Determination Of Parameters In 0-1 Emulsion Polymerization

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SUMMARY: Modeling of emulsion polymerization is a controversial subject because different models, based on contradictory assumptions, can describe the same set of experimental data. In order for the theoretical and experimental studies on emulsion polymerization to yield meaningful conclusions, the issue of parameter estimation with modeling consistency should be settled first. As a step in this direction, in this work, a dynamic nonlinear estimation approach[1] is used to determine the model parameters in a unique way and to assess the model-data consistency in the sense that the parameters are not time-varying, due to modeling errors. The proposed approach is compared with linear and nonlinear regression methods used before[2-5], and is illustrated with two examples: an interval II case with simulated experiments[3, 4], and an interval III case with experimental data[6].

Interval II System

The interval II of the 0-1 emulsion polymerization, with the first or second order exit rate mechanism, is described by two differential equations[3-5] ($\dot{c} = dc/dt$):

$$\dot{c} = A\tilde{n}, \quad \dot{\tilde{n}} = r - (2r + k)\tilde{n} \quad \text{or} \quad r - (2r + k\tilde{n})\tilde{n}; \qquad y = c, \quad [c(0), \tilde{n}(0)] = (0, 0) \qquad (1)$$

where c is the conversion, ñ is the average number of radicals, and y is the experimental measurement. Following Gilbert[4], A is given from independent experiments, and the parameter pair (r, k) must be estimated from the conversion-time data of a single experiment. In addition, the consistency of the model must be assessed in the sense that its parameters are indeed constant and not time-varying because of a modeling error. For this purpose, let us consider that the parameter pair (r, k) is estimated under the assumption that system (1) has a first-order exit rate, and that there are two sets of data: (i) in one case, there is model-data consistency because the data are indeed generated by system (1) with first-order exit rate and

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(A, r, k) = (4.3, 10, 15) 10^{-4} s^{-1}; and (ii) in another case, there is model-data inconsistency because the data are generated by system (1) with second-order exit rate and the above parameter set (A, r, k). The preceding notion of consistency is different from the one used[4] in previous studies in emulsion modeling, where self-consistency means a physicochemical foundation for the meaning and size of the parameters. Our notion of consistency must be seen as an additional tool to validate and construct understanding oriented models with physicochemical self-consistency.

Regression Methods

Let us recall the Slope and Intercept (SI) method[3,4], which amounts to finding the parameter pair (r, k) from a linear regression that, disregarding the initial data period where the number of radicals ñ approach their steady-state value, determines the slope-intercept pair associated to the limiting linear conversion-time behavior of the system. Since the first and second-order mechanisms both exhibit limiting linear behavior[3-5], the SI method provides parameter estimates that may fit the experimental data, but cannot detect the inconsistent case. As an attempt to overcome this problem, a nonlinear regression method was implemented to estimate the parameter pair (r, k) by minimizing the prediction-data error over the entire experimental time interval [0, 1000] s. In the consistent case, the parameter pair was reconstructed exactly. In the inconsistent case, the "pseudoparameter" pair (ρ*, κ*) = (1.0466, 0.516) 10^{-3} s^{-1} was obtained. In both cases the fitting reports were excellent: R^2 (squared mean error) = 0.99999. The corresponding conversion-time predictions (indistinguishable to the eye) are presented in Fig. 1, showing that the nonlinear regressor cannot detect the inconsistent case in spite of fitting the data very well.

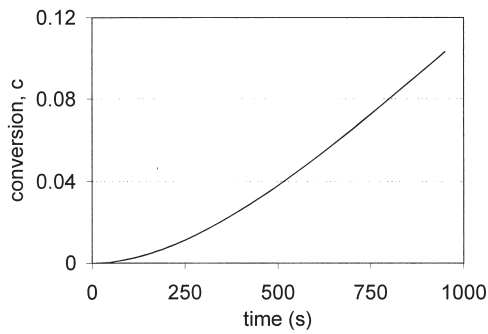

Fig. 1: Predicted conversion-time functions of the nonlinear regression scheme for the consistent (___), and inconsistent (---) cases in interval II.

Dynamic Parameter Estimation

To determine the parameter pair (r, k) with an assessment of model-data consistency, let us resort to a recently developed dynamic nonlinear state estimation design methodology[1], which adapted to our parameter problem amounts to the following steps: (i) regard the unknown parameters as dynamical states and augment the first-order exit rate candidate model (1) with two dynamic equations ($\dot{k} = 0$, and $\dot{r} = 0$); (ii) test the underlying parameter observability condition $A^3[-(2r + k) - r] \neq 0$ which is basically met in the period where the average number of radicals ñ approaches its steady-state value $\tilde{n}_s = r/(2r + k)$; and (iii) write the corresponding dynamic estimator:

$$\dot{\chi} = A\nu + g_1(y - \chi), \qquad \dot{\nu} = \rho - (2\rho + \kappa)\nu + g_2(y - \chi); \qquad [\chi(0),\nu(0)] = (0, 0)$$

$$\dot{\kappa} = g_3(y - \chi), \qquad \dot{\rho} = g_4(y - \chi); \qquad [\kappa(0), \rho(0)] = (\kappa_o, \rho_o)$$

whose integration yields the (time-varying) estimate (χ, ν, κ, ρ) of state-parameter set (c, ñ, k, r). g_i is a (χ, ν, κ, ρ, ω)-dependent nonlinear scalar function (given in the appendix), $\omega = 1.5s^{-1}$ is a (rate-of-convergence) tuning parameter, and $(\kappa_o, \rho_o) = (1, 1)\ 10^{-4}\ s^{-1}$ is an initial parameter guess. Fig. 2 shows the estimates (ρ_1, κ_1) (continuous plots) and (ρ_2, κ_2) (discontinuous plots) of the consistent and inconsistent cases, respectively. In the consistent case the parameters rapidly converge to their actual time-invariant values, and in the inconsistent case the parameters converge to time-varying functions. This leads us to conclude the incorrectness of the estimation model used in the inconsistent case. Moreover, the use of data on the approach to the steady-state is a key condition for the assessment of the of the model-data consistency.

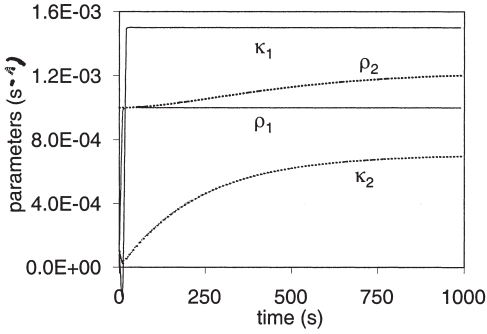

Fig. 2: Evolution of the parameter estimates of the consistent (ρ_1, κ_1; ____) and inconsistent (ρ_2, κ_2;---) cases in interval II

Interval III System

The interval III of the 0-1 emulsion polymerization is described by the following equation[4,6]

$$\dot{c} = k(1-c); \qquad y = c, \qquad c(t_o) = c_o, \qquad c_o \leq c \leq 1 \qquad (2)$$

where c is the conversion, and c_o its initial value at time t_o. The objective is to estimate the parameter k and to assess the consistency of the model on the basis of the experimental conversion-time discrete data set (shown in Fig. 3) reported in Weerts *et al.*[6] for two runs with different emulsifiers: Run 1 with $(c_o, t_o) = (0.59, 32375\ s)$ for $c \leq 0.85$, and Run 2 with $(c_o, t_o) = (0.60, 36357\ s)$ for $c \leq 0.85$.

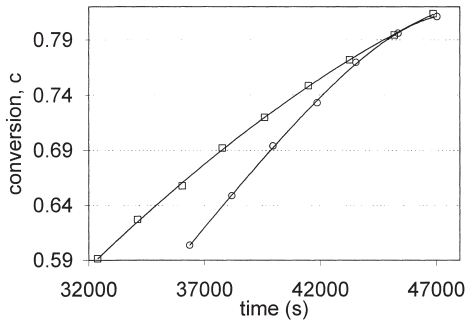

Fig. 3: Continuous representation of the two-run set of experimental (run 1: □; run 2: ○) data[6] of the interval III case.

Continuous Data Representation

In dynamic estimation[7] and emulsion modeling[2], it is known that the measurement-to-estimate error propagation limits the performance of any parameter estimation scheme. Thus, special care must be taken to design an adequate transient experiment, gather a sufficiently dense mesh of measurements, and set an appropriate noise-free continuous representation of the data. In emulsion systems this is an open subject of study, and here we circumscribe ourselves to set and *ad hoc* data processing scheme for our interval III problem. Let us introduce an auxiliary dynamical system:

$$\dot{z}_1 = [k_1 + k_2 t + \exp(k_3 t)](1-z_1)z_2\,, \quad \dot{z}_2 = k_4 \exp(k_5 t) + k_6 z_2^{k7}; \quad y = z_1,\ [z_1(t_o), z_2(t_o)] = (c_o, t_o)$$

whose structure and seven parameters (k_i) were adjusted, via a nonlinear regression, to produce the noise-free continuous data function y(t) of Fig. 3.

Dynamic Parameter Estimation

Following the dynamic estimation methodology[1], one reaches the conclusion that, except in a neighborhood before total conversion, the (possibly time-varying) parameter k can be estimated because the underlying observability condition $1 - c \neq 0$ is met, regardless of the emulsion system, and that the corresponding estimator is given by

$$\dot{\chi} = \kappa(1 - \chi) + 1.4\,\omega\,(y - \chi), \quad \dot{\kappa} = [\omega(\omega + 1.4\kappa)/(1-\chi)]\,(y - \chi); \qquad [\chi(t_o), \kappa(t_o)] = (c_o, \kappa_o)$$

where (χ, κ) is the estimate of (c, k). Fig. 4 presents the resulting parameter estimates for the two experimental runs when $(\kappa_o, \omega) = (0, 0.1)\ s^{-1}$, showing that in both runs the estimated parameters (κ) converge to slightly time-varying functions. On the basis of the seven-measurement of data of each run, one is led to conclude basically that model (2) is consistent with its two-run data set, and that a more conclusive confirmation would require a denser mesh of experimental data, information on the experimental errors, and a stochastic study on the error-to-estimate propagation mechanism.

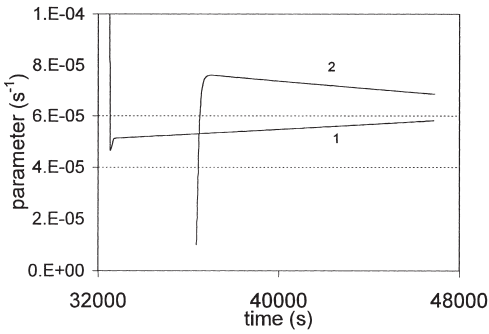

Fig. 4: Evolution of the parameter estimate of Runs 1 and 2 of the interval III case.

Conclusions

The problem of determining parameters with model-data consistency in 0-1 emulsion systems has been addressed. The study of the interval II case, with simulated experiments, showed that: (i) the SI and nonlinear regression techniques fail to detect a modeling inconsistency in spite of fitting the data well, (ii) using data from the approach to the steady state, the proposed

technique can determine the parameters and assess the consistency of the model. The study of the interval III, with actual experimental data, showed: (i) that the estimation-consistency problem is solvable, (ii) how to prepare a noise-free continuous representation of discrete experimental data, and (iii) the consistency of the candidate model. The interval III case exhibited better convergence properties, tolerated more errors in the measurement data, and was rather insensitive to the initial parameter. These observations coincide with the expressions that measure the degree of observability of the interval II and III cases. Practically speaking, the interval II case, with two parameters and less dynamic excitation, is an inherently more difficult problem, and this confirms the difficulties associated with the experimental modeling studies on interval II system[2-5]. Presumably, further work along the proposed methodological framework could lead to alleviating the dosage of experimental data required by the modeling studies[2-5] of the interval II case. Additional understanding and findings on the proposed methodology, and an application to a microemulsion system are presented in a subsequent work[8].

References

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Appendix: nonlinear gains g_i

$g_1 = 2.6\,\omega, \qquad g_2 = 3.4\omega^2/A, \qquad D = A(2\nu\rho + \nu\kappa - \rho), \qquad F = \omega^2/D$

$$g_3 = F\{3.4\nu\kappa^2 + (13.6\nu - 3.4)\rho\kappa + (13.6\nu - 6.8)\rho^2 + \omega[(10.4\nu - 2.6)\rho + 5.2\nu\rho] + \omega^2\nu^2\}$$

$$g_4 = F\{-6.8\nu\kappa^2 + (6.8 - 27.2\nu)\rho\kappa + (13.6 - 27.2\nu)\rho^2 + \omega[(10.4 - 20.8\nu)\rho + (2.6 - 10.4\nu)\kappa] + \omega^2(1 - 2\nu)\}$$