



# Modeling of molecular weight distribution of propylene slurry phase polymerization on supported metallocene catalysts



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## ABSTRACT

A mathematical model of the molecular weight distribution (MWD) based on a particle growth model and the kinetic scheme is developed to simulate the MWD of the slurry phase propylene polymerization on a silica-supported metallocene catalyst by means of the equations of moments. The model is used to predict molecular weight distribution, including the number-average molecular weight, the weight-average molecular weight, and the polydispersity index. The results show that the mass transfer has great influence on the polymerization reaction, and it can broaden the MWD especially; moreover, the MWD can be evaluated by simulation; the average molecular weight increases as pressure or temperature, and MWD shifts to long chain lengths as the effective diffusion coefficient increasing though the influence is not remarkable; furthermore, the MWD's simulation results are calculated, which fit greatly with the experimental data.

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## 1. Introduction

Olefin polymerization is catalyzed by using various catalysts such as Zeigler–Natta catalyst [1] and metallocene catalyst. Metallocene catalysts have become increasingly important recently for propylene polymerization due to the better flexibility and versatility for the synthesis and control of polyolefin structure in comparison to other olefin polymerization catalysts [2]. Polymerization of propylene catalyzed by metallocene catalysts is evidently complex and requires to be treated at different length scales, so that many mathematical models are available in the literature for heterogeneous catalytic polymerization. According to open literature on aspects of slurry phase polymerization of propylene with metallocene catalysts, several models have been suggested [3–28].

Nele et al. [3] developed a kinetic model to describe the propylene polymerization behavior of fluxional, two-state metallocene catalysts. Based on the propylene polymerization mechanism and the mass balance equations, Luo et al. [4–7] presented a model of the molecular weight distribution (MWD) of polypropylene produced in a loop reactor. Although the simulated data of these models were in agreement with the plant data, the mass transfer resistance was not considered in these models.

Dube et al. [8] developed a practical methodology for the computer modeling of multicomponent chain-growth polymerizations. The approach provided a common model framework which is applicable to many multicomponent systems. Diffusion-controlled termination, propagation, and initiation reactions are accounted for using the free-volume theory.

In 1966, Begley [9] proposed the first and simplest model, which is generally known as solid core model. The model was based on a spherical catalyst particle with a spherical shell of polymer growing around it. The polymeric core model was derived by Schmeal and Street [10]. In Schmeal and Street's model, expansion of the catalytic pellets was considered but the diameter of the catalytic pellet remained stable and only the thickness of the polymer shell grew. The increasing particle size during the polymerization was taken into account as well as the drift of the active sites in the 'polymeric flow model' [11].

The experimental evidence showed that the catalytic particles are broken into many small fragments, thus, a more complex but realistic model of the polymerizing particles was developed, which was also known as the multigrain model [12]. In this physical model, it was assumed that, a macroparticle consists of many small microparticles (the fragments), and each microparticle act like a 'solid core' pellet. This last model was derived for conventional Zeigler–Natta catalysts and only a complete fragmented particle is considered.

Bonini et al. [13] realized that the multigrain model cannot explain experimental data involving gradual particle fragmentation,

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**Nomenclatures**

$C^*$	catalyst active site, mol m <sup>-3</sup>
$C_L$	growth factor
$c_p$	specific heat, kcal kg <sup>-1</sup> K <sup>-1</sup>
$D_L$	monomer diffusion coefficient in the macroparticle, m <sup>2</sup> s <sup>-1</sup>
$D_c$	monomer diffusion coefficient in the microparticle, m <sup>2</sup> s <sup>-1</sup>
$D_n$	dead chain with length $n$
$E$	activation energy, cal mol <sup>-1</sup>
$h$	heat transfer coefficient in the external film, kcal m <sup>-2</sup> s <sup>-1</sup> K <sup>-1</sup>
$k_s$	mass transfer coefficient in the external film, m s <sup>-1</sup>
$k_r$	reactivation rate, mol m <sup>-3</sup> s <sup>-1</sup>
$k_p$	propagation rate, mol m <sup>-3</sup> s <sup>-1</sup>
$k_{tr}$	chain transfer rate, mol m <sup>-3</sup> s <sup>-1</sup>
$k_M$	thermal conductivity, kcal m <sup>-1</sup> s <sup>-1</sup> K <sup>-1</sup>
$L$	layer of the particle
$M$	propylene concentration, mol m <sup>-3</sup>
$M_B$	propylene concentration in bulk, mol m <sup>-3</sup>
$M_c$	monomer concentration on the surface of catalyst
$M_{n,j}$	average number molecule weight in the layer $j$
$M_W$	average weight molecule weight
$M_n$	average number molecule weight
$M_{W,j}$	average weight molecule weight in the layer $j$
$MW$	propylene molecular weight, g m <sup>-3</sup>
$PDI$	polydispersity index
$P_n$	concentration of living chain with chain length $n$ , mol m <sup>-3</sup>
$P$	pressure, bar
$PH$	temporary free site, mol m <sup>-3</sup>
$r_c$	variable along the microparticle radius, m
$r_L$	variable along the macroparticle radius, m
$R_L$	macroparticle radius of layer $L$ , m
$R_M$	macroparticle radius, m
$R_c$	microparticle initial radius, m
$R_p$	polymerization rate of ethylene, mol m <sup>-3</sup> s <sup>-1</sup>
$T$	temperature, K
$T_B$	external temperature of catalyst, K
$W_{Zr}$	Zr weight percent in the catalyst
$x$	chain length
$X_D$	ratio between the monomer diffusion constant in the macroparticle before and after fragmentation

**Greek letters**

$\alpha$	amorphous volume fraction of produced polymer
$\lambda_j$	living death with $j$ moment
$\rho_p$	average polymer density, kg m <sup>-3</sup>
$\xi^+$	radius of unfragmentation region, m
$\xi_k$	$k$ moment
$\varepsilon$	void fraction
$\varepsilon_0$	initial void fraction
$\Delta t$	time interval, s
$\Lambda_j$	dead chain with $k$ moment

and developed a particle growth model for silica supported metallocene catalysts. The model was based on the same ideas of the multigrain model but assumed a gradual fragmentation of the particle. In this way, the pellet was divided into two parts: a

fragmented (that behaves exactly like in the multigrain model) and an unfragmented one. In Bonini et al. [13], nevertheless, the unfragmented core was not precisely simulated and diffusion or polymerization in this region was basically ignored. This approach could be satisfactory only for fast reactions where all the monomer was consumed before arriving in the core, but in case of slower reaction a more specific modeling for this zone was needed.

Alexiadis et al. [14] proposed a more general approach directly derived from the Bonini's model but with the addition of a further part regarding the unfragmented core. The numerical results obtained by the model were compared with the experimental data, and the results allow extending the multigrain model to catalysts with lower activity.

We know that void fraction of the particle varied with reaction; therefore, Estenoz et al. [15] put forward a model on the basis of the multigrain model by taking into account the case of variable void fraction. However, this model neglected difference of mass transfer between fragmentation and unfragmentation region. It is clear that this idea is in contradiction with the experiment results as the monomer in two regions is different. Furthermore, Alexiadis et al. [14] compared the simulation results with the experimental data of polymerization rate, but not studied the molecular weight distribution (MWD); fewer articles were reported to simulate MWD of slurry phase propylene polymerization on metallocene catalysts.

In this paper, a model, which combines Alexiadis's model and Estenoz's model, is proposed. This model considers not only the evolution of void fraction, but also the difference of transfer mass in two regions.

**2. Theoretical part****2.1. Polymerization kinetics model**

To describe the kinetics of propylene polymerization on metallocene catalysts, a simple generalized and one-site kinetic model is developed on the basis of Alexiadis's study. The kinetics scheme comprises of a series of elementary reactions, including site activation, propagation, and site transfer reaction. Furthermore, the underlying assumptions made in the development of this model are instantaneous formation of sites and all reactions irreversible first-order with a pseudo-first-order-rate constant. Compared with Alexiadis's two-site kinetics model, only one-site was considered and site deactivation was ignored. With these analyses, the mechanism of propylene polymerization can be described as follows:

Instantaneous formation reaction:



Chain propagation reaction:



Chain transfer reaction:



Chain reactivation reaction:



where  $k_s$  ( $s = p, tr, r$ ),  $M$ ,  $P_n$ ,  $PH$ , and  $D_n$  represent the rate constants, the monomer, living polymer, the temporary free site and dead polymer, respectively. According to the above kinetic mechanism, the following live and bulk moments can be defined in order to

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