



Modeling of propylene polymerization with long chain branching



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HIGHLIGHTS

- A kinetic model is proposed for long chain branched polypropylene with binary catalyst system.
- Kinetic parameters are estimated by real coded genetic algorithm.
- Molecular properties are calculated and compared with the experimental findings.
- Molecular weight distribution is calculated by Schulz–Flory two parameter model.
- Kinetic parametric sensitivity study.

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ABSTRACT

A kinetic model has been proposed to describe the propylene polymerization process with long chain branching for a twin catalyst system to fit the experimental evolution of molecular weights, polydispersity index of atactic polypropylene, isotactic polypropylene and the grafting density at different catalyst and cocatalyst concentrations. Kinetic parameters are estimated by real coded genetic algorithm (an evolutionary optimization technique) from experimental data available in open literature. The validated model has the capability of predicting the branching density as a function of catalyst addition pattern, catalyst ratios and copolymerization time. Further, the validated model has been used to calculate the 'molecular weight long chain branching distribution'. Parametric sensitivity study has been conducted to analyze the effect of kinetic parameters on the long chain branching formation and other molecular properties of the polymer.

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1. Introduction

Branched polymers exhibit enhanced polymer processing properties as compared to their linear counterparts of similar molecular weight and this fact provides the former considerable edge over the latter for many practical applications. Significant numbers of experimental and theoretical studies have been conducted for various free-radical long chain branched systems. In general, Zeigler Natta and metallocene catalysts are known to produce highly linear polymers. After the discovery of constraint geometry catalyst, branched polyolefins synthesis was made possible. The unique feature of constraint geometry metallocene is that it incorporates the macromonomers into the growing chain. The lack of attention in synthesizing long chain branched polypropylene (LCB PP) is due to the limited knowledge of embedded chemistry to produce the LCB PP. To overcome this, various technologies, e.g. electron beam irradiation [1] and reactive

extrusion [2], have been developed. LCB polymers prepared by these methods are complex and sometimes the degree of branching of the resultant polymer is very difficult to control.

Due to the advantage of metallocene technology, Weng et al. [3] have synthesized long chain branched isotactic polypropylene (iPP) by the incorporation of in situ vinyl terminated macromonomers. The experiments are conducted at low and steady propylene concentration to allow accumulation of macromonomers in the reactor so that the probability of incorporation of macromonomers to the growing polymer chain increases. Shiono et al. [4] copolymerized atactic polypropylene (aPP) macromonomer with propylene by an isospecific metallocene catalyst. They used $rac\text{-Me}_2\text{Si}(2\text{-MeBenz}[e]\text{Ind})_2\text{ZrCl}_2$, the best isospecific catalyst available for the incorporation of macromonomers, for this purpose. Ye and Zhu [5] produced LCB PP with isotactic back bones and atactic side chains using binary catalyst system. Here, the catalyst (1) produces vinyl terminated macromonomers (having terminal double bonds) [6] and the catalyst (2) copolymerizes the polypropylene macromonomers with propylene. Under this mechanism the chains that have terminal unsaturation are

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Nomenclature

cat ₂	catalyst 2 concentration	v_0	zero th moment of iPP dead polymer
cocat	cocatalyst concentration	v_1	first moment of iPP dead polymer
aPP	atactic polypropylene	v_2	second moment of iPP dead polymer
iPP	isotactic polypropylene	k_{i1}	initiation rate constant (L/(mol min))
D_n^-	aPP macromonomer concentration of chain length “n”	k_β	β -H elimination constant (1/min)
C_1^H	Hydride activated complex	$k_{\beta r}$	reversible chain transfer to metal rate constant (L/(mol min))
$Q_{n,i}$	iPP copolymer of chain length “n” and “i” long chain branches	k_{p1}	propagation constant for the catalyst (1) system (L/(mol min))
$R_{n,i}$	dead iPP copolymer of chain length “n” and “i” long chain branches	αk_{lcb}	effective long chain branching rate constant (L/(mol min))
C_2^{Me}	methylated catalyst activated complex	k_{a2}	activation rate constant for the catalyst (2) system (L/(mol min))
[M]	monomer concentration (mol/L)	k_{i2}	initiation rate constant for the catalyst (2) system (L/(mol min))
GD	grafting density	k_{p2}	propagation rate constant for the catalyst (2) system (L/(mol min))
P_n	aPP live polymer of chain length “n”	k_{d2}	deactivation rate constant for the catalyst (2) system (L/(mol min))
λ_0	zero th moment of aPP live polymer	k_{a1}	chain transfer to cocatalyst for catalyst (2) system (L/(mol min))
λ_1	first moment of aPP live polymer	k_{ri1}	reinitiation with hydride metal complex (L/(mol min))
λ_2	second moment of aPP live polymer		
μ_0^-	zero th moment of aPP macromonomer		
μ_1^-	first moment of aPP macromonomer		
μ_2^-	second moment of aPP macromonomer		
μ_0	zero th moment of iPP live polymer		
μ_1	first moment of iPP live polymer		
μ_2	second moment of iPP live polymer		

inserted into the growing polymer chain to produce LCB PP. LCB PP has been produced by Paavola et al. [7] using non-conjugated diene comonomers, where the diene monomer provides a reactive functional group along the backbone to ease branching. Polymers produced by this method exhibit broad molecular weight distribution with a polydispersity index value greater than 5. Langston et al. [8] produced long chain branched isotactic polypropylene by metallocene catalyst and T-reagent. They conducted experiment by the combination of *rac*-Me₂-Si(2-Me-4-Ph-Ind)ZrCl₂/MAO as catalyst and *p*-(3-butenyl)styrene as T-reagent. In the presence of hydrogen, T-reagent acts as comonomer as well as chain transfer agent. LCB PP produced by this method has branching density of the order of ~ 3.3 per 10,000 carbon atoms. On the production of branched polyethylene, there has been considerable progress. Beigzadeh et al. [9] produced long chain branched polyethylene with binary metallocene catalyst system (2-ArN = C(Me))₂C₅H₃N}FeCl₂/MMAO (1) and *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂/MMAO (2)) and observed the extent of long chain branching by varying the two catalysts in the reactor. Zou et al. [10] synthesized long chain branched polyethylene by homopolymerization of ethylene with nickel α -diimine catalyst. They observed the influence of temperature and Al/Ni ratio on molecular weight and degree of long chain branching [10] in this work. Mathematical models have also been developed to explain long chain branched polyolefins. Mehdiabadi et al. [11] developed mathematical model for the general olefin polymerization in a series of two CSTRs, in which macromonomers produced in the first reactor is copolymerized with the propylene in the second reactor to produce PP with high LCB density. The Monte Carlo [12] models have been developed for branched polyolefins which are made with two single site catalysts. Soares and Hamielec [13] developed a simple analytical expression to calculate molecular weight distribution of chain length and long chain branching of polyolefins in a steady state CSTR. However, to the best of the knowledge of the authors, no mechanistic kinetic model has been reported in the literature for the synthesis of long chain branched polypropylene system which has been validated with experimental data.

There is no data available in open literature for industrial practices for LCB PP to the best of the knowledge of the authors (that too for a bi-catalyst system), though there are a plenty of industrial data available for industrial practices for linear PP. Lab scale data are the best possible option available for the authors to model the LCB PP process and validate the model. Authors have, therefore, developed kinetic model of the LCB PP process to replicate the experimental data available in literature which is probably the first step to build a model before it can be scaled up for pilot study and thereafter for industrial practices. Since the process modeled in this work is for PP with long chain branching, the operating conditions can be different from what is being practiced in industry for linear PP (without branching). To the best of the knowledge of the authors, this is the first LCB PP mechanistic model validated with the laboratory data available from literature. In this work, the authors have chosen the example of LCB PP (isotactic back bones and atactic side chains) with binary catalyst system (2-ArN = C(Me))₂C₅H₃N}FeCl₂/MMAO (1) and *rac*-Me₂Si(2-MeBenz[e]Ind)₂ZrCl₂/MMAO (2)) [5] and presented a model which can validate experimental findings [5] with a newly proposed kinetic mechanism. The catalyst (1) is capable of forming short chain atactic polypropylene macromonomers (having terminal double bonds) and the catalyst (2) can copolymerize propylene with macromonomers to form LCB PP. Both short chain atactic polypropylene macromonomer formation and copolymerization of propylene with macromonomers occur simultaneously in the same reactor to form LCB PP which has a potential to produce LCB PP with lesser fixed and operating cost.

Modeling study has been conducted by Zhu and Li [14] with the use of binary metallocene catalyst system to obtain highly comb-branched polymers in steady state CSTR and obtained an olefin polymer of narrow molecular weight distribution with a maximum polydispersity index of 2.25. By this catalyst systems, back bone and side chains provide a theoretical polydispersity index of 2 (Schulz-Flory distribution) [14] only. However, Ye and Zhu [5] obtained aPP macromonomers with polydispersity index to the order of 1.3 during their experiments which the above mentioned model [14] cannot explain. It has been identified that by taking the

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