

Final Program

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<p>Experimental Investigation and Modeling of Particle Growth in Propylene Polymerization A. Ramazani S.A.[*] <ramazani@sharif.edu> and A. Dashti <dashtiir@yahoo.com>, Sharif University of Technology.</p> <p>Experimental investigation and modelling of particle growth and morphology of produced polymer particles were studied in slurry phase propylene polymerization using synthesized Ziegler-Natta catalyst. Polymerization kinetic profile was obtained during polymerization time with repeating experiments to achieve reproduce results of kinetic profile and total yield of polymerization in the same conditions. The mathematical modelling of particle growth was carried out based on the combined model presented in our earlier work. Furthermore, some presented empirical relations were used for mass transfer resistances in the gas-liquid phase of propylene-heptane mixture in the experimental conditions. Most of the important kinetic rate constants were estimated by applying the deconvolution method of GPC data proposed by Soares and Hamielec (1995a) and also by modification on the curve fitting approach presented by Kissin et al. (1999). The proposed mathematical modelling incorporated with mentioned helpful methods show a good confirmation with experimental data particularly in average of particle size for produced PP during polymerization time. This significant advantage of this model cause to validate it for applicable features. Furthermore, the proposed model can be extended for other polyolefin polymerization system as a comprehensive experimental-based model which is an interesting issue in industrial and scientific topics</p>			

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EXPERIMENTAL INVESTIGATION AND MODELING OF PARTICLE GROWTH IN PROPYLENE POLYMERIZATION

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Abstract: Experimental investigation and modeling of particle growth and morphology of produced polymer particles were studied in slurry phase propylene polymerization using synthesized Ziegler-Natta catalyst. Polymerization kinetic profile was obtained during polymerization time with repeating experiments to achieve reproduce results of kinetic profile and total yield of polymerization in the same conditions. The mathematical modeling of particle growth was carried out based on the combined model presented in our earlier work. Furthermore, some presented empirical relations were used for mass transfer resistances in the gas-liquid phase of propylene-heptane mixture in the experimental conditions. Most of the important kinetic rate constants were estimated by applying the deconvolution method of GPC data proposed by Soares and Hamielec (1995a) and also by modification on the curve fitting approach presented by Kissin *et al.* (1999). The proposed mathematical modeling incorporated with mentioned helpful methods show a good confirmation with experimental data particularly in average of particle size for produced PP during polymerization time. Experimental validation of the model could provide industrial applicable features. Furthermore, the proposed model can be extended for other polyolefin polymerization systems as a comprehensive experimental-based model which is an interesting issue in industrial and scientific topics.

Keywords: Particle growth, Experimental investigation, Modeling, Propylene polymerization, Ziegler-Natta catalyst.

1. INTRODUCTION

Particle growth and morphology studies of produced polymer powders in polyolefin catalysis system is one of the most interesting issues in scientific and industrial topics particularly for the polyethylene (PE) and polypropylene (PP) as the two most important and applicable thermoplastics in the world. Although, there are many mathematical models presented to predict particle growth and morphology of various polyolefin systems (Singh and Merrill, 1971; Schmeal and Street, 1971; Floyd *et al.*, 1986; Sarkar and Gupta, 1991; Hutchinson *et al.*, 1992; Soares and Hamielec, 1995b; Kanellopoulos *et al.*, 2004; Dashti and Ramazani 2008), still a comprehensive study is necessary to validate the mathematical models with experimental results. Herein, our studies have been focused on PP polymerization using heterogeneous Ziegler-Natta (ZN) catalyst in slurry phase process concerning to its more complicated mathematical modeling and easier experimental investigation than gas and bulk phase processes. In fact, by this investigation we are able to develop desire results to other polyolefin system. To verify kinetic parameters, mass transfer and catalyst characteristics, some valid approaches were applied to confirm real and predicted data. GPC curves of final polymer samples were deconvoluted according to the methodology presented by Soares and Hamielec (1995). The average molecular weight of polymer produced at each site, as well as the mass fraction of polymer produced and k_{tr}/k_p kinetic ratio at each site, were determined by this method. Main kinetic parameters were calculated by modification in the method presented by Kissin *et al.* (1999) for PE homo and copolymerization system. Some offered empirical relations were used to estimate the transport and thermophysical properties between slurry media and propylene gas (Hutchinson *et al.*, 1992; Li *et al.* 1996).

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Earlier, we developed the combined model to predict the particle growth and morphology in olefin polymerization system (Dashti and Ramazani, 2008) which it has been correlated with new empirical relations concerning to gas-liquid phase interaction in slurry phase propylene polymerization in *n*-Heptane as solvent media. In addition, to achieve suitable kinetic parameters used in the simulation program, the mentioned approaches were added to modeling for estimating these required parameters. The simulated results show good agreement with experimental data including average particle growth factor and particle size of final polymer particles. In addition, the presented model could be easily developed for any polyolefin homo and copolymers systems produced with heterogenous ZN catalysts.

2. EXPERIMENTS AND MATHEMATICAL MODELING

2.1 Catalysts synthesis and polymerization

A Mg(OEt)₂-based TiCl₄/EB/MgCl₂ catalyst was prepared based on the patent (Terano *et al.*, 1987) with slight modification presented in previous paper (Dashti *et al.*, in press). Furthermore, the slurry polymerization of propylene was carried out in *n*-Heptane according the method mentioned in the same paper. Polymerization kinetic rate was obtained based on propylene gas consumption rate recorded by mass flow meter equipment (MFM, Kofloc series 3100, Japan) throughout reaction time.

2.2 Particle Size Distribution (PSD) and GPC data

The catalyst and obtained polymer particles were analyzed by scanning electron microscopy (SEM, JEOL JSM-6390). PSD of the catalyst was obtained by a laser diffraction particle size analyzer (HORIBA LA-920). The PSDs of the obtained polymers were directly measured from SEM pictures in a statistical way to study the morphology developments for the polymerization time. The molecular weight of the polymer sample was determined by high temperature gel permeation chromatography (GPC) (Senshu, SSC-7100) equipped with polystyrene gel columns Shodex HT-806M at 140°C using *o*-dichlorobenzene as a solvent.

2.3 Modeling

The comprehensive model for growing particle respect to fragmentation process of catalyst particle at early stage of olefin polymerization was presented by Floyd *et al.* (1986) and Hutchinson *et al.* (1992) well known as multigrain model (MGM). However, regarding to more difficulties and long run time for computer program of MGM, some modified models were proposed such as PMGM by Sarkar and Gupta (1991), PMLM by Soares and Hamielec (1995b). We developed a combined model based on these models concerning some advantages of each one (Dashti and Ramazani, 2008). The simplified scheme of this model can be shown in Fig. 1.

It is assumed that the growing polymer particle known as macroparticle has *N* polymeric layers which every layer was filled out with *N_i* microparticles calculated by Eq. 1. The microparticles are considered as fragmented particles with radius *R_{s,i}* with the same size or even different size in each layer. The subscript *i* indicates the *i*th layer and ϵ is the void fraction considered as a constant value in all layers or assumed as a function of the layer radius. It is clear that only one fragment must be present for the first layer.

$$N_i = 6(1 - \epsilon) \frac{\left[R_{s,i} + 2 \sum_{j=2}^{i-1} R_{s,j} + R_{s,i} \right]^2}{R_{s,i}^2} \quad i = 2, 3, \dots, N \quad (1)$$

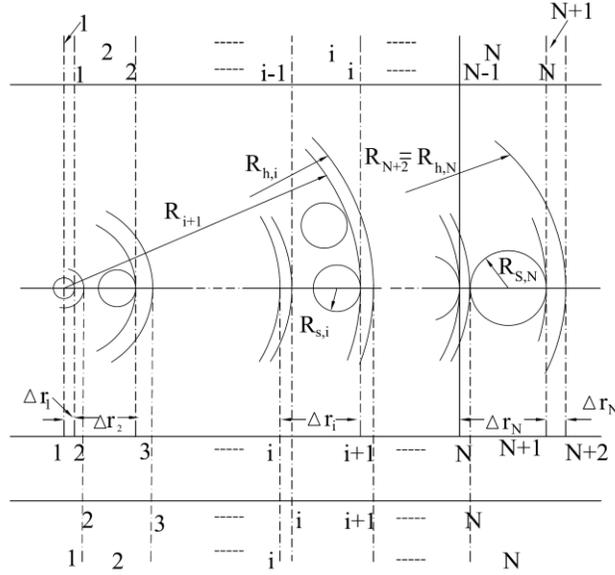


Fig. 1. Schematic of proposed model for particle growth modeling.

A general mechanism of polymerization kinetic was supposed according to the table 1 including activation, initiation, propagation, chain transfer and deactivation in which no hydrogen and external donor (ED) were used in polymerization to apply their effects on kinetic mechanism. In the first step, main kinetic parameters were calculated by modification in the method presented by Kissin *et al.* (1999) for PE homo and copolymerization system. In this method, overall polymerization profile, $R_{p,overall}$, and total yield, Q_{total} , are essential for curve fitting experimental data with following equation:

$$R_{p,overall} = Q_{total} \sum_{j=1}^{N_{site}} \frac{\exp(-k_a^j t) - \exp(-k_d^j t)}{1 - \exp(-k_d^j t_{reaction})} \frac{1}{k_a^j} ; R_{p,overall} = \sum_{j=1}^{N_{site}} R_p(j) \quad (2)$$

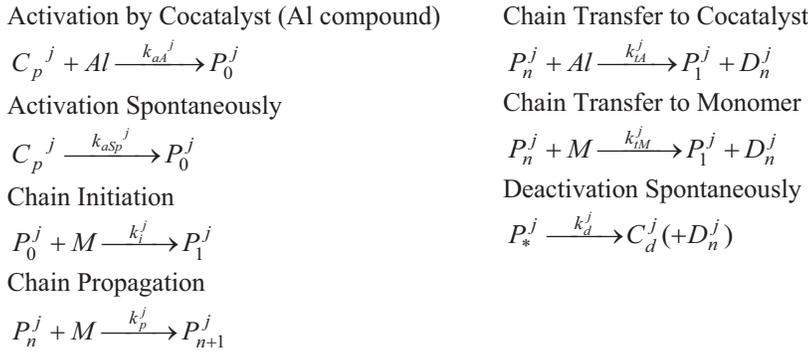
Furthermore, as can be seen in Eq. 2, kinetic constant rates are calculated for any active site type, thus instantaneous polymerization profile, $R_p(j)$, corresponding to active site type j is necessary. Mass fraction of each active site, $m(j)$, and total number of active sites, N_{site} , must be determined for calculating $R_p(j)$ from $R_{p,overall}$. In this way, the weight chain length distribution (WCLD) obtained from GPC data of final polymer samples were deconvoluted according to the methodology presented by Soares and Hamielec (1995a). The average molecular weights of produced polymer at each site, as well as the mass fraction of produced polymer and k_{tr}/k_p kinetic ratio at each site were determined by the Flory most probable distribution stated in following equations.

$$w(r, j) = \tau_j^{-2} r \exp(-\tau_j r) \quad ; \quad \tau_j = \frac{k_{tM}^j [M] + k_{tA}^j [AI]}{k_p^j [M]} \quad (3)$$

$$\hat{W}(r) = \sum_{j=1}^{N_{site}} m(j) w(r, j) \quad ; \quad \sum_{j=1}^{N_{site}} m(j) = 1 \quad (4)$$

In the presence of H_2 which is usually used in propylene polymerization, one can easily introduce its relating reactions in kinetic mechanism. Regarding to experiment results, the main effects of H_2 are included the control of molecular weight by chain transferring to H_2 and also the enhancement of polymerization activity by promoting the transformation of dormant sites into active sites and decreasing the lifetime of dormant sites.

Table 1. Polymerization kinetic mechanism (in the absence of H₂ and ED)



Figures 2 and 3 show the deconvolution of WCLD into 6 Flory most probable distributions and curve fitting of polymerization profile for a selected PP-s14 sample, respectively. The obtained kinetic rate constants from GPC deconvolution and curve fitting of polymerization rate applied as input data for the particle growth modeling. Details of kinetic parameters values were presented in table 2 for the PP-s14 sample.

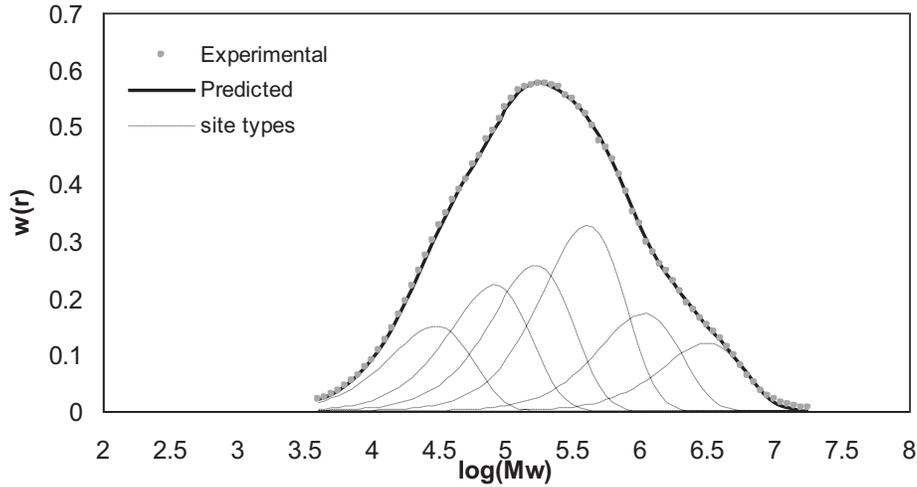


Fig. 2. Deconvolution of a WCLD of the PP-s14 sample into 6 most probable WCLDs.

In the next step, population balances for the active species were defined in each polymeric layer considering some assumptions to simplify set of equations and reduce stiffness of differential equations. More details of relations and assumptions are referred to our earlier article (Dashti and Ramazani, 2008). Average properties of the produced polymer were estimated by moments method.

$$\bar{M}_n = \frac{\sum_{j=1}^{N_{site}} \{X_1(j) + Y_1(j)\}}{\sum_{j=1}^{N_{site}} \{X_0(j) + Y_0(j)\}} \quad \bar{M}_w = \frac{\sum_{j=1}^{N_{site}} \{X_2(j) + Y_2(j)\}}{\sum_{j=1}^{N_{site}} \{X_1(j) + Y_1(j)\}} \quad (5)$$

In the Eq. 5, X_i(j) is defined as ith moment of the living polymer produced by site type j and Y_i(j) is defined as ith moment of the dead polymer produced by site type j.

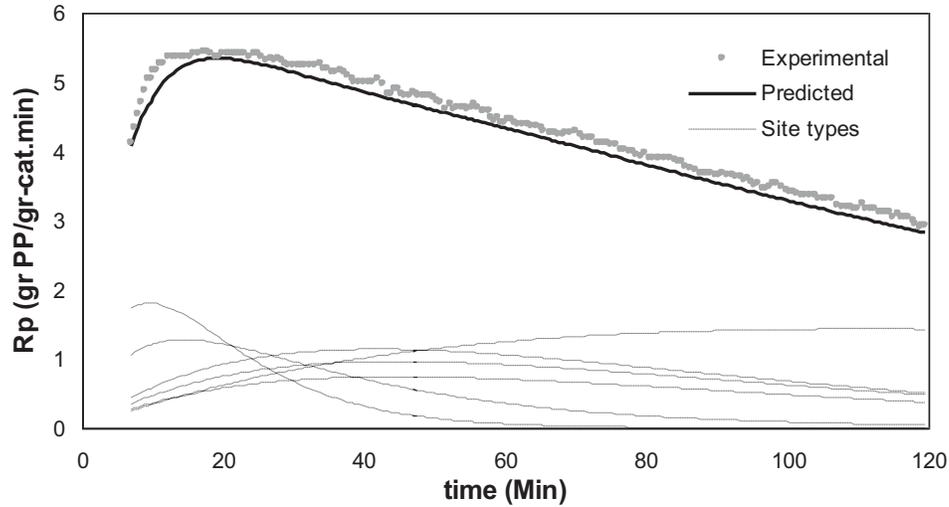


Fig. 3. Modeling of the experimental kinetic curve obtained for PP-s14 during propylene polymerization at 30 °C in the absence of hydrogen at 0.015 Mpa.

The final step of modeling algorithm is the way to calculate microparticle growth factor from mass balance of polymer produced at all active sites proposed by Hutchinson *et al.* (1992) as following equation:

$$\phi_i^3 = 1 + \frac{[Me]\bar{M}_n \sum_{k=1}^{N_{site}} (Y_0^k + X_0^k)}{\rho_{pol}} \quad (6)$$

[Me] is the concentration of active Titanium species and ϕ_i is defined as microparticle growth factor in the layer I of macroparticle. The ρ_{pol} indicates the bulk polymer density of typical PP. All equations and relations must be calculated at each step time Δt . The volume of each layer is updated according to the amount of produced polymer in that time interval. Volume changes affect on the radius of every layer, hence radius of all layers requires to be renewed in each time interval. It should be mentioned that number of equations directly relate to number of macroparticle layer and number of active sites ($N \cdot N_{site}$), therefore one should estimate appropriate number of these important parameters based on the requested output results to reduce run time of computer program and increase efficiency of modeling algorithm. The normal value for N is 20 and for N_{site} is 4 to 7 relating to GPC deconvolution method.

Table 2. Estimated kinetic rate constnts and mass fraction of produced polymer correspondig to each active site type for PP-s14

active site type	m(j)	$\tau(j)$	$k_{aA}(j)$ (1/min)	$k_{aSp}(j)$ (1/min)	$k_d(j)$ (1/min)	$k_p(j)$ (lit/mol.min)
1	0.1198	2.84e-3	0.172514	0.033591	0.120318	46810.5
2	0.0960	2.66e-5	0.210433	0.101859	0.104382	31900.0
3	0.1374	7.86e-5	0.178869	0.018125	0.024615	14446.4
4	0.2627	2.06e-4	0.304778	0.000158	0.017223	62837.1
5	0.1780	1.03e-3	0.226924	0.019134	0.022945	17365.9
6	0.2061	4.98e-4	0.259900	0.019847	0.024838	20903.2

3. RESULTS AND DISCUSSION

The main kinetic rate constants and mass fraction of produced polymer in each active site type can be estimated by applying curve fitting method on polymerization kinetic profile and WCLD deconvolution method on GPC data of final polymers as mentioned before. The related results are presented in table 2. After estimation of $\tau(j)$ for calculation of $k_{trM}(j)$ and $k_{trA}(j)$ a role of thumb was used in which $k_{trA}(j)$ is about 10 times greater than $k_{trM}(j)$ in the absence of hydrogen known as main chain transfer agent in olefin polymerization system.

Figure 4 shows the PSD evaluation for the produced polymer using synthesized ZN catalyst mentioned previously. The PSD was acquired from a statistical analysis of the taken SEM images over 200 polymer particles. Figure 4 demonstrates three representative particle sizes including the cumulative curve of the PSD with 90% particles, average particle sizes estimated from the kinetic curve (predicted by yield) and simulated results. The averaged particle sizes derived from the kinetic curve showed good coincidence with the particle size obtained from simulation for 15 min of the polymerization time in spite of the rough estimate from the kinetic curve, indicating good replication of the catalyst particles at the early stage without significant breakage or aggregation of the polymer (or catalyst) particles.

Table 3. Average polymer properties obtained from GPC analysis and simulation results

Average polymer property	GPC data (1)	GPC data (2)	Simulated
Mw	564043	600102	226631
PDI	14.5617	10.1637	16.2

However, as the polymerization time proceeded, the estimated value became smaller than the particle size at 90%, in consistent with the observed agglomeration phenomena in SEM pictures (not shown here) The formation of the agglomerates after the early stage of the polymerization was also observed by McKenna and Mattioli (2001).

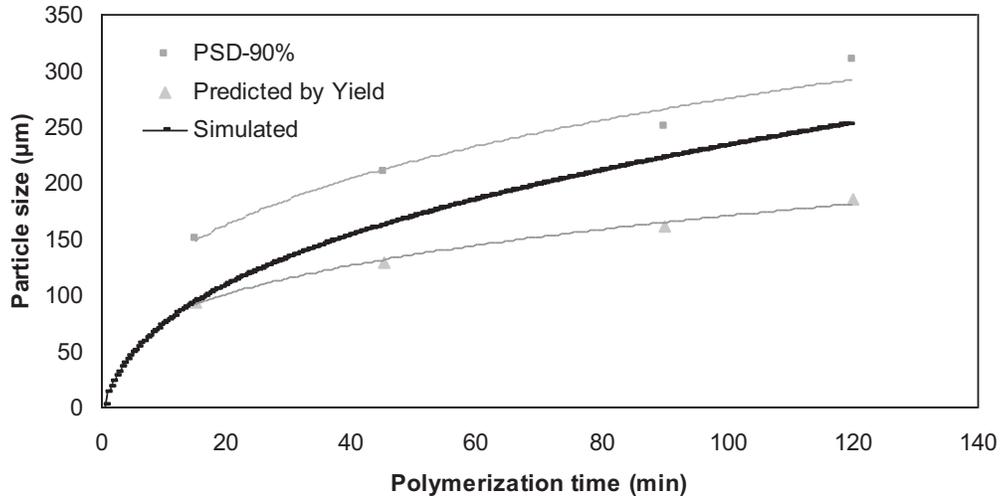


Fig. 4. Evaluation of polymer particle size at different polymerization time.

In addition, the simulated results of average particle size show the same trend as PSD data with almost constant deviation in observed time. These results can confirm validity of the proposed model to apply in particle growth of propylene polymerization to reach good prediction with experimental data. However, it should be considered that there are at least two origins for the deviation of simulated results with real data: the first one is that the GPC data are not reproduced easily (as shown in table 3 for the twice GPC analysis). Another one is related to the lack of real PSD of fragmented particles (microparticles) at early stage of polymerization. In our study, we found that the particle growth factor is so sensitive to the initial size of microparticles.

4. CONCLUSION

In this study, a developed model was described to predict particle growth and morphology of PP particles during propylene polymerization in slurry phase through heterogeneous ZN catalyst system. Most of the existing models describing particle growth and morphology of olefin polymerization system support the mathematical aspects of modeling with less consideration to experimental validity of the model. The proposed mathematical modeling incorporated with some helpful methods show a good confirmation with experimental data particularly in average of particle size for produced PP during polymerization time. Experimental validation of the model could provide industrial applicable features. Furthermore, the proposed model can be extended for other polyolefin polymerization system as a comprehensive experimental-based model which is an interesting issue in industrial and scientific topics.

5. ACKNOWLEDGMENT

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