Kinetics of the propylene polymerization with prepolymerization at high temperature using Ziegler-Natta catalyst

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ABSTRACT: The bulk polymerization of propylene in liquid monomers with Ziegler-Natta catalyst at 95°C is studied, using alkyl aluminum as the cocatalyst and dicyclopentyldimethoxysilane as the external donor. The highest catalyst activity is shown at the cocatalyst/Ti molar ratio of 300, which keeps relatively constant with the molar ratio increasing from 300 to 800. Besides, the catalyst activity is up to 65 kgPP/(gCat*h) in the range of cocatalyst/donor molar ratio from 12 to 16. The polymerization reaction rate curves with and without catalyst precontacting are similar, while the activity with catalyst precontacting are higher than that without precontacting. Furthermore, the kinetics of polymerization with and without prepolymerization are investigated in the range of the polymerization temperature from 70 to 95°C. It shows that at the high temperature, the polymerization rate increases with prepolymerization. Finally, the influence of prepolymerization at 95°C on the polymerization kinetics and particle properties is also described. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41816.

INTRODUCTION

Although the temperature of propylene polymerization is around 70–80°C with Ziegler-Natta catalyst in the most commercial plants, polymerization at higher temperatures, especially more than 80°C, is preferable industrially to reduce the burden of removing the heat of polymerization. Based on the advantage of polymerization at high temperature, supercritical olefin polymerization technology has been developed, which also requires a higher polymerization temperature, more than 90°C, for propylene polymerization. Therefore, it is important to improve the properties of Ziegler-Natta catalyst system at high temperature to fit the requirements of polymerization technology. However, the activity of conventional Ziegler-Natta catalyst is known to decrease with the temperature increasing.[1–6]

Prepolymerization step has been proved to play an important role in olefin polymerization technology for enhancing the catalyst activity. Prepolymerization is defined as a precisely controlled polymerization step under mild reaction conditions, such as relatively low temperature or low monomer concentration, typically carried out prior to the main polymerization step.[7–9]

It could be found that in many literatures the influence of prepolymerization on the polymerization kinetics was concerned. Pater

et al.[7] reported that the reaction rate of main polymerization kept increasing with the temperature increasing in the case of prepolymerization. They believed that the highest activity of the catalyst in the initial stage and a small outer surface area of the catalyst make the temperature of the particle strongly increased which in turn deactivate the catalyst due to overheating. At the beginning of prepolymerization, the outer surface area of the catalyst particles was slowly enlarged, which prevent the particle from runaway during the period of main polymerization. Samson et al.[10] reported that the polymerization rates were followed by relatively slow decay with prepolymerization compared to that without prepolymerization. The authors suggested that the prepolymerization gave the associated catalyst components adequate time to diffuse into the core of the primary catalyst particles forming active centers at all potentially catalyst sites. Coutinho et al.[11] also showed a similar result of the activity in propylene polymerization increasing after prepolymerization with different monomers (styrene, propylene, hexane-1, cyclopentadiene). They presumed that the growth of the polymer particles obtained by prepolymerization could expose occluded catalyst centers, which would enhance the catalyst activity.

However, most of experiments mentioned above investigate[7–11] prepolymerization based on the main polymerization

temperature below 80°C. Polymerization at the higher temperature (>80°C) is desired industrially to reduce the burden of removing the polymerization heat in commercial plants.[2,3] It is important to improve the performance of Ziegler-Natta catalyst at the higher temperature to meet the requirements of polymerization technology. Therefore, in this article, the effects of significant process parameters, such as molar ratio of cocatalyst/Ti, molar ratio of cocatalyst/donor, with/without prepolymerization, and with/without precontacting would be investigated on the polymerization of propylene with Ziegler-Natta catalysts at higher temperature. In this article, scanning electron microscopy (SEM) of cross-sectional cuts of polymer particles was used to study the internal structures of polymer particles, which were obtained with or without prepolymerization at different polymerization temperatures. Then modifying the performance of the Ziegler-Natta catalyst at high temperature polymerization was attempt by varying prepolymerization condition.

EXPERIMENTAL

Preparation of Catalyst

Preparation of Dialkoxy Magnesium Supporter. The 300 mL glass reactor vessel equipped with an internal stirrer was purified using nitrogen. 2-Ethyl hexanol (4 mL), 0.15 g iodine, and 0.1 g $MgCl_2$ dissolved in 130 mL ethanol, were added into the reactor. Under vigorous stirring, the reaction system was heated to the refluxing temperature. Then introducing 8 g magnesium powder to the reaction system, led to much hydrogen emerging. The reaction was stopped when hydrogen was no longer discharged from the reactor system. After subsequently washing, separating and drying, the final product, dialkoxy magnesium supporter was obtained and named as 1#.

Preparation of Catalyst Components. The suspension was compounded using 2 mL dibutyl phthalate (DNBP), 50 mL toluene and 10 g dialkoxy magnesium supporter 1# obtained by above experiment. The amount of 40 mL toluene and 60 mL $TiCl_4$ were added into the 300 mL glass reactor vessel which was purified using nitrogen. Then the reaction system temperature was decreased to −5°C. The previous suspension was subsequently introduced to the reactor. The system temperature was slowly raised to 110°C and maintained for 2 h. The solvent in the reactor was removed by filter pressing. Afterward, the mixture of 90 mL toluene and 60 mL $TiCl_4$ was added into the reactor, and stirred for 1 h at 110°C. The solvent was similarly removed by filter pressing. The previous experimental step was repeated once and solid would be obtained. After washed by 150 mL hexane for four times, the final product, catalyst components would be achieved. The concentration of titanium in the catalyst was 2.6 wt %.

Polymerization

Reactor Preparation. The reactor system used in the present work was a 1.8-L stainless steel jacketed batch reactor obtained from BuChi, which is suited for operating pressures up to 168 bars. The reactor was filled with nitrogen and evacuated during a period of 5 min. This was carried out at a jacket temperature of 95°C and repeated for at least five times. After purifying, the reactor was brought to a pressure of 20 bars with propylene gas and kept for 10 min to check for gas leakage before evacuation.

Polymerization Procedures and Kinetic Measurement. After purification and evacuation of the reactor system, it was subsequently filled with the prescribed amount of hydrogen and propylene. During polymerization, the impeller stirrer was used at 350 rpm and the reactor was heated to the required temperature. In the case where the catalyst was not precontacted before being injected, the mixed solution of cocatalyst, external donor and hexane was first injected by fresh propylene. After several minutes, the catalyst and hexane slurry was injected by fresh propylene. If the catalyst was required to be precontacted with the cocatalyst, hexane and electron donor, all catalyst components were injected together by fresh propylene after precontacted for 2 min. Then the catalyst was prepolymerized at the target temperature for setting-up time. After prepolymerization, the reactor temperature was rapidly raised to the main polymerization temperature.

When not using any form of prepolymerization, the catalyst components were subsequently injected into reactor at the main polymerization temperature. During polymerization, the polymerization rate could be determined by the flow rate technique, which was based on continuous compensation of monomer consumption such that the reactor pressure and temperature could keep constant. To end the experiment, the unreacted monomer was flashed off by opening the vent valve. The reactor, initially at polymerization temperature, would cool down due to flashing. After that, the reactor was flushed several times with nitrogen to remove the last monomer. Then the powder was taken from the reactor and dried 12 h in a vacuum oven at 80°C. The reactor was washed out with hexane, dried with nitrogen, and purified by using the method described above.

Characterization

The titanium content of catalyst solid was measured by 721 spectrophotometer. The particle size distribution of polymers was measured by the dynamic image analysis of CAMSIZER (Germany, Retsch). The samples of polymers were parceled into eight portions, and then randomly selected one portion to complete the test. The optimum of height and vibration amplitude of the filling hopper enabled the CAMSIZER to provide the measurements with the excellent reproducibility.

RESULTS AND DISCUSSION

Reproducibility

The reproducibility of experiments should be determined with respect to the polymerization kinetic results for obtaining solid conclusions from the experiments. Figure 1 shows that the polymerization reaction rate curves of three different experiments were obtained using the same procedures. In Experiment-1 and Experiment-2, the same amount of catalyst, 5.0 mg, was used. Furthermore, the influence of the amount of catalyst was examined, since the amount of catalyst used in the experiment was not exactly the same in all experiments. The double amount of catalyst of above experiments, 10.3 mg, was used in Experiment-3. It is clear that the results of three experiments are very similar. The kinetics of the polymerization was reproduced to an acceptable degree, and the variations in catalyst amount would not influence the kinetics of polymerization.
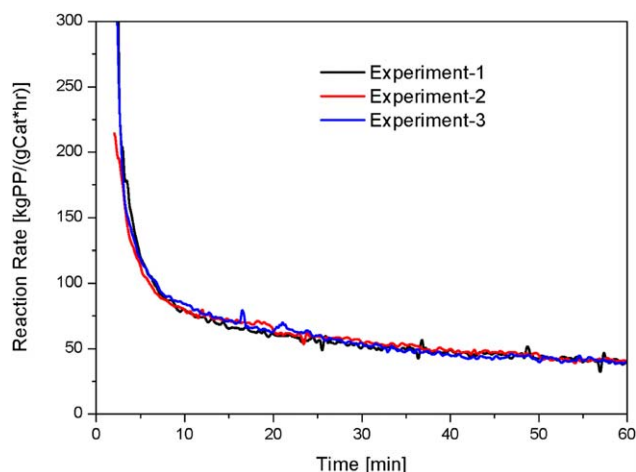
Figure 1. Reaction rate as a function of time of a repeated experiment at 70°C with different amount catalyst. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymerization Parameters

Influence of Al/Ti Ratios. Figure 2 shows the influence of the amount of the cocatlyst, triethylaluminum (TEAl), on the catalyst activity. Experiments were executed at 95°C for 1 h after the prepolymerization. The catalyst activity significantly increased with the ratios of TEAl to Ti (Al/Ti) increasing. From the data in Figure 2, it could be seen that polymerization yields reach a plateau value at about 65 kgPP/(gCat*h), and remain relatively constant until the Al/Ti molar ratio increasing to at least 800. The lowest Al/Ti ratio leading to the high polymerization yields was 300, which might be a minimum Al/Ti ratio to alkylate and activate all of the potentially active centers at high temperature polymerization.

Influence of Al/Si Ratios. It is well known that the use of Lewis bases as external donor could remarkably affect the polymerization kinetics and the activity of Ziegler-Natta catalysts.[12,13] The effect of the amount of dicyclopentyldimethoxysilane (D-donor) on the polymerization yields was summarized in Figure 3. Those

Figure 3. The effect of molar ratio TEAl/Donor on the activity of catalyst at 95°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polymerizations were carried out at 95°C for 1 h after prepolymerization. With the ratio of TEAl to D-donor (Al/Si) increasing, the polymerization yield would sharply increase in the range of lower Al/Si ratios, which could subsequently reach a stable value of about 65 kgPP/(gCat*h) in the range of Al/Si ratios from 12 to 16. When Al/Si ratios were above 16, the polymerization yield would obviously decrease as Al/Si ratios increased.

Influence of Precontacting. The catalyst activity might be strongly influenced by the sequence in which the catalyst solid, cocatalyst and electron donor was injected into reactor. The effect of precontacting in hexane at ambient temperature on polymerization rates was tested for a polymerization at the temperature of 95°C, as shown in Figure 4. The figure displayed the polymerization reaction rate curves obtained with and without precontacting, respectively. Notice that the polymerization rate of the catalyst with precontacting was higher than that without precontacting. When the catalyst solid was not precontacted
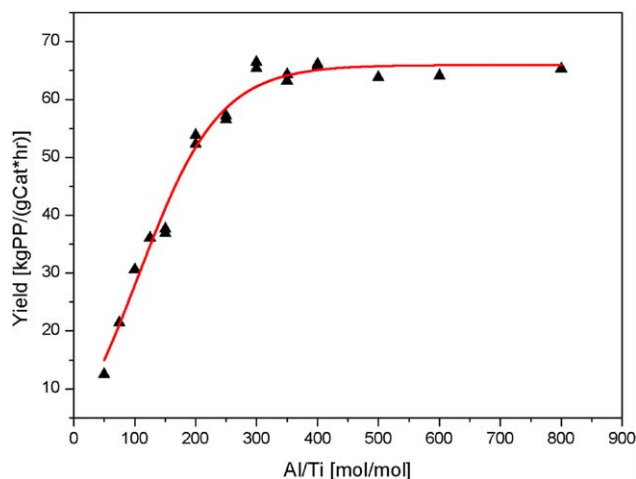

Figure 2. The effect of TEAl/Ti molar ratio on the activity of catalyst at 95°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
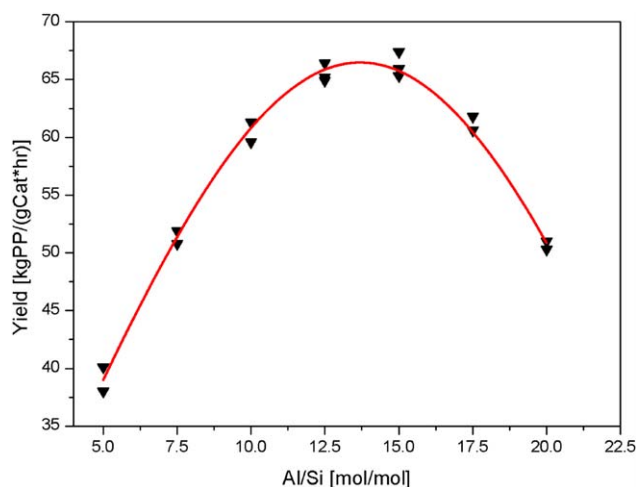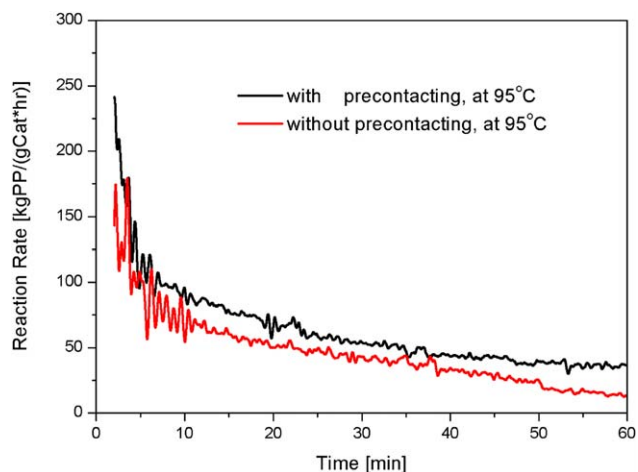

Figure 4. Reaction rates of polymerization at 95°C with and without precontacting. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with a mixed solution of TEAl, D-donor and hexane before being injected into the reactor, the cocatalyst TEAl had to diffuse to the temporarily poisoned sites to form active centers in the bulk propylene during the polymerization period. However, the concentration of TEAl was diluted by a mass of liquid propylene, so that the significant portions of the active centers were not activated, which resulted in lower polymerization rates.[12,14]

In addition, from the data in Figure 4, the decay of curve obtained without precontacting more rapidly increased than that obtained with precontacting after the polymerization was carried out for 40 min. It is possible that after the catalyst system was injected into the liquid propylene, the active centers of the particle surface were activated immediately, which made a polymer layer forming on the particle before activation of all of the potentially active sites was completed.[15] Because the growth of polymer particles could occlude active sites to enhance the mass-transfer limitation in such a polymer layer,[16] the deactivation rate of the catalyst without precontacting would be faster than with precontacting during the latter polymerization.

Influence of Prepolymerization on Polymerization Kinetics
Influence of Main Polymerization Temperature. A series of experiments was performed to investigate the influence of prepolymerization on polymerization kinetics at various temperatures. In the case of polymerization with prepolymerization, the catalyst system was injected into the liquid propylene at a temperature of 20°C. The catalyst system was prepolymerized for 10 min, and then the reactor temperature was quickly raised to execute the polymerization at desired polymerization temperature during the remaining reaction time. For the case of polymerization without prepolymerization, the catalyst system was directly injected into the reactor at the target temperature of main polymerization. In both cases, a fixed ratio of the catalyst solid, cocatalyst and electron donor had been precontacted for 2 min before being injected into reactor. The results of this series of experiments are show in Figure 5. Each thumbnail of Figure 5 shows the polymerization reaction rate curves of two experiments carried out at the same main polymerization temperature: one experiment executed with prepolymerization and the other experiment executed without prepolymerization. From these curves, in the experiments without prepolymerization, the catalyst activity significantly decayed fastest during the period of 2–5 min, and then swiftly reached a plateau, which indicated that the catalyst activity were followed by relatively slow decay after 2–5 min in the temperature range of above experiments. The polymerization reaction rates were significantly higher after prepolymerization than that without prepolymerization, but the polymerization reaction rate curves obtained with prepolymerization decayed obviously during the whole main polymerization time. The tendency of those decays became more pronounced as temperature increased. Of course, again with increasing temperature of the main polymerization, the decay of catalyst activity was improved. The reaction-rate curves of polymerization with and without prepolymerization are given for the temperature of 70 and 80°C in Figure 5(a,b), respectively. It is clear that in the lower temperature range the polymerization reaction rate curves obtained without prepolymerization lie below those

obtained with prepolymerization justly during the first 30–40 min; after that, the rate of polymerization without prepolymerization followed the same course as that with prepolymerization. Figure 5(c–e) shows the polymerization reaction rate curves of polymerization with and without prepolymerization obtained at 85, 90, and 95°C, respectively. It is noted that the polymerization reaction rate curves with prepolymerization and without prepolymerization are almost coincided during the first 3–5 min, and then they are separated into two curves. The polymerization reaction rate curves with prepolymerization always lie above those without prepolymerization. Figure 6 shows the ratios of the polymerization yield obtained with prepolymerization to that obtained without prepolymerization, named as $r_{\text{with/without}}$ for a function of temperature. At the temperature from 70 to 80°C, the polymerization yields obtained with prepolymerization and without prepolymerization are practically identical. Above 80°C, the $r_{\text{with/without}}$ value increased sharply with increasing temperature, which would be up to a value of about 4.46 at 95°C.

Cross-Morphology of Polymer. The polymer particles produced by polymerization with and without prepolymerization, which were executed at 70, 85, and 95°C for 10 min under the conditions of the experiments presented above, were analyzed with SEM. Figure 7(a–f) shows the image of the cross-sectional surface of those polymer particles which have been cut. It is interesting to note that there is a compact core in all of particles. The structure of the polymer particle cores is more compact than that of the polymer core around. As expected, the catalysts under different polymerization conditions could produce different porous polymer particles. The different effective diffusion coefficients of different polymer particles could be related to the internal structures of polymer particles observed by SEM.[17,18] It could be presume that the reaction rate of catalyst was controlled by mass-transfer after the initial polymer particles were produced. At first, the monomers were convectively transported to particle surface from bulk propylene and then through pores throughout particle. Finally, the monomers were diffused from pore to active site through the polymer particles, which would become a control step for the reaction rate.[19,20]

Figure 7(a,d) shows the internal structure of polymer particles obtained by 70°C with and without prepolymerization, respectively. It is noticed that the polymer particles produced with prepolymerization have similar internal structure comparing with that produced without prepolymerization, and the $r_{c/o}$ value, which is determined as the ratio of compact structure polymer to open structure polymer, of two particles are almost identical. Nevertheless, the effective diffusion coefficient of polymer particles produced by polymerization with and without prepolymerization should be equal. Coming back to the polymerization reaction rate curves in Figure 5(a), as we have already noted above, it seems that the reaction rate curves coincide after a period of reaction time. Figure 7(b,e) shows the internal structure of the polymer particles obtained at 85°C for 10 min with prepolymerization and without prepolymerization, respectively. The internal structure of the polymer particles produced with prepolymerization is observed to be more open
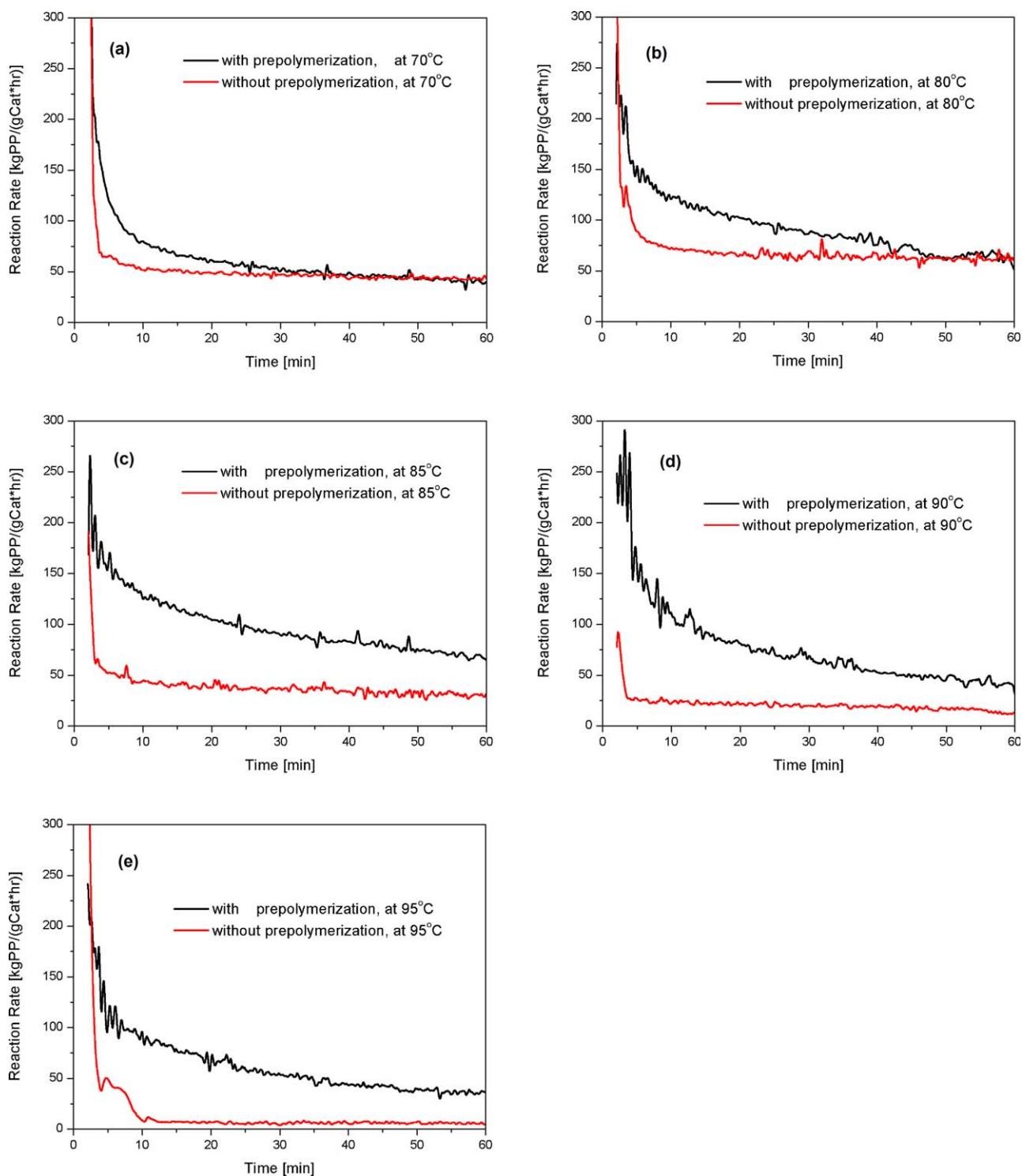
Figure 5. Reaction rates of polymerizations with and without prepolymerization: (a) $Tr = 70°C$, (b) $Tr = 80°C$, (c) $Tr = 85°C$, (d) $Tr = 90°C$, (e) $Tr = 95°C$; and $t_{prepoly} = 10$ min, $T_{prepoly} = 20°C$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

than that without prepolymerization. In other words, the $r_{c/o}$ value of polymer particles produced with prepolymerization is lower than that without prepolymerization. In Figure 5(e), after prepolymerization the reaction rate is significantly higher than that without prepolymerization. Figure 7(c,f) shows the internal structure of the polymer particle obtained at 95°C for 10 min

with and without prepolymerization, respectively. Since the polymer particles produced by polymerization without prepolymerization consisted of almost compact polymers, the monomer transport to the active sites was difficult, which resulted in a completely deactivated catalyst and a relatively low polymerization yield.[19]
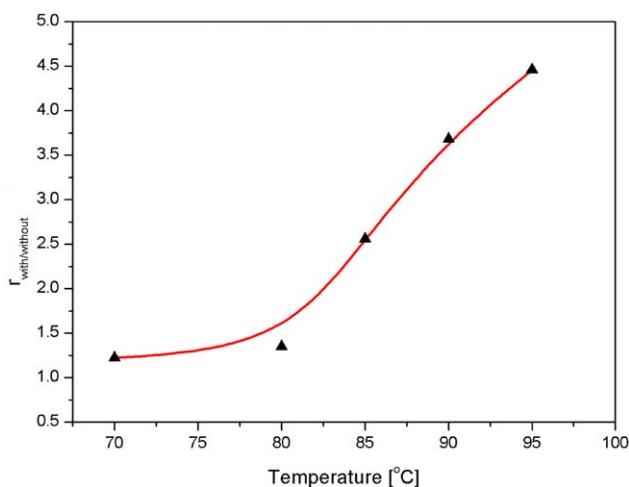
Figure 6. Ratio $r_{with/without}$ of polymerization with and without prepolymerization as function of the main temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 8. The effect of temperature of prepolymerization on reaction rate of polymerizations at 95°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Process Parameter of Prepolymerization. For investigating the influence of prepolymerization temperature on polymerization reaction rates, a series of experiments were performed, in which the catalyst system was injected into the liquid propylene at the target temperature. The catalyst system was prepolymerized for 10 min, and then the reactor temperature was quickly raised to the main polymerization temperature of 95°C during the remaining reaction time. In the experiments, a fixed ratio of the catalyst, cocatalyst, and electron donor had been precontacted for 2 min before being injected into reactor. The results of the experiments are shown in Figure 8. It could be seen that the decay behavior curves of the catalyst was not changed significantly with the fluctuation of temperature, but the reaction rates were influenced by the prepolymerization temperature. The reaction rates obtained by the polymerization with prepolymerization at 20 and 40°C
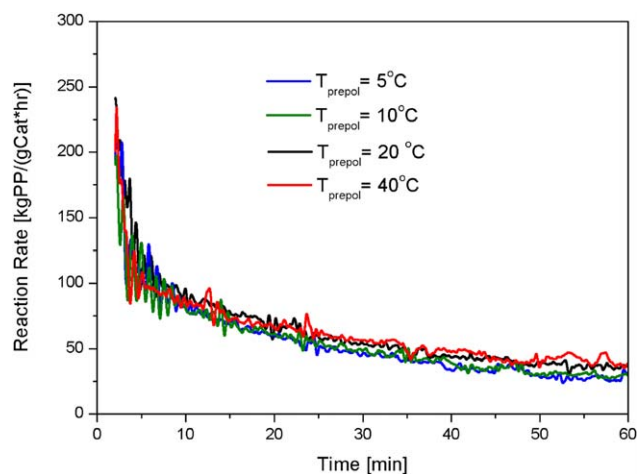
are almost identical, and slightly higher than that with prepolymerization at 5 and 10°C. With the prepolymerization at the temperature of 5°C, the entire reaction rate curves lie below those at higher prepolymerization temperature.

Figure 9 shows that the particle size distribution (PSD) of the polymers particle obtained by the experiments presented above did not change obviously at various temperatures. Although it could not make a clear distinction among these PSD results, PSD of the particles obtained with prepolymerization at 20 and 40°C were slightly narrower than that obtained with prepolymerization at 5 and 10°C.

As described above, when a prepolymerization step was applied, the polymer shell would slowly grow on outer surface area of the catalyst particles for preventing the catalyst particles from
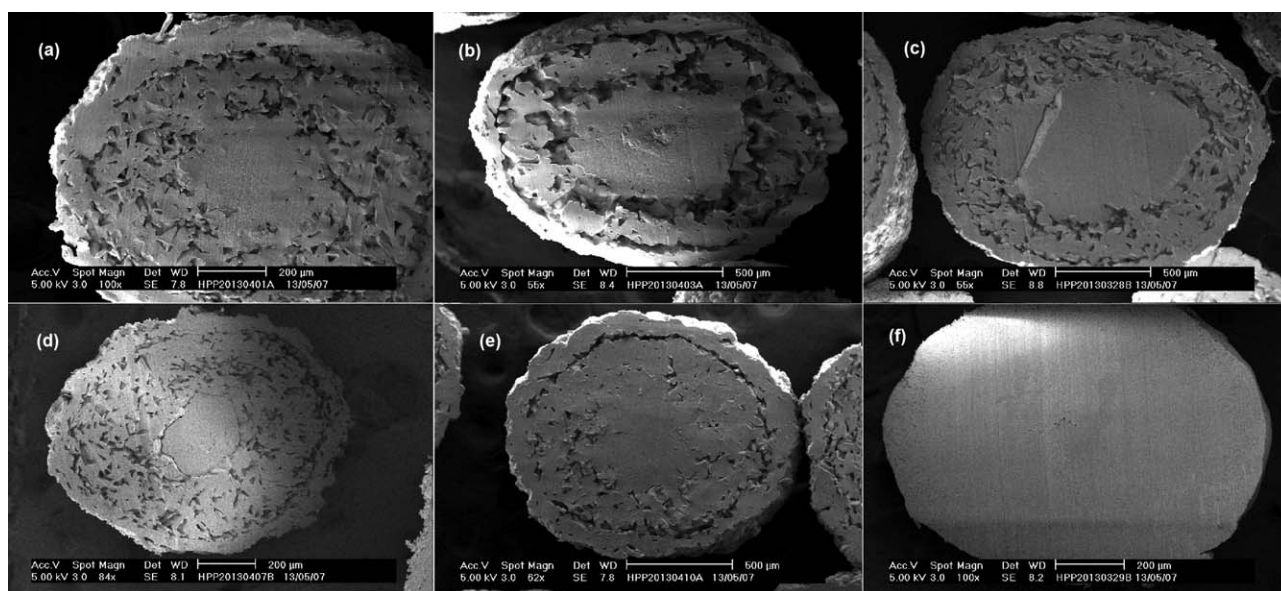

Figure 7. Cross-sectional SEM pictures of polymer particle produced with and without prepolymerization, at different main polymerization temperature for 10 min: (a) and (d) Tr = 70°C, (b) and (e) Tr = 85°C, (c) and (f) Tr = 95°C.
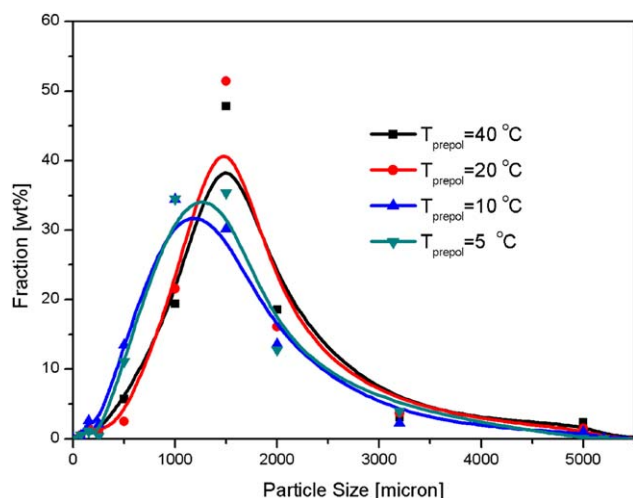
Figure 9. PSD curves for particles produced at varied prepolymerization temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 11. PSD curves for particles produced at varied prepolymerization time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

thermal runaway. It is attributed to that at the lower prepolymerization temperature the polymer shell produced by prepolymerization would not grant sufficient yields and mechanical stability to prevent the active sites from overheating. However, when the polymer shell was prepolymerized reaching adequate yields and mechanical stability, the changes of the reaction rates and fragmentation could not be observed.[21]

A further proof for the fact that the reaction rates and the fragmentation of polymer particles are indeed determined in the initial stage of the prepolymerization yields is given in Figures 10 and 11. Figures 10 and 11 show the polymerization reaction rate curves of polymerization and PSD of the polymer particles with different prepolymerization time, respectively. When prolonging the prepolymerization time, the catalyst activity could also be increased. From the data in Figure 10, the experiment with prepolymerization for 0 min, which is so-called non-isothermal prepolymerization, was similar in the kinetic behavior
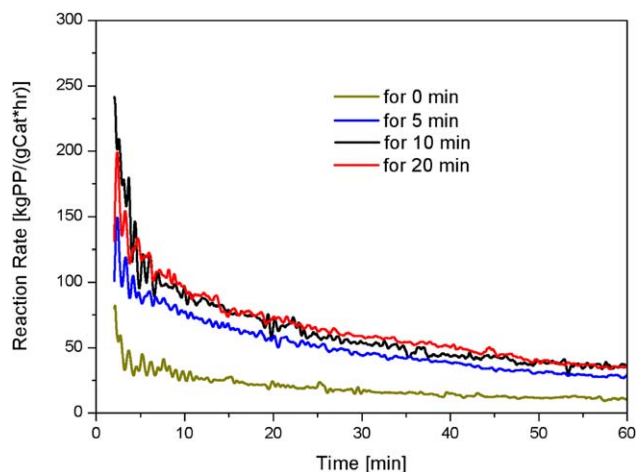

Figure 10. The effect of time of prepolymerization on reaction rate of polymerizations at 95°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
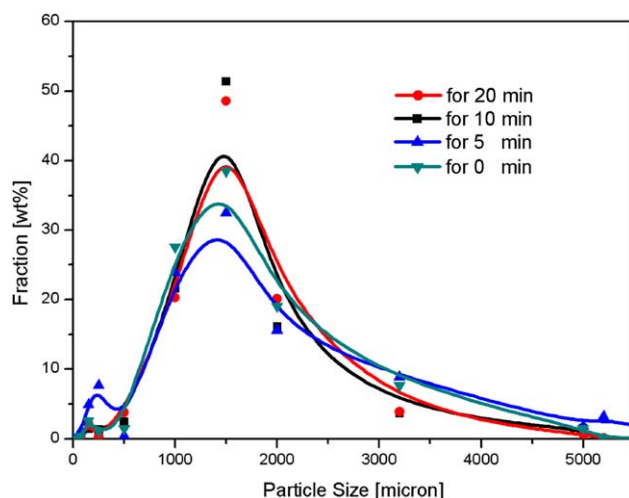
of reaction rates curve comparing with the experiment without prepolymerization, which are shown in Figure 5, while the reaction rate with prepolymerization was higher than that without prepolymerization. When the prepolymerization time was less than 10 min, the PSD of polymer particles showed a small peak in the range of 0–500 μm, which might be resulted from the high reaction rate at the initial stage of polymerization as shown in Figure 11. The high reaction rate would lead to those particles which did not grant sufficient mechanical stability,[11,21] quickly and extensively to rupture. However, the PSD of polymer particles obtained from the non-isothermal prepolymerization was broadest in this series of polymerizations and did not show a small peak in the range of 0–500 μm, because the polymer particles could form the agglomerates under the higher polymerization temperature at the polymerization initial stage.

CONCLUSIONS

The influence of alkyl aluminum, alkoxysilane, and precontacting on the activation and kinetics of Ziegler-Natta catalyst was studied at the main polymerization temperature of 95°C under industrially relevant condition. When the Al/Ti molar ratio was up to 300, the Ziegler-Natta catalyst showed the highest activity, which could reach 65 kgPP/(gCat*h). The catalyst activity showed no obvious improvement if kept increase Al/Ti molar ratio. In the range of Al/Si ratios from 12 to 16, higher polymerization activities were obtained. The polymerization reaction rate curves are similar, while the activity of catalyst with precontacting was higher than that without precontacting.

It was demonstrated that, the prepolymerization step can increase the polymerization reaction rate in the main polymerization stage when high polymerization temperature used. In the range of lower main polymerization temperature (70–80°C), the value of $r_{with/without}$ was about 1 and increases as the temperature increasing. Above 80°C, $r_{with/without}$ increases sharply with increasing temperature, up to a value of about 4.46 at 95°C. This effect is ascribed to the internal structure of polymer particles, which was produced in the initial stage of main polymerization. Moreover,

the influences of prepolymerization parameters on kinetics and particle properties were also studied at a main polymerization temperature of 95°C. Changes in the prepolymerization temperature or the prepolymerization time could slightly affect the polymerization rates and PSD of the polymer particles.

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