

Worst-case and Distributional Robustness Analysis of the Full Molecular Weight Distribution During Free Radical Bulk Polymerization

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Abstract—A novel approach is proposed to quantify the effects of parameter uncertainties on state distributions in finite-time nonlinear distributed parameter systems, and this approach is applied to a free radical bulk polymerization reactor. For worst-case uncertainty descriptions, parameters are computed that result in worst-case deviations in the monomer conversion, average molecular properties, and the full molecular weight distribution. For probabilistic uncertainty descriptions, a constructive procedure is provided for computing the stochastic distribution of the state distribution. This more sophisticated robustness analysis enables a deep investigation into the effects of parameter uncertainties, control implementation uncertainties, and disturbances for systems with state distributions.

I. INTRODUCTION

Robustness analysis quantifies the effects of uncertainties on the states and/or outputs of dynamical systems. This information can be used for model-based experimental design, the synthesis of robust controllers, and for assessing whether further laboratory experiments are necessary to obtain a model accurate enough for open-loop or closed-loop control purposes. In recent years nonconservative and computationally-efficient algorithms for analyzing the robustness of nonlinear lumped and distributed parameter dynamical systems have become available for finite-time systems (e.g., see [1] and citations therein), which describe the batch and semibatch operations commonly used in the pharmaceuticals, fine chemicals, and microelectronics industries. Such algorithms have been applied to both batch crystallization [1], [2] and semiconductor processes [3], in which the uncertainty descriptions were quantified from experimental data. Although the processes were distributed parameter systems, the analysis was applied to lumped variables, which enabled the interpretation of results in the same manner as for lumped parameter systems.

This paper considers the robustness analysis of distributed parameter systems in which there are states that take the form of a distribution. Such processes involving a state distribution are ubiquitous in the biomedical (e.g., cell populations), pharmaceuticals (e.g., drugs, proteins, peptides), photographic (e.g., silver halides), agricultural (e.g., solid fertilizers), automotive (e.g., combustion gas-liquid mixtures), military (rocket propellants), and chemical industries, as well as in the environment (dust, cloud, and

pollutant particles). This paper shows, for the first time, how to analyze the robustness for batch and semibatch processes in which some of the *main states take the form of a distribution*. More specifically, it is shown how to compute worst-case deviations and probability density functions of state distributions, and how to interpret this information to provide deep insights into the fundamental nature of how uncertainties affect the state distributions. The application problem is free radical polymerization, in which the full molecular weight distribution (MWD) is considered.

The paper begins with a summary of worst-case and stochastic uncertainty analysis for finite-time nonlinear lumped and distributed parameter dynamical systems, presented in a general enough form to include the effects of disturbances, measurement noise, and parameter and control implementation uncertainties. A brief summary of the free radical polymerization model is presented next. This includes the modeling of the batch process by the method of moments and direct solution of the discrete population balance equation. Optimal control trajectories are described. Worst-case and distributional analysis is applied to free radical polymerization, followed by discussion and conclusions.

II. UNCERTAINTY ANALYSIS

This section summarizes methods to compute both worst-case deviations and distributions for a state or output y due to uncertainties in the model parameters θ and control trajectory u , and describes how to extend these methods to analyze the robustness of state distributions. The vector of model parameters can be augmented to include disturbances, measurement noise, and perturbations in the control trajectory.

A. Uncertainty Description

The vector of parameter uncertainties is

$$\theta = \hat{\theta} + \delta\theta \quad (1)$$

in which $\hat{\theta}$ is the nominal parameter vector of dimension $n \times 1$ and $\delta\theta$ is a perturbation about the nominal parameter value.

A general uncertainty representation can be defined in terms of the Hölder p -norm. This general description includes the hyperellipsoid on the model parameters, as produced by most model identification algorithms [4],

$$\varepsilon_\theta = \left\{ \theta : (\theta - \hat{\theta})^T \mathbf{V}_\theta^{-1} (\theta - \hat{\theta}) \leq r^2(\alpha) \right\}, \quad (2)$$

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where \mathbf{V}_θ is an $n \times n$ positive definite covariance matrix, α is the specified confidence level, and r is the distribution function.

The set of parameters and control trajectories including Hölder norm-bounded perturbations $\delta\theta$ is represented as

$$\varepsilon_\theta = \left\{ \theta : \theta = \hat{\theta} + \delta\theta, \|\mathbf{W}_\theta \delta\theta\|_p \leq 1 \right\} \quad (3)$$

where \mathbf{W}_θ is a positive definite weighting matrix with dimension $n \times n$. The uncertainty description (2) can be written in the form (3) using $p = 2$ and

$$\mathbf{W}_\theta = \frac{1}{r(\alpha)} \mathbf{V}_\theta^{-1/2}. \quad (4)$$

The nominal state or output scalar, \hat{y} , is defined when the system is operated under the nominal control trajectory \hat{u} with nominal model parameters $\hat{\theta}$. The observed or true output or state, y , is realized with control trajectory $u = \hat{u} + \delta u$ and model parameters θ .

The parameter deviations and values are computed from a low-order power series expansion about the nominal control trajectory. Although the overall approach applies when there are either independent or coupled descriptions for perturbations in the parameters and control trajectories [5], to simplify the presentation, the vectors θ and u are combined to form a single vector

$$\lambda = \begin{bmatrix} \theta \\ u \end{bmatrix} \quad (5)$$

with nominal and perturbed vectors

$$\hat{\lambda} = \begin{bmatrix} \hat{\theta} \\ \hat{u} \end{bmatrix} \text{ and } \delta\lambda = \lambda - \hat{\lambda}. \quad (6)$$

Basing the robustness analysis on a first-order power series expansion results in analytic expressions for the worst-case deviations and uncertainties and analytic expressions for the distributions. Structured singular value calculations and Monte Carlo methods are required for worst-case and distributional analysis, respectively, based on higher order series expansions [1].

B. First-order Series Expansion

First consider the case where the deviation in the output δy at a fixed point in time is described by a first-order power series expansion

$$\delta y = L\delta\lambda \quad (7)$$

which is valid for small $\|\delta\lambda\|$. This equation is not as restrictive as it first appears, because such a representation can be derived as a linearization about the nominal trajectory, which is much more accurate than a linearization about a single operating point, which is typically what is done to derive a linear model for a nonlinear system. For δy differentiable in $\delta\lambda$,

$$L_i = \left. \frac{\delta y}{\delta \lambda_i} \right|_{\lambda=\hat{\lambda}} \text{ for } i = 1, \dots, n+m \quad (8)$$

The row vector L contains the sensitivities, which can be computed using finite differences [6], [7], [8], [9] or by integrating the original differential-algebraic equations augmented with an additional set of differential equations known as sensitivity equations [10], [11]. These sensitivities are computed automatically by some differential-algebraic equation solvers, even for distributed parameter systems [10], [12]. The higher order series expansions should be used when $L_i = 0$ or $\|\delta\lambda\|$ is large.

1) *Worst-case Uncertainty Analysis:* The worst-case deviation at the fixed point in time is defined by

$$\delta y_{w.c.} = \max_{\|\mathbf{W}_\lambda \delta\lambda\|_p \leq 1} |L\delta\lambda| \quad (9)$$

Analytical expressions can be derived for the worst-case deviation and the worst-case uncertainties, $\delta\lambda_{w.c.}$ (for details see [1]). The worst-case uncertainties are not unique, for example, another worst-case vector of uncertainties is obtained by multiplying by minus one. Both vectors represent the maximum output deviation $\delta y_{w.c.}$. Some of these vectors represent the worst-case increase in y and others the worst-case decrease in y .

2) *Probabilistic Uncertainty Analysis:* Consider the use of a multivariate normal distribution

$$f(\theta) = \frac{1}{\sqrt{2\pi} \det(\mathbf{V}_\theta)^{1/2}} \exp \left[-\frac{1}{2} (\theta - \hat{\theta})^T \mathbf{V}_\theta^{-1} (\theta - \hat{\theta}) \right] \quad (10)$$

to represent the uncertainty in the parameters, as is produced by most parameter estimation algorithms [4]. For a first-order series expansion (7), the normal distribution for y is

$$f(y) = \frac{1}{\sigma_y \sqrt{2\pi}} \exp \left[-\frac{(y - \hat{y})^2}{2\sigma_y^2} \right] \quad (11)$$

with the variance

$$\sigma_y^2 = L\mathbf{V}_\theta L^T. \quad (12)$$

C. Uncertainty Analysis for States Described by Distributions

Both the worst-case and probabilistic uncertainty analysis methods can be applied to a discrete state distribution, by applying the above methods to each element of the distribution. For a continuous state distribution, apply the methods to each element of a discretization of the continuous state distribution. For a probabilistic uncertainty description, the robustness results have the form of a probability density function of the state distribution, in other words, a *distribution of a distribution*. Such a distribution of a distribution is a function of time since the nominal state distribution, \mathbf{y} , and the matrix of sensitivities, \mathbf{L} , are functions of time.

To illustrate this approach for the case in which a first-order series expansion is used, consider the determination of the normal distribution for each element y_i of a state distribution \mathbf{y} :

$$f(y_i) = \frac{1}{\sigma_{y_i} \sqrt{2\pi}} \exp \left[-\frac{(y_i - \hat{y}_i)^2}{2\sigma_{y_i}^2} \right] \quad (13)$$

with the variance

$$\sigma_{y_i}^2 = L^i \mathbf{V}_\theta L^{iT} \quad (14)$$

where the superscript i on L refers to the first-order sensitivity vector for element i of the state distribution, with the matrix of sensitivities being

$$\mathbf{L} = \begin{bmatrix} \vdots \\ L^i \\ \vdots \end{bmatrix}. \quad (15)$$

This approach is illustrated through application to the molecular weight distribution in free radical polymerization.

For the worst-case analyses, a full dynamic simulation is carried out at the worst-case parameter values, to verify the accuracy of the power series expansion at those values.

III. FREE RADICAL POLYMERIZATION SIMULATION

This section describes the process model and an algorithm for its simulation.

A. Free Radical Polymerization

The reaction mechanism and the reaction rates for free radical polymerization with a single monomer and initiator are reported in Table I. The molar balances for a well-mixed batch reaction are, for initiator decomposition,

$$\frac{1}{V} \frac{d([I_2]V)}{dt} = -k_d[I_2] \quad (16)$$

free radical concentration,

$$\frac{1}{V} \frac{d([I\cdot]V)}{dt} = -k_i[I\cdot][M] + 2fk_d[I_2] \quad (17)$$

monomer concentration,

$$\frac{1}{V} \frac{d([M]V)}{dt} = -k_i[I\cdot][M] - (k_p + k_{trm})[M] \sum_{j=1}^{\infty} [P_j] \quad (18)$$

live polymer chains,

$$\frac{1}{V} \frac{d([P_1]V)}{dt} = k_i[I\cdot][M] - k_p[M][P_1] - k_{trm}[M] \left([P_1] - \sum_{j=1}^{\infty} [P_j] \right) - (k_{tc} + k_{td}) [P_1] \sum_{j=1}^{\infty} [P_j] \quad (19)$$

$$\frac{1}{V} \frac{d([P_m]V)}{dt} = k_p[M] ([P_{m-1}] - [P_m]) - k_{trm}[M][P_m] - (k_{tc} + k_{td}) [P_m] \sum_{j=1}^{\infty} [P_j] \text{ for } m = 2, \dots, n \quad (20)$$

and dead polymer chains

$$\frac{1}{V} \frac{d([D_m]V)}{dt} = k_{trm}[M][P_m] + k_{td}[P_m] \sum_{j=1}^{\infty} [P_j] + \frac{1}{2} k_{tc} \sum_{j=1}^{m-1} [P_j][P_{m-j}] \text{ for } m = 2, \dots, n. \quad (21)$$

The parameters $k_d, k_i, k_p, k_{trm}, k_{tc},$ and k_{td} are rate constants and f is the initiator efficiency. The short average lifetime ($\ll 1$ s) of an initiator radical molecule, $I\cdot$, implies that the quasi-steady state assumption can be applied:

$$\frac{1}{V} \frac{d([I\cdot]V)}{dt} = 0 \longrightarrow k_i[I\cdot][M] = 2fk_d[I_2].$$

The total concentrations of live polymer molecules and monomer are

$$[P] = \sum_{j=1}^{\infty} [P_j] \text{ and } [M] = \frac{[M_0](1-x)}{1+\varepsilon x} \quad (22)$$

where x is the conversion and

$$\varepsilon = \frac{\rho_m(T) - \rho_p(T)}{\rho_p(T)}$$

is the volume contraction factor that takes into account the density differences between the polymer and monomer. Initially, the reactor consists of pure monomer. Throughout the reaction, the volume of the reactant/product mixture changes according to

$$V = V_0(1 + \varepsilon x), \quad \frac{dV}{dt} = V_0 \varepsilon \frac{dx}{dt}.$$

B. Gel Effect

In this work, the gel effect or ‘‘Trommsdorf effect’’ is modeled using free volume correlation [13]. The void volume in a monomer/polymer solution is defined as the free volume. As the conversion increases, the free volume decreases. Established methods are implemented to account for the decrease in propagation and termination due to strong diffusion limitations. The overall termination rate, k_t , takes the form

$$k_t = k_{td} + k_{tc} = k_t^0 g_t \quad (23)$$

where

$$g_t = \begin{cases} 0.10575e^{17.15\nu_f - 0.01715(T-273.15)}, & \nu_f > \nu_{f,cr} \\ 0.23 \times 10^{-5} e^{75\nu_f}, & \nu_f \leq \nu_{f,cr} \end{cases} \quad (24)$$

and the propagation rate takes the form

$$k_p = k_p^0 g_p \quad (25)$$

$$g_p = \begin{cases} 1, & \nu_f > \nu_{f,cr} \\ 0.71 \times 10^{-4} e^{71.53\nu_f}, & \nu_f \leq \nu_{f,cr} \end{cases} \quad (26)$$

The free volume, ν_f , is defined by

$$\nu_f = \phi_m \nu_{f,m} + \phi_p \nu_{f,p} \quad (27)$$

where ϕ_m and ϕ_p is the volume fraction of monomer and polymer and the monomer $\nu_{f,m}$ and polymer $\nu_{f,p}$ free volume is defined by

$$\nu_{f,m} = 0.025 + 0.001(T - 167) \quad (28)$$

$$\nu_{f,p} = 0.025 + 0.00048(T - 387) \quad (29)$$

The critical free volume, $\nu_{f,cr}$ is defined by

$$\nu_{f,cr} = 0.1856 - 2.965 \times 10^{-4}(T - 273.15). \quad (30)$$

$I_2 \xrightarrow{k_d} 2I\cdot$	$r_d = 2fk_d[I_2]$	initiator decomposition
$I\cdot + M \xrightarrow{k_i} P_1$	$r_i = k_i[M][I\cdot]$	initiation
$P_n + M \xrightarrow{k_p} P_{n+1}$	$r_p = k_p[M][P_n]$	propagation
$P_n + M \xrightarrow{k_{trm}} D_n + P_1$	$r_{trm} = k_{trm}[M][P_n]$	monomer transfer
$P_n + P_m \xrightarrow{k_{tc}} D_{n+m}$	$r_{tc} = k_{tc}[P_m][P_n]$	termination by combination
$P_n + P_m \xrightarrow{k_{td}} D_n + D_m$	$r_{td} = k_{td}[P_m][P_n]$	termination by disproportionation

TABLE I

FREE RADICAL POLYMERIZATION MECHANISM. “[A]” REFERS TO THE CONCENTRATION OF SPECIES A.

C. Simulating the MWD Using Parallel CVODE

As the average lifetime of live polymer chains is very short, the quasi-steady state approximation (QSSA) was applied

$$\frac{1}{V} \frac{d([P_m]V)}{dt} = 0, \quad \text{for } m = 1, \dots, \infty, \quad (31)$$

which reduced the stiffness to $\sim 10^4$. This leads to the system of ordinary differential equations:

$$\frac{d[I_2]}{dt} = - \left(k_d + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} \right) [I_2] \quad (32)$$

$$\frac{dx}{dt} = \frac{2fk_d[I_2](1 + \varepsilon x)}{[M]_0} + (k_p + k_{trm})(1 - x)[P] \quad (33)$$

$$\frac{d[P]}{dt} = 2fk_d[I_2] - (k_{td} + k_{tc})\lambda_0^2 - \frac{\varepsilon\lambda_0}{1 + \varepsilon x} \frac{dx}{dt} \quad (34)$$

$$[P_1] = \frac{2fk_d[I_2] + k_{trm}[M][P]}{(k_p + k_{trm})[M] + (k_{td} + k_{tc})[P] + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt}} \quad (35)$$

$$[P_n] = \frac{k_p[M][P_{n-1}]}{(k_p + k_{trm})[M] + (k_{td} + k_{tc})[P] + \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt}} \quad (36)$$

$$[P] = \sum_{i=1}^n [P_i] = \lambda_0 \quad (37)$$

$$\begin{aligned} \frac{d[D_2]}{dt} &= k_{trm}[M][P_2] + k_{td}[P_2][P] \\ &+ \frac{1}{2}k_{tc}[P_1]^2 - \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} [D_2] \end{aligned} \quad (38)$$

$$\begin{aligned} \frac{d[D_n]}{dt} &= k_{trm}[M][P_n] + k_{td}[P_n][P] \\ &+ \frac{1}{2}k_{tc} \sum_{j=1}^{n-1} [P_j][P_{n-j}] - \frac{\varepsilon}{1 + \varepsilon x} \frac{dx}{dt} [D_n] \end{aligned} \quad (39)$$

These molar balances were directly integrated using Parallel CVODE [14]. For a more in-depth description of the architecture of the algorithm, the reader is referred to the user documentation [14] and a Ph.D. thesis [15].

Experiment	MMA (g)	BPO (g)	Initiator Concentration (wt%)
1	400.0	4.00	1.0

TABLE II

EXPERIMENTAL CONDITIONS FOR FREE RADICAL POLYMERIZATION OF METHYL METHACRYLATE AND BENZOYL PEROXIDE AT 50 °C.

IV. ROBUSTNESS ANALYSIS

Here the robustness is analyzed for the isothermal free radical polymerization of methyl methacrylate and benzoyl peroxide. The conditions used in the polymerization experiment [15] are reported in Table II. The nominal vector of kinetic parameters in this study is

$$\hat{\theta} = [f, k_{trm}, k_{td}^o, k_p^o]^T \quad (40)$$

with the nominal values fit to experimental data: $f = 0.0658$, $k_{trm} = 1.236$ L/mol·min, $k_{td}^o = 1.9735 \times 10^9$ L/mol·min, and $k_p^o = 3.354 \times 10^4$ L/mol·min [15]. A parametric uncertainty description (2) was constructed from experimental data, with the covariance matrix

$$\mathbf{V}_\theta = \begin{bmatrix} 4.83 \times 10^{-6} & -1.96 \times 10^{-4} & 1.34 \times 10^5 & -7.09 \times 10^{-2} \\ -1.96 \times 10^{-4} & 1.12 \times 10^{-2} & -5.50 \times 10^6 & 2.38 \\ 1.34 \times 10^5 & -5.50 \times 10^6 & 3.78 \times 10^{15} & -1.71 \times 10^9 \\ -7.09 \times 10^{-2} & 2.38 & -1.71 \times 10^9 & 1.10 \times 10^4 \end{bmatrix} \quad (41)$$

Here is the analysis of the robustness of the MWD to the parameter uncertainties identified from experimental data. Gel permeation chromatography was applied to an experimental reactor to determine the maximum number of equations ($n = 200,000$) needed to simulate the MWD throughout the batch runs. The MWD for an entire batch run was simulated in ~ 10 min (see Ref. [15] for details).

Using the 2-norm ($p = 2$) and setting $\mathbf{W}_\theta = 1/r(\alpha) \cdot \mathbf{V}_\theta^{-1/2}$, the worst-case variation in each D_n and the worst-case parameter vector for the first-order series expansion was computed. Because reporting the worst-case parameter vector for *each* n -mer using would take up too much space, the maximum parameter deviation

$$\delta\theta_{i,w.c.} = \max_{D_n \in [2, 2 \times 10^5]} \left| \frac{r(\alpha)}{(L^n \mathbf{V}_\theta (L^n)^T)^{1/2}} (\mathbf{V}_\theta (L^n)^T)_i \right| \quad (42)$$

is reported instead for the i^{th} element in the parameter vector, where L^n is the first-order sensitivity vector for D_n .

$\delta\theta_{i,w.c.}$				
Experiment	f	k_{trm}	$k_{td}^o \times 10^{-9}$	$k_p^o \times 10^{-4}$
1	0.0097	0.359	0.0098	0.248

TABLE III

WORST-CASE PARAMETER UNCERTAINTIES USING FIRST-ORDER SERIES EXPANSION FOR THE FULL MWD.

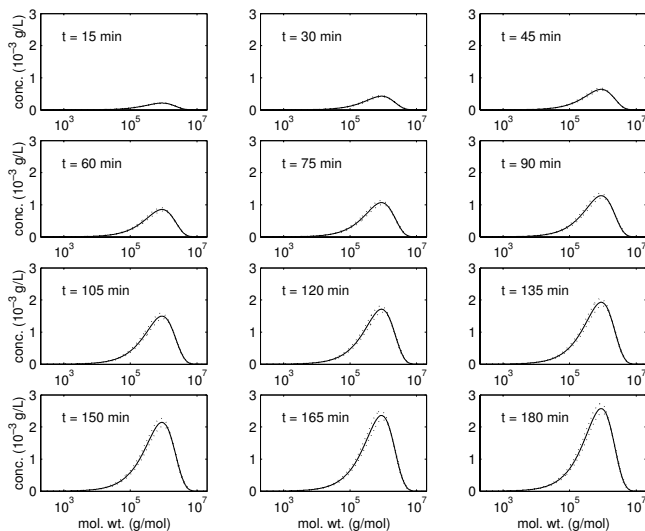


Fig. 1. Two worst-case MWDs, $\hat{y}(\dots)$, for $\alpha = 0.95$ computed using first-order analysis and the nominal MWD, $\hat{y}(-)$, (1.0 wt% BPO).

The worst-case parameters based on deviations in the MWD are reported in Table III. These worst-case parameters are very different from those computed using the method of moments (see [15]), indicating that robustness analysis based on moments of the distribution does not accurately describe the true robustness of the molecular weight distributions.

The molecular weight distributions computed from the first-order series expansion using the worst-case parameters computed for $\alpha = 0.95$ are reported in Figure 1 for Experiment 1. The effects of parameter uncertainties become larger as the batch progresses, and the results of first-order robustness analysis are consistent with the dynamic simulations.

Although the worst-case outputs and parameter vectors for varying confidence levels (i.e., $\alpha \in (0, 1)$) can be constructed using the techniques in this paper, it is much more informative to visualize the effect of model uncertainties in terms of distribution functions (13). Usually in statistical analyses the distribution function traces a single output variable during the course of the batch time. In this case, a distribution function of a molecular weight distribution is considered. This MWD distribution function has too many independent variables to be directly visualized as a function of time. However, it is possible to construct and plot distribution functions for each n -mer, individual distribution

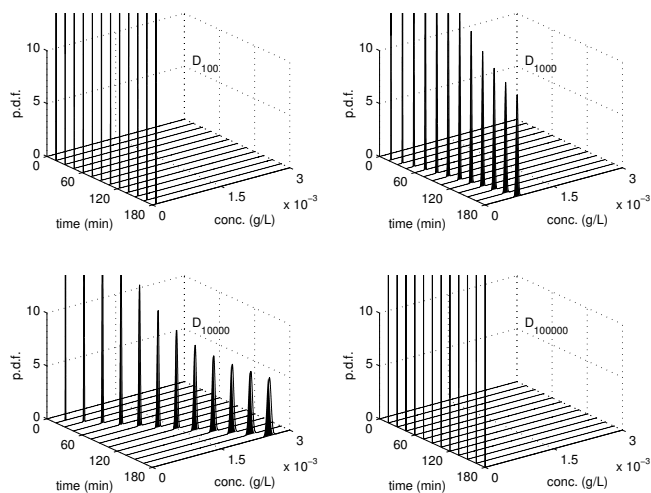


Fig. 2. Evolution of individual D_n distribution functions (1.0 wt% BPO) for $n = 10^2, 10^3, 10^4$, and 10^5 .

functions for each n -mer, D_n , for $n = 10^2, 10^3, 10^4$, and 10^5 (see Figure 2). The concentrations of D_{1000} and D_{10000} increase with time, as expected, and the variance of the distribution due to parameter uncertainties also increases. The concentrations for $n = 10^2$ and $n = 10^5$ are small throughout the batch and so are not as pronounced. The broadest distributions were observed in the molecular weight range of 10^5 - 10^6 g/mol.

It is very important to note that *the robustness analysis in terms of full MWD gives very different qualitative conclusions than robustness analysis in terms of average molecular weights*. The robustness analysis with respect to average molecular weights in Ref. [15] indicates that the effects of parameter uncertainties are fairly uniform throughout the batch, whereas the robustness analysis with respect to the full MWD indicates that the effects of parameter uncertainties significantly increase during the batch. The reason for these qualitative differences is that the average molecular weights, being averaged properties, average out the effect of parameter uncertainties. Since the true product quality variable is the full MWD, performing robustness analysis only on averaged properties such as the average molecular weights, or moments, can lead to incorrect conclusions as to the importance of parameter uncertainties on the product quality. That is, this notion of a “distribution of a distribution” to represent the effects of uncertainties on state distributions provides information on robustness for distributed parameter systems that is not obtained with the “lumped parameter” methods of robustness analysis which currently dominate the literature.

The ability to represent the effects of uncertainties on the full MWD enables a much more thorough and accurate understanding of the process and the differences between the process and its model. This greater understanding can improve the formulation of open- and closed-loop optimal control problems in which a MWD is the product quality

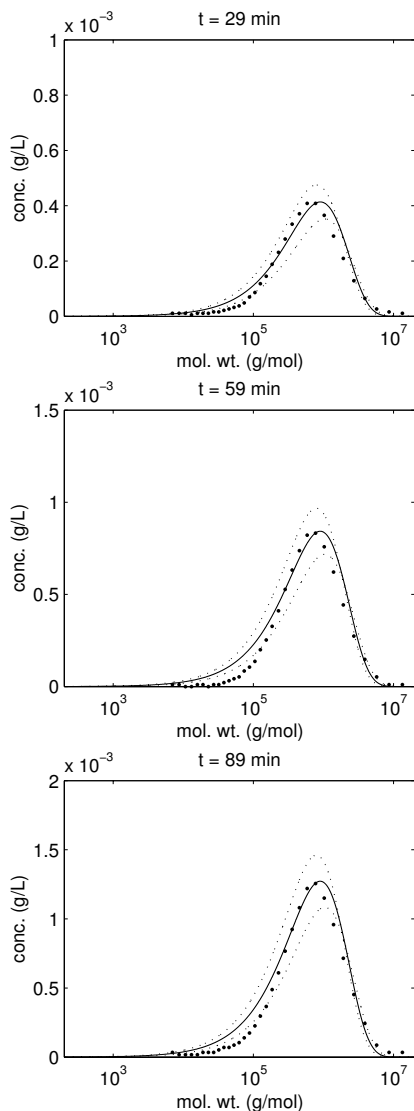


Fig. 3. Nominal MWD (solid line), experimental MWD (dots), and upper and lower bounds on the MWD computed from first-order robustness analysis applied to the 95% confidence region on the parameter uncertainties, for Experiment 1.

variable.

Figure 3 compares the upper and lower bounds on the MWD computed from first-order robustness analysis to measured MWDs [15] for the experiment reported in Table IV. The experimental MWD is mostly between the lower and upper bounds. Overall, the upper and lower bounds computed from the first-order robustness analysis are sufficiently accurate for making engineering decisions regarding the adequacy of the model quality and the accuracy of model predictions, and would be suitable for inclusion in robust optimal control algorithms.

V. CONCLUSIONS

This paper presented an approach to quantifying the robustness to uncertainties for processes with state distributions, and applied the approach to the optimal control of

Experiment	MMA (g)	BPO (g)	Initiator Concentration (wt%)
1	400.6	4.01	1.0

TABLE IV
EXPERIMENTAL CONDITIONS FOR THE FREE RADICAL
POLYMERIZATION OF METHYL METHACRYLATE AND BENZOYL
PEROXIDE AT 50°C.

free radical polymerization. It was observed that the notion of a “distribution of a distribution” to represent the effects of uncertainties on state distributions provided a more accurate evaluation of the robustness of product quality to uncertainties than obtained by the lumped-parameter methods of robustness analysis that currently dominate the literature. The robustness results were highly consistent with molecular weight distributions measured by gel permeation chromatography for an experimental polymerization reactor. Although the focus on the application was on the effects of uncertainties, the same approach applies to quantifying the effects of disturbances on state distributions. The robustness analysis results motivate their incorporation into robust optimal control algorithms for processes in which the product quality is specified in terms of state distributions.

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