 | 930 | 92.3 | 9.17 | 2357 |

https://doi.org/10.1007/s10118-020-2473-z
CONCLUSIONS

The polymerization temperature and time have complex influences on the propylene polymerization. The lamellar thickness of PP crystals in the range of 8.9−9.4 nm was almost unaffected by the polymerization temperature and time, which was less than the most size of the nanopores in the catalyst.

The activity of the propylene polymerizations with MgCl$_2$-supported Z-N catalyst increased rapidly during the first 3 min to reach a maximum value and then decreased gradually with the increase in the polymerization time. The largest activity observed in the first 3 min was attributed to the large number of active centers produced by the fragmentation of the catalyst and the highest $k_p$. However, C$_i$ as the majority ones increased gradually with polymerization time prolonging and occupied 91% of the total C$^*$ at 30 °C for 30 min. The active centers producing iPP, mIPP, and aPP showed decreased $k_p$ with the polymerization time extension, which was blamed on the increased diffusion limitation, explained the decay activity of the propylene polymerization with time increasing.

The polymerization activity increased obviously with the temperature increasing, which can be attributed to the extremely higher $k_p$ at higher temperature. However, the total [C$^*$] as well as [C$_i$] increased to the highest value when the temperature increased to 30 °C, and then decreased greatly.

Fig. 10  (a, d) The mass percentage, (b, e) [C$^*$]/[Ti] and (c, f) $k_p$ of three PP fractions (a−c) under different polymerization temperatures for 10 min of polymerization or (d−f) at 30 °C for different polymerization time.
with the temperature further increase. The $C_i^*$ as the major-
ity ones showed much higher $k_\text{d}$ and higher temperature
sensitivity than the active centers with lower stereoselecti-
vity and produced IPP with higher $M_\text{w}$. Therefore, appro-
priate polymerization temperature ($30 \, ^\circ\text{C}$) and time (10 min)
are essential for the achievement of both $C_i^*$ and $C_j^*$ with
the highest values. A higher temperature ($60 \, ^\circ\text{C}$) is favor to
the activity increasing accompany with the highest IPP com-
ponents.

ACKNOWLEDGMENTS

This work was financially supported by the Major Scientific and
Technological Innovation Project of Shandong Province (No.
2019JZZY010352), Natural Science Foundation of Shandong
Province (No. ZR2019MB072) and Taishan Scholar Program.

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