

Polynomial ARMA Model Identification for a Continuous Styrene Polymerization Reactor Using On-Line Measurements of Polymer Properties

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ABSTRACT: The multiinput–multioutput identification for a continuous styrene polymerization reactor using a polynomial ARMA model is carried out by both simulation and experiment. The pseudorandom multilevel input signals are applied for model identification in which input variables are the jacket inlet temperature and the feed flow rate, whereas the output variables are the monomer conversion and the weight-average molecular weight. The use of a polynomial ARMA model for identification of the multivariable polymerization reaction system is validated by simulation study. For the experimental corroboration, correlations are developed to convert the on-line measurements of density and viscosity of the reaction mixture to the monomer conversion and the weight-average molecular weight. The on-line values of the conversion and weight-average molecular weight turn out to be in good agreement with the off-line measurements. Despite the complex and nonlinear features of the polymerization reaction system, the polynomial ARMA model is found to satisfactorily describe the dynamic behavior of the polymerization reactor. Therefore, one may apply the polynomial ARMA model to the optimization and control of polymerization reactor systems. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1889–1901, 2000

Key words: identification; ARMA model; input–output model; continuous polymerization reactor; on-line measurement

INTRODUCTION

A polymerization reaction system is subject to a complex reaction mechanism and shows highly nonlinear features. Thus, the first-principle model of a polymerization reactor may contain a large number of kinetic parameters and nonlinear terms. These parameters are neither readily found from the literature nor easily determined by experiments. As an alternative to the first-principle model, it may be advantageous to use a

model structure whose parameters can be identified from input–output data. Because input–output models can effectively describe a nonlinear system, a number of those models have been employed for the construction of model-based controllers, such as the model predictive controller (MPC).

A wide variety of nonlinear input–output models have been proposed for use in identification and control of chemical processes. These include Volterra series models, bilinear models, Hammerstein models, Wiener models, and autoregressive moving-average (ARMA) models. Bartee and Georgakis¹ used a bilinear model for the identification of a continuous stirred tank reactor (CSTR) and implemented the model in a reference system

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control structure. A binary distillation column was identified by Eskinat et al.² by using the Hammerstein model. Fruzzetti et al.³ employed the Hammerstein model in a nonlinear MPC scheme for the pH control of a chemical reactor and for the control of a binary distillation column. Although the Hammerstein model is convenient for the controller design and also for handling the process noise, it is incapable of modeling systems that exhibit output multiplicities as displayed by various chemical systems.

Maner and Doyle III⁴ used the autoregressive plus Volterra model to identify a continuous methyl methacrylate (MMA) polymerization reactor and implemented the model in the control of polymer properties using a nonlinear MPC. Hernandez and Arkun⁵ identified a single-input–single-output (SISO) polynomial ARMA model for a CSTR in which first-order exothermic reaction occurred. The authors examined the steady-state multiplicity by using the model, and proposed a nonlinear MPC scheme based on the polynomial ARMA model.

The main advantage of polynomial ARMA models is that it can describe the process nonlinearities as polynomial nonlinearities, and can greatly simplify the estimation of the parameters from the input–output data. Moreover, polynomial ARMA models are superior to Volterra series models in the sense that the number of parameters needed to approximate a system is, in general, much less with polynomial models. There are numerous studies for identification of chemical processes using input–output models. However, applications to the polymerization reactor systems are scarce, and furthermore, most of them are limited to simulation studies.

In this study, we perform the multiinput–multioutput (MIMO) identification for a continuous styrene polymerization reactor using the polynomial ARMA model not only by simulation but also by experimentation. The identified ARMA model is validated by comparison of the open-loop response of the model with that of the plant in simulation and experiment. Especially, the output data in the experimental identification are obtained from on-line measurements, which is proven very effective for the property control of the polymerization reactor system.

NONLINEAR MODEL STRUCTURE

The polynomial ARMA model is defined as follows:

$$\begin{aligned}
 y_i(k) = & y_{i0} + \sum_{l=1}^{q_y} \sum_{j=1}^{n_y} \theta_{l,j}^1 y_l(k-j) + \sum_{l=1}^{q_u} \sum_{j=1}^{n_u} \theta_{l,j}^2 u_l(k-j) \\
 & + \sum_{l=1}^{q_y} \sum_{j=1}^{n_y} \sum_{m=l}^{q_y} \sum_{n=1}^j \theta_{l,j,m,n}^3 y_l(k-j) y_m(k-n) \\
 & + \sum_{l=1}^{q_u} \sum_{j=1}^{n_u} \sum_{m=l}^{q_u} \sum_{n=1}^j \theta_{l,j,m,n}^4 u_l(k-j) u_m(k-n) \\
 & + \sum_{l=1}^{q_y} \sum_{j=1}^{n_y} \sum_{m=l}^{q_u} \sum_{n=1}^{n_u} \theta_{l,j,m,n}^5 y_l(k-j) \\
 & \times u_m(k-n) + \dots \quad (1)
 \end{aligned}$$

where q_y and q_u denote the number of outputs and inputs, respectively, while n_y and n_u indicate the number of lags on the outputs and inputs, respectively. The model is linear in the parameters θ , and its regressors and parameters may be identified from input–output data. In this study, input variables are the jacket inlet temperature and the feed flow rate, whereas output variables are the monomer conversion and the weight-average molecular weight.

CONTINUOUS STYRENE POLYMERIZATION REACTOR MODEL

To perform the simulation study, we consider the mathematical model of a continuous stirred-tank reactor in which solution polymerization of styrene occurs. The reaction kinetics is assumed to follow the free radical polymerization mechanism including chain transfer reactions to both solvent and monomer. The free radical polymerization mechanism for styrene is summarized in Table I.

One can derive the mass balance equations for the initiator, solvent, and monomer, respectively, as follows:

$$\frac{d(IV)}{dt} = q_f I_f - qI + (-k_d)IV$$

$$\frac{d(SV)}{dt} = q_f S_f - qS + (-k_{trs}SG_0)V$$

$$\frac{d(MV)}{dt} = q_f M_f - qM - \{2fk_d I + (k_p + k_{trm})MG_0\}V$$

(2)

Table I Reaction Mechanism for Free Radical Styrene Polymerization

Initiation	$I \xrightarrow{k_d} 2\varphi^\bullet$
	$\varphi^\bullet + M \xrightarrow{k_i} R_1^\bullet$
Propagation	$R_1 + M \xrightarrow{k_{p1}} R_2^\bullet$
	$R_j + M \xrightarrow{k_{pj}} R_{j+1}^\bullet$
Termination by combination	$R_i + R_j \xrightarrow{k_{tc}} P_{i+j}$
Chain transfer to monomer	$R_i + M \xrightarrow{k_{trm}} P_i + R_1^\bullet$
Chain transfer to solvent	$R_i + S \xrightarrow{k_{trs}} P_i + S^\bullet$

For the first three moments of living and dead polymer concentrations, the balance equations can be expressed as

$$\frac{d(G_0V)}{dt} = -qG_0 + (2fk_dI - k_{tc}G_0^2)V$$

$$\frac{d(G_1V)}{dt} = -qG_1 + \{2fk_dI + k_pMG_0 - k_{tc}G_0G_1 + (k_{trm}M + k_{trs}S)(G_0 - G_1)\}V$$

$$\frac{d(G_2V)}{dt} = -qG_2 + \{2fk_dI + k_pM(G_0 + 2G_1) - k_{tc}G_0G_2 + (k_{trm}M + k_{trs}S)(G_0 - G_2)\}V$$

$$\frac{d(F_0V)}{dt} = -qF_0 + \{0.5k_{tc}G_0^2 + (k_{trm}M + k_{trs}S)G_0\}V$$

$$\frac{d(F_1V)}{dt} = -qF_1 + \{(k_{tc}G_0 + k_{trm}M + k_{trs}S)G_1\}V$$

$$\frac{d(F_2V)}{dt} = -qF_2 + \{k_{tc}(G_0G_2 + G_1^2) + (k_{trm}M + k_{trs}S)G_2\}V \quad (3)$$

The energy balances for the reactor and the jacket give rise to the following equations

$$\frac{d((\rho C_p)_m VT_r)}{dt} = (\rho C_p)_m q_f T_f - (\rho C_p)_m q T_r + (-\Delta H_p)k_p MG_0 V - UA(T_r - T_j)$$

$$\frac{d((\rho C_p)_c V_j T_j)}{dt} = (\rho C_p)_c q_c T_{jin} - (\rho C_p)_c q_c T_{jout} + UA(T_r - T_j) + U_a A_a (T_a - T_j) \quad (4)$$

To take into account the gel effect, we use the empirical correlation suggested by Hamer et al.,⁶ which is listed in Table II. The physical properties and kinetic parameters were taken from the literature and are also listed in Table II.

Table II Physico-Chemical Data and the Gel Effect Correlation Used in the Mathematical Model for Styrene Polymerization

Parameters	Values	Reference
Physical Properties		
ρ_m [g/L]	$924.0 - 0.981 \times (T - 273.15)$	Schuler and Suzhen (1985)
ρ_s [g/L]	$885.5 - 0.955 \times (T - 273.15)$	Schuler and Suzhen (1985)
ρ_p [g/L]	$1084.0 - 0.605 \times (T - 273.15)$	Takamatsu et al. (1988)
Rate Constants		
k_d [s ⁻¹]	$1.58 \times 10^{15} \exp(-30780/RT)$	Duerksen et al. (1967)
k_p [L/mol/s]	$1.051 \times 10^7 \exp(-7064/RT)$	Duerksen et al. (1967)
k_{t0} [L/mol/s]	$1.255 \times 10^9 \exp(-1680/RT)$	Duerksen et al. (1967)
k_{trm} [L/mol/s]	$1.186 \times 10^7 \exp(-11767/RT)$	Yoo and Rhee (1999)
k_{trs} [L/mol/s]	$3.148 \times 10^9 \exp(-16264/RT)$	Yoo and Rhee (1999)
Gel Effect Correlation		
$g_i(X, T) \equiv \frac{k_t}{k_{t0}} = \exp[-2(AX + BX^2 + CX^3)]$		Hamer et al. (1981)

where

$$A = 2.57 - 5.05 \times 10^{-3}T$$

$$B = 9.56 - 1.76 \times 10^{-2}T$$

$$C = -3.03 - 7.85 \times 10^{-3}T$$

Table III Reference Conditions for Simulation and Experiment

Simulation and Experimental Conditions		
Condition	Item	Value
Initial charge	Monomer (styrene)	400 mL
	Solvent (toluene)	400 mL
	Initiator (AIBN)	8 g
Feed concentration	Monomer	4.34 mol/L
	Solvent	4.70 mol/L
	Initiator	0.06 mol/L
Operating conditions	Reactor temperature	50–85°C
	Feed flow rate	5–30 mL/min
	Simulation Conditions	
Reactor volume (V)		1 L
Jacket volume (V_j)		0.8 L
Feed temperature (T_f)		20°C
Ambient temperature (T_a)		20°C
Initiator efficiency (f_i)		0.5
Heat of reaction for propagation (ΔH_p)		74,500 cal/mol
Thermal conductance		
UA		16 cal/s/K
$U_a A_a$		3.2 cal/s/K
Heating or cooling water flow rate (q_c)		2.5 L/min

SIMULATION STUDY

Reference conditions of simulation study are summarized in Table III. The regressors and model parameters were obtained by using a stepwise model building algorithm.⁷ In this algorithm, we used both popular F -test¹³ and Akaike's information criterion⁷ as model verification methods. Because the F -test seems to have the disadvantage of being difficult to choose the proper levels of significance, Akaike's information criterion was used together in model identifications. The procedure of stepwise model building algorithm quits if the F -test shows that the model equation is not significant or if Akaike's information criterion gives a value greater than that for the previous model.

The nonlinear order of the model and the number of lags on the inputs and outputs were specified as $n = 2$, $n_u = 3$, and $n_y = 3$, respectively. The mathematical model was considered as the plant in simulations. The inputs and outputs were scaled as follows:

$$y_1 = X, \quad y_2 = \frac{M_w - M_{w \min}}{M_{w \max} - M_{w \min}} \quad (5)$$

$$u_1 = \frac{T_{jin} - T_{jin \min}}{T_{jin \max} - T_{jin \min}}, \quad u_2 = \frac{q_f - q_{f \min}}{q_{f \max} - q_{f \min}} \quad (6)$$

where X , M_w , T_{jin} , and q_f denote the monomer conversion, the weight-average molecular weight, the jacket inlet temperature, and the feed flow rate, respectively. The scaling factors in eqs. (5) and (6) are listed in Table IV.

Although a three-level sequence is persistently exciting, the results of preliminary study revealed that a four-level sequence was superior to a three-level sequence. Hence, the input signals, u_1 and u_2 , were drawn from a uniform distribution with four levels. Just like the pseudorandom binary signals (PRBS), the pseudorandom multilevel signals are persistently exciting for a system, but the latter have several additional features.⁸ The pseudorandom multilevel signals include interior points of input region, are closer to white autocorrelation function, and excite nonlinear modes that PRBS cannot. Because of these features, we used the pseudorandom multilevel input signals rather than the PRBS. The process white noise with zero mean and standard deviation of 0.02 was added to both the conversion and the molecular weight.

The output data obtained by the mathematical model against the pseudorandom multilevel input signals and the response of the identified polynomial ARMA model are shown in Figure 1. In this case, the sample time was 2 min and switching probability P_S , which represents the probability of input change at the end of any sampling interval, was assumed to be 0.1. To investigate the reliability of the identified model, the percentage variance accounted for (VAF) index was introduced, which is defined as follows:

Table IV Scaling Factors for the Inputs and Outputs

Input and Output	Scaling Factor	Value
Weight-average	$M_{w \max}$	60,000
Molecular weight	$M_{w \min}$	10,000
Jacket inlet	$T_{jin \max}$	85°C
Temperature	$T_{jin \min}$	55°C
Feed flow rate	$q_{f \max}$	30 mL/min
	$q_{f \min}$	5 mL/min

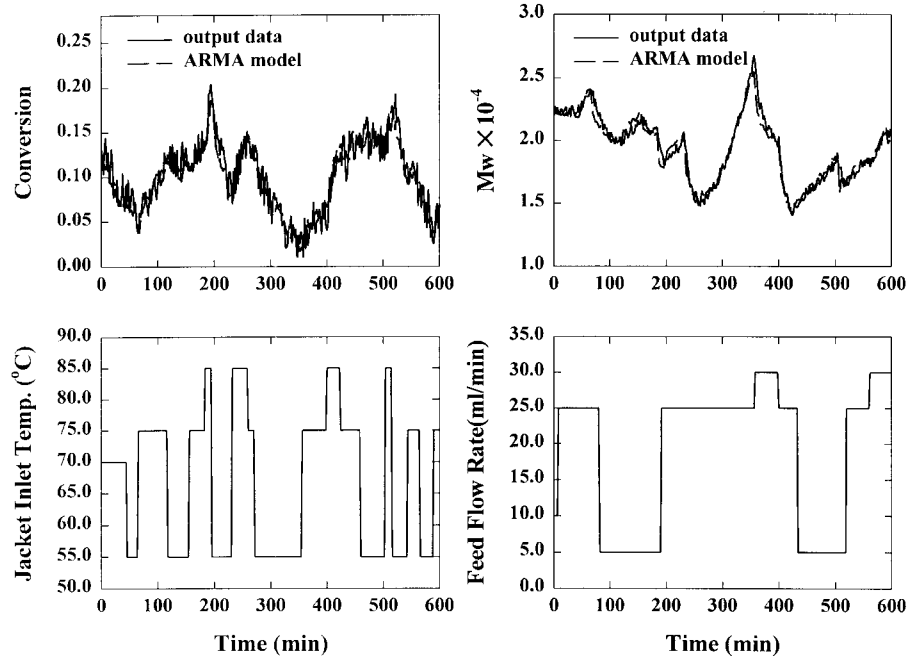


Figure 1 Output data obtained by the mathematical model against the pseudorandom multilevel input signals with $P_S = 0.1$ and four levels and the response of the identified polynomial ARMA model.

$$\text{VAF} \equiv 100 \left(1 - \frac{\sqrt{\sum_{i=1}^N (y_i - \hat{y}_i)^2}}{\sqrt{\sum_{i=1}^N y_i^2}} \right) \% \quad (7)$$

where N , y , and \hat{y} denote the number of data points, the plant (or the mathematical model) output, and the identified model output, respectively. The VAF index is used as a measure of the relative accuracy of the model and its range is between $-\infty$ and 100%. The identified model for the conversion was constituted of nine regressors and had a VAF of 89.66%. For the molecular weight, 20 regressors were included in the model and a VAF of 95.30% was obtained. The results of the identification are summarized in Table V.

Figure 2 presents the input–output data used to identify the models for the conversion and the molecular weight and the response of the identified polynomial ARMA model when $P_S = 0.5$. In this case, 8 and 16 regressors were included in the models of the conversion and the molecular weight, respectively. The VAF was found to be 90.48 and 95.54% for the respective model. The results of the identification are summarized in

Table VI. As shown in Figures 1 and 2, the higher switching probability would be more accurate. Because, however, the difference between the results for the case of $P_S = 0.1$ and $P_S = 0.5$ is very small, and input signals with $P_S = 0.5$ are too demanding for practical implementation, we chose 0.1 for P_S in experiments. Considering the large time constants of the polymerization reaction system, this choice of P_S is found more desirable.

Figure 3 shows the responses of the mathematical model and the polynomial ARMA model, which is identified in the case of Figure 1, to a series of step changes in both inputs. In addition, the responses of the linear ARMA model and the autoregressive-plus Volterra model, which was used in the work of Maner and Doyle III, are compared with those of the polynomial ARMA model. The linear ARMA model and the autoregressive-plus Volterra model were identified by the same method and under the same conditions as for the case of the polynomial ARMA model. The results of the identifications are summarized in Table VII. The outputs estimated from the polynomial ARMA model for both conversion and the molecular weight are in good agreement with those of the mathematical model, whereas the

Table V Simulation Results of the Identification Using Pseudorandom Multilevel Input Signals with $P_S = 0.1$ and Four Levels

VAF	Conversion $y_1(k)$		Weight-Average Molecular Weight $y_2(k)$	
	89.66%		95.3%	
	Parameters	Regressors	Parameters	Regressors
Models	0.02	1	-0.08	1
	0.20	$y_1(k - 1)$	0.40	$y_2(k - 1)$
	0.34	$y_1(k - 2)$	-0.48	$y_2(k - 2)u_2(k - 3)$
	0.04	$u_1(k - 1)u_1(k - 2)$	0.59	$y_2(k - 2)$
	-0.18	$y_1(k - 2)u_2(k - 1)$	0.15	$y_1(k - 3)u_2(k - 3)$
	0.32	$y_1(k - 3)$	0.49	$y_2(k - 3)$
	-0.02	$y_2(k - 1)$	0.05	$y_1(k - 1)^2$
	-0.09	$y_1(k - 1)u_1(k - 1)$	-0.22	$u_1(k - 1)u_1(k - 2)$
	-0.0025	$u_1(k - 2)u_1(k - 3)$	0.11	$y_1(k - 2)u_1(k - 1)$
			0.04	$u_1(k - 2)$
			0.05	$u_1(k - 1)u_2(k - 1)$
			-0.19	$y_2(k - 2)u_1(k - 2)$
			-0.22	$y_2(k - 2)y_2(k - 3)$
			-0.22	$y_2(k - 1)y_2(k - 2)$
			-0.27	$y_2(k - 3)^2$
			0.25	$u_1(k - 1)$
			0.21	$y_1(k - 2)$
			-0.03	$u_2(k - 1)^2$
			0.03	$u_2(k - 1)u_2(k - 2)$
			0.16	$u_1(k - 1)u_1(k - 3)$

linear ARMA model and the autoregressive-plus Volterra model show some discrepancies in both the molecular weight and the conversion, especially in the latter part of the reaction course. For the case of a linear ARMA model or an autoregressive-plus Volterra model, therefore, we have to include more regressors by increasing the order of nonlinearity or the number of time lags on inputs and outputs to improve the output to the extent of a polynomial ARMA model.

ON-LINE MEASUREMENTS AND EXPERIMENTAL STUDY

In this section, we consider the on-line measurements of the conversion and the molecular weight that are to be used for the identification. The on-line measurements are essential for the property control of a continuous polymerization reactor system.

The density of polymer can be used effectively to follow the course of polymerization and to examine the variation of monomer conversion X .

Ahn et al.⁹ proposed the correlation equation, which may be used to calculate the monomer conversion from the on-line density measurement. This equation is given as follows:

$$X = \frac{\left(\frac{1}{\rho_d} - \frac{1}{\rho_m}\right) - W_{sf} \left(\frac{1}{\rho_s} - \frac{1}{\rho_m}\right)}{\left(\frac{1}{\rho_p} - \frac{1}{\rho_m}\right)} \quad (8)$$

in which ρ_m , ρ_s , and ρ_p denote the densities of monomer, solvent, and polymer, respectively. Here, ρ_d and W_{sf} represent the measured density of reaction mixture and the weight fraction of solvent in reactor, which may be assumed constant.

Several correlations have been reported to describe the relationship between the specific viscosity η_{sp} and the intrinsic viscosity $[\eta]$. Lyons and Tobolsky¹⁰ suggested the following equation

$$\eta_{sp} = C[\eta] \exp \frac{k_H[\eta]C}{1 - bC} \quad (9)$$

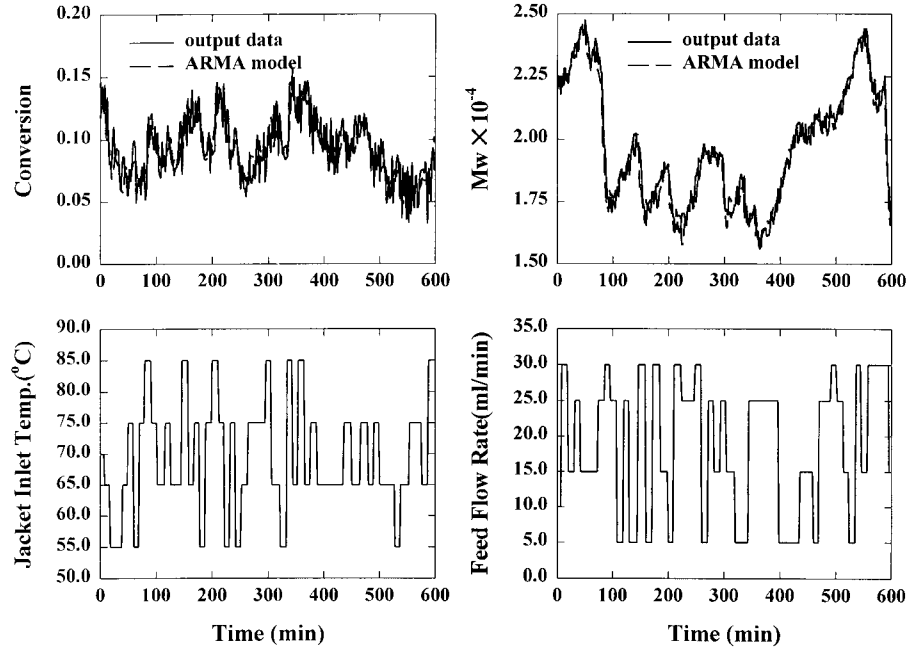


Figure 2 Output data obtained by the mathematical model against the pseudorandom multilevel input signals with $P_S = 0.5$ and four levels and the response of the identified polynomial ARMA model.

where C indicates the mass concentration (g/mL) of the polymer in the reactor. For the styrene polymerization system of this study, the param-

eter k_H and b were obtained as 0.9 and 0.8, respectively. When the intrinsic viscosity $[\eta]$ is determined by eq. (9) with on-line measurement of the

Table VI Simulation Results of the Identification Using Pseudorandom Multilevel Input Signals with $P_S = 0.5$ and Four Levels

VAF	Conversion $y_1(k)$		Weight-Average Molecular Weight $y_2(k)$	
	90.48%		95.54%	
	Parameters	Regressors	Parameters	Regressors
Models	0.05	1	0.03	1
	2.77	$y_1(k - 1)y_1(k - 2)$	0.33	$y_2(k - 1)$
	0.09	$y_1(k - 3)u_1(k - 1)$	0.07	$u_1(k - 1)u_1(k - 2)$
	-0.02	$y_2(k - 1)u_2(k - 1)$	0.50	$y_2(k - 3)$
	0.62	$y_1(k - 3)^2$	-0.32	$y_2(k - 3)u_1(k - 1)$
	0.02	$u_1(k - 1)u_1(k - 2)$	0.27	$u_1(k - 1)$
	0.03	$y_1(k - 1)u_2(k - 2)$	-0.55	$u_1(k - 1)^2$
	0.06	$y_1(k - 3)y_2(k - 2)$	0.05	$y_2(k - 2)u_1(k - 1)$
			-0.11	$y_2(k - 3)u_1(k - 2)$
			-0.10	$y_2(k - 3)u_2(k - 1)$
			0.07	$y_2(k - 1)u_2(k - 1)$
			-1.58	$y_1(k - 2)^2$
			2.00	$y_1(k - 3)u_1(k - 1)$
			-4.92	$y_1(k - 3)^2$
		0.34	$y_1(k - 3)y_1(k - 2)$	
		0.26	$y_2(k - 2)$	

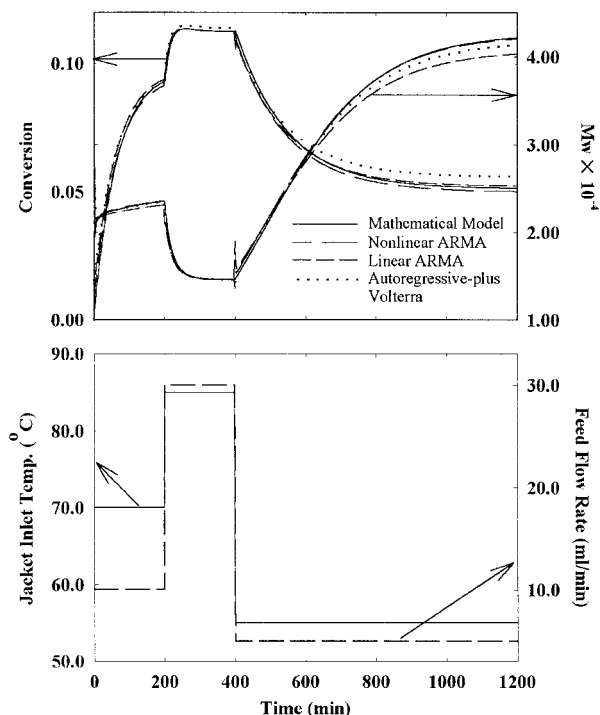


Figure 3 Open-loop responses of the plant (mathematical model), the polynomial ARMA model, the linear ARMA model, and the autoregressive-plus Volterra model to a series of step changes in inputs.

specific viscosity, one can calculate the weight-average molecular weight from the Mark-Houwink equation, which is given in the form

$$[\eta] = K(M_w)^a \quad (10)$$

Here, K and a are Mark-Houwink constants, which may be assumed independent of the temperature. The value of K is given as 3.3×10^{-3} for the case of polystyrene. According to the experimental results of this study, the parameter a is determined by

$$a = 0.62 + 0.002(\eta - \eta_{X=0}) \quad (11)$$

The schematic diagram of the experimental system is shown in Figure 4. The jacketed glass reactor has a capacity of 1 L and the overflow line is installed at the upper part of the reactor, so that the volume of reaction mixture is kept constant. An inverter maintains the stirring speed at 300 rpm. Heating or cooling of the reaction mixture is carried out by heating-cooling water through the jacket. The valve stem positions of the hot and cold water lines are adjusted, in a

cascade control configuration, in such a way that the jacket inlet temperature is kept equal to the desired value specified by the master controller. A variable-speed, remote setpoint pump is used for pumping the solution of monomer, solvent, and initiator into the reactor. This is a piston-operated metering pump from FMI LAB (Model QVG50). The reaction product flows out of the reactor via an overflow line.

To measure the density and viscosity of the reaction mixture, the circulation line is attached to the reactor. The reaction mixture is circulated by the diaphragm metering pump through the circulation line, in which the on-line densitometer and the viscometer are installed. The on-line densitometer is DMA 401 YHEW from Anton Paar, whereas the on-line viscometer is MIVI 6002 from SOFRASER. The set of reference conditions for the experiment are summarized in Table III. The reaction mixture is sampled at successive times, and the conversion is measured by the gravimetric method, while the average molecular weights are measured by the gel permeation chromatography (GPC).

Figure 5 shows the results of the experiment, which is performed to examine the validity of the on-line measurements. The solid curve in Figure 5(a) represents the conversion calculated from eq. (8) using the measured density, while the solid dot denotes the conversion measured off-line by the gravimetric method. In Figure 5(b), the solid curve and the solid dot represent the weight-average molecular weight obtained from the on-line measurement and the off-line GPC, respectively. In both diagrams the two results are in good agreement, and this indicates that the on-line measurements may be used for identification of a continuous styrene polymerization reactor using a polynomial ARMA model.

Presented in Figure 6 are the experimental input-output data used to identify the models for the conversion and the molecular weight. The output data were obtained from the correlations (8), (9), and (10) using the density and viscosity data measured by the on-line densitometer and viscometer, respectively. The input sequences were drawn from a uniform distribution with $P_S = 0.1$ and four levels. Because polymerization processes have large time constants, it may be desirable to incorporate a clock period, T_{cl} , which is an integer number of sample periods for which the inputs are held constant before possibly switching again, as is done in identification of autoregressive plus Volterra model.⁴ In the ex-

Table VII Simulation Results of the Identification for Linear ARMA Models and Autoregressive-Plus Volterra Models Using Pseudorandom Multilevel Input Signals with $P_S = 0.1$ and Four Levels

VAF		Conversion $y_1(k)$		Weight-Average Molecular Weight $y_2(k)$	
		89.5%		94.4%	
		Parameters	Regressors	Parameters	Regressors
Linear ARMA	Models	0.004	1	0.03	1
		1.422	$y_1(k - 1)$	1.892	$y_2(k - 1)$
		0.144	$y_1(k - 2)$	-1.111	$y_2(k - 2)$
		0.013	$u_1(k - 1)$	-0.086	$u_1(k - 1)$
		-0.008	$u_2(k - 1)$	0.029	$u_1(k - 3)$
		0.003	$u_2(k - 2)$	0.118	$y_2(k - 3)$
		-0.008	$u_1(k - 3)$	0.04	$u_1(k - 2)$
		0.008	$u_1(k - 2)$	-0.035	$y_1(k - 1)$
		-0.629	$y_1(k - 3)$		
		0.003	$u_2(k - 3)$		
VAF		89.2%		95.0%	
		Parameters	Regressors	Parameters	Regressors
Autoregressive-plus Volterra	Models	0.012	1	0.016	1
		0.898	$y_1(k - 1)$	1.647	$y_2(k - 1)$
		0.154	$y_1(k - 2)$	-0.520	$y_2(k - 2)$
		0.017	$u_1(k - 1)^2$	-0.073	$u_1(k - 1)^2$
		-0.008	$u_2(k - 1)$	0.085	$u_1(k - 1)u_1(k - 3)$
		0.006	$u_2(k - 2)^2$	-0.057	$u_1(k - 3)^2$
		0.005	$u_1(k - 2)u_1(k - 3)$	0.037	$u_1(k - 1)u_1(k - 2)$
		-0.011	$u_2(k - 2)$	-0.039	$u_1(k - 1)$
		0.004	$u_2(k - 1)u_2(k - 2)$	0.002	$u_2(k - 1)$
		-0.007	$u_1(k - 3)u_2(k - 1)$	0.034	$u_1(k - 3)$
		0.003	$u_1(k - 3)u_2(k - 2)$	-0.179	$y_2(k - 3)$
		-0.003	$u_1(k - 1)u_1(k - 3)$	-0.001	$u_2(k - 1)^2$
		-0.188	$y_1(k - 3)$		
		-0.001	$u_1(k - 1)u_2(k - 1)$		

periment, sample period was 2 min and T_{cl} was empirically determined as 10. In Figure 6, the dashed line represent the output data obtained by the identified ARMA models. The model of the conversion consisted of nine regressors, and a VAF of 98.5% was obtained. For the model of the molecular weight, 10 regressors were included, and a VAF of 97.2% was obtained. The results of the identification experiment are listed in Table VIII. As shown in Tables V, VI, and VIII, the experimentally identified models were superior to the models identified by simulation. This indicates that the input sequences randomly determined in the experiments were

more relevant than in the simulation, and hence, the nonlinearities of the process were better included in the experimental input-output data.

Figure 7 shows the response of the experimentally identified ARMA model to a series of step changes in inputs in comparison with the on-line and off-line measurements. The small discrepancies are present in the high conversion range, probably because the input-output data in that range were not used in identification (see Fig. 6). If the identification is performed by including the input-output data in the higher polymer concentration range, the identified ARMA model is ex-

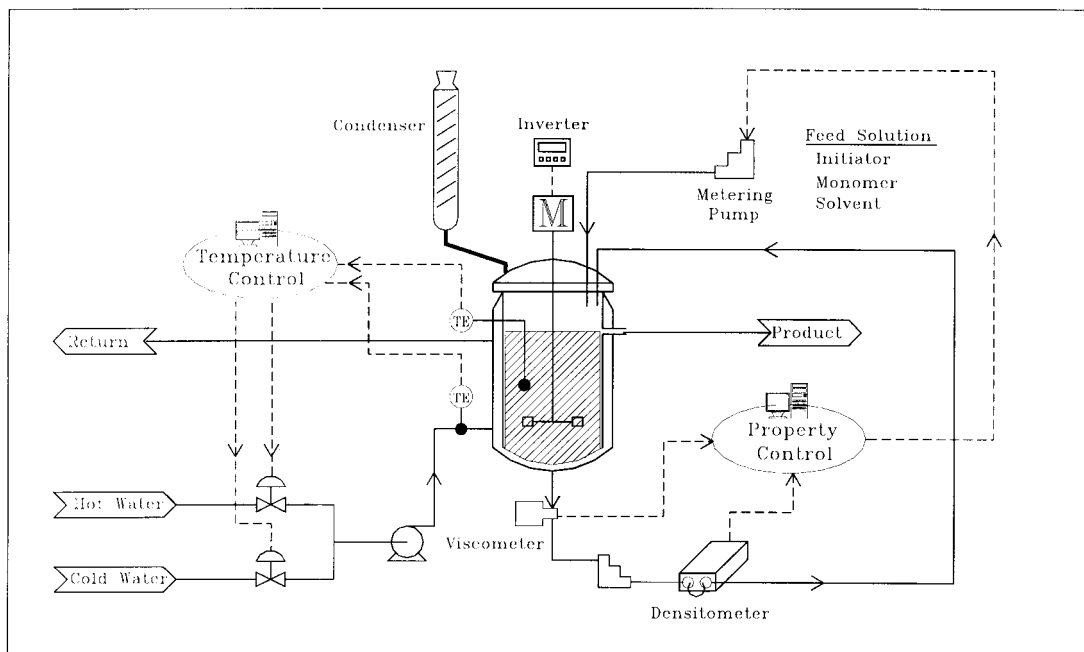


Figure 4 Schematic diagram of the experimental system.

pected to more accurately estimate the conversion and the weight-average molecular weight in that range. Here again, the on-line and off-line measurements are found to be in good agreement with each other.

CONCLUSIONS

The multivariable polynomial ARMA model identification for a continuous styrene polymerization reactor was performed by simulation and experi-

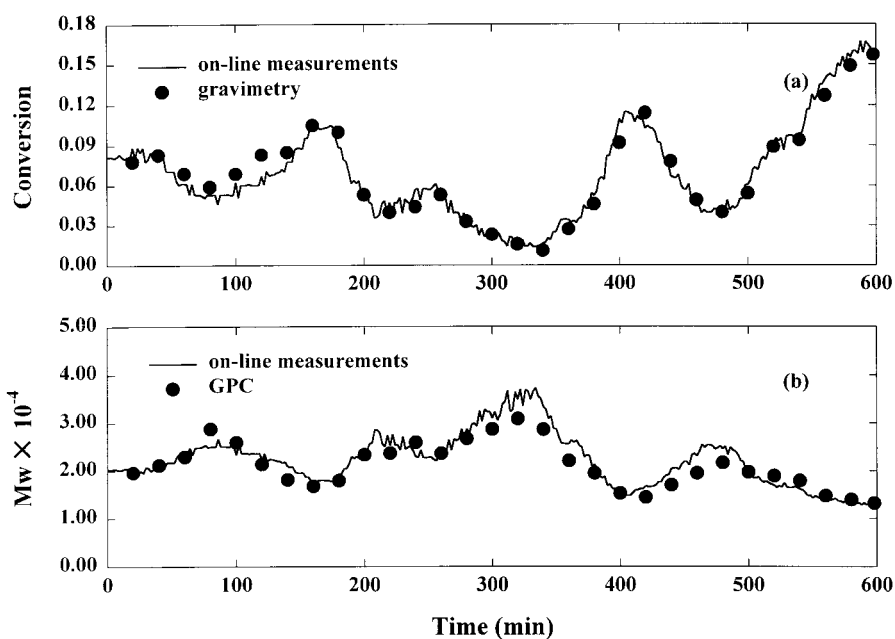


Figure 5 Comparison of monomer conversion and the weight-average molecular weight between the on-line measurements and the results of off-line analysis.

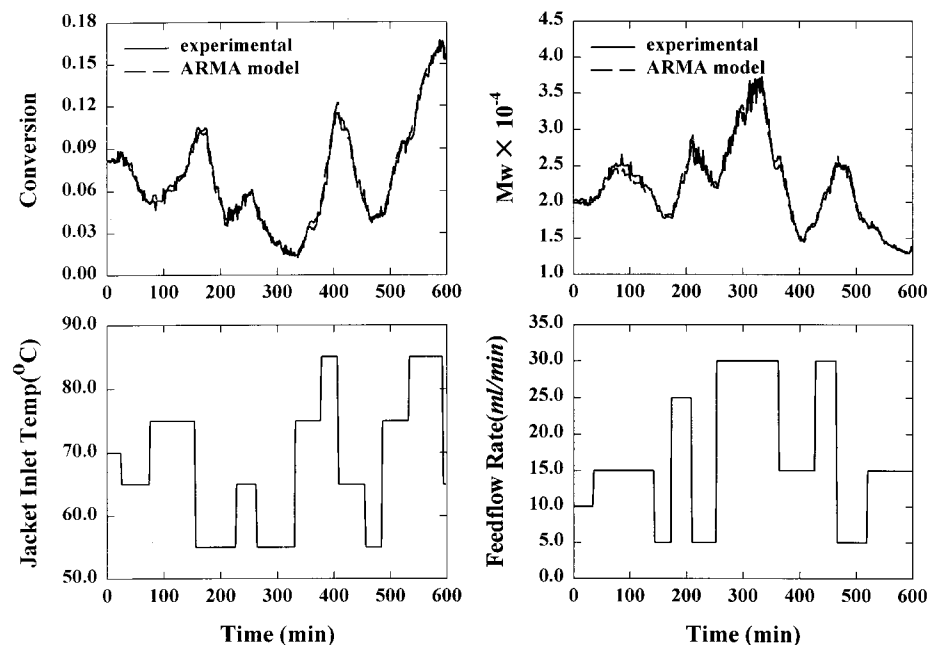


Figure 6 Output data obtained experimentally against the pseudorandom multilevel input signals with $P_s = 0.1$ and four levels and the response of the experimentally identified polynomial ARMA model.

ment. The on-line measurements for the monomer conversion and the weight-average molecular weight are found very effective in identification of a polymerization reactor system. The conversion and the weight-average molecular weight data determined by the on-line measurements are in good agreement with the off-line data obtained by the analysis of the samples of reaction mixture. The polynomial ARMA model, identified by using the on-line measurements, turns out to satisfac-

torily describe the dynamic behavior of the continuous styrene polymerization reactor system. Therefore, the polynomial ARMA model may be effectively employed for the property control and optimization of a continuous polymerization reactor.

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Table VIII Experimental Results of the Identification Using On-Line Measurements

VAF	Conversion $y_1(k)$		Weight-Average Molecular Weight $y_2(k)$	
	98.5%		97.2%	
	Parameters	Regressors	Parameters	Regressors
Models	0.01	1	-0.002	1
	0.49	$y_1(k-1)$	0.58	$y_2(k-1)$
	-0.001	$u_1(k-2)^2$	0.37	$y_2(k-2)$
	0.32	$y_1(k-2)$	-0.15	$y_2(k-3)u_1(k-2)$
	-0.14	$y_1(k-1)u_2(k-2)$	-0.03	$u_2(k-2)$
	0.07	$y_1(k-3)$	2.19	$y_1(k-1)y_2(k-1)$
	0.02	$u_1(k-1)u_1(k-3)$	-1.17	$y_1(k-3)y_2(k-1)$
	-0.008	$y_2(k-3)u_1(k-1)$	0.06	$y_2(k-1)u_1(k-2)$
	-0.01	$y_2(k-3)$	-0.02	$u_1(k-3)u_2(k-2)$
			-0.07	$y_2(k-3)u_1(k-1)$

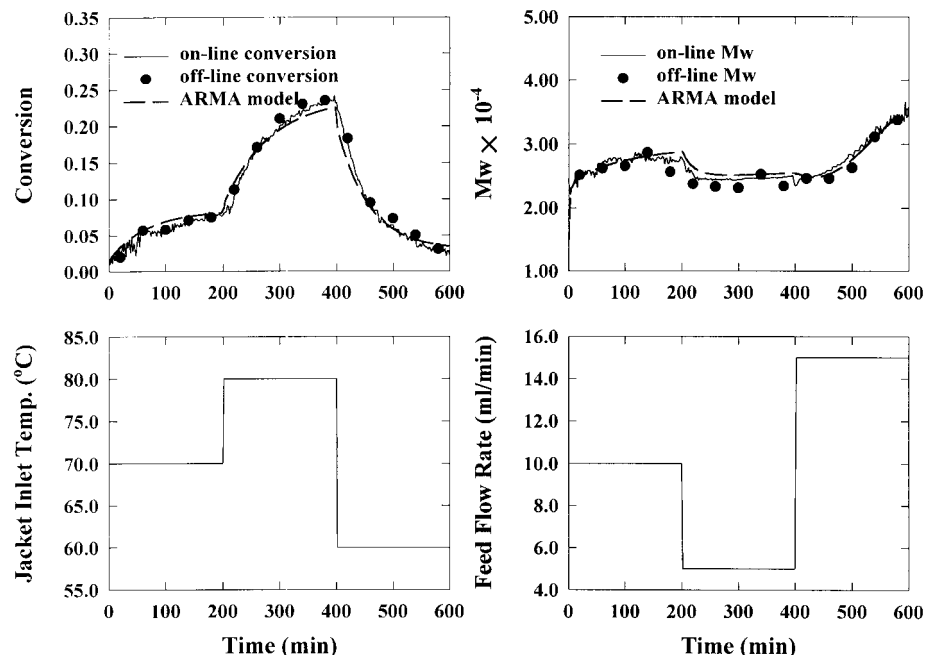


Figure 7 Experimental result of the open-loop test for the experimentally identified ARMA model and its comparison with the on-line and off-line measurements.

NOTATION

- A = heat exchange area [m^2]
 C = mass concentration of polymer [g/mL]
 f = initiator efficiency [-]
 F_k = k th moment of dead polymer concentration ($k = 0, 1, 2$) [mol/L]
 G_k = k th moment of living polymer concentration ($k = 0, 1, 2$) [mol/L]
 ΔH_p = heat of reaction for propagation [cal/mol]
 I = initiator or its concentration [mol/L]
 k = reaction rate constant [s^{-1}] or [$1/(\text{mol} \cdot \text{s})$]
 M = monomer or its concentration [mol/L]
 M_w = weight-average molecular weight [g/mol]
 n = number of lags on output or input [-]
 q = volumetric flow rate or number of inputs or outputs [mL/min] or [-]
 S = solvent or its concentration [mol/L]
 t = time [s]
 u = process input [-]
 U = overall heat transfer coefficient [$\text{cal}/(\text{m}^2 \cdot \text{K} \cdot \text{s})$]
 V = volume of reaction mixture [L]
 W_{sf} = weight fraction of solvent [-]
 X = monomer conversion [-]
 y = process output [-]
 \hat{y} = estimated output [-]

Greek Letters

- η = viscosity [centipoise]
 $[\eta]$ = intrinsic viscosity [mL/g]
 η_{sp} = specific viscosity [-]
 θ = parameter in the polynomial ARMA model [-]
 ρ = density [g/L]

Subscripts

- a = ambient
 c = coolant
 d = initiator decomposition or densitometer
 f = feed
 j = jacket
 m = monomer
 p = propagation or polymer
 r = reactor
 s = solvent
 t = termination
 tc = termination by combination
 trm = chain transfer to monomer
 trs = chain transfer to solvent

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