Recipes for Synthesizing Polyolefins with Tailor-Made Molecular Weight, Polydispersity Index, Long-Chain Branching Frequencies, and Chemical Composition Using Combined Metallocene Catalyst Systems in a CSTR at Steady State

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ABSTRACT: Polymerization of ethylene in a CSTR using a combined metallocene catalyst system (combination of an open-face catalyst, such as Constrained Geometry Catalyst, and a conventional metallocene catalyst) was studied. Using the model developed by Soares and Hamielec, and expanded by Beigzadeh et al., a steady-state simulator was prepared. The effects of different process parameters (such as reactor residence time) and kinetic parameters of the combined catalyst system on steady-state values of molecular weight, polydispersity index, long-chain branching frequency, and copolymer composition (in the case of copolymerization with α -olefins) were investigated. It was shown how recipes for synthesizing polyolefins with tailor-made MWD, CCD, and LCB frequencies can be designed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1753–1770, 1999

Key words: polyethylene; combined metallocene catalyst system; constrained geometry catalyst; long-chain branching

INTRODUCTION

Lai et al.^{1,2} were the first to introduce the production of polyethylenes with long-chain branches using metallocene catalysts. They employed an open-face metallocene catalyst (Constrained Geometry Catalyst), which is a monocyclopentadienyl metallocene catalyst, to incorporate macromonomers into the polymer backbone and synthesize polyethylenes with long-chain branches. These macromonomers are dead polymer chains with terminal double bonds formed via β -hydride elimination reaction.

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Swogger and Kao,³ and Sugawara⁴ used the procedure proposed by Lai et al.^{1,2} and made polyethylenes with different branching degrees.

Soares and Hamielec^{5,6} proposed a reaction mechanism for homo- and copolymerization of ethylene with other α -olefins with long-chain branch formation using metallocene catalysts. They obtained an analytical solution for the chain length and chemical composition distributions of the populations containing a different number of long chain branches per molecule for a CSTR operating at steady state.

Beigzadeh et al.⁷ expanded the kinetic model proposed by Soares and Hamielec,^{5,6} and proposed a reaction mechanism for homo- and copolymerization of ethylene with other α -olefins using a combined metallocene catalyst system. They in-

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Kinetic Constant	Value
$k_{i,11} \; (\text{L/mol} \cdot \text{s})$	40,000
$k_{i,12} \; (\text{L/mol} \cdot \text{s})$	10,000
$k_{i,21} \; (\text{L/mol} \cdot \text{s})$	40,000
$k_{i,22} \; (\text{L/mol} \cdot \text{s})$	320
$k_{1,11} \; (\text{L/mol} \cdot \text{s})$	40,000
$k_{1,12} \; (\text{L/mol} \cdot \text{s})$	10,000
$k_{1,21} (\text{L/mol} \cdot \text{s})$	35,000
$k_{1,22}$ (L/mol · s)	8750
$k_{2,11} \; (\text{L/mol} \cdot \text{s})$	40,000
$k_{2,12} \; (\text{L/mol} \cdot \text{s})$	320
$k_{2,21}$ (L/mol · s)	35,000
$k_{2,22} \; (\text{L/mol} \cdot \text{s})$	280
$k_{pLCB,11}$ (L/mol · s)	6000
$k_{pLCB,12}$ (L/mol · s)	4500
$k_{p \text{LCB}, 21}$ (L/mol · s)	1500
$k_{pLCB,22}$ (L/mol · s)	100
$k_{\beta,11}$ (s ⁻¹)	0.01
$k_{\beta,12}^{(-1)}$ (s ⁻¹)	0.01
$k_{da,1}^{(-1)}$ (s ⁻¹)	0.02
$k_{da,2}^{-1}$ (s ⁻¹)	0.02
$k_{\mathrm{CTA},11}$ (L/mol \cdot s)	0.1
$k_{\text{CTA},12}$ (L/mol · s)	0.1
$k_{\text{CTA},21}$ (L/mol · s)	0.1
$k_{\text{CTA},22}$ (L/mol · s)	0.1

Table IKinetic Constants for Ethylene/1-Octene Copolymerization

vestigated the effect of different process conditions and also characteristics of the combined catalyst system on the microstructure of the polymer made in a CSTR operating dynamically. They used the method of moments to calculate molecular weight, polydispersity index, long-chain branching frequency, and cumulative copolymer composition.

Based on the model proposed by Beigzadeh et al.,⁷ a computer simulator has been designed for the steady-state homo- and copolymerization of ethylene with other α -olefins using a combined catalyst system in a CSTR. The effects of different process conditions and kinetic parameters of the combined catalyst system on long-chain branching frequency, molecular weight, polydispersity index, and cumulative copolymer composition have been investigated. Using the obtained results, it has been shown how recipes for synthesizing polyolefins with predetermined chemical structure can be designed.

POLYMERIZATION MECHANISM

Olefin copolymerization with long-chain branch formation includes steps of initiation, propaga-

Table II	Operating Conditions Used in
Ethylene	Copolymerization Simulation

Total catalyst concentration in feed (mol/L) Ethylene concentration in reactor (mol/L)	4E-6 0.002
1-octene concentration in reactor (mol/L)	0.0012
Chain transfer agent concentration in feed (mol/L)	0

tion, addition of dead polymer chains with terminal double-bonds to active centers (formation of long-chain branches), transfer to chain transfer agent (formation of dead polymer chains with saturated chain-ends), β -hydride elimination (formation of dead polymer chains with terminal double bonds), and catalyst deactivation.⁷ In this model the combination of two catalyst types has been considered. Catalyst type 1 (LCB catalyst) is capable of polymerizing both monomers and macromonomers (incorporating long-chain branches), whereas catalyst type 2 (linear catalyst) can only polymerize monomers (unable to incorporate macromonomers).

Based on the proposed reaction mechanism, balances for different populations can be derived (Appendix 1). Chain-length averages and polydispersity indices for different chain populations, calculated by the method of moments, can be stated as follows:

$$\bar{r}_n = \frac{\text{First Moment}}{\text{Zeroth Moment}} \tag{1}$$

$$\bar{r}_w = rac{ ext{Second Moment}}{ ext{First Moment}}$$
 (2)

$$PDI = \frac{\bar{r}_2}{\bar{r}_n}$$
(3)

where, \bar{r}_n is the number-average chain length; \bar{r}_w is the weight-average chain length; and PDI is the polydispersity index.

Table III	β-Hydride Elimination Reaction Rate
Constants	of Three Linear Catalysts Employed
in Polyme	rization Simulation

Catalyst	Kinetic Constant (s^{-1})
Linear Catalyst 1 Linear Catalyst 2 Linear Catalyst 3	$\begin{array}{rcl} k_{\beta,21} &=& k_{\beta,22} &=& 0.02 \\ k_{\beta,21} &=& k_{\beta,22} &=& 0.03 \\ k_{\beta,21} &=& k_{\beta,22} &=& 0.04 \end{array}$

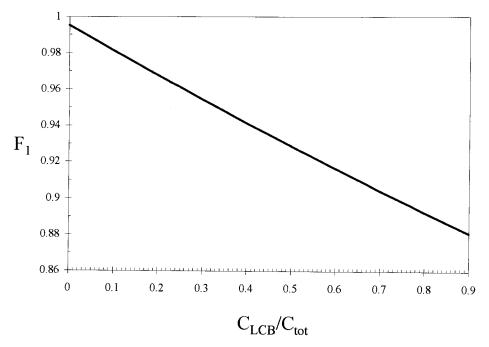


Figure 1 Variation in copolymer composition (F_1) vs. mol fraction of LCB catalyst (in catalyst feed) for different reactor residence times $(F_1$ is independent of reaction residence time) of a copolymer made with catalyst system 1 $(k_{\beta,21} = k_{\beta,22} = 0.02 \text{ s}^{-1})$.

The equations for moments and the balance equations for monomers, catalysts, and chain transfer agent (total of 26 nonlinear algebraic equations) (Appendix 2) should be solved simultaneously. Newton's method⁸ was used to solve the obtained system of nonlinear algebraic equations.

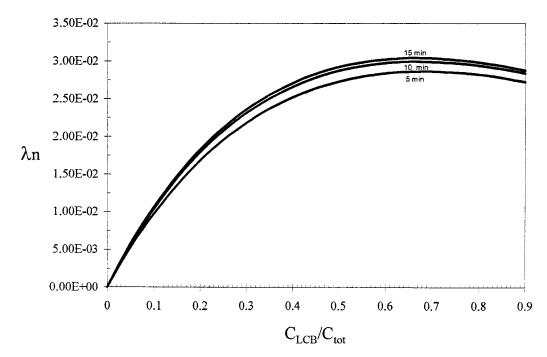


Figure 2 Variation in the number of branching points per 1000 carbon atoms (λn) vs. mol fraction of LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 1 ($k_{\beta,21} = k_{\beta,22} = 0.02 \text{ s}^{-1}$).

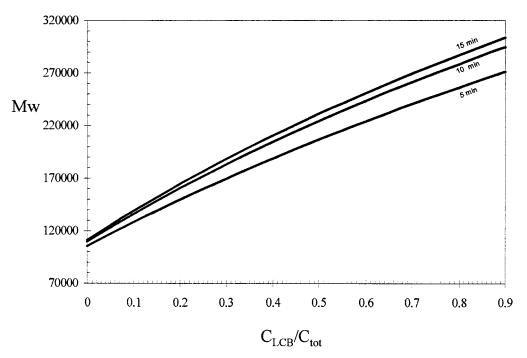


Figure 3 Variation in weight-average molecular weight (M_w) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 1 $(k_{\beta,21} = k_{\beta,22} = 0.02 \text{ s}^{-1})$.

Average values for long-chain branching frequency can also be easily obtained by noticing that:

$$\bar{B}_{\rm N} = \frac{R_{\rm LCB}}{R_{\rm cf}} = \frac{R_{\rm LCB}}{R_{\beta} + R_{\rm da} + R_{\rm CTA} - R_{\rm LCB}}$$
 (4)

where $B_{\rm N}$ is the average number of LCB per polymer chain; $R_{\rm LCB}$ is the rate of macromonomer propagation; $R_{\rm cf}$ is the net rate of dead polymer chain formation; R_{β} is the rate β -hydride elimination reaction; $R_{\rm da}$ is the rate of deactivation reaction; $R_{\rm CTA}$ is the rate of transfer reaction.

The number of branching points per 1000 carbon atoms (λ_n) can also be easily calculated:

$$\bar{\lambda}_n = 500 \, \frac{R_{\rm LCB}}{R_p} \tag{5}$$

where R_p is the rate of monomer propagation.

RECIPE DESIGN

To design a recipe for synthesizing a particular polyolefin, one should follow these steps: (1) the moment equations (Appendix 2) should be solved simultaneously using corresponding kinetic parameter values of employed catalysts and monomers. (2) The effect of process parameters such as reactor residence time and the ratio of the two catalysts, and the effect of the characteristics of the catalyst system on chemical structure of final product should be investigated and plotted. (3) By implementing the preferred characteristics into the obtained plots, the best recipe can be selected. This procedure can be better understood in the following examples. In these examples, the copolymerization of ethylene and an α -olefin (such as 1-octene) has been considered using a combined metallocene catalyst system. The catalyst system consists of an LCB catalyst (such as CGC) and a conventional metallocene catalyst (linear catalyst). The behavior of the polymerization system for three different cases using three different conventional metallocene catalysts in combination of CGC has been investigated.

Typical values for kinetic rate constants used in the computer simulations are tabulated in Tables I and II. Values of reactivity ratios were taken from the data obtained by Knight and Lai.⁹ The values of β -hydride elimination rate constants for the three metallocene catalysts employed in these examples are tabulated in Table III.

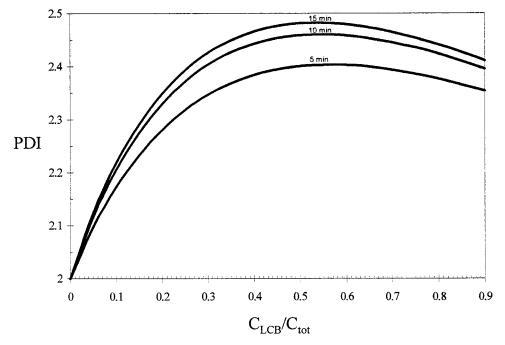


Figure 4 Variation in polydispersity index (PDI) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 1 ($k_{\beta,21} = k_{\beta,22} = 0.02 \text{ s}^{-1}$).

Table II shows the operating conditions used in computer simulations for homo- and copolymerization of ethylene, respectively. According to the proposed kinetic model, the produced macromonomers may have vinyl or vinylidene chain ends (Appendix 1). The mac-

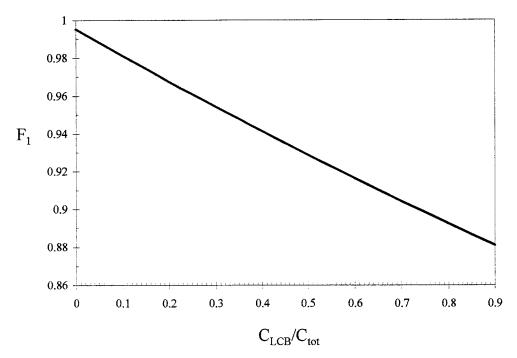


Figure 5 Variation in copolymer composition (F_1) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times $(F_1$ is independent of reaction residence time) of a copolymer made with catalyst system 2 $(k_{\beta,21} = k_{\beta,22} = 0.03 \text{ s}^{-1})$.

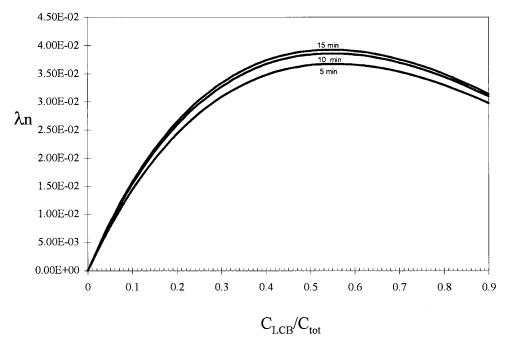


Figure 6 Variation in the number of branching points per 1000 carbon atoms (λn) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 2 ($k_{\beta,21} = k_{\beta,22} = 0.03 \text{ s}^{-1}$).

romonomers with vinylidene chain ends have much lower polymerization activity than the ones with vinyl unsaturations (because of their bulky chain ends). However, their polymerization rate constant is not zero and they can be polymerized.^{10,11} This has been considered in Table I,

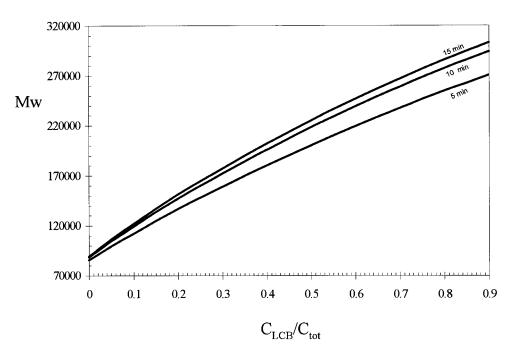


Figure 7 Variation in weight average molecular weight (M_w) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 2 $(k_{\beta,21} = k_{\beta,22} = 0.03 \text{ s}^{-1})$.

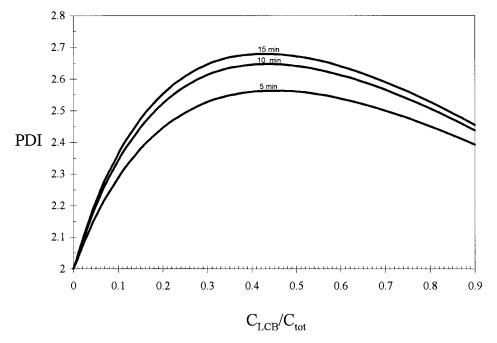


Figure 8 Variation in polydispersity index (PDI) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 2 ($k_{\beta,21} = k_{\beta,22} = 0.03 \text{ s}^{-1}$).

where the values of $k_{pLCB,11}$, $k_{pLCB,12}$ are much higher than the ones of $k_{pLCB,21}$, $k_{pLCB,22}$, respectively.

According to Tables II and III, the following catalyst systems have been used in recipe design examples: catalyst system 1: CGC and linear cat-

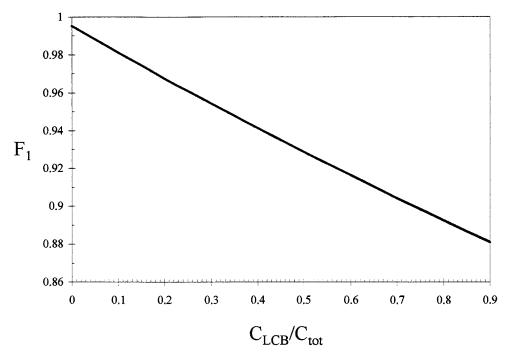


Figure 9 Variation in copolymer composition (F_1) vs. mol fraction of the LCB catalyst (in catalyst) feed for different reactor residence times $(F_1$ is independent of reaction residence time) of a copolymer made with catalyst system 3 $(k_{\beta,21} = k_{\beta,22} = 0.04 \text{ s}^{-1})$.

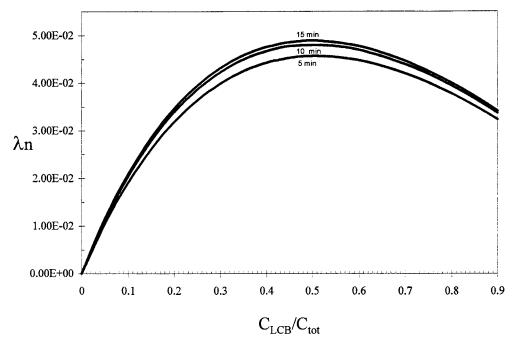


Figure 10 Variation in the number of branching points per 1000 carbon atoms (λn) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 3 $(k_{\beta,21} = k_{\beta,22} = 0.04 \text{ s}^{-1})$.

alyst 1; catalyst system 2: CGC and linear catalyst 2; and catalyst system 3: CGC and linear catalyst 3.

As shown in Tables II and III, it has been assumed that all of the kinetic parameters for linear metallocene catalysts are the same ex-

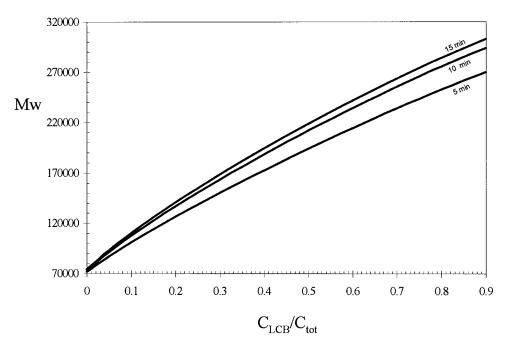


Figure 11 Variation in weight average molecular weight (M_w) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 3 $(k_{\beta,21} = k_{\beta,22} = 0.04 \text{ s}^{-1})$.

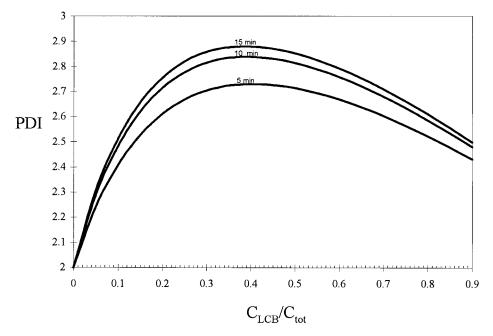


Figure 12 Variation in polydispersity index (PDI) vs. mol fraction of the LCB catalyst (in catalyst feed) for different reactor residence times of a copolymer made with catalyst system 3 ($k_{\beta,21} = k_{\beta,22} = 0.04 \text{ s}^{-1}$).

cept the β -hydride elimination reaction constants.

It should be mentioned that operating conditions and catalyst system characteristics (shown in Tables I–III) can be altered according to the operating conditions of each particular polymerization system and the recipe design procedure proposed in this article will be applicable to any kind of operating conditions and catalyst system.

Considering constant values for total catalyst concentration in feed and constant monomer concentration in the reactor (Table II), the proper type of linear catalyst, the mol fraction of the LCB catalyst, and the reactor residence time should be determined.

Figures 1 to 12 illustrate the effect of different LCB catalyst mol fractions and reactor residence times on several properties of the produced copolymer.

Table IV The C_{LCB}/C_{tot} Limits Satisfying λn > 1.5E-2 for Catalyst System 1

Reactor Residence Time (min)	C_{LCB}/C_{tot}
5 10	0.17-0.90 0.15-0.90
15	0.14-0.90

As stated in Figure 1, copolymer composition is not a function of reactor residence time. The content of 1-octene in the copolymer increases with increasing the $C_{\rm LCB}/C_{\rm tot}$ ratio, because the comonomer reactivity ratio for the LCB catalyst is higher than that of the linear catalyst (see Table I).

Figure 2 shows the variations of LCB per 1000 carbon atoms as a function of LCB catalyst mol fraction at different reactor residence times for catalyst system 1. As expected, higher LCB levels are obtained at higher residence times,⁷ but by increasing the LCB catalyst mol fraction, λn passes through a maximum. This behavior can be related to the lower macromonomer concentration as the mol fraction of linear catalyst decreases. As shown in Tables II and III, all employed linear catalysts have higher β -hydride elimination rate constants than the LCB catalyst. Therefore, at

Table VThe C_{LCB}/C_{tot} Limits Satisfying150,000 < M_w < 160,000 for Catalyst System 1</td>

Reactor Residence Time (min)	C_{LCB}/C_{tot}
5	0.21 - 0.25
10	0.16 - 0.20
15	0.15-0.18

Reactor Residence Time (min)	C_{LCB}/C_{tot}
5 10 15	$\begin{array}{c} 0.23 - 0.90 \\ 0.17 - 0.30 \\ 0.15 - 0.26 \end{array}$

Table VI The C_{LCB}/C_{tot} Limits Satisfying 2.3 < PDI < 2.4 for Catalyst System 1

higher mol fraction ratios of the LCB catalyst, the rate of formation of macromonomers will be lower.

Figure 3 shows the variations of weight-average molecular weight as a function of LCB catalyst mol fraction ratio for different reactor residence times.

In the presence of the LCB catalyst, long-chain branching takes place. Because higher reactor residence times favors long-chain branching reaction (high polymer concentration) and because LCB formation reaction increases molecular weight, higher M_w values will be obtained at higher residence times. This can explain the diverging behavior of the plots of M_w vs. C_{LCB}/C_{tot} for different reactor residence times.

Figure 4 illustrates the variations of polydispersity index (PDI) as a function of the LCB catalyst mol fraction for different reactor residence times. As shown in this figure, as C_{LCB}/C_{tot} ratio increases, PDI passes through a maximum. This behavior can be attributed to two phenomena. First, the β -hydride elimination reaction rate constant considered for the linear catalyst is higher than the one of CGC (while their propagation rate constants are equal, Tables I and III). Therefore, the molecular weight of chains made by the linear catalyst will be lower than the ones made by CGC. This difference in molecular weights of polymer chains increases PDI as the molar fraction of CGC in the catalyst inlet stream increases. By increasing the molar fraction of CGC, after a certain C_{LCB}/C_{tot} ratio, this site type will be the major component in the combined catalyst system and as the fraction of CGC in the catalyst inlet increases, more uniform chains will be formed and PDI starts decreasing. Secondly, at different $C_{\rm LCB}/C_{\rm tot}$ ratio values, different LCB degrees will be obtained. By increasing the C_{LCB}/C_{tot} ratio, the concentration of LCB active sites increases, but the rate of formation of macromonomers decreases (due to higher β -hydride elimination reaction rate constant of linear catalysts). Therefore, the plot of PDI as a function of $\mathrm{C}_{\mathrm{LCB}}/\mathrm{C}_{\mathrm{tot}}$ passes through a maximum value that will be in accordance with the maximum LCB formation rate.

The plots of F_1 , M_w , λn , and PDI for other catalyst systems follow the same trends (Figs. 5–12) as explained for catalyst system 1.

The following examples show how recipes can be designed by employing the plots of F_1 , λn , M_w , and PDI obtained for different catalyst systems (Figs. 1–12). In each of these examples a particular polyolefin with a certain chemical structure has been considered as the main target, and suitable catalyst systems and operation conditions have been determined.

Example 1

An ethylene/1-octene copolymer with the following characteristics is to be synthesized in a CSTR at steady state. Mol fraction of ethylene in copolymer, F_1 : 0.96-0.97; long-chain branches per 1000 carbon atoms, λn : > 1.5E-2;

Reactor Residence Time Characteristic (min) C_{LCB}/C_{tot} $F_1 = 0.96 - 0.97$ (Fig. 5) all 0.19 - 0.26 $\lambda n > 1.5$ E-2 (Fig. 6) 5 0.11 - 0.9010 0.10 - 0.900.09 - 0.9015 $M_{iv} = 150,000-160,000$ (Fig. 7) $\mathbf{5}$ 0.26 - 0.3110 0.21 - 0.25150.20 - 0.24PDI = 2.3-2.4 (Fig. 8) 5 0.11 - 0.1710 0.09 - 0.140.08 - 0.1215

Table VII The C_{LCB}/C_{tot} Limits Satisfying the Desired Polymer Characteristics of Example 1 for Catalyst System 2

Characteristic	Reactor Residence Time (min)	C_{LCB}/C_{tot}
$F_1 = 0.96 - 0.97$ (Fig. 9)	all	0.19-0.26
$\lambda n > 1.5$ E-2 (Fig. 10)	5	0.08-0.90
	10	0.07 - 0.90
	15	0.06-0.90
$M_w = 150,000 - 160,000$ (Fig. 11)	5	0.30 - 0.35
	10	0.25 - 0.29
	15	0.24 - 0.27
PDI = 2.3-2.4 (Fig. 12)	5	0.07 - 0.10
	10	0.05 - 0.08
	15	0.04 - 0.07

Table VIII The C_{LCB}/C_{tot} Limits Satisfying the Desired Polymer Characteristics of Example 1 for Catalyst System 3

weight-average molecular weight, M_w : 150,000– 160,000; and polydispersity index, PDI: 2.3–2.4.

Starting with the catalyst system 1, according to Fig. 1, F_1 values between 0.96–0.97 correspond to C_{LCB}/C_{tot} values between 0.19–0.26 and because F_1 is not a function of reactor residence time (Rt), C_{LCB}/C_{tot} values will be the same for all residence times.

According to Figure 2, the C_{LCB}/C_{tot} limits satisfying $\lambda n > 1.5E-2$ (Fig. 2) are shown in Table IV.

Figure 3 can be employed for determining suitable limits of $C_{\rm LCB}/C_{\rm tot}$ at different reactor residence times for the desired weight-average molecular weight between 150,000–160,000. According to this figure, different $C_{\rm LCB}/C_{\rm tot}$ limits at different residence times satisfying the required M_w values are tabulated in Table V.

Figure 4 illustrates the variations of PDI as a function of $C_{\rm LCB}/C_{\rm tot}$ at different reactor residence times. The $C_{\rm LCB}/C_{\rm tot}$ limits satisfying PDI values between 2.3–2.4 can be obtained from this plot for different reactor residence times. These limits are summarized in Table VI.

This shows that catalyst system 1 can be used in production of the desired polyolefin. The conditions that satisfies the required chemical structure are: Catalyst system 1: Rt = 5 min, C_{LCB}/C_{tot} $C_{tot} = 0.23-0.25$; and Rt = 10 min, C_{LCB}/C_{tot} = 0.19-0.20.

As can be seen, there are two conditions satisfying the desired polymer characteristics. Depending on the catalyst cost and/or limitations of the residence time, either of the above conditions can be used.

If the same type of investigation is done for catalyst system 2, the $C_{\rm LCB}/C_{\rm tot}$ values at differ-

ent residence times satisfying the required properties can be summarized in Table VII.

As can be seen, there is no common operating conditions satisfying all of required values. For example F_1 limits requires C_{LCB}/C_{tot} values between 0.19–0.26. But none of the C_{LCB}/C_{tot} limits satisfying PDI = 2.3–2.4 are in the same range.

Repeating this investigation for catalyst system 3 the $C_{\rm LCB}/C_{\rm tot}$ values at different residence times satisfying the required properties can be summarized in Table VIII.

As for catalyst system 2, there is no common operating conditions satisfying all of required values. For example F_1 limits requires C_{LCB}/C_{tot} values between 0.19–0.26. But none of the C_{LCB}/C_{tot} limits satisfying PDI = 2.3–2.4 are in the same range.

Example 2:

An ethylene/1-octene copolymer with following characteristics is to be synthesized in a CSTR at steady state. Mol fraction of ethylene in copolymer, $F_1: 0.89-0.90$; long-chain branches per 1000 carbon atoms, $\lambda n: > 3.5$ E-2; weight-average molecular weight, $M_w: 260,000-270,000$; and polydispersity index, PDI: 2.5–2.6.

Starting with the catalyst system 1 and doing the same kind of investigation as in Example 1, the C_{LCB}/C_{tot} values at different residence times, satisfying the required properties, are tabulated in Table IX.

As can be seen, there is no common operating conditions satisfying all of required values. Therefore, catalyst system 1 cannot be employed to synthesize the desired polyolefin.

If the same sort of investigation is done for catalyst system 2, the C_{LCB}/C_{tot} values at differ-

Characteristic	Reactor Residence Time (min)	$\rm C_{LCB}/\rm C_{tot}$
$F_1 = 0.89 - 0.90$ (Fig. 1)	all	0.74-0.83
$\lambda n > 3.5$ E-2 (Fig. 2)	5	not applicable
J. J	10	not applicable
	15	not applicable
$M_w = 260,000-270,000$ (Fig. 3)	5	0.81-0.88
	10	0.69 - 0.75
	15	0.65 - 0.70
PDI = 2.2-2.3 (Fig. 4)	5	not applicable
	10	not applicable
	15	not applicable

Table IX The C_{LCB}/C_{tot} Limits Satisfying the Desired Polymer Characteristics of Example 2 for Catalyst System 1

ent residence times satisfying the required properties can be summarized in Table X.

This shows that catalyst system 2 can be employed in production of the desired polyolefin. The conditions that satisfies the required chemical structure are: catalyst system 2: Rt = 10 min, $C_{LCB}/C_{tot} = 0.74-0.78$.

Doing the same type of investigation on catalyst system 3, the $C_{\rm LCB}/C_{\rm tot}$ values at different residence times satisfying the required properties are tabulated in Table XI.

The obtained C_{LCB}/C_{tot} limits show that catalyst system 3 can be employed in production of the desired polyolefin. The conditions that satisfies the required chemical structure are: catalyst system 3: (1) Rt = 5 min, $C_{LCB}/C_{tot} = 0.83$; (2) Rt = 10 min, $C_{LCB}/C_{tot} = 0.78-0.79$.

Catalyst systems 2 and 3 can be used for synthesizing the required polyolefin in Example 2. Depending on the availability of the catalyst types and economical feasibility, catalyst systems 2 or 3 might be used. For the case of catalyst system 2, there are two process conditions to choose. Depending on the efficiency, prices of the two metallocene catalysts, and other economical and/or operational limitations of the process, either of the conditions can be selected.

CONCLUDING REMARKS

Homo- and copolymerization of ethylene with other α -olefins using combined catalyst systems were studied. Based on the kinetic model proposed by Beigzadeh et al.,⁷ a computer simulator for a CSTR operating at steady state was designed. The variations of molecular weight, polydispersity index, LCB frequency, and copolymer composition as functions of process conditions and

Table X The C_{LCB}/C_{tot} Limits Satisfying the Desired Polymer Characteristics of Example 2 for Catalyst System 2

Characteristic	Reactor Residence Time (min)	$\rm C_{LCB}/C_{tot}$
$F_1 = 0.89 - 0.90$ (Fig. 5)	all	0.74-0.83
$\lambda n > 3.5 \text{E-2} \text{ (Fig. 6)}$	5	0.41 - 0.72
C C	10	0.36 - 0.78
	15	0.34 - 0.80
$M_w = 260,000-270,000$ (Fig. 7)	5	0.82 - 0.90
<i>a</i>	10	0.73 - 0.78
	15	0.67 - 0.72
PDI = 2.5-2.6 (Fig. 8)	5	0.29 - 0.70
	10	0.19-0.29
		0.63 - 0.81
	15	0.17 - 0.25
		0.68 - 0.84

Characteristic	Reactor Residence Time (min)	C_{LCB}/C_{tot}
$F_1 = 0.89 - 0.90$ (Fig. 9)	all	0.74-0.83
$\lambda n > 3.5 \text{E-}2 \text{ (Fig. 10)}$	5	0.24 - 0.85
	10	0.22 - 0.87
	15	0.21 - 0.88
$M_w = 260,000-270,000$ (Fig. 11)	5	0.83 - 0.90
	10	0.72 - 0.79
	15	0.68 - 0.73
PDI = 2.5-2.6 (Fig. 12)	5	0.71 - 0.83
5	10	0.78 - 0.89
	15	0.81 - 0.90

Table XI The $\rm C_{LCB}/\rm C_{tot}$ Limits Satisfying the Desired Polymer Characteristics of Example 2 for Catalyst System 3

characteristics of the combined catalyst system were investigated.

It was shown how for a given set of polymer characteristics, suitable catalyst system, and process conditions can be chosen. The proposed procedure is a step forward in designing recipes for production of ethylene-based homo- and copolymers.

NOMENCLATURE

\bar{B}_{N}	average number of LCB per polymer
11	chain
C_1	the LCB catalyst.
$\overline{C_2}$	the linear catalyst.
CTA	chain transfer agent.
$D_{m,r,i}^{=}$	dead polymer of chain length r contain-
	ing <i>i</i> long-chain branches and termi-
	nal vinyl or vinylidene unsaturation
	ended with monomer m ($m = 1$ or
	2).
$D_{r,i}$	dead polymer of chain length r contain-
	ing i long-chain branches and a sat-
	urated chain end.
DC	dead catalyst
$k_{i,jq}$	initiation rate constant for catalyst site
	type j reacting with monomer q .
$k_{j,mq}$	propagation rate constant for incorpo-
	ration of monomer q to a chain made
	on catalyst site type j ended with
	monomer <i>m</i> .
$k_{p \text{LCB}, jm}$	propagation rate constant for incorpora-
	tion of macromonomers ended with
	monomer m to a living chain ended
	with monomer <i>j</i> .
$k_{\mathrm{CTA},jq}$	transfer rate for a living chain made on
	catalyst site type <i>j</i> ended with mono-

mer q.

_	
$k_{eta,jq}$	β -hydride elimination rate constant of
	a living chains made on catalyst site
	type j ended with monomer q .
k_{daj}	deactivation rate constant for catalyst
-	site type j .
M_1, M_2	monomers 1 and 2.
PDI	polydispersity index.
$P_{1.0.}$	living polymer of chain length one con-
_,	taining no long-chain branches.
$P_{r,i}$	living polymer of chain length r con-
7,0	taining i long-chain branches made
	on catalyst 1 ended with monomer 1.
Q_r	linear living polymer of chain-length r
C/	made on catalyst site type 2 ended
	with monomer 1.
r_n	number-average kinetic chain length
r_w	weight-average kinetic chain length
$\ddot{R}_{ m LCB}$	rate of macromonomer propagation
R_{cf}^{LCD}	net rate of dead polymer chain forma-
<i>c)</i>	tion
R_{β}	rate β -hydride elimination reaction
R_{da}^{P}	rate of deactivation reaction
R_{CTA}^{aa}	rate of chain transfer to chain transfer
UIA	agent
8	reciprocal of the mean residence time
	in the reactor
S_{ri}	living polymer of chain length r con-
- 11,	taining i long-chain branches made
	on catalyst site type 1 ended with
	monomer 2.
T_r	linear living polymer of chain length r
- <i>r</i>	made on catalyst site type 2 ended
	with monomer 2.

Greek Letters

 λ_j *j*th moment of living polymer chains made on the linear catalyst, ended with monomer 1.

- η_j *j*th moment of the living polymer chains made on the LCB catalyst ended with monomer 1.
- λ_n average number of branching points per 1000 carbon atoms.
- λ_j jth moment of the dead polymers with terminal double-bond ended with monomer 1.
- μ_j *j*th moment of the dead polymers with saturated chain end.
- σ_j jth moment of the dead polymers with terminal double-bond ended with monomer 2.
- τ_j *j*th moment of living polymer chains made on the linear catalyst, ended with monomer 2.
- Ψ_j jth moment of the living polymer chains made on the LCB catalyst ended with monomer 2.

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APPENDIX 1

Reaction mechanism and population balances of different species for the copolymerization of ethylene with α -olefins using combined metallocene catalyst systems are as follows⁷:

Reaction Mechanism

Initiation:

$$C_1 + M_1 \longrightarrow P_{1,0} \qquad \qquad k_{i,11}$$

$$C_1 + M_2 \quad o \quad S_{1,0} \qquad \qquad k_{i,12}$$

$$C_2 + M_1 \quad o \quad Q_1 \qquad \qquad k_{i,21}$$

$$C_2 + M_2 \quad
ightarrow T_1 \qquad \qquad k_{i,22}$$

Propagation:

$$egin{array}{rl} P_{r,i}+M_1&
ightarrow P_{r+1,i}&k_{1,11}\ P_{r,i}+M_2&
ightarrow S_{r+1,i}&k_{1,12} \end{array}$$

$$S_{ri} + M_1 \rightarrow P_{r+1i} \qquad k_{121}$$

$$S_{r,i} + M_2 \quad
ightarrow S_{r+1,i} \qquad k_{1,22}$$

$$egin{array}{rll} Q_r+M_1&
ightarrow Q_{r+1}&k_{2,11}\ Q_r+M_2&
ightarrow T_{r+1}&k_{2,12} \end{array}$$

$$egin{array}{cccc} T_r+M_1&
ightarrow Q_{r+1}&k_{2,21}\ T_r+M_2&
ightarrow T_{r+1}&k_{2,22} \end{array}$$

Long-chain branching:

$$\begin{array}{rcl} P_{r,i} + D_{1,q,j}^{=} & \to & P_{r+q,i+j+1} & k_{p\text{LCB},11} \\ \\ S_{r,i} + D_{1,q,j}^{=} & \to & P_{r+q,i+j+1} & k_{p\text{LCB},21} \\ \\ P_{r,i} + D_{2,q,j}^{=} & \to & S_{r+q,i+j+1} & k_{p\text{LCB},12} \\ \\ S_{r,i} + D_{2,q,j}^{=} & \to & S_{r+q,i+j+1} & k_{p\text{LCB},22} \end{array}$$

Transfer:

 β -Hydride elimination:

$P_{r,i}$	$\rightarrow D_{1,r,i}^{=} + C_1$	$k_{eta,11}$
${m S}_{r,i}$	$\rightarrow D^{=}_{2,r,i} + C_1$	$k_{eta,12}$
Q_r	$\rightarrow D_{1r0}^{=} + C_2$	$k_{\scriptscriptstyle B21}$

$$T_r \longrightarrow D^{=}_{2,r,0} + C_2 \quad k_{\beta,22}$$

Deactivation:

$$egin{array}{ccccc} C_1 & o & {
m DC} & k_{da,1} \ C_2 & o & {
m DC} & k_{da,2} \ P_{r,i} & o & D_{r,i} & k_{da,1} \ S_{r,i} & o & D_{r,i} & k_{da,2} \ Q_r & o & D_{r,0} & k_{da,2} \ T_r & o & D_{r,0} & k_{da,2} \end{array}$$

where:

- $P_{r,i}$ living polymer of chain length r containing i long-chain branches made on catalyst site type 1 ended with monomer 1.
- $S_{r,i}$ living polymer of chain length r containing i long-chain branches made on catalyst site type 1 ended with monomer 2.
- Q_r linear living polymer of chain length rmade on catalyst site type 2 ended with monomer 1.
- T_r linear living polymer of chain length rmade on catalyst site type 2 ended with monomer 2.
- $D_{m,r,i}^{=}$ dead polymer of chain length r containing i long-chain branches and terminal vinyl or vinylidene unsaturation ended with monomer m (m = 1 or 2).
- $D_{r,i}$ dead polymer of chain length r containing i long-chain branches and a saturated chain end.
- C_i catalyst site type i.
- DC dead catalyst site (or inactive).
- M_1, M_2 monomers 1 and 2.
- CTA chain transfer agent.
- $k_{i,jq}$ Initiation rate constant for catalyst site type j reacting with monomer q.
- $k_{j,mq}$ propagation rate constant for incorporation of monomer q to a chain made on catalyst site type j ended with monomer m.
- $k_{p \text{LCB},jm}$ propagation rate constant for incorporation of macromonomers ended with monomer *m* to a living chain ended with monomer *j*.
- $k_{\text{CTA},jq}$ transfer rate constant for a living chain made on catalyst site type jended with monomer q.

 $\begin{array}{ll} k_{\beta,jq} & \beta \text{-hydride elimination rate constant of} \\ & a \text{ living chains made on catalyst site} \\ & type \ j \ \text{ended with monomer} \ q. \\ k_{daj} & \text{deactivation rate constant for catalyst} \\ & \text{site type } \ j. \end{array}$

Population Balances

Based on the above reaction mechanism, balances for different populations for steady-state conditions can be derived as follows:

Catalysts:

$$\begin{aligned} \frac{dC_1}{dt} &= 0 = s(C_{1,in} - C_1) - (k_{i,11}M_1 \\ &+ k_{i,12}M_2 + k_{da,1})C_1 + \text{CTA}(k_{\text{CTA},11}\eta_0 + k_{\text{CTA},12}\Psi_0) \\ &+ (k_{\beta,11}\eta_0 + k_{\beta,12}\Psi_0) \quad (6) \end{aligned}$$

$$\begin{aligned} \frac{dC_2}{dt} &= 0 = s(C_{2,in} - C_2) \\ &- (k_{i,21}M_1 + k_{i,22}M_2 + k_{da,2})C_2 + \text{CTA}(k_{\text{CTA},21}\gamma_0 \\ &+ k_{\text{CTA},22}\tau_0) + (k_{\beta,21}\gamma_0 + k_{\beta,22}\tau_0) \end{aligned}$$
(7)

where s is the reciprocal of the mean residence time in the reactor

Monomers:

$$\begin{aligned} \frac{dM_1}{dt} &= 0 = s(M_{1,in} - M_1) - (k_{1,11}\eta_0 + k_{1,21}\Psi_0 \\ &+ k_{2,11}\gamma_0 + k_{2,21}\tau_0)M_1 \end{aligned} (8)$$

$$\frac{dM_2}{dt} = 0 = s(M_{2,in} - M_2) - (k_{1,12}\eta_0 + k_{1,22}\Psi_0 + k_{2,12}\gamma_0 + k_{2,22}\tau_0)M_2 \quad (9)$$

Dead Polymer Chains:

$$\begin{aligned} \frac{dD_{1,r,0}^{=}}{dt} &= 0 = k_{\beta,11}P_{r,0} + k_{\beta,21}Q_r \\ &- (k_{p\text{LCB},11}\eta_0 + k_{p\text{LCB},21}\Psi_0 + s)D_{1,r,0}^{=} \\ &\qquad (i=0) \quad (10) \end{aligned}$$

$$\begin{aligned} \frac{dD_{1,r,i}^{=}}{dt} &= 0 = k_{\beta,11} P_{r,i} \\ &- (k_{p\text{LCB},11} \eta_0 + k_{p\text{LCB},21} \Psi_0 + s) D_{1,r,i}^{=} \\ &\qquad (i > 0) \quad (11) \end{aligned}$$

$$\frac{dD_{2,r,0}^{=}}{dt} = 0 = k_{\beta,12}S_{r,0} + k_{\beta,22}T_{r} - (k_{p\text{LCB},12}\eta_{0} + k_{p\text{LCB},22}\Psi_{0} + s)D_{2,r,0}^{=}$$

$$(i = 0) \quad (12)$$

$$\begin{aligned} \frac{dD_{2,r,i}^{=}}{dt} &= 0 = k_{\beta,12} S_{r,i} \\ &- (k_{p\text{LCB},12} \eta_0 + k_{p\text{LCB},22} \Psi_0 + s) D_{2,r,i}^{=} \\ &\qquad (i > 0) \quad (13) \end{aligned}$$

$$\begin{aligned} \frac{dD_{r,0}}{dt} &= 0 = (k_{\text{CTA},11}P_{r,0} + k_{\text{CTA},12}S_{r,0} \\ &+ k_{\text{CTA},21}Q_r + k_{\text{CTA},22}T_r)\text{CTA} + k_{da,1} \\ &\times (P_{r,0} + S_{r,0}) + k_{da,2}(Q_r + T_r) - sD_{r,0} \\ &\qquad (i = 0) \quad (14) \end{aligned}$$

$$\begin{aligned} \frac{dD_{r,i}}{dt} &= 0 = (k_{\text{CTA},11}P_{r,i} + k_{\text{CTA},12}S_{r,i}) \\ &\times \text{CTA} + k_{da,1}(P_{r,i} + S_{r,i}) - sD_{r,i} \\ &(i > 0) \quad (15) \end{aligned}$$

Living Polymer Chains:

$$\begin{aligned} \frac{dP_{1,0}}{dt} &= 0 = k_{i,11} C_1 M_1 \\ &- (k_{1,11} M_1 + k_{1,12} M_2 + k_{p\text{LCB},11} \lambda_0 + k_{p\text{LCB},12} \sigma_0) \end{aligned}$$

$$\times P_{1,0} - (k_{\text{CTA},11}\text{CTA} + k_{\beta,11} + k_{da,1} + s)P_{1,0} \quad (16)$$

$$\frac{dP_{r,i}}{dt} = 0 = k_{1,11}M_1(P_{r-1,i} - P_{r,i}) + k_{1,21}M_1S_{r-1,i}$$

$$-k_{1,12}M_2P_{r,i} - (k_{p\text{LCB},11}\lambda_0 + k_{p\text{LCB},12}\sigma_0)$$

$$\times P_{r,i} + k_{p\text{LCB},11}\sum_{s=1}^{r-1}\sum_{j=0}^{i-1} P_{r-s,j}D_{1,s,i-1-j}^{=}$$

$$r-1 \ i-1$$

+
$$k_{pLCB,21} \sum_{s=1}^{\infty} \sum_{j=0}^{\infty} S_{r-sj} D_{1,s,i-1-j}^{=}$$

$$- (k_{\text{CTA},11}\text{CTA} + k_{\beta,11} + k_{da,1} + s)P_{r,i} \quad (17)$$

$$\begin{aligned} \frac{dS_{1,0}}{dt} &= 0 = k_{1,12} C_1 M_2 \\ &- (k_{1,21} M_1 + k_{1,22} M_2 + k_{p\text{LCB},21} \lambda_0 + k_{p\text{LCB},22} \sigma_0) S_{1,0} \\ &- (k_{\text{CTA},12} \text{CTA} + k_{\beta,12} + k_{da,1} + s) S_{1,0} \quad (18) \end{aligned}$$

$$\frac{dS_{r,i}}{dt} = 0 = k_{1,22}M_2(S_{r-1,i} - S_{r,i}) + k_{1,12}M_2P_{r-1,i}$$

$$-k_{1,21}M_1S_{r,i} - (k_{pLCB,21}\lambda_0 + k_{pLCB,22}\sigma_0)S_{r,i}$$

+
$$k_{p\text{LCB},12} \sum_{s=1}^{r-1} \sum_{j=0}^{i-1} P_{r-s,j} D_{2,s,i-1-j}^{=}$$

+
$$k_{p\text{LCB},22} \sum_{s=1}^{r-1} \sum_{j=0}^{i-1} S_{r-s,j} D_{2,s,i-1-j}^{=}$$

$$- (k_{\text{CTA},12}\text{CTA} + k_{\beta,12} + k_{da,1} + s)S_{r,i} \quad (19)$$

$$\frac{dQ_1}{dt} = 0 = k_{i,21}M_1C_2 - (k_{2,11}M_1 + k_{2,12}M_2)Q_1$$

$$- (k_{\text{CTA},21}\text{CTA} + k_{\beta,21} + k_{da,2} + s)Q_1 \quad (20)$$

$$\frac{dQ_r}{dt} = 0 = k_{2,11}M_1(Q_{r-1} - Q_r) - k_{2,12}M_2Q_r + k_{2,21}M_1T_{r-1}$$

$$- (k_{\text{CTA},21}\text{CTA} + k_{\beta,21} + k_{da,2} + s)Q_r \quad (21)$$

$$\frac{dT_1}{dt} = 0 = k_{i,22}M_2C_2 - (k_{2,21}M_1 + k_{2,22}M_2)T_1 - (k_{\text{CTA},22}\text{CTA} + k_{\beta,22} + k_{da,2} + s)T_1 \quad (22)$$

$$\frac{dT_r}{dt} = 0 = k_{2,22}M_2(T_{r-1} - T_r) + k_{2,12}M_2Q_{r-1} - k_{2,21}M_1T_r - (k_{\text{CTA},22}\text{CTA} + k_{\beta,22} + k_{da,2} + s)T_r \quad (23)$$

In the above equations, the Greek letters stand for the moments of different populations, defined as follows:

- λ_j *j*th moment of the dead polymers with terminal double-bond ended with monomer 1.
- σ_j jth moment of the dead polymers with terminal double-bond ended with monomer 2.
- μ_j *j*th moment of the dead polymers with saturated chain end (see Appendix 1).
- η_j *j*th moment of the living polymer chains made on the LCB catalyst ended with monomer 1.

- Ψ_j jth moment of the living polymer chains made on the LCB catalyst ended with monomer 2.
- γ_j *j*th moment of living polymer chains made on the linear catalyst, ended with monomer 1.
- au_j jth moment of living polymer chains made on the linear catalyst, ended with monomer 2.

where these moments are defined by the following equations:

$$\lambda_{j} = \sum_{r=1}^{\infty} \sum_{i=0}^{\infty} (r \cdot i)^{j} D_{1,r,i}^{=}$$
(24)

$$\sigma_{j} = \sum_{r=1}^{\infty} \sum_{i=0}^{\infty} (r \cdot i)^{j} D_{2,r,i}^{=}$$
(25)

$$\mu_{j} = \sum_{r=1}^{\infty} \sum_{i=0}^{\infty} (r \cdot i)^{j} D_{r,i}$$
(26)

$$\eta_j = \sum_{r=1}^{\infty} \sum_{i=0}^{\infty} (r \cdot i)^j P_{r,i}$$
(27)

$$\Psi_{j} = \sum_{r=1}^{\infty} \sum_{i=0}^{\infty} (r \cdot i)^{j} S_{r,i}$$
(28)

$$\gamma_j = \sum_{r=1}^{\infty} r^j Q_r \tag{29}$$

$$\tau_j = \sum_{r=1}^{\infty} r^j T_r \tag{30}$$

APPENDIX 2

Moment Equations:

Zeroth Moments

Dead chains with terminal double bonds:

$$\begin{aligned} \frac{d\lambda_0}{dt} &= 0 = k_{\beta,11}\eta_0 + k_{\beta,21}\gamma_0 - (k_{p\text{LCB},11}\eta_0 \\ &+ k_{p\text{LCB},21}\Psi_0 + s)\lambda_0 \end{aligned} (31)$$

$$\frac{d\sigma_0}{dt} = 0 = k_{\beta,12}\Psi_0 + k_{\beta,22}\tau_0 - (k_{p\text{LCB},12}\eta_0 + k_{p\text{LCB},22}\Psi_0 + s)\sigma_0 \quad (32)$$

Dead chains with saturated chain end:

$$\begin{aligned} \frac{d\mu_0}{dt} &= 0 = (k_{\text{CTA},11}\eta_0 + k_{\text{CTA},12}\Psi_0 \\ &+ k_{\text{CTA},21}\gamma_0 + k_{\text{CTA},22}\tau_0)\text{CTA} + k_{da,1}(\Psi_0 + \eta_0) \\ &+ k_{da,2}(\gamma_0 + \tau_0) - s\mu_0 \quad (33) \end{aligned}$$

Living chains with LCB:

$$\begin{aligned} \frac{d\eta_0}{dt} &= 0 = k_{i,11} C_1 M_1 - k_{1,12} M_2 \eta_0 \\ &+ k_{1,21} M_1 \Psi_0 - k_{p\text{LCB},12} \eta_0 \sigma_0 + k_{p\text{LCB},21} \Psi_0 \lambda_0 \\ &- (k_{\text{CTA},11} \text{CTA} + k_{\beta,11} + k_{da,1} + s) \eta_0 \quad (34) \end{aligned}$$

$$\frac{d\Psi_0}{dt} = 0 = k_{i,12}C_1M_2 + k_{1,12}M_2\eta_0$$

= k = M \Psi_1 + k_2 = 2 P_0 \Psi_2 - k_2 = 2 P_0 \Psi_2

$$- (k_{\text{CTA},12}\text{CTA} + k_{\beta,11} + k_{da,1} + s)\Psi_0 \quad (35)$$

Linear living chains:

$$\frac{d\gamma_0}{dt} = 0 = k_{i,21}C_2M_1 - k_{2,12}M_2\gamma_0 + k_{2,21}M_1\tau_0 - (k_{\text{CTA},21}\text{CTA} + k_{\beta,21} + k_{da,2} + s)\gamma_0$$
(36)

$$\frac{d\tau_0}{dt} = 0 = k_{i,22}C_2M_2 + k_{2,12}M_2\gamma_0 - k_{2,21}M_1\tau_0 - (k_{\text{CTA},22}\text{CTA} + k_{\beta,22} + k_{da,2} + s)\tau_0 \quad (37)$$

First Moments: Dead chains with terminal double bonds:

$$\frac{d\lambda_{1}}{dt} = k_{\beta,11}\eta_{1} + k_{\beta,21}\gamma_{1} - (k_{p\text{LCB},11}\eta_{0} + k_{p\text{LCB},21}\Psi_{0} + s)\lambda_{1} \quad (38)$$

$$\begin{aligned} \frac{d\sigma_1}{dt} &= k_{\beta,12} \Psi_1 + k_{\beta,22} \tau_1 \\ &- (k_{p\text{LCB},12} \eta_0 + k_{p\text{LCB},22} \Psi_0 + s) \sigma_1 \quad (39) \end{aligned}$$

Dead chains with saturated chain end:

$$\frac{d\mu_{1}}{dt} = 0 = (k_{\text{CTA},11}\eta_{1} + k_{\text{CTA},12}\Psi_{1} + k_{\text{CTA},21}\gamma_{1} + k_{\text{CTA},22}\tau_{1})\text{CTA} + k_{da,1}(\Psi_{1} + \eta_{1}) + k_{da,2}(\gamma_{1} + \tau_{1}) - s\mu_{1} \quad (40)$$

Living chains with LCB:

$$\begin{aligned} \frac{d\eta_1}{dt} &= 0 = k_{i,11}C_1M_1 + k_{1,11}M_1\eta_0 \\ &- k_{1,12}M_2\eta_1 + k_{1,21}M_1(\Psi_1 + \Psi_0) - k_{p\text{LCB},12}\eta_1\sigma_0 \\ &+ k_{p\text{LCB},11}\eta_0\lambda_1 + k_{p\text{LCB},21}(\Psi_1\lambda_0 + \Psi_0\lambda_1) \\ &- (k_{\text{CTA},11}\text{CTA} + k_{\beta,11} + k_{da,1} + s)\eta_1 \quad (41) \end{aligned}$$

$$\begin{aligned} a_{l} &+ k_{1,22}M_{2}\Psi_{0} + k_{1,12}M_{2}(\eta_{1} + \eta_{0}) - k_{p\text{LCB},21}\Psi_{1}\lambda_{0} \\ &+ k_{p\text{LCB},22}\Psi_{0}\sigma_{1} + k_{p\text{LCB},12}(\eta_{1}\sigma_{0} + \eta_{0}\sigma_{1}) \\ &- (k_{\text{CTA},12}\text{CTA} + k_{\beta,12} + k_{da,1} + s)\Psi_{1} \quad (42) \end{aligned}$$

Linear living chains:

$$\frac{d\gamma_1}{dt} = 0 = k_{i,21}C_2M_1 + k_{2,11}M_1\gamma_0$$
$$-k_{2,12}M_2\gamma_1 + k_{2,21}M_1(\tau_1 + \tau_0)$$
$$-(k_{\text{CTA},21}\text{CTA} + k_{\beta,21} + k_{da,2} + s)\gamma_1 \quad (43)$$

$$\begin{aligned} \frac{d\tau_1}{dt} &= 0 = k_{i,22} C_2 M_2 - k_{2,21} M_1 \tau_1 \\ &+ k_{2,22} M_2 \tau_0 + k_{2,12} M_2 (\gamma_1 + \gamma_0) \\ &- (k_{\text{CTA},22} \text{CTA} + k_{\beta,22} + k_{da,2} + s) \tau_1 \quad (44) \end{aligned}$$

Second Moments

Dead chains with terminal double bonds:

$$\begin{aligned} \frac{d\lambda_2}{dt} &= 0 = k_{\beta,11}\eta_2 + k_{\beta,21}\gamma_2 \\ &- (k_{p\text{LCB},11}\eta_0 + k_{p\text{LCB},21}\Psi_0 + s)\lambda_2 \quad (45) \end{aligned}$$

$$\frac{d\sigma_2}{dt} = 0 = k_{\beta,12}\Psi_2 + k_{\beta,22}\tau_2 - (k_{p\text{LCB},12}\eta_0 + k_{p\text{LCB},22}\Psi_0 + s)\sigma_2 \quad (46)$$

Dead chains with saturated chain end:

$$\begin{aligned} \frac{d\mu_2}{dt} &= 0 = (k_{\text{CTA},11}\eta_2 + k_{\text{CTA},12}\Psi_2 \\ &+ k_{\text{CTA},21}\gamma_2 + k_{\text{CTA},22}\tau_2)\text{CTA} + k_{da,1}(\Psi_2 + \eta_2) \\ &+ k_{da,2}(\gamma_2 + \tau_2) - s\mu_2 \quad (47) \end{aligned}$$

Living chains with LCB:

$$\begin{split} \frac{d\eta_2}{dt} &= 0 = k_{i,11}C_1M_1 - k_{1,12}M_2\eta_2 + k_{1,11}M_1 \\ &\times (2\eta_1 + \eta_0) + k_{1,21}M_1(\Psi_2 + 2\Psi_1 + \Psi_0) \\ &- k_{p\text{LCB},12}\eta_2\sigma_0 + k_{p\text{LCB},11}(2\eta_1\lambda_1 + \eta_0\lambda_2) \\ &+ k_{p\text{LCB},21}(\Psi_2\lambda_0 + 2\Psi_1\lambda_1 + \Psi_0\lambda_2) \\ &- (k_{\text{CTA},11}\text{CTA} + k_{\beta,11} + k_{da,1} + s)\eta_2 \quad (48) \end{split}$$

$$\begin{aligned} \frac{d\Psi_2}{dt} &= 0 = k_{i,12}C_1M_2 - k_{1,21}M_1\Psi_2 + k_{1,22}M_2 \\ &\times (2\Psi_1 + \Psi_0) + k_{1,12}M_2(\eta_2 + 2\eta_1 + \eta_0) \\ &- k_{p\text{LCB},21}\Psi_2\lambda_0 + k_{p\text{LCB},12}(\eta_2\sigma_0 + 2\eta_1\sigma_1 \\ &+ \eta_0\sigma_2) + k_{p\text{LCB},22}(2\Psi_1\sigma_1 + \Psi_0\sigma_2) \\ &- (k_{\text{CTA},12}\text{CTA} + k_{\beta,12} + k_{da,1} + s)\Psi_2 \end{aligned}$$
(49)

Linear living chains:

$$\begin{aligned} \frac{d\gamma_2}{dt} &= 0 = k_{i,21}C_2M_1 - k_{2,12}M_2\gamma_2 \\ &+ k_{2,11}M_1(2\gamma_1 + \gamma_0) + k_{2,21}M_1(\tau_2 + 2\tau_1 + \tau_0) \\ &- (k_{\text{CTA},21}\text{CTA} + k_{\beta,21} + k_{da,2} + s)\gamma_2 \quad (50) \end{aligned}$$

$$\begin{aligned} \frac{d\tau_2}{dt} &= 0 = k_{i,22}C_2M_2 - k_{2,21}M_1\tau_2 \\ &+ k_{2,22}M_2(2\tau_1 + \tau_0) + k_{2,12}M_2(\gamma_2 + 2\gamma_1 + \gamma_0) \\ &- (k_{\text{CTA},22}\text{CTA} + k_{\beta,22} + k_{da,2} + s)\tau_2 \quad (51) \end{aligned}$$