



# Simultaneous cross-linking as a way to control physical growth of random ethylene-propylene copolymer during formation of high-impact polypropylene



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## ABSTRACT

An effective chemistry for controlling the physical growth of random ethylene-propylene copolymer (EPR) during formation of high-impact polypropylene (hiPP), i.e., PP/EPR in-reactor alloy, is proposed, by prompting EPR chains to be simultaneously cross-linked right during its polymerization. A sufficient degree of cross-linking in EPR effectively prevents its fleeing away from the catalyst fragments and into the pore network of pre-formed PP particles during the late E/P copolymerization of hiPP process, thus transforming EPR's dispersion morphology in PP particles from segregated droplet aggregates with mobility to catalyst fragment-adhered discrete particles with stability. This research not only contributes to the understanding of particle growth mechanism of hiPP but also provides a promising strategy for continuing innovating as well as expanding the scope of the industrially important in-reactor alloy technology.

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## 1. Introduction

Polyolefins, including polypropylene (PP) and polyethylene (PE), are the most important synthetic polymer family with an extremely wide application range that exhibits little shrinkage with time. PP, in particular, with a successful transformation from being a long-time commodity polymer to an emerging new engineering plastic thanks to the many available advanced modification techniques [1,2], is being increasingly used in areas which are traditionally the strongholds of those high-priced engineering plastics. As of now, PP has been the No.1 choice of polymeric material in auto industry. Of the technologies that have made all these happen, the so-called in-reactor alloy is surely one of the most prominent, which in effect has enabled the great commercial success of high-impact PP (hiPP) (or thermoplastic olefin, TPO). With a spherical  $\text{MgCl}_2/\text{TiCl}_4$  catalyst (presently the most industrially important catalyst type) catalyzing propylene homopolymerization in a rather well-defined particle growth mode and the resultant PP replicating particle morphology of the catalyst and being composed of solid polymer subparticles

and a network of pores (both macro- and micro-) in the polymer particle whole, a late, successive ethylene/propylene (E/P) copolymerization enabled by the dispersed catalyst fragments will be allowed inside the pre-formed PP particles, thus creating, in a more efficient way (catalytic vs. post compounding), the highly demanding PP/random EP copolymer (EPR) alloys of broad-ranged properties and applications [3].

Though industrially very successful, producing millions of tonnes of hiPP and TPO resins worldwide annually, the current PP in-reactor alloy technology in essence is still more of a spontaneous polymerization process without much controllability. One prime aspect of this lack of controllability lies in an absence of effective control of the physical growth of EPR inside the PP particles. According to Debbling and Ray and McKenna et al. [4–7], though formed by the well-dispersed catalyst fragments inside the PP microparticles, EPR does not remain encapsulated within them but progressively expands into the small micropores between the PP microparticles and then into the larger macropores between the PP mesoparticles. Several other reports on hiPP particle morphology also prove that EPR is largely located in the interstitial pores between different-leveled PP subparticles [8–11]. This controllability inadequacy in EPR growth causes multiple problems in both scientific and technological fronts. First, particle growth mechanism

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for hiPP is still a controversial issue without final resolution. Though most people agree that it is the migration of EPR from the catalyst fragments located at the center of PP microparticles that causes the actual observation of EPR in the interstitial pores of PP, Cecchin et al. however argued that the catalyst fragments might be segregated at the end of prior propylene homopolymerization to the surface of the PP mesoparticles where they render the rear E/P copolymerization and form EPR in between the PP mesoparticles [12–14]. In fact, this latter proposition has recently gained so much popularity that it is often cited as a general particle growth mechanism of propylene polymerization over  $\text{MgCl}_2/\text{TiCl}_4$  catalysts [15,16]. Second, since the hierarchical pores inside a PP particle are interconnected each other forming an actual pore network opening at the surface of the polymer particle, it is very likely that EPR will continuously grow in the network and be mobile, and once it accumulates to a certain level of amount it will expand outside and “pool” on the surface of the PP particle. That is when polymer particles lump and reactor sheeting takes places, both of which are highly undesirable in actual application.

In this paper, we introduce a chemical strategy which we have found quite effective in controlling EPR physical growth during the formation of hiPP. With the effective control of EPR growth, we go on to clarify the presently inconclusive views on particle growth mechanism of hiPP and discuss its technological implications in polyolefin in-reactor alloy technology innovation.

## 2. Experimental section

### 2.1. Materials

The spherical  $\text{MgCl}_2/\text{TiCl}_4$  catalyst used contains a 1,3-diether internal electron donor 9,9-bis(methoxymethyl)fluorine (BMMF), synthesized according to literature [17], which contains 3.57 wt.% of Ti and 16.2 wt. % of BMMF. Triethylaluminium (TEA) as cocatalyst (1.8 M in heptane) was purchased from Albemarle and used as received. Polymerization grade propylene and ethylene were supplied by Yanshan Petrochemical Co. of China. 1,9-decadiene (97%) was purchased from Alfa Aesar and distilled over  $\text{CaH}_2$  before use. Hexane (AR grade) was from Beijing Chemical Works and refluxed over Na before use.

### 2.2. Sole E/P copolymerization

In a typical reaction (run 2 in Table 1), a 450 mL Parr stainless steel autoclave reactor equipped with a mechanical stirrer was first prepared by vacuum drying at 90 °C for 1 h, followed by the feeding of atmospheric ethylene/propylene mixed gas ( $P_E/P_P = 1$ ) and 50 mL dry hexane as the polymerization medium in sequence. Then 1.0 mL (1.8 mmol) of TEA in heptanes and 3.0 mL (16.5 mmol) of 1,9-decadiene was syringed into the reactor which at this time was maintained a temperature of 60 °C. The dropping of the solid

$\text{MgCl}_2/\text{TiCl}_4/\text{BMMF}$  catalyst (25 mg) initiated the copolymerization which lasted for 15 min under a total pressure of 0.4 MPa. After the reaction was terminated with acidic ethanol, the retrieved product was stirred vigorously in ethanol, filtered and washed with ethanol and water several times, and then dried overnight under vacuum at 60 °C.

### 2.3. hiPP Polymerization

In a typical reaction (run 3 in Table 2), a 450 mL Parr stainless steel autoclave reactor equipped with a mechanical stirrer was first prepared by vacuum drying at 90 °C for 1 h, followed by the feeding of atmospheric propylene gas and 50 mL dry hexane as the polymerization medium in sequence. Then 1.0 mL (1.8 mmol) of TEA in heptane was syringed into the reactor which at this time was maintained a temperature of 60 °C. The dropping of the solid  $\text{MgCl}_2/\text{TiCl}_4/\text{BMMF}$  catalyst (25 mg) initiated the first stage propylene homopolymerization which lasted for 30 min under a propylene pressure of 0.4 MPa before the polymerization was temporally halted by cutting the propylene feed. Hexane and other liquid substances were removed by vacuum evaporation and the inside of the autoclave was only left of the solid polymerization produce of PP. To this reactor was then fed a mixed ethylene and propylene (1/1) and 3.0 mL (16.5 mmol) of 1,9-decadiene under a pressure of 4 atm at a polymerization temperature of 90 °C. This second-stage polymerization was allowed a period of 10 min before the whole polymerization was permanently stopped by releasing the monomer pressure and pouring in 100 mL acidified ethanol. The eventual polymer product was thoroughly washed with ethanol to remove the un-reacted 1,9-decadiene. After drying under vacuum, 32.6 g polymer was obtained in white granular powder.

### 2.4. Characterization

All high-temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker DMX 300 spectrometer at 110 °C using *o*-dichlorobenzene- $d_4$  as solvent. Differential scanning calorimetry (DSC) was performed on a Pyris 1 Perkin–Elmer instrument operating at a scan rate of 10 °C/min $^{-1}$  under a flowing nitrogen atmosphere. GPC molecular weight and molecular weight distribution measurement was done by Waters Alliance PL-GPC 220 instrument equipped jointly with a two-angle laser light scattering detector, a viscosity detector, and a differential refractive index detector. The measurement was performed at 150 °C with 1,2,4-trichlorobenzene as the eluent at a flow rate of 1.0 mL/min. Compositional determination of EPR was done using Fourier Transform Infrared Spectroscopy (FTIR, Nicolet 6700) with an ATR accessory [18]. Scanning electron microscopy (SEM) was performed by a JEOL JSM-6700 field emission SEM at an accelerating voltage of 5 kV. Transmission electron microscopy (TEM) was by a JEOL JEM-2200FS TEM. For

**Table 1**  
Conditions<sup>a</sup> and results of sole E/P copolymerization in the presence of 1,9-DD with  $\text{MgCl}_2/\text{TiCl}_4/\text{BMMF}$  catalyst.

Run	E/P copolymerization		Catalyst activity (g/g cat.h)	EPR characterization					
	[1,9-DD] (M)	Duration (min)		[E] <sup>b</sup> (mol%)	[P] <sup>b</sup> (mol%)	$T_m^c$ (°C)	$\Delta H_f^c$ (J/g)	$T_g^c$ (°C)	Gel content <sup>d</sup> (%)
1	0	15	2435.0	47.1	52.9	117.8	2.2	−45.2	0
2	0.33	15	2514.0	48.4	51.6	116.0	1.4	−43.8	13.1
3	0.54	15	2281.0	48.9	51.1	113.6	1.4	−40.3	31.4
4	0.76	15	2308.0	50.6	49.4	115.2	1.3	−41.9	48.2

<sup>a</sup> General conditions:  $\text{MgCl}_2/\text{TiCl}_4/\text{BMMF}$  catalyst, 25 ± 1 mg, [TEA]/[Ti] = 100, 50 ml hexane; 0.4 MPa, 60 °C,  $P_E/P_P = 1/1$ .

<sup>b</sup> From FTIR analysis,  $[E] = [1.263 - 1.575 \times (A_{1379}/A_{1460})] \times 100\%$ ,  $E + P = 100\%$  [18].

<sup>c</sup> Data obtained from the second heating scan of DSC measurement.

<sup>d</sup> Percentage insoluble portion by boiling xylen extraction.

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