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An Experimental Investigation of the Impact of Gas Phase Prepolymerization of Propylene

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ABSTRACT

A systematic investigation has been carried out on the gas phase of propylene during the initial instants of polymerization. The results confirm the positive impact of small amounts of mineral oil on the initial reaction rate and morphology. In addition, it is shown that simply polymerizing under conditions of mild temperature and pressure alone are not enough to achieve the same result. It has been found that the presence of mineral oil, and low temperature of polymerization can be used to control the morphology of polymer particles and to obtain high activity in the main reaction. Furthermore, if enough oil is used, moderate to high temperatures of prepolymerization are acceptable in terms of controlling morphology but can compromise the activity of the main polymerization. It was also observed that the way in which the oil is introduced has an impact on the kinetics and particle morphology.

Particularly, separate addition of oil from the precatalyst gives rise to relatively flat kinetics during prepolymerization and highest rate during main polymerization. To account for the activity enhancement, a selective quench-labeling study employing methyl propargyl ether shows that the presence of appears to increase the fraction of active Ti by a factor of almost 2.

KEY WORDS: Polypropylene; gas phase; prepolymerization; effect of mineral oil; number of active sites.

INTRODUCTION

Polypropylene can be made in bulk slurry phase reactors (i.e. polymerization in liquid propylene), gas phase reactors, or a combination of the two. When slurry phase polymerization is used the main homopolymerization is carried out in bulk loop reactors, which can be followed by gas phase fluidized bed reactor(s) for the production of amorphous copolymers in situ. In such processes a first, smaller reactor dedicated to continuous prepolymerization, and is run under much milder conditions of temperature and pressure than those of the main reactor.¹ Prepolymerization can also be conducted off-line to prepare so-called “prepolymerized catalyst”.²⁻¹⁰ Regardless of how it is carried out, for the early generations of TiCl_3 -based catalysts, prepolymerization could reduce the amorphous fraction of the final product, enhance the catalyst stability and improve the particle morphology.¹¹⁻¹³ For the modern high yield MgCl_2 -supported catalysts, prepolymerization has been employed mainly to allow the polymer/catalyst particles to fragment in a controlled manner so that the particle morphology and the activity can be improved, sometimes improving the stability of the catalyst and preventing the clogging of the catalyst transfer lines are also purposes.^{3, 13-17}

Over the past few decades, academic studies on prepolymerization focused almost entirely on prepolymerization in slurry processes. Weickert et al. used a reactor adapted as a calorimeter to study the kinetics of liquid pool (liquid monomer slurry) prepolymerization of propylene and its impact on full polymerization under various conditions.¹⁸⁻²⁶ They demonstrated that the final particle morphology greatly depends on the initial stage of polymerization. They also showed that conducting prepolymerization under mild conditions (at lower temperature

mostly) greatly enhanced activity and improved particle morphology, and that higher extent of prepolymerization at milder conditions is needed for polymerization at higher temperature. Furthermore, they found that during catalyst fragmentation the particle firstly breaks into large fragments and then decreases in size, providing direct evidences for the fragmentation mechanism of MgCl_2 -supported catalysts under controlled conditions. Interestingly enough, they also did not observe an impact of the catalyst porosity on the fragmentation process. This is coherent with other studies, where quasi-instantaneous fragmentation was observed for the Borealis Sirius catalyst^{27, 28} which is prepared through an emulsion technology and has extremely low porosity and specific surface area²⁹⁻³¹.

While these conclusions are valid for slurry phase polymerizations, very little is known about prepolymerization in the gas phase. Previous studies from our group showed that overheating of the catalyst in the very early stages of polymerization can have a negative impact on catalyst productivity and can have a strong influence on the morphology of the particles obtained.^{32, 33} They also showed that using a hydrocarbon (heptane or mineral oil) can have a positive effect on particle morphology. When catalyst particles were injected into the reactor “dry” (i.e. without an alkane or mineral oil), the morphology was poor, with the formation of broken, or flakey particles. In addition, dry inject also led to lower overall activities during full scale polymerization. On the other hand, injecting the catalyst in an alkane slurry seemed to alleviate the problems linked to poor morphology and activity. It is noted that some patents disclose the advantages of using mineral oil in the polymerization system in terms of the catalyst stability and uniformity, but do not provide an explanation as

to why this might be.³⁴⁻³⁶ It is possible that the presence of an alkane, in particular mineral oil, blocks the pores and helps to “slow down” the initial phase of the polymerization, thereby avoiding overheating. In the current paper we carried out a more systematic investigation of the factors influencing gas phase propylene during the nascent phase of propylene polymerization and investigate whether or not a (pre)polymerization step helps to optimize the overall performance of a commercial Ziegler-Natta catalyst under typical gas phase conditions.

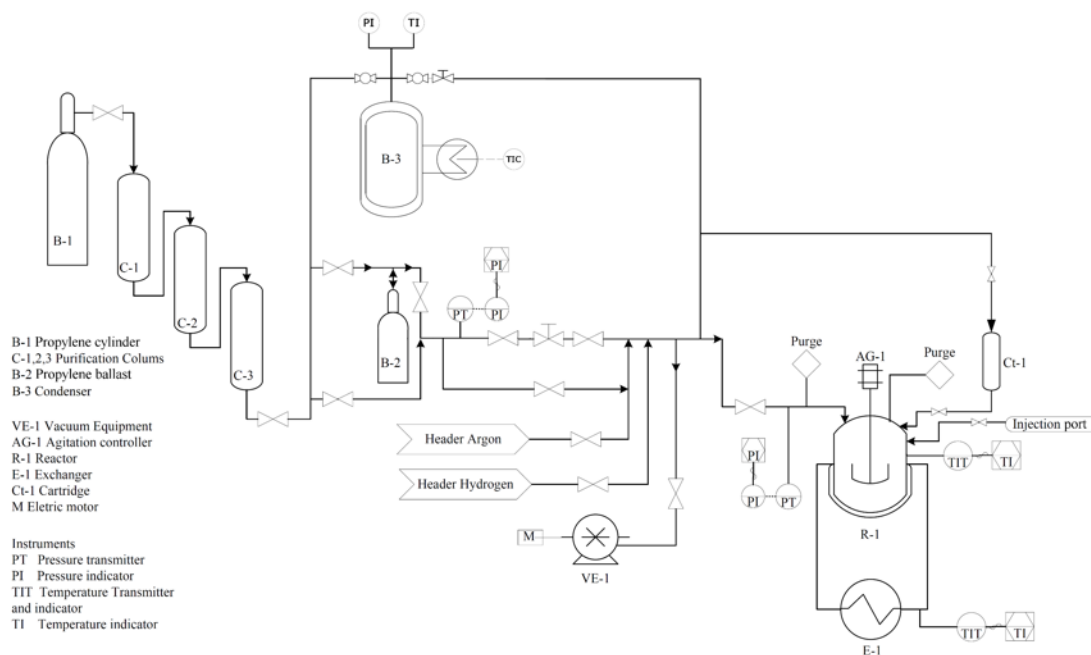
EXPERIMENTAL PROCEDURES

Chemicals

A classic four-generation industrial Ziegler-Natta catalyst (ZNC, 2 wt% Ti) was used in this study. Triethylaluminium (TEAL, from SGS) was used as received. *n*-Heptane (from Biosolve Chemicals) was purified using an MBraun SPS-800 solvent purification unit. Dicyclopentylmethoxysilane (DCPDMS, from ABCR GmbH) was degassed and then stored over dehydrated zeolite under argon. NaCl (from Carl Roth GmbH) was treated at 400 °C under high vacuum for 5 h and then stored in the glovebox. Mineral oil (Fina Vestan A36) was degassed and then stored over dehydrated zeolite in the glovebox. High purity propylene was purchased from Air Liquide S.A. and passed through three different purification columns before use: a first one filled with reduced BASF R3-16 catalyst (CuO on alumina), a second one filled with molecular sieves (13X, 3A, Sigma-Aldrich), and a last one filled with Selexsorb COS (Alcoa). H₂ (ALPHAGAZTM high purity gas) was purchased from Air Liquide and was used as received. Quenching agents: ethanol (EtOH, absolute anhydrous from Carlo Erba) is used as received; methyl propargyl ether (MPE, from TCI) was purified through distillation over CaH₂. NMR solvent is prepared by mixing 1,2-dichlorobenzene-*d*₄ (*o*-DCB-*d*₄, 98% D, used as received from Euroisotop) with the non-deuterated counterpart (*o*-DCB, 99%, used as received from Sigma-Aldrich) in the volume ratio 1:9.

Polymerization

Gas phase polymerization was conducted in a turbosphere reactor system illustrated in Scheme 1. Thermally treated NaCl grain was used as catalyst dispersant. 50 g NaCl was introduced into the reactor before polymerization. Certain amounts of cocatalyst TEAL and external donor (ED) were successively and quickly injected into the reactor at room temperature before precatalyst injection. The total volume of cocatalyst and ED solution was kept lower than 0.5 mL in order to avoid the impact of alkanes on the polymerization in so far as possible.³²



Scheme 1 Process flow diagram of the turbosphere reactor system equipped with condenser (B-3).

Conventional low pressure ($P_{C3} \leq 6$ bar) (pre)polymerization experiments without precontact: A mixture of 50 mg precatalyst and 20 g salt was placed in the cartridge. In the case of employing wet precatalyst, the precatalyst was covered by 0.1 mL of mineral oil before being

mixed with the salt grain. In the case of employing extra oil, another 1 mL of oil was injected into the reactor before the introduction of cocatalyst and ED. After the desired gas phase temperature has stabilized under agitation, the precatalyst/salt mixture was injected with monomer backpressure to initiate the polymerization. A predetermined partial pressure of monomer was reached instantaneously and maintained within ± 0.02 bar. Pressure drop in the ballast B-2 was recorded and converted into a yield of polymer. Polymerization activity was calculated as the derivative of the t_p -yield profile. Low pressure (pre)polymerization experiments with precontact were conducted in a similar manner to the experiments without precontact. The difference exists in the way of injecting the precatalyst. In the case of employing precontact, the precatalyst was injected with N_2 . After 2 min of precontact, the monomer was filled into the reactor to initiate the polymerization. For all the conventional low pressure experiments, 0.70 mmol cocatalyst TEAL (Al/Ti = 33 mol/mol) in 2 M heptane solution and 0.14 mmol external donor (ED) DCPDMS (Al/Si = 5 mol/mol) in 1 M heptane solution were used.

For the quenching experiments, three folds (150 mg) of precatalyst with respect to the conventional experiments was employed for the sake of weighing accuracy at short t_p . 1.90 mmol cocatalyst TEAL (Al/Ti = 30 mol/mol) in neat form and 0.38 mmol external donor (ED) DCPDMS (Al/Si = 5 mol/mol) in 1 M heptane solution were used. The reactor was cooled to 10 °C under agitation (100 rpm) before 6 bar (about 30 g) of propylene was filled into the reactor. The polymerization was initiated by injecting precatalyst (contained in the cartridge Ct-1 in Scheme 1) into the reactor using high pressure (20 bar) N_2 flow. At each

pre-determined time 4 mL of quenching agent (neat EtOH or MPE/heptane solution, in the quenching tube) was sprayed into the reactor under N₂ pressure to stop the polymerization. In the case of MPE, living polypropylene (PP) chains were at the same time labeled by the enchainment of MPE units (details about the methodology can be found in literature³⁷). The quenching tube in Scheme 1 was installed each time after the injection of cocatalyst and ED because they were introduced from the same injection port of the reactor. The quenching tube was flushed with Ar for 5 min after installation to expel air from the system. The quenching agent MPE, was stored and protected under Ar all the time.

High-pressure ($P_{C3} = 20$ bar) polymerization was conducted by using the condenser (B-3 in Scheme 1) which contained liquified propylene. When the condenser was heated to 65 °C, a monomer pressure of ~28 bar was obtained in the ballast, allowing the reactor to be pressurized to 20 bar. The monomer was fed in an intermittent manner. The pressure in the reactor was maintained between 20 and 21 bar. Once the monomer inlet was closed, the pressure in the reactor started to drop. The time required by the pressure-drop of 0.3 bar was recorded. The activity of high-pressure polymerization was calculated by dividing the amount of the consumed monomer (~1.8 g, corresponding to the pressure drop 0.3 bar) over the time of consumption.

A full process consists of a prepolymerization stage and a main polymerization stage. There are three protocols of full process employed in this work:

#1. This protocol consists of 15 min of prepolymerization at 10 °C with $P_{C_3} = 6$ bar and 30 min of main polymerization at 70 °C with $P_{C_3} = 20$ bar. The reactor is evacuated between prepolymerization and main polymerization (*Figure 1a*).

#2. Here, the same temperature and pressure profiles are employed (*Figure 1b*). The difference compared to protocol #1 is that the reactor is not evacuated.

#3. 20 bar of propylene is maintained throughout the whole process. In order to maintain the gaseous state at this pressure, a relatively high temperature 50 °C is employed for the prepolymerization. This is also meant to mimic the environment near the catalyst injection port in a gas phase reactor where propylene is often injected in liquid phase and a cooler local space is probable to exist.

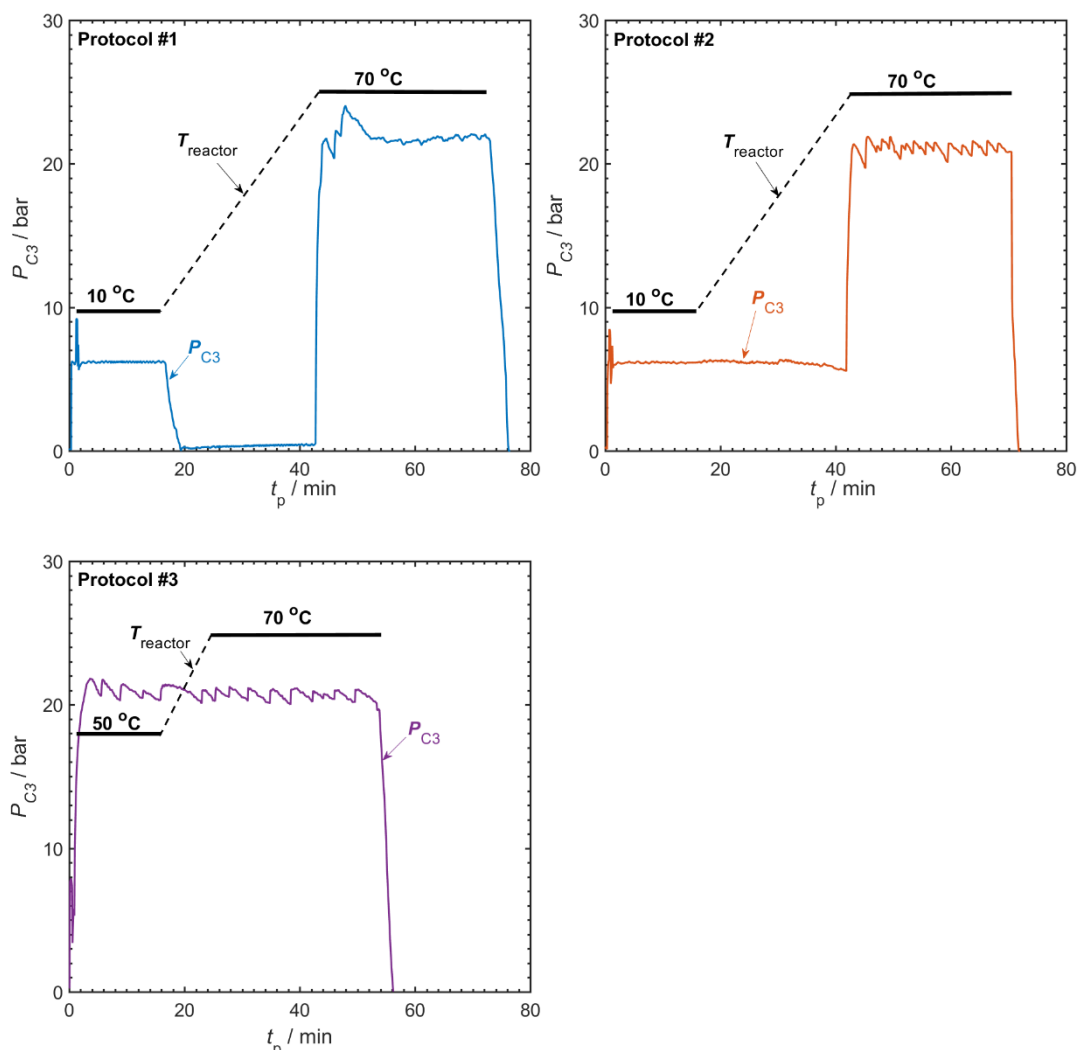


Figure 1. T_p - P_{C3} profiles in prepolymerization and main polymerization of protocol #1,#2 and #3.

After polymerization is complete, the reactor was vented and opened. The product was retrieved and washed with acidified water to remove NaCl and catalyst residue. In the cases with wet precatalyst (mixed with mineral oil, see the text for details), product was sufficiently washed with acetone thereafter. All polymer samples were dried under vacuum at 70 °C for 2 hours.

Differential scanning calorimetry (DSC) characterization

DSC analyses were performed with Mettler Toledo DSC 1 system equipped with an auto-sampler and a 120 thermocouple sensor. The temperature and the heat flow of the equipment were calibrated with an indium standard. All samples were accurately weighed (6 ± 0.1 mg) and sealed in aluminium pans of volume 40 μ L. An empty aluminium pan was employed as the reference. Dry nitrogen with a flow rate at 50 mL min^{-1} was used as the purging gas. The STARe thermal analysis software was used to process the collected data. Melting temperature (T_m) was defined as the temperature corresponding to the melting peak point; the crystallinity (by weight, w_c) of the samples was calculated through $w_c = \Delta H_f / \Delta H_{f0}$, where ΔH_f (J g^{-1}) is the melting enthalpy of the sample and $\Delta H_{f0} = 209 \text{ J g}^{-1}$ is the melting enthalpy of a 100 % crystalline polypropylene. Samples were heated to 200 $^{\circ}\text{C}$ to erase thermal history and then cooled to -20 $^{\circ}\text{C}$ before being heated to 200 $^{\circ}\text{C}$. Heating rate 10 $^{\circ}\text{C min}^{-1}$, cooling rate -10 $^{\circ}\text{C min}^{-1}$.

Gel permeation chromatography (GPC) characterization

High temperature GPC analyses were performed using a Viscotek system (from Malvern Instruments) equipped with three columns (PLgel Olexis 300 mm \times 7 mm I.D. from Agilent Technologies). 200 μ L of sample solutions with a concentration of 3 mg mL^{-1} were eluted in 1,2,4-trichlorobenzene using a flow rate of 1 mL min^{-1} at 150 $^{\circ}\text{C}$. The mobile phase was stabilized with 2,6-di-tert-butyl-4-methylphenol (butylated hydroxytoluene, BHT, 400 mg L^{-1}). Online detection was performed with a differential refractive index detector and a dual

light scattering detector (LALS and RALS) for absolute molar mass measurement. The OmniSEC 5.02 software was used for calculations.

Particle size distribution (PSD) measurement

Particle size distribution of polymer (reactor powder) was performed with Malvern Mastersizer 3000 particle analyzer with Aero S dry powder disperser.

SEM observation

Scanning electron microscope (SEM) observations of the polymer particles were made with a FEI Quanta FEG 250 scanning electron microscope. Micrographs were taken at 5 KV acceleration voltage. The samples for SEM observation were prepared by attaching the reactor powder to conductive tape. Before SEM observations, all the sample surfaces were coated with a layer of 15 nm of copper.

Active sites counting through ^1H NMR

The number of active sites was counted through ^1H NMR characterization on the labeled PP samples prepared by quenching the polymerization with the quench-labeling agent MPE (MPE/Ti = 15). This methodology has been recently established; and the details can be found in the literature.³⁷ MPE has been proved able to selectively insert into the Ti-C bond regardless of the regiochemistry (1,2- or 2,1-orientation) of the last inserted monomer without noticeable multiple insertion. Although the labeling reaction has been showed having fast

completion, the system was let react for 25 min before depressurization. The PP samples were washed one time by dissolving them in boiling xylene and precipitating in ethanol.

For each NMR sample, about 35 mg washed polypropylene was dissolved in 0.6 mL *o*-DCB-*d*₄/*o*-DCB (1/9, v/v) in a 5 mm tube. ¹H NMR spectra were recorded at 400 MHz with a Bruker Avance III spectrometer at 110 °C. The following NMR operating conditions were used: zgig30 sequence, acquisition time 2.0 s, relaxation delay 10 s, 2K scans. The chemical shift of methyl branch (PP) was used as internal reference (δ 0.87 ppm). The integral of -OMe peak (δ 3.18 ppm) of the labeling group (produced by the insertion of MPE into living chains) and the integral of total alkyl protons were employed to calculate the content of labeled chain ends.

The content of labeling group/labeled chain ends in mol mol(C3)⁻¹ was obtained as

$$[\text{LbG}] = \frac{A_{\text{NMR,OMe}}/3}{A_{\text{NMR,alkyl}}/6} \quad (1)$$

where $A_{\text{NMR,OMe}}$ is the integral of the peak of -OMe (δ 3.18 ppm, belonging to the enchainned MPE units) and $A_{\text{NMR,alkyl}}$ is the integral of the alkyl region (protons of C3 units).

The fraction of active Ti was calculated as:

$$\chi^* = \frac{[\text{LbG}] \cdot \frac{Y}{MM_{C3}}}{N_{Ti}} \quad (2)$$

where [LbG] is the content of labeling group in PP measured against the total monomeric units, in mol(LbG) mol(C3)⁻¹; Y is the yield of polymer, in g(PP) g(cat)⁻¹; MM_{C3} is the molar mass of propylene, 42.08 g mol⁻¹; N_{Ti} is the amount of Ti in 1 g of catalyst, 4.18×10^{-4} mol in this study.

RESULTS AND DISCUSSION

Summary of polymer characteristics

All the polymer samples involved in this paper are homopolymer of propylene prepared in the presence of ED. Polymer properties are briefly listed in Table 1.

Entries 1-13 are samples prepared with quenching experiments (the polymerization was quenched with EtOH at each given t_p). Entries 14-21 are samples prepared with conventional low pressure polymerization. And entries 22-26 are samples prepared with full process of polymerization.

Table 1 Properties of the polymer obtained under various conditions.

Entry	T_p^a	oil ^b	t_p^c	T_m^d	w_c^d	M_n^e	M_w^e	\mathcal{D}^e
1	10 ^k	0+0	5	162.13	42.26	64	244	3.8
2			15	162.76	41.82	73	313	4.3
3			30	162.81	42.01	72	343	4.8
4			60	163.38	44.09	109	465	4.3
5			120	162.56	44.42	93	452	4.8
6		0.2+0	15	162.65	42.93	-	-	-
7			30	162.21	43.67	87	371	4.3
8			60	161.40	43.07	95	404	4.3
9			120	161.42	41.01	98	464	4.7
10		0.2+1	15	162.40	42.84	76	288	3.8
11			30	161.73	43.22	86	347	4.0
12			60	162.70	43.33	108	393	3.6
13			120	162.02	43.15	107	431	4.0
14	10	0.1+0	1800	161.33	41.51	104	488	4.7
15		0+0		161.60	42.18	129	608	4.7
16		0.1+1		161.12	41.82	120	574	4.8
17		1.1+0		160.80	40.03	113	488	4.3
18 ^f		0.1+0		162.34	44.90	35	155	4.4
19 ^g		0.1+0		160.24	47.32	27	111	4.1
20		40		0.1+0	164.33	46.70	225	937
21	70	0.1+0	166.13	47.48	284	1130	4.0	
22 ^h	10+70	0.1+0	see text	163.21	49.34	264	1160	4.4
23 ⁱ	10+70	0.1+0		163.05	49.45	233	1081	4.6
24 ⁱ		0.1+1		162.71	49.66	215	1010	4.7
25 ⁱ		1.1+0		165.07	49.05	260	1040	4.0
26 ^j		50+70		1.1+0	165.11	48.15	310	1276

^a Temperature of polymerization, °C.

^b Amount of mineral oil in mL added into the system, including two parts: one mixed with precatalyst + extra one injected separately into the reactor before the injection of precatalyst.

^c Time of polymerization in s.

^d Melting temperature T_m in °C and crystallinity w_c in weight percentage measured by DSC.

^e Number-average molecular weight M_n in KDa, weight-average molecular weight M_w in KDa and dispersity \mathcal{D} measured by GPC.

^f With 2% H₂.

^g With 6% H₂.

^h Full process consisting of prepolymerization and main polymerization, protocol #1, see the text for details.

ⁱ Full process using protocol #2.

^j Full process using protocol #3.

^k Quenching experiments.

Effects of initial conditions

As it is reasonably well accepted that the morphology of polymer particles produced on heterogeneous catalysts is at least in part a result of a trade-off between the deformability of the polymer and the rate of polymerization. We therefore ran tests under mild conditions with dry catalyst to see if changing the reaction conditions (lower T and P) led to any improvement in the final morphologies. The activity curves are shown in Figure 2, and the resulting morphologies are shown in Figure 3. Once again, we observe poor morphologies with dry injections for temperatures as low as 10°C and pressures of 3 bars, and for a temperature of 40°C and 1 bar (these conditions were shown as they led to the similar activities). Clearly, reducing the monomer pressure and/or temperature during prepolymerization is not enough to allow us to obtain suitable control of the particle morphology. This also implies that the evolution of the physical properties of the polymer being produced at the nascent stage is perhaps the most important issue in terms of morphology control in the case of gas phase propylene polymerization.

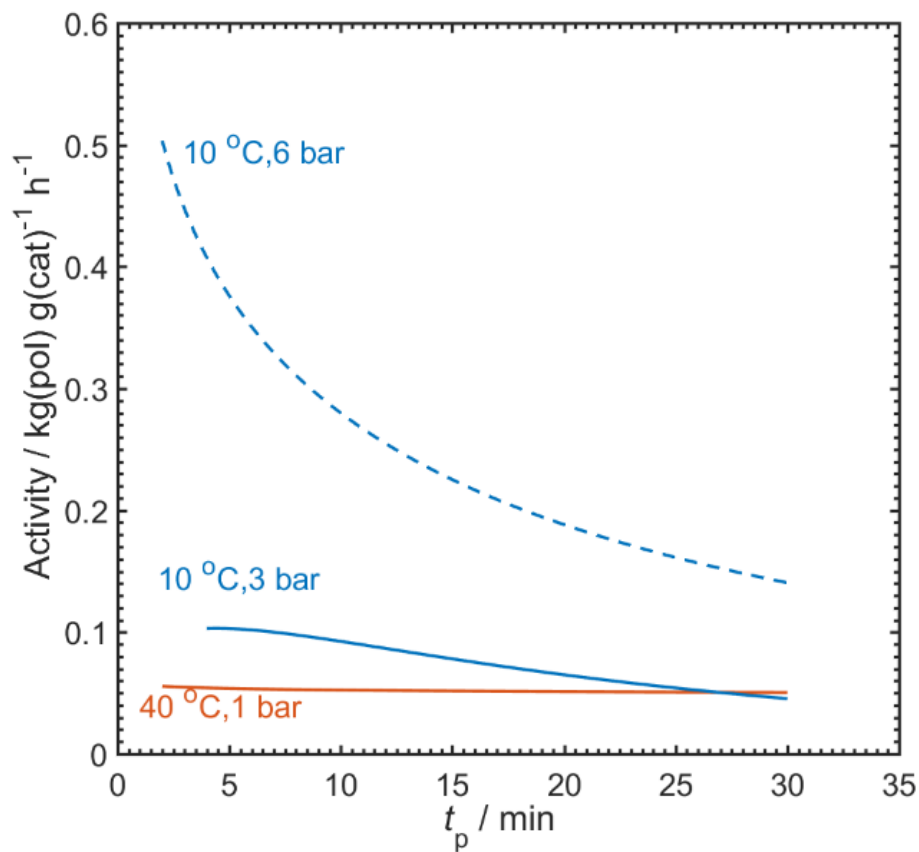


Figure 2. Propylene polymerization kinetics with dry precatalyst. Agitation speed was 200 rpm.

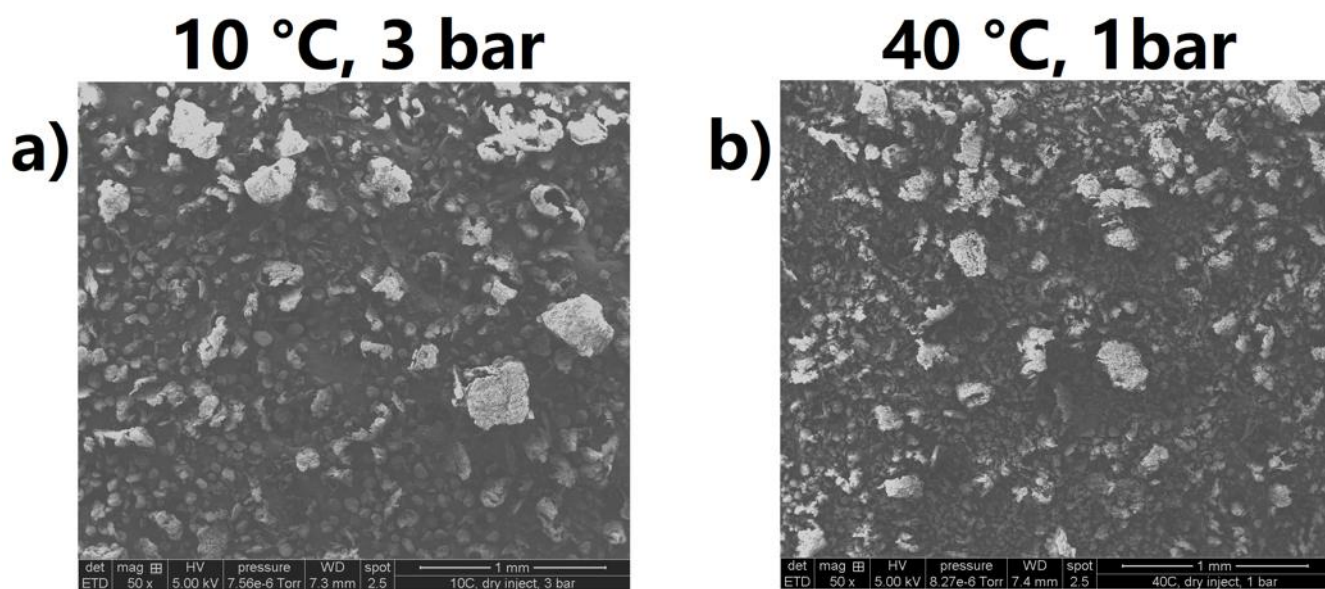


Figure 3. SEM pictures of polypropylene particles prepared with dry precatalyst. Agitation speed was 200 rpm.

Another series of experiments was carried out with wetted precatalyst under different reaction conditions. The precatalyst was mixed with very small amount of mineral oil (~0.1 mL, just enough to theoretically fill the pores of the catalyst being injected) before being loaded into the injection cartridge. The paste-like wet precatalyst was mixed with salt and then carefully loaded into the cartridge, and the effects of T_p and P_{C3} on polymerization kinetics and particle morphology under prepolymerization were investigated.

Figure 4 shows that, as expected, decreasing T_p from 40 °C to 10 °C results in the polymerization rate dropping by roughly 50%, and decreasing P_{C3} also causes a corresponding decrease of polymerization rate. Note also that different combinations of temperature and pressure give rise to similar rates of polymerization (and thus supposedly to similar rates of pressure build that provokes particle fragmentation and expansion). For instance [$T_p = 40$ °C, $P_{C3} = 3$ bar] and [$T_p = 40$ °C, $P_{C3} = 1$ bar] have similar rates as [$T_p = 10$ °C, $P_{C3} = 6$ bar] and [$T_p = 10$ °C, $P_{C3} = 3$ bar], respectively. However, it can be seen clearly in Figure 5 that although these runs have similar rates, they do not give rise to the same particle morphology. All the samples prepared at 40 °C show broken morphology whereas the samples prepared at 10 °C show well-preserved morphology. If we compare these results to those shown above for the dry catalyst, it appears that adding the oil can improve the particle morphology, but that this is not true for all of the conditions examined. Note also that the observations from the previous gas phase study cited above (reference [33]) were obtained in a stopped flow experiment – in other words the growing particles are not mixed, but rather held in place in a fixed bed of salt with gas flowing over them. Here, the particles

are agitated in a free-flowing salt bed. It is possible that the good morphologies obtained in the cited work at 40°C, but not observed here could also be due to an external factor such as the agitation of the stirred bed. Therefore, before going further, we wished to consider the possibility that an agitation speed of 200 rpm, combined with the use of salt (which could serve as a grinding material) would enhance the break-up of the growing particles. A series of comparative experiments with lower agitation speeds (100 rpm and 0 rpm) were therefore conducted.

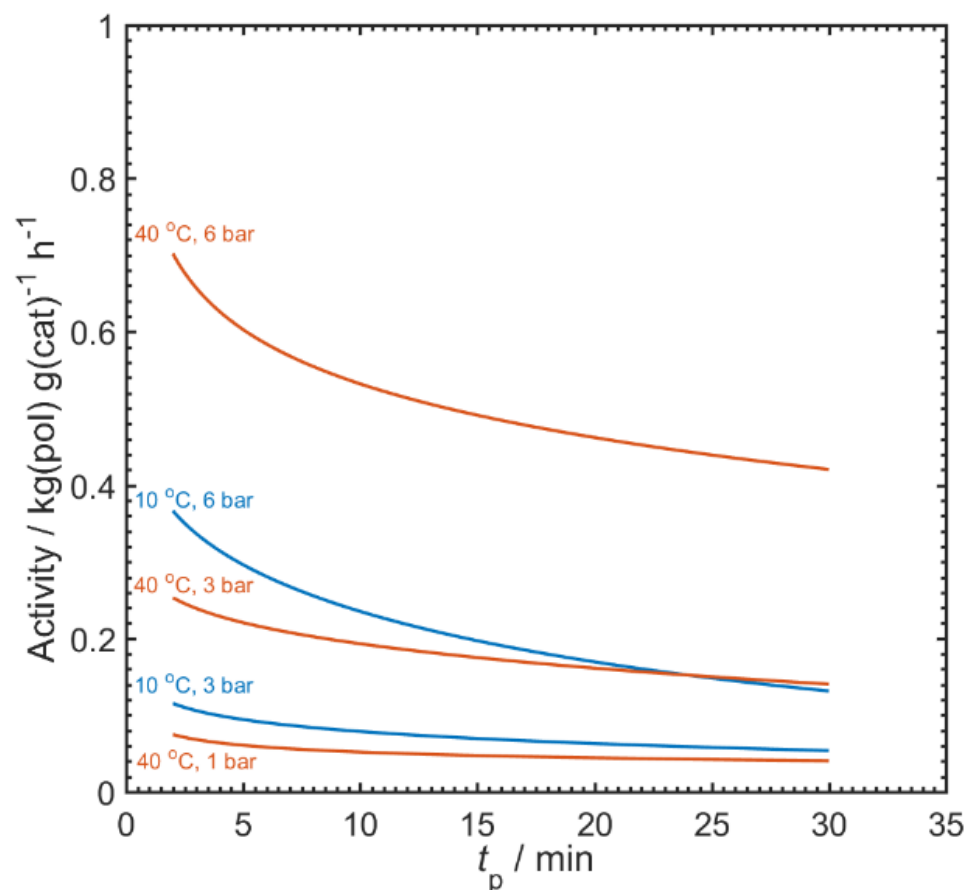


Figure 4. Polymerization kinetics with wet precatalyst (precatalyst was mixed with 0.1 mL oil before injection). Agitation speed was 200 rpm.

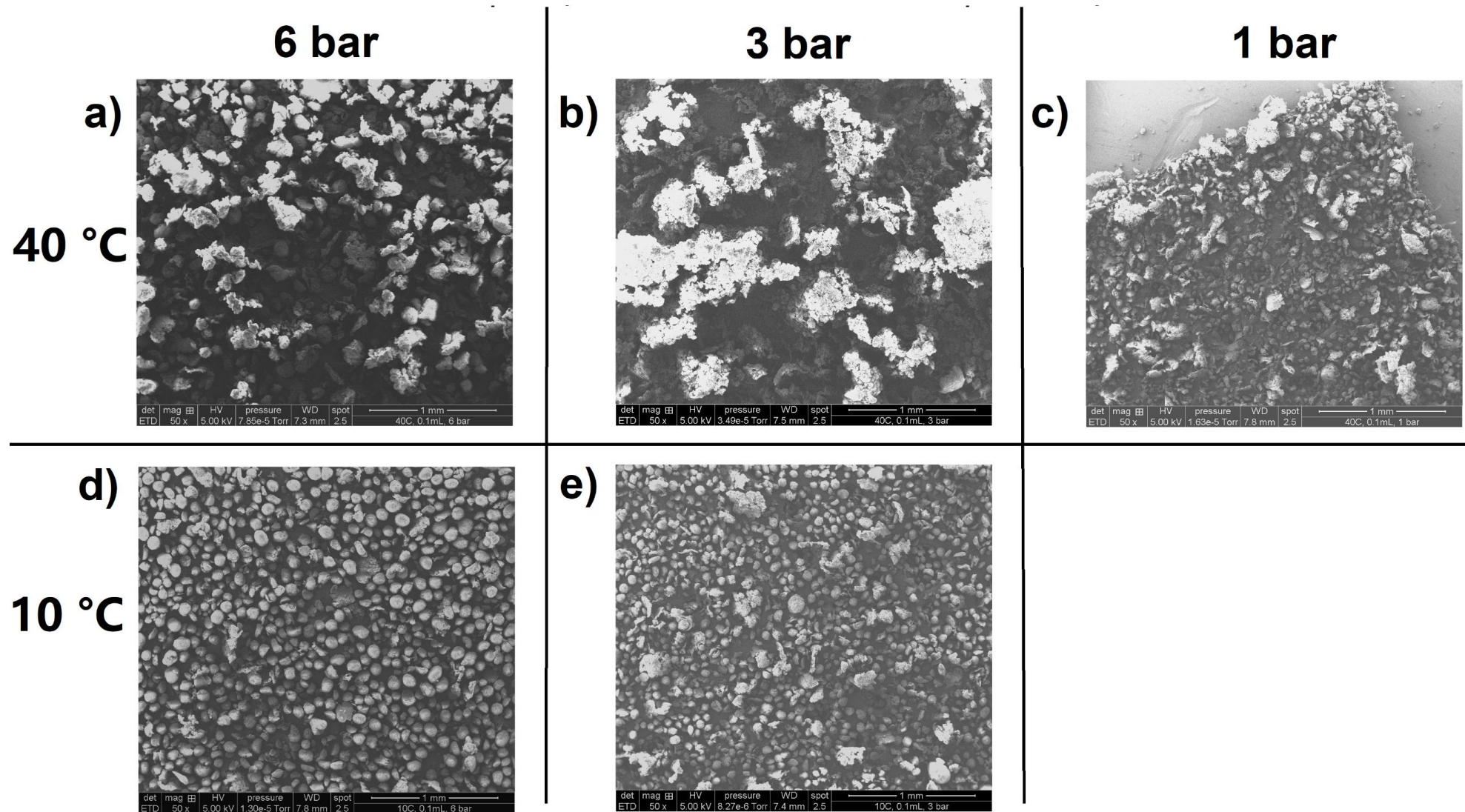


Figure 5. SEM pictures of polypropylene particles prepared with wet precatalyst. Agitation speed was 200 rpm. The scale bar in every picture stands for 1 mm.

Effects of agitation

When precatalyst was injected in dry form at 10 °C, it can be seen from Figure 6 that the final particle size distribution of the powder made at 200 rpm shows a significantly lower peak particle size, and a much longer tail of fines than one obtains with the powder made at 100 rpm. However, when precatalyst was injected in wet form at 10°C, a higher agitation speed had a negligible impact on the final PSD, and once again the morphology of the resulting polymer was more spherical and regular than in the dry case. For this reason, an agitation speed of 100 rpm was employed in the remainder of the study. This result is actually quite important as it shows that the presence of the oil has a clear and definite impact on the morphology. The oil most likely plasticizes the PP matrix, eventually slowing down crystallization, and allowing the particle to deform to compensate for the stresses caused by the agitator. It is also quite reasonable to suppose that if plasticization by the oil helps maintain the morphology in the face of stress caused by the agitator, it will also do the same thing when one has stresses generated by particle fragmentation and expansion.

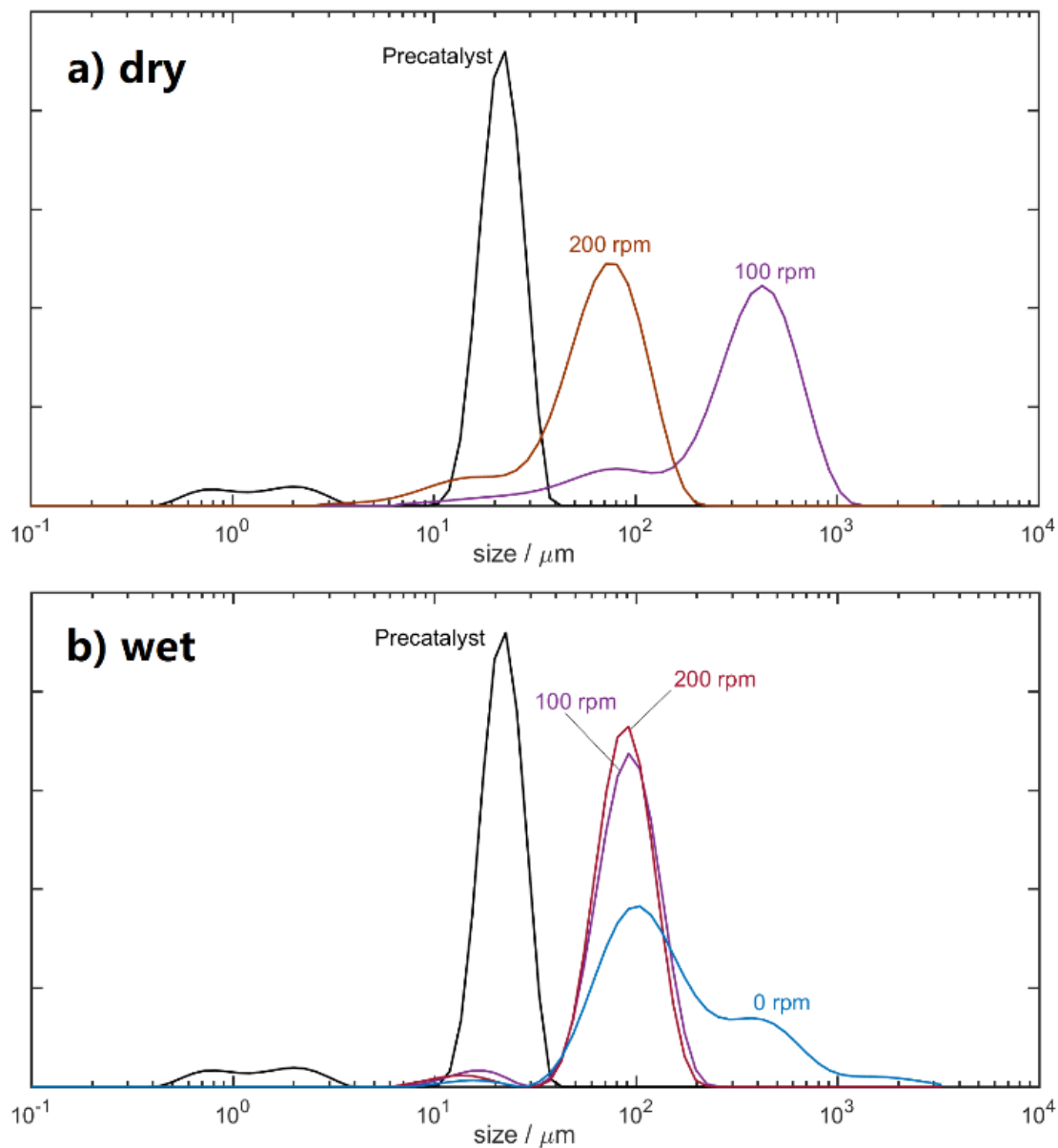


Figure 6. PSD of PP particles prepared under different agitation speeds. The precatalyst was injected in (a) dry form and (b) wet form, respectively. $T_p = 10 \text{ }^\circ\text{C}$ and $P_{C3} = 6 \text{ bar}$.

Nascent polymerization with quenching experiments

It has been recognized in a number of studies^{28, 33, 38-51} that nascent stage of polymerization plays a critical role in morphogenesis. However, conventional experiments did not allow one to obtain the nascent kinetics of polymerization in a reliable manner due to the fluctuation of monomer pressure in the beginning. Thus, we carried out a series of polymerization quenched at given times of polymerization ($t_p = 5 - 120$ s) in order to evaluate the influences of the mineral oil on the nascent stage of polymerization.

When precatalyst is injected in dry form, the polymerization has the highest initial activity but decays rapidly (Figure 7). When a little amount of oil, which is only enough to wet the precatalyst, is mixed with precatalyst, the initial activity is reduced to 60%. And the activity is stabilized. Adding extra oil into the reactor separately from precatalyst further reduces the initial activity and gives rise to similarly stable activity. Overall the presence of mineral oil moderates the polymerization especially in the initial stage and stabilizes the kinetics.

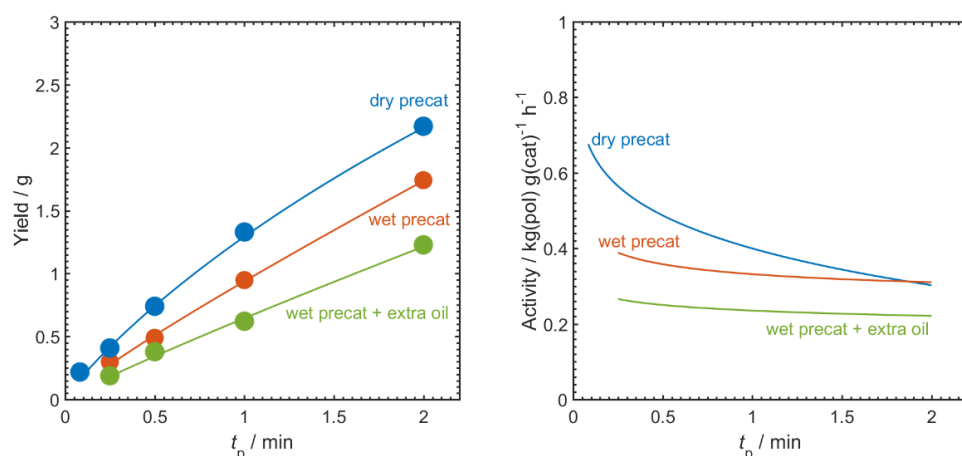


Figure 7 Effects of oil on the kinetics of early stage of prepolymerization.

The PSD of pre-catalyst (in Figure 6) show two peaks: major fraction and fine fraction. For the case of dry pre-catalyst, the emerging peaks of PSD of the polymer particles (1-3 in Figure 8) indicate that larger particles break into smaller ones and contribute to the fine fraction. The normalized PSD data (in Figure 8 b) seem to suggest that particle breakup reaches a steady state from $t_p = 30$ s. SEM pictures demonstrate that dry pre-catalyst resulted in highly rough particle surface with sharp cracks while wet pre-catalyst resulted in smooth particle surface. Adding extra oil for the wet pre-catalyst interestingly induced cauliflower-like morphology with pores in the particle surface.

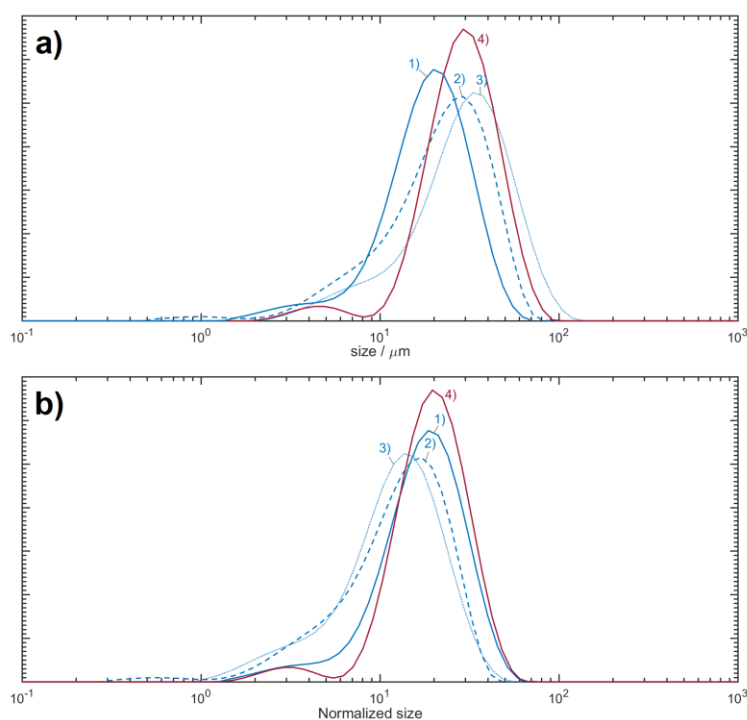


Figure 8. PSD of PP particles prepared under various conditions: a) original size data; b) normalized size equals to the original size divided by the cubic root of productivity ($\text{g(PP)} \text{g(cat)}^{-1}$). 1) Dry pre-catalyst, $t_p = 5$ s; 2) dry pre-catalyst, $t_p = 30$ s; 3) dry pre-catalyst, $t_p = 120$ s; 4) wet pre-catalyst, $t_p = 30$ s.

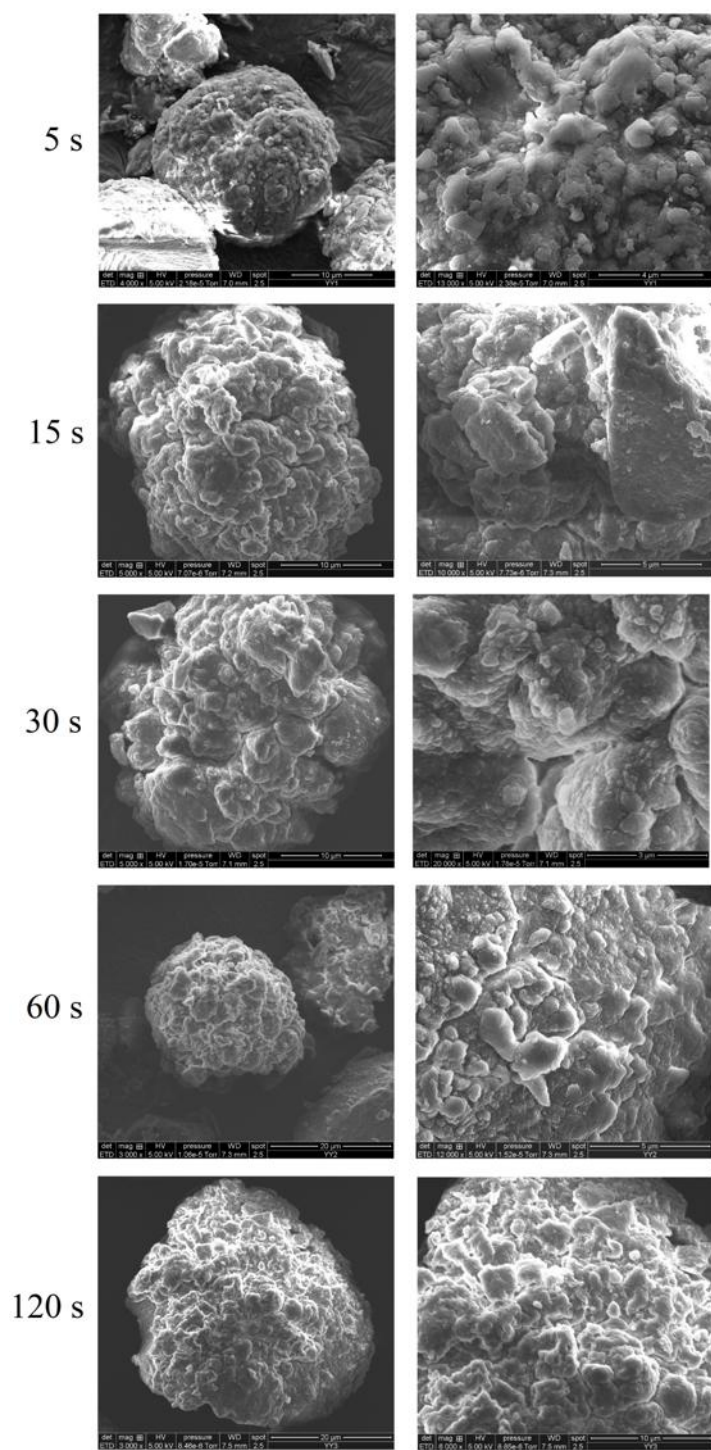


Figure 9. SEM pictures of PP particles prepared with dry precatalyst at various t_p .

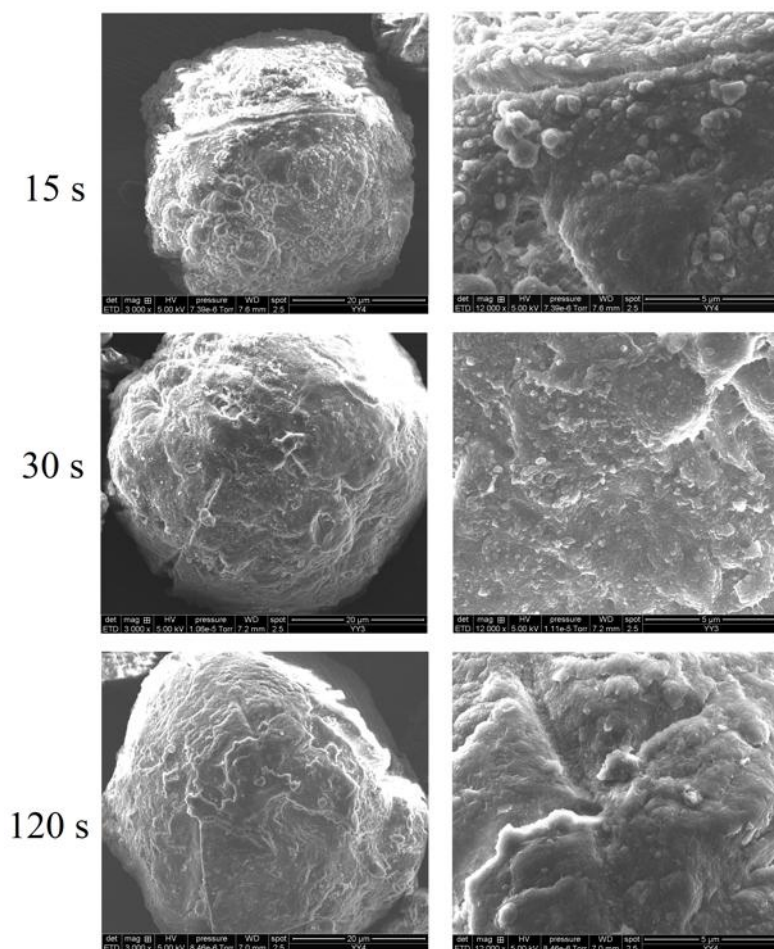


Figure 10. SEM pictures of PP particles prepared with wet (0.2 mL oil with 150 mg precatalyst) precatalyst at various t_p . Particles were washed with cold acetone before SEM observation.

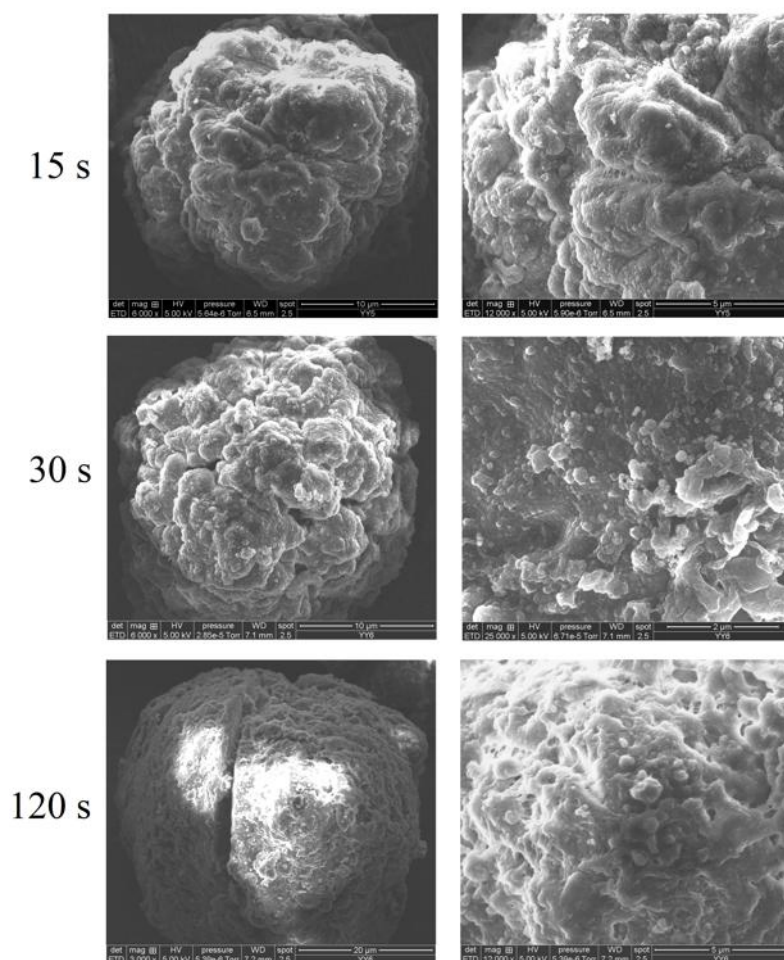


Figure 11. SEM pictures of PP particles prepared with wet (0.2 mL oil with 150 mg precatalyst) precatalyst and extra oil (1 mL oil) at various t_p . Particles were washed with cold acetone before SEM observation.

Effects of H₂ on prepolymerization

H₂ is commonly used as chain transfer agent in catalytic olefin polymerization to modulate the molecular weight distribution (MWD), and it is known to boost the activity of propylene polymerization mediated by many catalysts. In this work, 2% and 6% (in partial pressure) of H₂ were tested in the system. Figure 12 shows that, as expected, one sees a slight activity boost at higher H₂ concentrations. However, a comparison of the particle size distributions of the prepolymer powder shown in Figure 13 shows that there is an increase in the agglomeration of larger particles as the hydrogen concentration increases, but no additional fines generation.

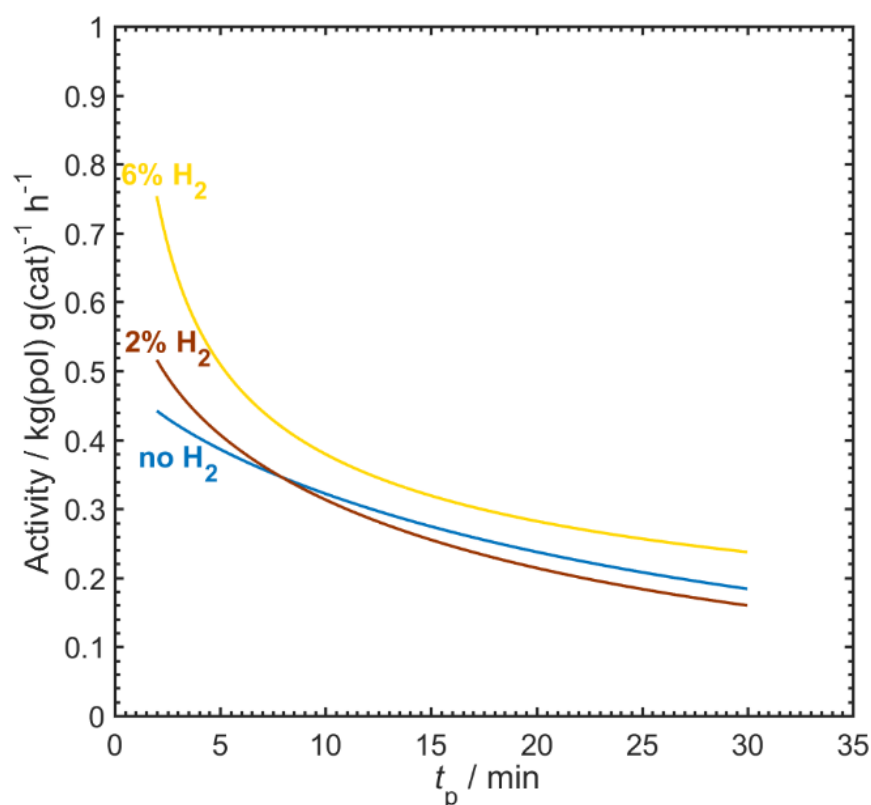


Figure 12. Kinetics of polymerization affected by the content of H₂. Polymerization was conducted using wet precatalyst, $T_p = 10$ °C and $P_{C3} = 6$ bar.

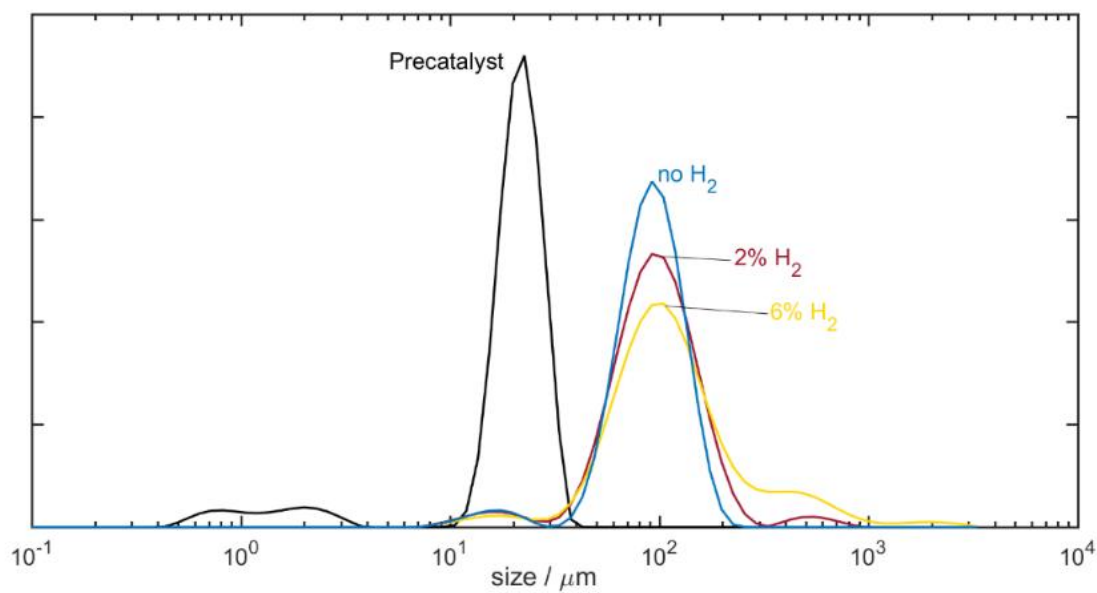


Figure 13. PSD of PP particles affected by the content of H_2 . Polymerization was conducted using wet precatalyst, $T_p = 10\text{ }^\circ\text{C}$ and $P_{C3} = 6\text{ bar}$.

Evaluation of the number of active sites: Oil vs dry

A selective labeling method³⁷ that has been recently developed was applied in gas phase prepolymerization. This method allows to selectively label the living chains so that the number of living chains/active sites can be directly obtained. Details can be found in the experimental part and in reference [37]. Figure 14 shows ¹H NMR spectra of labeled PP samples prepared at $t_p = 15$ s with different dosages of mineral oil. A qualitative comparison of active sites number between the samples can be made with the signal intensity of the labeling group (-OMe) illustrated in the inset c. When precatalyst was employed in dry form, only 8% of Ti was active. And apparently this fraction was already reached by $t_p = 15$ s since the number of active sites did not change between 15 s and 120 s.

Mixing a little amount of oil with the precatalyst resulted in an increase in the fraction of active Ti to 12% (increased by 46%). And addition of extra oil further increases the value to 15% (1.8 times of the entry with dry precatalyst). However, the macrokinetics (Figure 7) showed a decreasing trend over the addition of oil. Skoumal et al. employed oil to separate catalytic system from the monomer-saturated heptane solution, and demonstrated the high mass transfer resistance of monomer in oil.⁵² Thus there are reasons to believe that the lower activity of gas phase prepolymerization we obtained in the presence of oil is attributed to the mass transfer resistance imposed by the mineral oil covering on the surface of the catalyst particle. As an additional argument, the activity in the main stage polymerization (see Figure 15 and the following text) was higher for the entry with extra oil compared to the entry without extra oil, in accordance with the data of the active sites number reported here. The oil

was believed to be well-dispersed in the polymer matrix at high yield of polymer during main polymerization so that the mass transfer-limiting effect by oil was diminished. Thus the effects of higher active sites content played the main role.

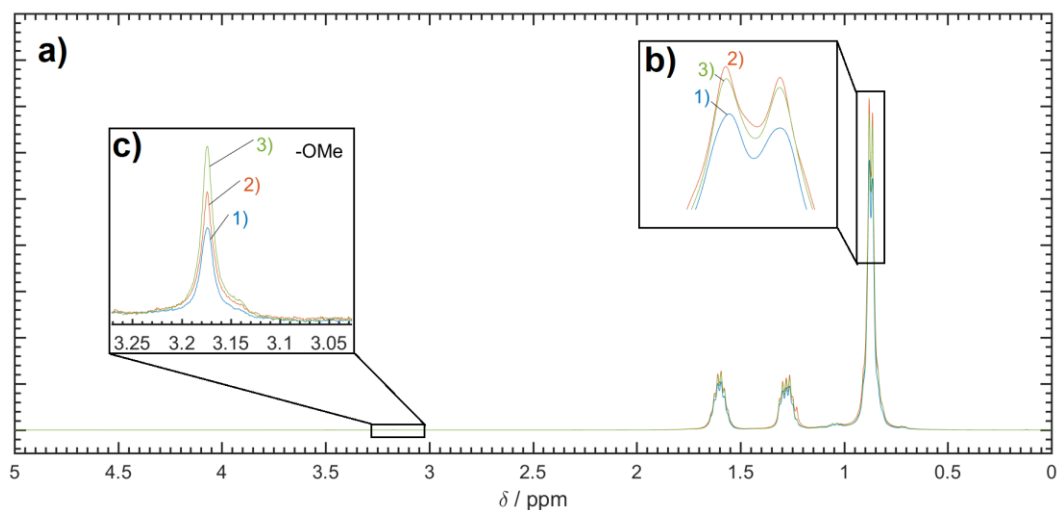


Figure 14 ^1H NMR spectra of PP samples labeled with MPE. The area under each curve has been normalized to the corresponding sample yield. Samples: 1) Dry precatalyst, 2) wet precatalyst, 3) wet precatalyst + extra oil. Time of polymerization for all samples $t_p = 15$ s. Plots: a) Overview, b) methyl region showing the signals of alkyl protons of PP have been normalized to the yield, c) the signal of -OMe belonging to the enchaind labeling unit.

Table 2 Results summary of labeling experiments.

oil ^a	t_p ^b	Yield ^c	[LbG] ^d	χ^{*e}
0+0	120	18.1	0.80	8.1
0+0	15	4.3	3.3	8.0
0.2+0	15	5.3	3.9	11.7
0.2+1	15	4.9	5.3	14.5

^a Amount of mineral oil in mL added into the system, including two parts: one mixed with precatalyst + extra one injected separately into the reactor before the injection of precatalyst.

^b Time of polymerization in s.

^c Polymer yield in $\text{g}(\text{PP}) \text{g}(\text{cat})^{-1}$.

^d Content of labeling group in $10^{-4} \text{mol mol}(\text{C3})^{-1}$.

^e The fraction of active Ti over the total Ti in %.

Full process of polymerization and impact of oil

In order to understand the importance (or not) of prepolymerization on the evolution of powder properties during later stages of polymerization under full conditions, a 15 min prepolymerization step (using the different protocols described above) was combined with 30 min of polymerization at **70 °C and 20 bars**. In this section of work, prepolymerization using precatalyst wet with 0.1 mL oil adopting $T_p = 10\text{ °C}$ and $P_{C3} = 6\text{ bar}$ has been used as the benchmark given the results of the previous sections.

Mineral oil clearly plays a critical role in determining the activity of the catalyst and the particle morphology during early stages of propylene polymerization, so different protocols of adding oil have been applied in order to study the effects of mineral oil on the morphology of the final product, with oil being added in one or two shots: one shot mixed with precatalyst and loaded into cartridge + an eventual second shot injected into the reactor separately before the injection of precatalyst.

If we compare the impact of the quantity and injection protocol of oil, it can be seen from Figure 15a that the highest rate of prepolymerization is obtained when 0.1 + 0 mL (0.1 mL with precatalyst and 0 mL injected separately into the reactor) of oil was employed. Figure 15b shows that, for this same oil injection method, using protocol #1 or #2 gives rise to relatively low but similar activity during the main polymerization step.

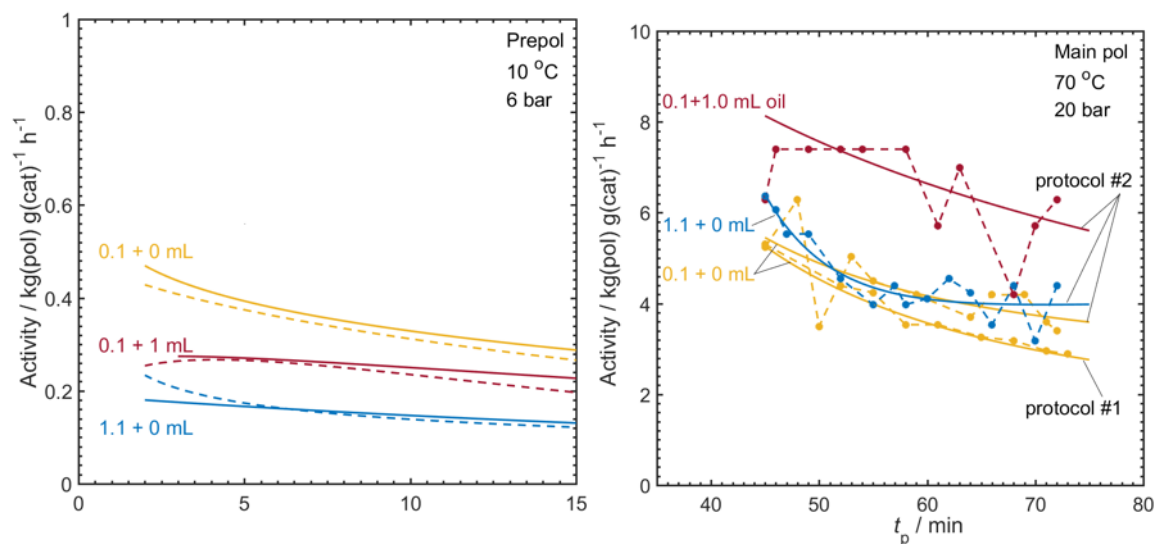


Figure 15. Kinetics of prepolymerization (a) and main polymerization (b) with various ways of oil introduction. The dashed lines in (a) are duplicates. Final yield of PP by protocol #1: (0.1+0 mL oil) 2.8 kg(PP) g(cat)⁻¹; protocol #2: (0.1+0 mL) 3.8 kg(PP) g(cat)⁻¹, (0.1+1 mL) 5.4 kg(PP) g(cat)⁻¹, (1.1+0 mL) 3.8 kg(PP) g(cat)⁻¹.

Increasing the dosage of mineral oil came to be a possible approach for improving the particle morphology of the final product. There are two options to increase the dosage of oil: 1) directly increasing the amount of the oil mixed with precatalyst and 2) introducing the extra oil separately into the reactor.

It has been found that a direct increase in the amount of oil which is totally mixed with precatalyst (Figure 15a – 1.1+0 mL of oil) resulted in lower activity in prepolymerization stage than was seen when 0.1 mL is injected with the catalyst after injecting 1 mL separately (0.1+1 mL oil). However, both methods gave a much lower rate of prepolymerization than was observed for 0.1 mL of oil. During main polymerization, the case with 1.1+0 mL oil showed similar activity to the one with 0.1+0 mL oil but significantly lower activity than the one with 0.1+1 mL oil. Clearly the kinetics of main polymerization was not governed by the total amount of oil but rather by the second shot of oil.

Some lump formation was observed for all three cases without the second shot of oil (Figure 16). The case with 0.1+0 mL oil employing protocol #2 produced particles presenting a “shoulder” with PSD (Figure 17) and agglomerate morphology (Figure 18 d-f). Adding the second shot of oil (0.1+1 mL) eliminated the lump formation. For the normal particles apart from the lump, the case of 0.1+0 mL showed smooth particle surface (Figure 18 a-c) while the both cases with 1.1 mL (1.1+0 mL and 0.1+1 mL) showed similar rough and porous surface (Figure 18 g-l). SEM examination on the prepolymer produced with 1.1+0 mL and 0.1+1 mL oil was performed (Figure 19). The original particles were coated by a layer of oil which

interfered the observation. Washing the particles with cold acetone removed oil and showed similar morphology between the two cases. Apparently the surface morphology at $t_p = 2$ min (see Figure 11) is already alike the one at $t_p = 30$ min.

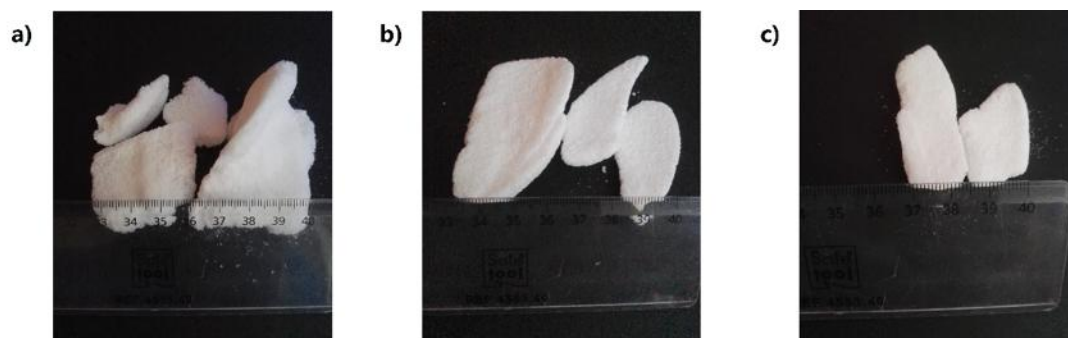


Figure 16. Pictures of lump formed under a) protocol #1, 0.1 + 0 mL oil; b) protocol #2, 0.1+0 mL oil and c) protocol #2, 1.1+0 mL oil.

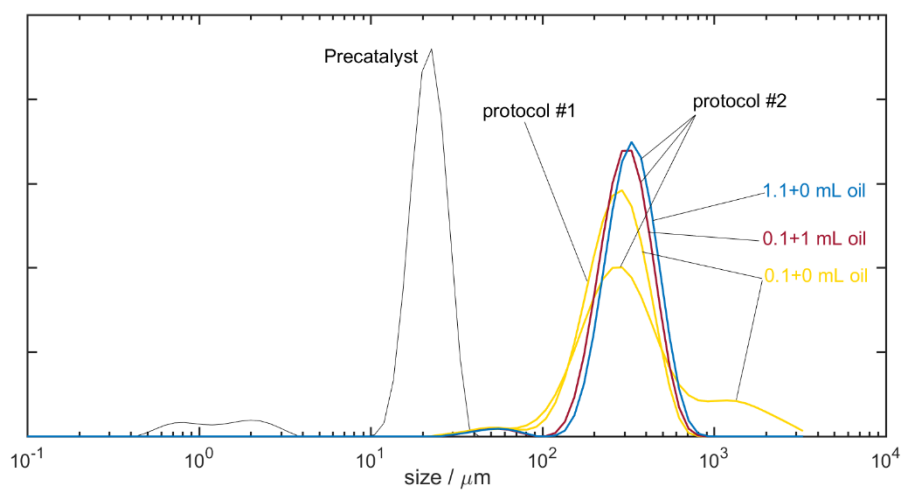


Figure 17. PSD of PP particles prepared with protocol #1 and #2.

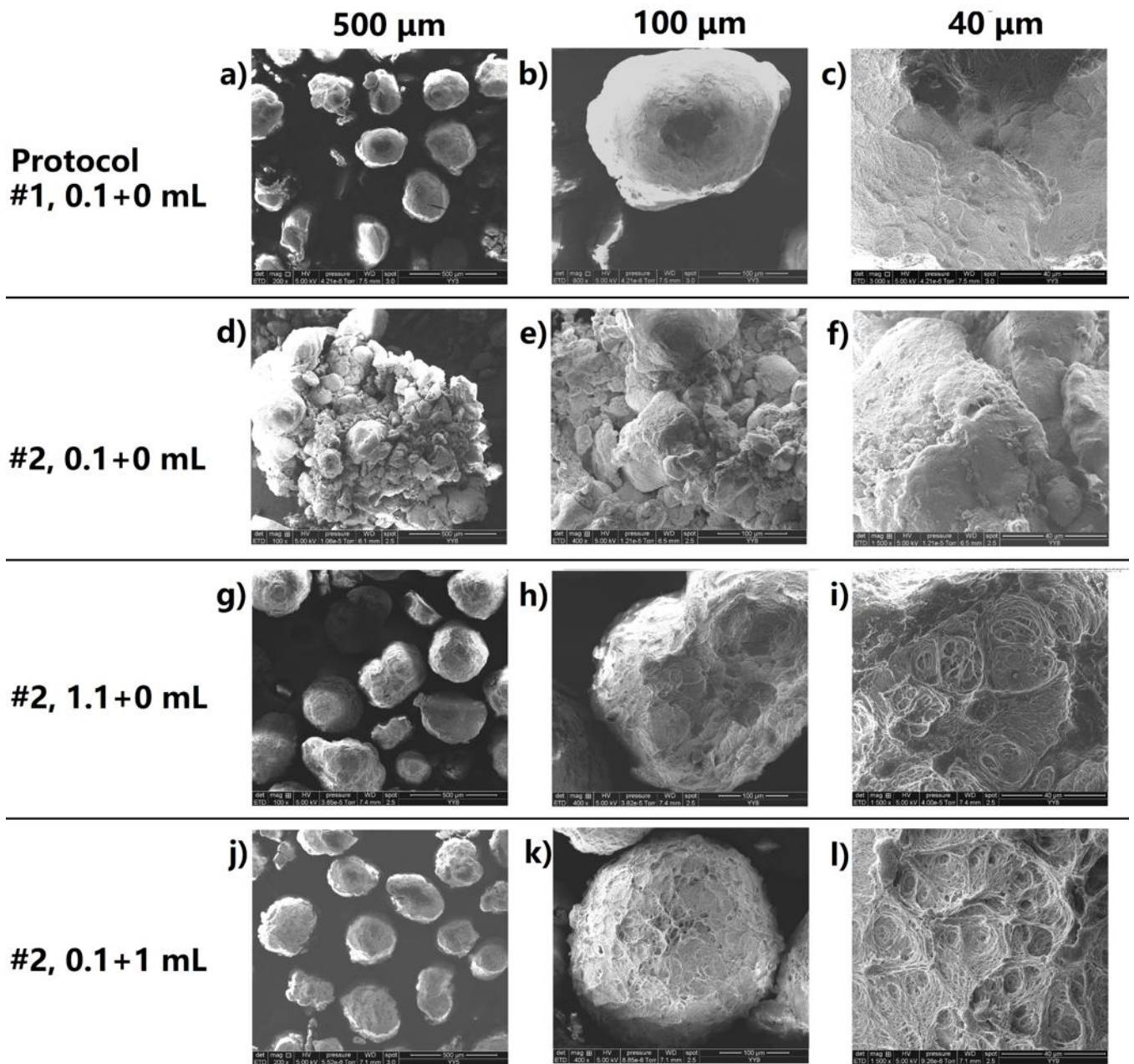


Figure 18. SEM pictures of PP particles prepared through protocol #1 and #2 with various ways of oil injection. The scale bar in each column of pictures stands for 500 μm, 100 μm and 40 μm, respectively.

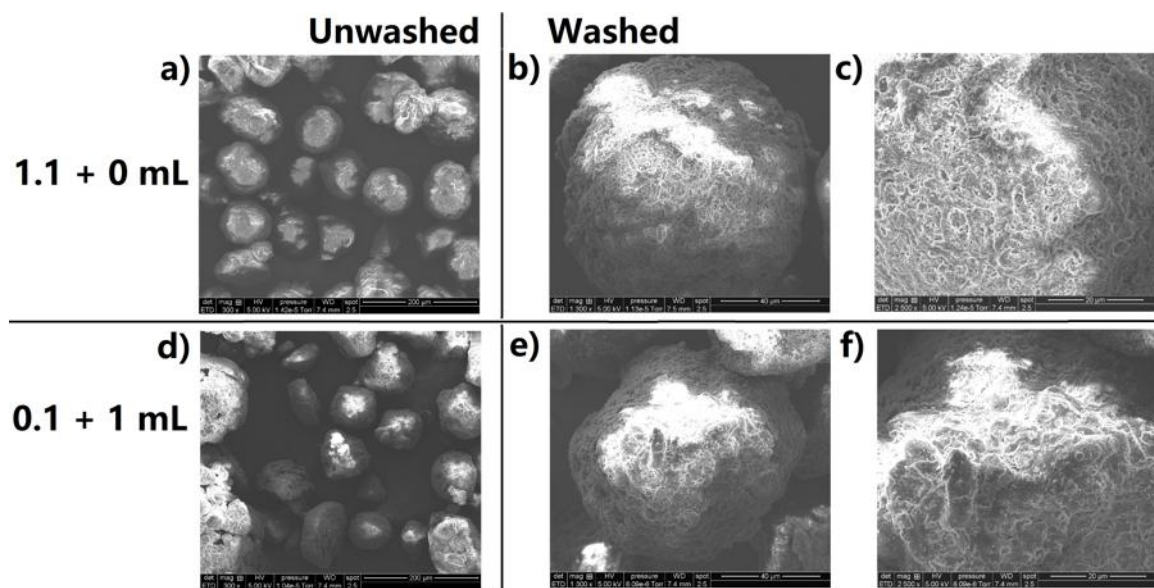


Figure 19. SEM pictures of PP prepolymer particles prepared in the presence of 1.1 mL total amount of oil in two ways of introduction. $t_p = 30$ min. The scale bar in each column of pictures stands for 200 μm (300 \times), 40 μm (1300 \times) and 20 μm (2500 \times), respectively.

To better understand to what extent the extra oil (the second shot of oil) can influence the polymerization and the roles of the extra oil, a series of experiments with various amounts of extra oil have been carried out in this section.

It has been found that an increased amount of extra oil from 0.3 mL to 1 mL results in slightly decreased activity of prepolymerization but almost identical activity of the main polymerization (Figure 20). PSD (Figure 21) and SEM (Figure 22) results suggest that changing the amount of extra oil in this range does not significantly impact the particle morphology.

The decreased activity in prepolymerization can be explained by the oil covering the particles and imposing mass transfer resistance towards the monomer diffusion. However, the amount of oil clearly was not an essential factor to determine the morphology of the final product or the kinetics of main polymerization. To some extent, the existence of the oil in the reactor before the injection of precatalyst might be important for obtaining the enhanced activity and improved morphology for the main polymerization. A speculation based on the observed facts is that the effective concentration of cocatalyst in the system is reduced by the presence of oil, and thus it slows down the contact between cocatalyst and precatalyst and therefore as well as the initial rate of prepolymerization. As a matter of fact, there have been some reports showing that lower temperature of prepolymerization, which should result in lower initial rate, is accompanied by faster main polymerization.^{23, 53} In this work it has been ascribed to that the lower initial rate of prepolymerization produced particles having more active titanium (see

the text above for active sites counting and Table 2). Apparently somehow the lower initial rate of prepolymerization may allow a better fragmentation of catalyst particle to occur and a higher fraction of active Ti to form.

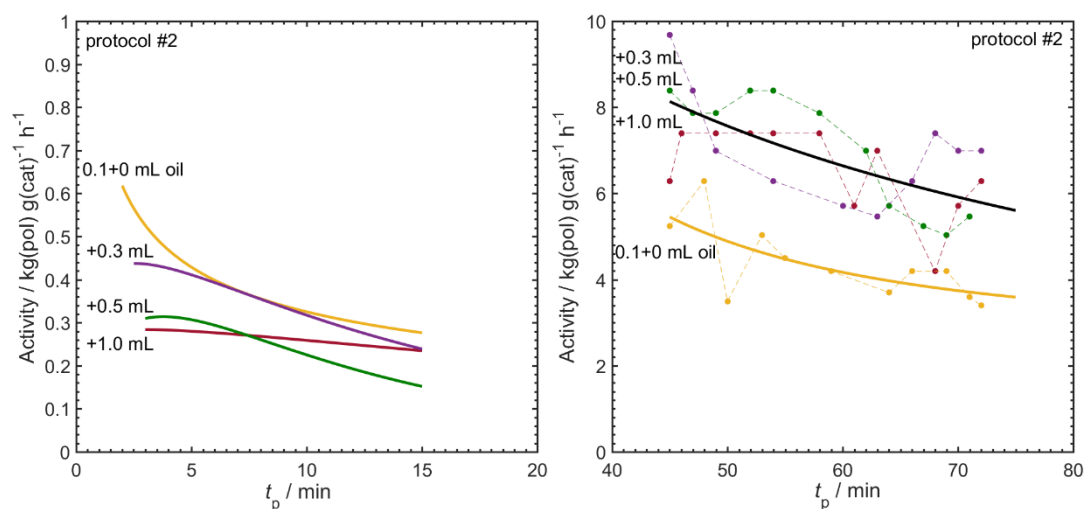


Figure 20. Kinetics of prepolymerization stage (left) and main polymerization stage (right) with various amounts of extra oil (V_{ex}) separately injected into the reactor. Precatalyst is mixed with 0.1 mL oil and injected in a wet form. Polymerization followed protocol #2. For $V_{\text{ex}} = 0, 0.3, 0.5$ and 1 mL, final yield is 3.8, 5.7, 5.3 and 5.4 kg(PP) g(cat)⁻¹, respectively.

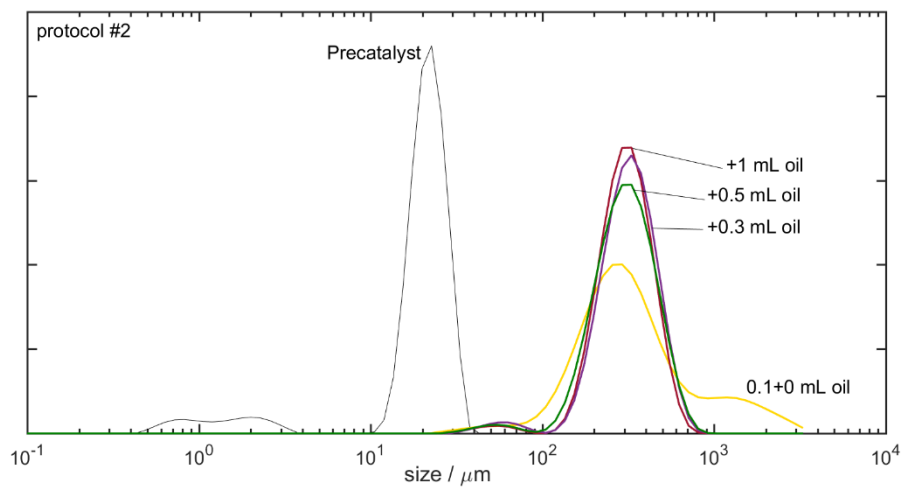


Figure 21. PSD of PP particles prepared through protocol #2 with various amounts of extra oil.

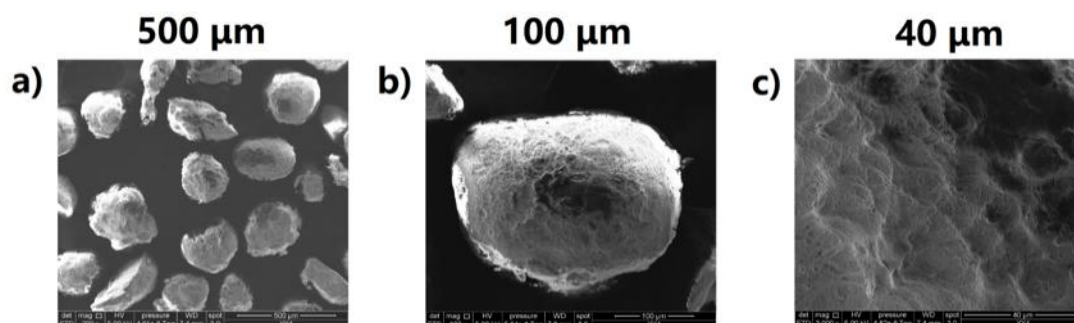


Figure 22. SEM pictures of PP particles prepared through protocol #2 with 0.1+0.3 mL oil (0.1 mL oil was mixed with precatalyst and extra 0.3 mL oil was injected separately into the reactor). The scale bar in each picture stands for 500 μm (200 \times), 100 μm (800 \times) and 40 μm (3000 \times), respectively.

As a gas phase prepolymerization at lower pressure is not always explicitly present in a gas phase process, it could be informative to compare the previous protocols with protocol #3.

The precatalyst was introduced in the same way as previously described: 50 mg precatalyst was dispersed in 1.1 mL of oil to form slurry and then injected into the salt bed in the cartridge. It has been found that the prepolymerization at 50 °C and 20 bar of propylene showed a fast decay in the activity and then tended to be stabilized (Figure 23 a). The activity of the main polymerization stage of the protocol #3 is significantly lower than protocol #2 with the same oil introduction (Figure 23 b). The former one was found to have lump formation. However, the remaining part of the polymer showed surprisingly well-preserved morphology which is reflected by the narrow PSD (Figure 24) and regular shape under SEM (Figure 25). The SEM pictures also demonstrate that the polymer particles prepared with protocol #3 are smoother and less porous in the surface than the one prepared with protocol #2 (Figure comparing with Figure 18 g-i). However, again, the morphology in the surface does not necessarily reflect the internal structure. Comparing the PSD of the samples prepared with protocol #2 and #3 indicates that the latter one has slightly larger size but lower yield. It means the particles of #3 are more porous internally than #2. It is noticed that the fine part of the polymer particles is absent when protocol #3 was employed, implying the fines possibly contribute to the lump formation and eventually are contained in the lump.

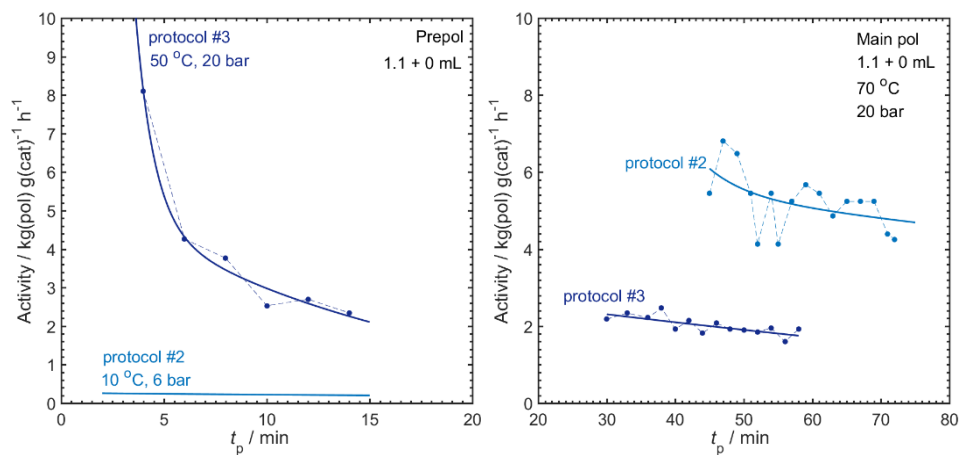


Figure 23. Kinetics of prepolymerization stage (a) and main polymerization stage (b) using protocol #3 compared with protocol #2.

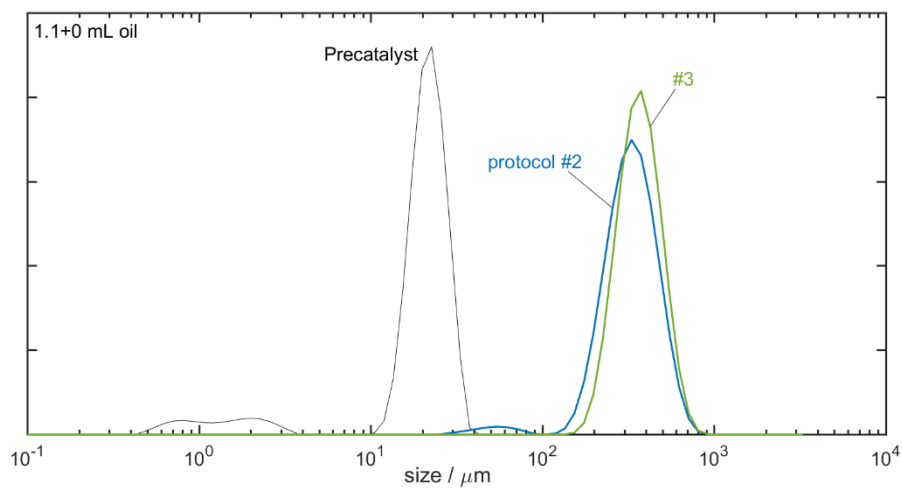


Figure 24. PSD of PP particles prepared through protocol #2 and #3. 1.1 mL oil was wholly mixed with precatalyst. Yield of PP by protocol #2 and #3: 3.8 kg (PP) g(cat)⁻¹ and 3.1 kg(PP) g(cat)⁻¹, respectively.

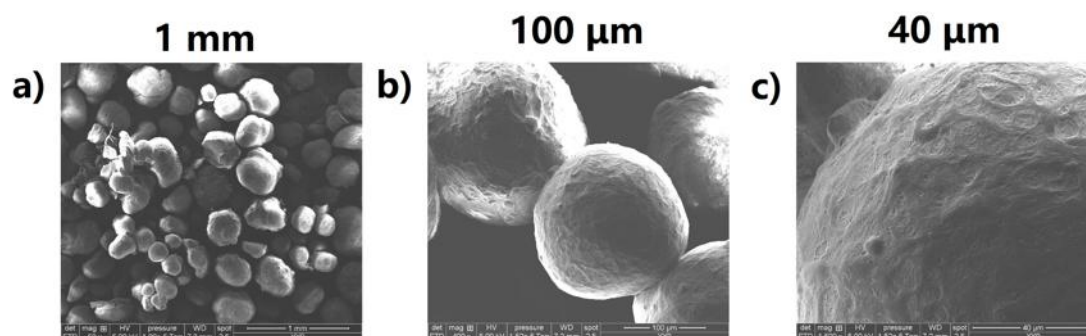


Figure 25. SEM pictures of PP particles prepared through protocol #3 with 1.1+0 mL oil (total 1.1 mL oil was wholly mixed with precatalyst to form a slurry state and injected into the salt bed in the cartridge). The scale bar in each picture stands for 1 mm (50 \times), 100 μ m (400 \times) and 40 μ m (1500 \times), respectively.

CONCLUSIONS

In this paper, we showed that mineral oil plays essential roles in the kinetics and morphogenesis of gas phase propylene polymerization. Through a comprehensive investigation on the effects of mineral oil, we have concluded:

- i. Precatalyst must be wet with mineral oil in order to obtain well-preserved polymer morphology.
- ii. The presence of oil significantly slows down the prepolymerization in the initial stage, and stabilizes the kinetics.
- iii. The presence of oil increases the fraction of active Ti in the catalyst as well as the mass transfer resistance of monomer during the prepolymerization.
- iv. Low temperature of prepolymerization is necessary for the morphology preservation when the amount of oil is low; whereas higher temperature is feasible when the oil is sufficient although it compromises the activity of the main polymerization stage.
- v. The way of introducing oil matters for both activity and particle morphology. Compared to the case where oil is totally mixed with precatalyst, a significantly higher activity of the main polymerization stage is obtained if a portion of oil is introduced separately into the reactor before the injection of precatalyst. And the amount of the extra oil is irrelevant within the range of this study (from 0.3 to 1 mL).

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