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Global Parametric Identifiability of Mechanistic Models in Chain Polymerization

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Abstract—Mechanistic models of chain homopolymerization systems in isothermal batch reactors are analyzed in terms of their global parametric identifiability with respect to state-of-art measurements. The analyses include identifiability of the individual parameters (reaction rate constants) from the measurements and distinguishability of models that arise from different reaction networks. Particular systems of interest are the high-temperature batch chain homopolymerization systems. Advantages of adding spectroscopic measurements to conventional (e.g., gravimetric and chromatographic) measurements in parameter estimation studies are also discussed.

I. INTRODUCTION

Recent efforts in the modeling and monitoring of polymerization reactors have been focused on understanding the underlying reaction mechanisms in broader ranges of process operation. For example, such efforts have been motivated by the increasing average temperature used in industrial polymerization reactors (e.g., batch chain-polymerization reactor for acrylics [1] and continuous chain-polymerization reactor for styrene [2]). Broadening the range of process operations often leads to increasing complexities in the underlying polymerization chemistry (e.g., in alkyl acrylate polymerization at 25–140 °C [3]). The added complexity requires one to revisit/re-evaluate models that were developed in the narrower range of process operation, and subsequently, obtain a more representative set of reaction mechanisms (reaction network) and the corresponding parameter (rate constant) values.

The parameter estimation problem has been formulated as follows. Given a set of process measurements, postulate a set of reaction mechanisms and estimate the corresponding set of parameters. While such formulation may seem straight-forward, the simultaneous parameter estimation is often hindered by (i) limited number and type of available measurements, (ii) limited knowledge of dominant reaction mechanisms, and (iii) the obtainment of more than one set of parameters that give comparable model predictions. Hence, what at first seems to be a simple parameter estimation problem is also a kinetic model identification problem. The problem is inherently complex, as one needs

to simultaneously consider the nature of the measurements (outputs), the underlying polymerization chemistry, the modeling techniques, and all the elements of the parameter estimation problem (e.g., optimization/search algorithms [4], optimization problem formulation [5]). A more comprehensive treatment of the problem has been called *design of experiments* [6], where the quality (e.g., sampling frequency) of output measurements and the type of input sequences are also of interest. Often times, estimates are solely based on available (conventional) measurements (e.g., in polymerization of styrene [7] and methyl methacrylate [8]). Currently, estimates are based on both advanced and conventional measurements (e.g., in high-temperature acrylates polymerization [9], [10]). Spectroscopic measurements help reveal characteristic polymer chain structures that are formed by specific reactions.

What is not always understood is how such inclusion help alleviate the parameter estimation or kinetic model identification problem. Therefore, this question brings to light other questions such as (i) whether a unique set of parameter values can be inferred from the available measurements (e.g., parametric identifiability [11], parametric observability [12], [13]) and (ii) how sensitive a measurement is to a parameter (e.g., sensitivity analyses [14]). Recent case studies mostly deal with biological/biochemical systems [15], [16], and a few with catalytic chemical systems [17], [18]. Several methods for analyzing identifiability have been put forth, they include; analyses of explicit solutions through series expansions [11], analyses of the state isomorphism matrix [11], [16] and analyses of the linearized structures of the output (or input-output) functions through differential algebra manipulations [19], [20]

Motivated by the need to understand the nature of parametric identifiability, particularly in relevance to kinetic model identification and parameter estimation in polymerization systems, this study aims to (i) analyze the degree of identifiability of the individual parameters (reaction rate constants) from state-of-art measurements [21] and (ii) assess the distinguishability of process models that arise from different reaction networks. Chain homopolymerization systems considered in this study are those that represent the high-temperature polymerization kinetics of alkyl acrylates.

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II. SCOPE AND PRELIMINARIES

This section describes the scope of this study and reviews the notions of local and global identifiability of model structure and model parameter, and distinguishability of model structures.

A. Local and Global Identifiability of Model Parameter and Model Structure

Consider the class of processes that can be represented by a parameterized non-linear state-space model of the form:

$$M(\theta) : \begin{cases} \dot{x} &= f(x, \theta, u) \\ y &= h(x, \theta, u) \end{cases} \quad (1)$$

where $x = [x_1 \cdots x_n]^T$ denotes the vector of model state variables, $\theta = [\theta_1 \cdots \theta_l]^T$ denotes the vector of model parameters, $u = [u_1 \cdots u_p]^T$ denotes the vector of model inputs, and $y = [y_1 \cdots y_m]^T$ denotes the vector of model outputs. The vector of output measurements is represented by $\hat{y} = [\hat{y}_1 \cdots \hat{y}_m]^T$. It is assumed that continuous measurements of the outputs are available; that is, $\hat{y} = \hat{y}(t)$.

Model parameter values are commonly obtained by solving the least squared-error (non-linear regression) problem:

$$\min_{\theta} \sum_{i=1}^N \int_0^T [h_i(x, \theta, u) - \hat{y}_i(t)]^2 dt \quad (2)$$

Definition 1 [22]: A model structure is *locally identifiable* from a given set of output measurements, $\hat{y}_1(t), \dots, \hat{y}_m(t)$, generated by the vector of parameter values $\hat{\theta}$, if $\theta = \hat{\theta}$ is a *local* minima of (2). The *model structure* is *globally identifiable*, if $\theta = \hat{\theta}$ is a *global* minima of (2). In other words, if the model is not identifiable, then there are more than one parameter vectors that correspond to exactly the same input-output behavior, and it is impossible to eliminate them from the data alone.

Remark 1: The *model structure* generally refers to the vector function $f(x, \theta, u)$ which represents analytical relationships between model states, model parameters and model inputs.

Remark 2: The notion of *structural identifiability* is associated with the nature of the solution to the parameter estimation problem. Hence in this study the notion of *parametric identifiability* is interchangeably used in place of *structural identifiability*.

B. Distinguishability of Model Structures

Definition 2 [11]: A model structure, $\tilde{M}(\cdot)$, is distinguishable from a model structure, $M(\cdot)$, if and only if for almost any parameter vector value, $\hat{\theta}$, there is no other parameter vector value, θ , such that

$$\tilde{M}(\hat{\theta}) \equiv M(\theta) \quad (3)$$

where M denotes the *model structure*, and (3) reads $M(\hat{\theta})$ has the same input-output behavior as $M(\theta)$. In other words, if $\tilde{M}(\cdot)$ is not distinguishable from $M(\cdot)$, then there is no way to discover from experimental data that the structure $M(\cdot)$ of the model does not correspond to that $M(\cdot)$ of the process that has generated the data.

C. Scope of the Study

In this study, we limit the scope to the special form of the model of (1):

$$M(\theta) : \begin{cases} \dot{x} &= \theta f(x) \\ y &= h(x) \end{cases} \quad (4)$$

where θ is a parameter matrix and $m = n$. It is assumed that the model outputs are not redundant; that is, the $n \times n$ matrix

$$\frac{\partial}{\partial x} h(x)$$

is nonsingular locally. Then it is possible to write:

$$G(y) = Hx$$

where H is a constant nonsingular $n \times n$ matrix, and the states can be expressed in terms of the outputs:

$$x = H^{-1}G(y)$$

The model in terms of the outputs takes the form:

$$\frac{d}{dt} [H^{-1}G(y)] = \theta f(H^{-1}G(y)) \quad (5)$$

Then linear regression can be used to estimate the parameter matrix [19]. The parameter matrix θ will be unique (model will be globally identifiable), if the right hand side of equation (5) depends on elements of θ .

III. CHALLENGES IN FREE-RADICAL POLYMERIZATION

Current issues in mechanistic models for free radical polymerization chemistry include:

- Measurements of the concentration of intermediate radicals are not available, as the intermediate radicals exist in very low concentrations and have very short life time.
- Batch free-radical models are usually not in the form of (4); the optimization problem of the parameter estimation is non-convex.
- Role of measurements on parametric identifiability is not well understood yet.
- More than one postulated network is able to capture the dynamics of a given set of measurements; more than one set of parameters is able to capture the given set of measurements.

Before carrying out polymerization and collecting data on the reactor, one should check to see if there is any possibility of selecting the best model structure and estimating uniquely its parameters from the experiments considered, irrespective of the quality of the experimental data. To this end, the global identifiability of mechanistic models with different sets of measurements and the distinguishability of globally identifiable model structures are assessed. A review of current state-of-art on-line measurements for polymerization reactors can be found in [21].

TABLE I
POLYMERIZATION REACTION NETWORKS FOR
INITIATION-PROPAGATION-TERMINATION SCHEME

R1		R2	
I	$\xrightarrow{k_d}$ 2R	I	$\xrightarrow{k_d}$ 2R
R + M	$\xrightarrow{k_p}$ R	R + M	$\xrightarrow{k_p}$ R
2R	$\xrightarrow{k_t}$ D	2R	$\xrightarrow{k_t}$ 2D + TDB

A. Example 1

Consider a polymerization system in which only the primary chain polymerization reactions take place; i.e., chain initiation, chain propagation and chain termination by combination (reaction network R1 in Table 1). Using species mass balances, one can develop the chain-polymerization batch-reactor model:

$$\begin{aligned}
 \dot{x}_1 &= -\theta_1 x_1, & x_1(0) &= x_{1,0} \\
 \dot{x}_2 &= -\theta_2 x_2 x_4, & x_2(0) &= x_{2,0} \\
 \dot{x}_3 &= \theta_3 x_4^2, & x_3(0) &= 0 \\
 \dot{x}_4 &= \theta_1 x_1 - \theta_3 x_4^2, & x_4(0) &= 0 \\
 y_1 &= x_1 \\
 y_2 &= 1 - \frac{x_2}{x_{2,0}} \\
 y_3 &= \frac{x_{2,0} - x_2}{x_3}
 \end{aligned}$$

where $x = [x_1 \ x_2 \ x_3 \ x_4]^T = [[I] \ [M] \ [D] \ [R]]^T$ is the vector of state variables, $\theta = [\theta_1 \ \theta_2 \ \theta_3]^T = [k_d \ k_p \ k_t]^T$ is the vector of parameters, and $y = [y_1 \ y_2 \ y_3]^T = [[I] \ x_m \ M_n/M_m]^T$ is the vector of measurements. Invoking quasi steady state assumption (QSSA) for the molar concentration of radicals, x_4 , and writing the states in terms of the outputs, we obtain:

$$\frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} -\theta_1 & 0 \\ 0 & -\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \\ \theta_1 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ x_1^{0.5} x_2 \end{bmatrix}$$

$$G(y) = \begin{bmatrix} y_1 \\ x_{2,0}(1 - y_2) \\ x_{2,0} \frac{y_2}{y_3} \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix}$$

The following observations can be made:

- The parameters θ_1 and $\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$ are globally identifiable from the set of measurements.
- The individual parameters of θ_2 and θ_3 are not identifiable from the set of measurements.
- Inclusion of measurement of y_3 does not improve the parametric identifiability of the system.

Considering the above observations, one can experimentally determine the globally identifiable lumped parameters, and not rely on the measurement of number-average molecular weight (M_n) on improving the quality of the parameter estimates. Also note that the measurement of y_1 (concentration of initiator) is a measurement where the solution to the globally identifiable parameter θ_1 and lumped parameter $\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$ are dependent upon.

B. Example 2

One may also consider a reaction network that is the same as the above, except for the chain termination mechanism (reaction network R2 in Table 1). Such a case is considered when one is not certain of the path by which the propagating chain terminates. To our advantage, terminal double bonds (TDBs) are created whenever the chain termination by disproportionation occurs. Therefore, the TDBs can be used as a measure of how often (reaction rate constant) the chain termination by disproportionation occurs. The structure of TDB is typically measured by using proton nuclear magnetic spectroscopy ($^1\text{H-NMR}$) [3], [23], [10]. By using the same modeling approach we arrive at the following model:

$$\begin{aligned}
 \dot{x}_1 &= -\theta_1 x_1, & x_1(0) &= x_{1,0} \\
 \dot{x}_2 &= -\theta_2 x_2 x_4, & x_2(0) &= x_{2,0} \\
 \dot{x}_3 &= 2\theta_3 x_4^2, & x_3(0) &= 0 \\
 \dot{x}_4 &= \theta_1 x_1 - \theta_3 x_4^2, & x_4(0) &= 0 \\
 \dot{x}_5 &= \theta_3 x_4^2, & x_5(0) &= 0 \\
 y_1 &= x_1 \\
 y_2 &= 1 - \frac{x_2}{x_{2,0}} \\
 y_3 &= \frac{x_{2,0} - x_2}{x_3} \\
 y_4 &= \frac{x_5}{x_{2,0} - x_2}
 \end{aligned} \tag{6}$$

where $x = [x_1 \ x_2 \ x_3 \ x_4]^T = [[I] \ [M] \ [D] \ [R] \ [TDB]]^T$ is the vector of state variables, $\theta = [\theta_1 \ \theta_2 \ \theta_3]^T = [k_d \ k_p \ k_t]^T$ is the vector of parameters, and $y = [y_1 \ y_2 \ y_3 \ y_4]^T = [[I] \ x_m \ M_n/M_m \ TDB]^T$ is the vector of measurements. Making QSSA for the molar concentration of the intermediate radicals, x_4 , we obtain:

$$\frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_5 \end{bmatrix} = \theta \begin{bmatrix} x_1 \\ x_1^{0.5} x_2 \\ x_3 \\ x_5 \end{bmatrix}$$

where

$$\theta = \begin{bmatrix} -\theta_1 & 0 \\ 0 & -\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \\ 2\theta_1 & 0 \\ \theta_1 & 0 \end{bmatrix}$$

$$G(y) = \begin{bmatrix} y_1 \\ x_{2,0}(1-y_2) \\ x_{2,0}\frac{y_2}{y_3} \\ x_{2,0}y_2y_4 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_5 \end{bmatrix}$$

Note that the two models are indistinguishable from the measurements and the addition of the spectroscopic measurement of TDB does not improve the parametric identifiability of the system. Such prior knowledge is useful as the measurement of TDB requires a time-consuming procedure and is not always obtainable on-line. It should also be noted, however, that the experimental evidence of the existence of TDBs does suggest that the network R2 is the more accurate description of the system.

IV. GLOBAL PARAMETRIC IDENTIFIABILITY OF CHAIN HOMOPOLYMERIZATION SYSTEMS

Considered here are models that are postulated for homopolymerization systems which show polymer chain branch formations. Based on current NMR techniques, short- and long-chain branches are not always experimentally distinguishable [23]. Two reaction networks are considered. The first one attributes branching formation to the preceding intra-molecular chain transfer reaction (reaction network R3 in Table 2), and the second reaction network attributes the branching formation to the preceding inter-molecular chain transfer (reaction network R4 in Table 2). In the reaction network R1, short chain branches (SCB) are formed through the intra-molecular chain transfer (backbiting) followed by propagation of the tertiary radical (Q). While in the reaction network R2, the long chain branches (LCB) are formed through the inter-molecular chain transfer (chain transfer to polymer) followed by the propagation of the tertiary radical (P). The two reaction networks are typical representations of how chain branches are formed. From experimental measurements, it is difficult to distinguish one reaction network from the other. Currently, branch quantities are determined through carbon nuclear magnetic spectroscopy (^{13}C -NMR) [3], [23], [10]. Often times, both reaction networks can capture the dynamics of the concentration of chain branches.

A. Example 3

Similar to Examples 1 and 2, based on species mass balances, we can develop an isothermal chain-polymerization batch-reactor model [10]:

$$\begin{aligned} \dot{x}_1 &= -\theta_1 x_1, & x_1(0) &= x_{1,0} \\ \dot{x}_2 &= -\theta_2 x_2 x_4 - \theta_5 x_2 x_5, & x_2(0) &= x_{2,0} \\ \dot{x}_3 &= \theta_3 x_4^2, & x_3(0) &= 0 \\ \dot{x}_4 &= 2\theta_1 x_1 - \theta_4 x_4 + \theta_5 x_2 x_5 - 2\theta_3 x_4^2, & x_4(0) &= 0 \\ \dot{x}_5 &= \theta_4 x_4 - \theta_5 x_2 x_5, & x_5(0) &= 0 \\ \dot{x}_6 &= \theta_5 x_2 x_5, & x_6(0) &= 0 \end{aligned}$$

(7)

TABLE II
POLYMERIZATION REACTION NETWORKS FOR
INITIATION-PROPAGATION-TRANSFER TO POLYMER-TERMINATION
SCHEME

R3		R4	
I	$\xrightarrow{k_d} 2R$	I	$\xrightarrow{k_d} 2R$
R + M	$\xrightarrow{k_p} R$	R + M	$\xrightarrow{k_p} R + \text{TC}$
2R	$\xrightarrow{k_t} D$	2R	$\xrightarrow{k_t} D$
R	$\xrightarrow{k_{bb}} Q$	R + TC + D	$\xrightarrow{k_{tp}} P$
Q + M	$\xrightarrow{k_{pq}} R + \text{SCB}$	P + M	$\xrightarrow{k_{pp}} R + \text{TC} + \text{LCB}$

$$\begin{aligned} y_1 &= x_1 \\ y_2 &= 1 - \frac{x_2}{x_{2,0}} \\ y_3 &= \frac{x_{2,0} - x_2}{x_3} \\ y_4 &= \frac{x_6}{x_{2,0} - x_2} \end{aligned}$$

where $x = [x_1 \ x_2 \ x_3 \ x_4 \ x_5 \ x_6]^T = [[I] \ [M \ D] \ [R] \ [Q] \ [SCB]]^T$ is the vector of state variables, $\theta = [\theta_1 \ \theta_2 \ \theta_3 \ \theta_4 \ \theta_5]^T = [k_d \ k_p \ k_t \ k_{bb} \ k_{pq}]^T$ is the vector of parameters, and $y = [y_1 \ y_2 \ y_3 \ y_4]^T = [[I] \ x_m \ M_n/M_m \ SCB]^T$ is the vector of measurements. Again, making QSSA for the concentration of free radicals, we obtain:

$$\frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_6 \end{bmatrix} = \theta \begin{bmatrix} x_1 \\ x_1^{0.5} x_2 \\ x_1^{0.5} \end{bmatrix}$$

where

$$\theta = \begin{bmatrix} -\theta_1 & 0 & 0 \\ 0 & -\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} & -\theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \\ \theta_1 & 0 & 0 \\ 0 & 0 & \theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \end{bmatrix}$$

$$G(y) = \begin{bmatrix} y_1 \\ x_{2,0}(1-y_2) \\ x_{2,0}\frac{y_2}{y_3} \\ x_{2,0}y_2y_4 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_6 \end{bmatrix}$$

Observations:

- The parameters θ_1 , $\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$ and $\theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$ are globally identifiable from the measurements.
- The parameters θ_2 , θ_3 , and θ_4 are not identifiable from the measurements.

- The measurements y_3 and y_4 do not improve the parametric identifiability of the model.
- The parameter θ_5 does not have any effect on the measurements; it is not identifiable due to the model structure.

As in Example 2, measurement of the number-average molecular weight (y_3) does not improve the global identifiability of the model. The spectroscopic measurement of the short chain branches (SCB) also does not improve the identifiability of the model. By analyzing the parameter matrix, we can also see that the parameter θ_5 does not at all effect the set of measurements. This is contrary to the common intuition which assumes that once we have included the measurement of branch quantities (y_4) that we would obtain a more reliable measurement of the rate of branch formation (θ_5).

B. Example 4

One can also postulate a reaction network where the branch formation is attributed to the inter-molecular chain transfer to polymer (reaction network R4 in Table 2). Note that in the reaction network, TC (tertiary carbon) is not a reactive species, it is only used to represent how the rate of chain transfer to polymer reaction is governed by the number of tertiary carbons on the polymer chain. Again species mass balances lead to [10]:

$$\begin{aligned}
\dot{x}_1 &= -\theta_1 x_1, & x_1(0) &= x_{1,0} \\
\dot{x}_2 &= -\theta_2 x_2 x_4 - \theta_5 x_2 x_5, & x_2(0) &= x_{2,0} \\
\dot{x}_3 &= \theta_3 x_4^2 - \theta_4 x_4 x_6, & x_3(0) &= 0 \\
\dot{x}_4 &= 2\theta_1 x_1 - \theta_4 x_4 x_6 + \theta_5 x_2 x_5 - 2\theta_3 x_4^2, & x_4(0) &= 0 \\
\dot{x}_5 &= \theta_4 x_4 x_6 - \theta_5 x_2 x_5, & x_5(0) &= 0 \\
\dot{x}_6 &= \theta_2 x_2 x_4 - \theta_4 x_4 x_6 + \theta_5 x_2 x_5, & x_6(0) &= 0 \\
\dot{x}_7 &= \theta_5 x_5 x_2, & x_7(0) &= 0 \\
y_1 &= x_1 \\
y_2 &= 1 - \frac{x_2}{x_{2,0}} \\
y_3 &= \frac{x_{2,0} - x_2}{x_3} \\
y_4 &= \frac{x_7}{x_{2,0} - x_2}
\end{aligned} \tag{8}$$

where $x = [x_1 \ x_2 \ x_3 \ x_4 \ x_5 \ x_6]^T = [[I] \ [M] \ [D] \ [R] \ [P] \ [TC] \ [LCB]]^T$ is the vector of state variables, $\theta = [\theta_1 \ \theta_2 \ \theta_3 \ \theta_4 \ \theta_5]^T = [k_d \ k_p \ k_t \ k_{tp} \ k_{pp}]^T$ is the vector of parameters, and $y = [y_1 \ y_2 \ y_3 \ y_4]^T = [[I] \ x_m \ M_n/M_m \ LCB]^T$ is the vector of measurements. Upon the rearrangement of the output equations,

$$\frac{d}{dt} \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_7 \end{bmatrix} = \theta \begin{bmatrix} x_1 \\ x_1^{0.5} x_2 \\ x_1^{0.5} (x_2 + x_7) \end{bmatrix}$$

where

$$\theta = \begin{bmatrix} -\theta_1 & 0 & 0 \\ 0 & -\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} & \theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \\ \theta_1 & 0 & \theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \\ 0 & 0 & -\theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5} \end{bmatrix}$$

$$G(y) = \begin{bmatrix} y_1 \\ x_{2,0}(1 - y_2) \\ x_{2,0} \frac{y_2}{y_3} \\ x_{2,0} y_2 y_4 \end{bmatrix} = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_7 \end{bmatrix}$$

Observations:

- The parameters θ_1 , $\theta_2 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$, and $\theta_4 \left(\frac{\theta_1}{\theta_3}\right)^{0.5}$ are globally identifiable from the set of measurements.
- The parameters θ_2 , θ_3 , and θ_4 are not globally identifiable from the set of measurements.
- The measurements y_3 and y_4 do not improve the parametric identifiability of the system.
- The parameter θ_5 does not have any effect on the measurements; it is not identifiable due to the model structure.

Note that the dynamics of state x_6 can be represented by a combination of states x_2 and x_7 . The reaction networks R3 and R4 are therefore indistinguishable from one another from the set of outputs considered.

V. CONCLUSIONS

A class of chain-homopolymerization systems has been analyzed in terms of its global parametric identifiability. This study considers identifiability analyses as an integral part of parameter estimation efforts in polymerization systems. The advantages or disadvantages of including measurements were evaluated and presented. Globally identifiable parameters or lumped parameters were obtained, and the implications of their global identifiability properties were discussed. The study can be readily extended to more complex polymerization systems, and can also consider alternate models that are developed by different modeling techniques. The importance of the identifiability and distinguishability analyses in developing complex polymerization models is also re-emphasized, particularly for parameter estimation and modeling efforts in high-temperature polymerization systems. Lastly, the study also signifies the need for both non-redundant measurements and identifiable model structures, to avoid issues associated with different sets of models and parameters that can explain a given set of measurements.

VI. NOTATION

[A]	Concentration of species A in reactor, A = M, TDB, etc.
I	Initiator
M	Monomer

D	'Dead' polymer chain
R	'Live' polymer chain, secondary radical species
P	'Dead' polymer chain, mid-chain tertiary radical species
Q	'Dead' polymer chain, near-chain-end tertiary radical species
x_m	Monomer conversion
M_n	Number-average molecular weight
M_m	Molecular weight of monomer
TDB	Number of terminal double bonds
SCB	Number of short chain branches
LCB	Number of long chain branches
k_d	Rate constant of thermal initiator decomposition
k_p	Rate constant of propagation reactions
k_t	Rate constant of termination by combination or disproportionation reactions
k_{bb}	Rate constant of backbiting reactions (intra-molecular chain-transfer)
k_{tp}	Rate constant of chain-transfer to polymer reactions (inter-molecular chain-transfer)
k_{pq}	Rate constant of SCB formation reactions
k_{pp}	Rate constant of LCB formation reactions

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