Modeling and Optimization of propylene polymerization with branching

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Abstract

A kinetic model has been proposed to fit the experimental data (2003) available from the open literature for branched propylene polymerization system. The present system considered is a binary catalyst system, in which the first catalyst produces the atactic polypropylene macromonomer whereas the second one grafts the atactic polypropylene macromonomers to isotactic polypropylene backbone leading to branching. The proposed kinetic model, first of its kind that has been validated with experimental data, is extended to find the optimal process conditions for the desired combination of conflicting objectives. For this purpose, multi-objective optimization technique non-dominating sorting genetic algorithm II (NSGA II) has been utilized. A wide variety of process choices have been obtained for the optimization set up which shows improvement in process performance as compared to similar process performances reported in the open literature.
Keywords: Long chain branching, polypropylene, NSGA II, multi-objective optimization
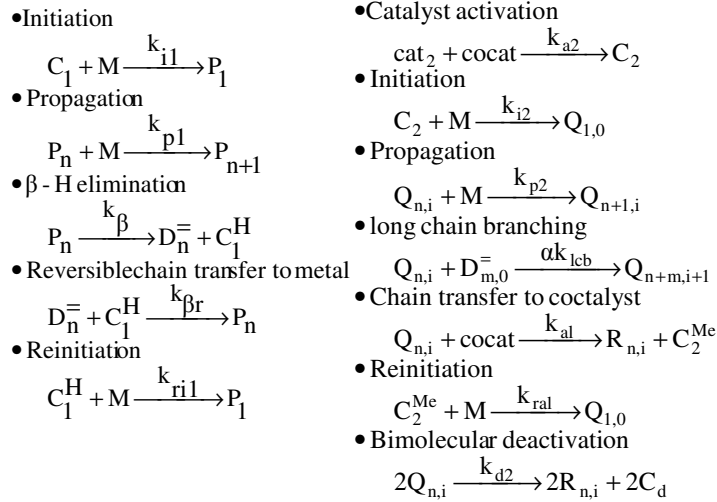.

1. Introduction

Polypropylene (PP) has good properties in terms of high melting point, low density as compared to other thermoplastics. Highly linear polypropylene can be produced by Ziegler-Natta and metallocene catalysts. Due to the poor melt strength of linear PP, it cannot be processed easily. Processing techniques like thermoforming, film blowing, blow molding etc. demand high melt strength, which can be achieved by the long chain branched polypropylene (LCBPP). Due to the difficult embedded chemistry in producing LCBPP by direct synthesis methods, various techniques have been developed in the open literature. Weng et al (2002) utilized the previously prepared polypropylene macromonomers to copolymerize with the propylene monomer leading to branching. Shiono et al (1999) synthesized LCBPP by copolymerizing the atactic polypropylene (aPP) macromonomers with propylene monomer by using an isospecific catalyst. Ye and Zhu (2003) used two catalysts to produce LCBPP (isotactic back bones and atactic side chains). By this technique, first catalyst has the capability of producing aPP macromonomers, while the latter one copolymerizes the aPP macromonomers with the propylene monomer to produce LCBPP. By using the metallocene catalyst and T-reagent, Langston et al (2008) synthesized LCBPP. In the present effort, we have chosen the experimental data (Ye and Zhu, 2003) from open literature to develop a kinetic model for the long chain branched polypropylene system. However, to the best of the knowledge of the authors, this is the only model for propylene polymerization system with long chain branching which has been validated with experimental data and extending this validated model to optimize and control the extent of branching rather is

even rare. Multi-objective optimization techniques are excellent to find out optimal trade-off solutions which are conflicting in nature. From the perspective of branched PP system, the polymer of high grafting density (number of aPP side chains per 1000 back bone monomer units) and high weight average molecular weight (M_w) are required in less polymerization time. It is known that higher molecular weight polymer can be obtained at the higher polymerization time. Here, the main aim is to attain polymers with higher grafting density and higher molecular weight in less polymerization time.

2. Model and problem formulation

Kinetic model developed for the long chain branched polypropylene system in this study is shown in Table 1. Motivated by the work of Hustad et al. (2008), reversible chain transfer to metal has been considered for the first catalyst system to obtain polydispersity index of nearer to 1.3 instead of 2. Since we know that the catalysts with single site behavior give theoretical polydispersity index of 2 for irreversible reactions (Hustad et al., 2008), it is very difficult to obtain PDI value less than 2 without considering reversible reaction. Bimolecular deactivation has been considered for the second catalyst system (Soares and Mckenna, 2012).

Table 1: Kinetic mechanism for the twin catalyst system

• Initiation

$$C_1 + M \xrightarrow{k_{i1}} P_1$$

• Propagation

$$P_n + M \xrightarrow{k_{p1}} P_{n+1}$$

• β - H elimination

$$P_n \xrightarrow{k_\beta} D_n^= + C_1^H$$

• Reversible chain transfer to metal

$$D_n^= + C_1^H \xrightarrow{k_{\beta r}} P_n$$

• Reinitiation

$$C_1^H + M \xrightarrow{k_{ri1}} P_1$$

• Catalyst activation

$$cat_2 + cocat \xrightarrow{k_{a2}} C_2$$

• Initiation

$$C_2 + M \xrightarrow{k_{i2}} Q_{1,0}$$

• Propagation

$$Q_{n,i} + M \xrightarrow{k_{p2}} Q_{n+1,i}$$

• long chain branching

$$Q_{n,i} + D_{m,0}^= \xrightarrow{\alpha k_{lcb}} Q_{n+m,i+1}$$

• Chain transfer to cocatalyst

$$Q_{n,i} + cocat \xrightarrow{k_{al}} R_{n,i} + C_2^{Me}$$

• Reinitiation

$$C_2^{Me} + M \xrightarrow{k_{ral}} Q_{1,0}$$

• Bimolecular deactivation

$$2Q_{n,i} \xrightarrow{k_{d2}} 2R_{n,i} + 2C_d$$

Where P_n and $D_n^=$ are the live and the unsaturated dead polymers (vinyl terminated macromonomers) for aPP of chain length n, Whereas, $Q_{n,i}$ and $R_{n,i}$ depicts the live and the dead polymer chains of branched polypropylene having "n" numbers of chain length and "i" number of long chain branches. Direct kinetic modeling, if used for modeling polymer systems, leads to huge number of equations since the number of repeating unit in a polymer (say, n) can assume a very large value. So, the method of moments (equation 1 and 2) has been applied to keep the dimensional explosion under control. However, by using the overall method of moments, we can calculate total molecular weight and PDI of molecular population. Polymer properties like number average

molecular weight, weight average molecular weight, polydispersity index (PDI) and grafting density (GD) are calculated by the following equations 3 and 4.

$$\lambda_x = \sum_{n=1}^{\infty} n^x P_x \qquad \mu_x^= = \sum_{n=1}^{\infty} n^x D_x^= \qquad (1)$$

$$\mu_x = \sum_{n=1}^{\infty} n^x Q_x \qquad v_x = \sum_{n=1}^{\infty} n^x R_x \qquad (2)$$

$$M_n = \left(\frac{v_1}{v_0}\right) MW \qquad M_w = \left(\frac{v_2}{v_1}\right) MW \qquad PDI = \left(\frac{M_w}{M_n}\right) \qquad (3)$$

$$GD = 1000 \left(\frac{\text{Long chain branching formation rate}}{\text{Propagation rate}}\right) \qquad (4)$$

where M_n and M_w are number average molecular weight and weight average molecular weight of the polymer, respectively. MW and GD represent molecular weight of monomer unit and grafting density of the polymer, respectively.

Maximization of M_w, maximization of grafting density (GD) and minimization of polymerization time are taken as objective functions. Addition amounts of two catalysts, cocatalyst, time gap between the two catalyst additions and total polymerization time are taken as decision variables. All decision variables are kept within the ±10% experimental limit to avoid possible extrapolation error from the original process. To perform multi-objective optimization, model is integrated with real coded NSGA II (Deb, 2001).

Multi-objective optimization problem formulation for the LCBPP system is shown below.

$$\underset{u_1, u_2, u_3, u_4, t_p}{Maximize} \quad M_w$$

$$\underset{u_1, u_2, u_3, u_4, t_p}{Maximize} \quad GD$$

$$\underset{u_1, u_2, u_3, u_4, t_p}{Minimize} \quad t_p$$

$$500000 \leq M_w \leq 700000$$

$$4500 \leq \frac{cocat}{cat_2} \leq 8000$$

$$M_{w, app} \geq 2500$$

$$PDI_{app} \leq 1.45$$

$$GD \geq 7$$

Decision variables:

$$u_1^{min} = 14e^{-6}; u_1^{max} = 82.5e^{-6}$$

$$u_2^{min} = 9e^{-6}; u_2^{max} = 16.5e^{-6}$$

$$u_3^{min} = 0.045; u_3^{max} = 0.0825$$

$$u_4^{min} = 0.2t_p; u_4^{max} = 0.8t_p$$

$$t_p^{min} = 70 \, min; t_p^{max} = 180 \, min$$

In u_n^{min} and u_n^{max}, subscript "n" is from 1 to 4. In this, 1 to 4 represents addition amount of two catalysts, cocatalyst and time gap between the two catalyst additions, whereas superscript min and max represents lower and upper limits. t_{poly}^{min} and t_{poly}^{max} represents lower and upper limits of total processing time.

3. Results and discussion

Polymer molecular properties such as M_w, PDI of aPP and branched polypropylene system including GD are validated with the experimental polymerization of propylene which was conducted by Ye and Zhu (2003) for a binary catalyst system at inputs (concentration of two catalysts and cocatalyst, second catalyst addition time and total polymerization time). Comparison of model predicted and experimental M_w, polydispersity index (PDI) of aPP macromonomers and branched polypropylene (iPP) is shown in Table 2. Grafting density (number of aPP side chains per 1000 iPP backbone monomer units) for various experimental runs is shown in the same table. Grafting density of the experimental (Ye and Zhu, 2003) and simulated values for the first three runs are matching quite well. Last two runs are predicted from model. These branching density data are compared with the melting points (Ye and Zhu, 2003) of the iPP copolymer. Isotactic polypropylene (iPP) copolymer melting point decreases with the increase of grafting density (Ye and Zhu, 2003).

Table 2. Comparison of model predictions with experimental

Run No.	aPP Experiment		aPP Predicted		iPP Experiment		iPP Predicted	
	$M_w \times 10^3$ (gm/mol)	PDI	$M_w \times 10^3$ (gm/mol)	PDI	$M_w \times 10^3$ (gm/mol)	PDI	$M_w \times 10^3$ (gm/mol)	PDI
1	3.6	1.3	4.4	1.4	631.8	2.7	632	2.2
2	3.6	1.4	3.2	1.34	564.7	2.5	544	2.2
3	3.3	1.3	4.5	1.4	447.3	2.3	485	2.4
4	3.1	1.3	2.5	1.34	395.2	2.4	378	2.4
5	3.0	1.3	2.6	1.33	514.4	2.3	554	2.4

Run No.	GD		Melting Point
	Experiment	Predicted	
1	8.4	8.2	144.4
2	1.7	1.7	148.6
3	8.6	7.5	145.6
4		0.31	149.7
5		0.008	153.5

Polymerization time and molecular weight of the polymer are conflicting objectives, similarly polymerization time and grafting density are two opposing factors. So, there is a need to perform multi-objective optimization to find the optimal process conditions for the desired combination of conflicting objective functions. Multi-objective Pareto solutions for optimization are obtained among three conflicting objectives which is given in Figure 1. Various combinations of two catalyst additions, cocatalyst addition and time gap between the two catalyst additions are possible. There are multiple numbers of solutions (as shown in Figure 1) which are equally important (i.e. non-dominated solutions). Two experimental points (which are having grafting density

greater than 8, the largest grafting density reported in the experiments) represented in the Figure 1 as square points. Several Pareto optimal solutions are found to be better than the experimental points. A wide variety of process choices have been obtained for the optimization set up which shows improvement in process performance as compared to the same reported in the open literature. As opposed to single optimal solution obtained during single objective optimization, the number of solutions in multi-objective optimization is more than one and these solutions are non-dominated in nature. It is obvious that one needs to choose one solution from the set of Pareto optimal solutions. This can be calculated by the min-max method (Belegundu and Chandrupatla, 1999), where deviations from the best values such as $Z_1 = t - t_{min}$, $Z_2 = GD_{max} - GD$, $Z_3 = M_{w,max} - M_w$ can be calculated first and then from this set of points of deviations, a single Pareto solution can be calculated by using the formula of $\min[\max\{Z_1, Z_2, Z_3\}]$. This point is shown as a filled point in Figure 1.
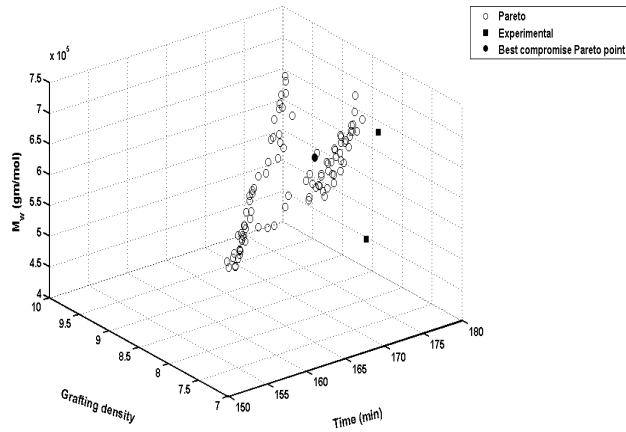

Figure 1: Pareto optimal solutions

The corresponding decision variables have been represented as a contour like plot (in shades) is depicted from Figure 2a-d. These four plots describe the trade off solutions for the entire search space.
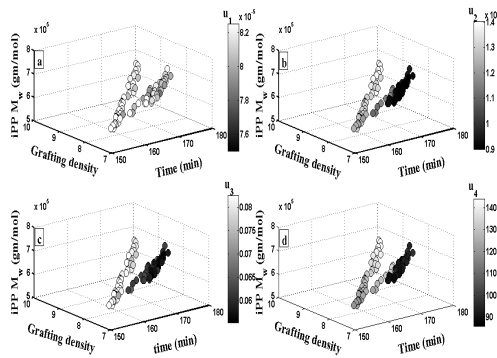
Figure 2: Pareto optimal solutions with total search space

4. Conclusions

Moment based modeling has been applied to the long chain branched polypropylene system to reduce the large set of equations. To obtain polymer with enhanced properties in less polymerization time, multi-objective optimization problem has been formulated for conflicting objectives with relevent constraints. Real coded non-domonated sorting genetic algorithm-II is used to find the optimal process conditions. Optimization routine provided a variety of solutions in the entire search space. One of the objective function grafting density strongly depends on the ratio of the two catalysts, time gap between the two catalyst additions (second catalyst addition time), and copolymerization time. Other objective function branched copolymer M_w depends on cocatalyst concentration (due to chain transfer to cocatalyst) and cocatalyst/catalyst$_2$ ratio which is due to bimolecular deactivation.

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