

Online Estimation and Control of Polymer Quality in a Copolymerization Reactor

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The validity of an online state estimator for a semi-batch MMA/MA solution copolymerization reactor was established using online densitometer and viscometer. Using the conventional extended Kalman filter (EKF) as the state estimator, the experiment was conducted under both isothermal and nonisothermal conditions for application to the control of copolymer properties. Further analysis was made by using offline measurement data for the mol fraction of MMA in the remaining monomers and the solid content. The EKF was found to provide a good estimate for the state of the copolymerization system. A model predictive controller was designed and implemented to obtain copolymers with uniform copolymer composition and the desired weight average molecular weight by adopting the feed flow rate of MMA and the reaction temperature as control inputs. The controller was proven effective with a satisfactory performance for the control of polymer properties in the semi-batch copolymerization reactor.

Introduction

Copolymer has a variety of better properties than homopolymer, because two monomers having different characteristics are used to compose the structure of a polymer chain. However, the use of two monomers brings about a greater complexity and requires several factors to be determined for the production of copolymers with desired end-user properties. Hence, a great deal of research interest has been focused on the development of the operation technique for the control of these factors.

Copolymer composition is one of the most important factors that affect the properties of copolymer. It is well known that copolymer composition drift occurs in a batch or semi-batch free radical copolymerization reactor due to the different reactivities of two monomers. Choi and Butala (1989) proposed open-loop control policies for both molecular weight and copolymer composition by using an inverse feedback control method. On the other hand, Kozub and MacGregor (1992a) applied the optimal instantaneous property

condition in such a way that the instantaneous polymer being produced at every instant of time might have the desired properties. This method, which has been used by many researchers in recent years (Saldivar and Ray, 1997; Sayer et al., 2000), suffers from several features such as the existence of disturbances appearing in most chemical reactors, or mismatches between the real system and the model used for the calculation of optimal trajectory.

To overcome these difficulties, offline measurements or online measurements with time delay were used to update the optimal trajectory. A midcourse correction policy was employed by Yabuki and MacGregor (1997), who used online measurement of the reactor temperature and offline measurements of the residual monomer concentration by gas chromatography and the volume average particle size by dynamic light scattering in order to make the midcourse adjustment. Gattu and Zafiriou (1999) used the temperature as the primary measurement and the average molecular weights and conversion as the secondary measurements.

As reported by Congalidis and Richards (1998), polymerization reactors lack the online measurements of polymer properties and this has been the major obstacle in the appli-

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cation of control strategies to industrial reactors. To make an estimation for the state of a polymerization reactor, Dimitratos et al. (1989, 1991) implemented the conventional extended Kalman filter (EKF) to the semicontinuous emulsion copolymerization reactor and developed a filter with parameter adaptation and noise adaptation algorithms. Kozub and MacGregor (1992b) augmented the EKF with a second EKF to improve the convergence, whereas Kazantzis et al. (2000) designed the model based nonlinear observer for process monitoring.

Recently, the development of online measurement devices such as a densitometer, a calorimeter, and a viscometer has shed light on the implementation of the state estimation and the feedback control. Hammouri et al. (1999) and Santos et al. (2000) adapted a calorimeter to estimate the states of copolymerization reactors like the concentrations of two monomers. Ellis et al. (1994) obtained good experimental results for the estimation of the molecular weight distribution (MWD) in a batch polymerization reactor by using online densitometer and online size exclusion chromatograph (SEC), and then controlled the polymer quality with a PID controller. The application of online measurement devices has also been reported in other research works (Echevarria et al., 1998; Chylla et al., 1997; Chang and Liao, 1999) and an excellent review on the online measurement techniques has been presented by Ohshima and Tanigaki (2000).

For the control of polymer properties, several advanced control algorithms were adapted to the polymerization reactor. Soroush and Zambare (2000) derived a nonlinear output feedback control law on the basis of the input-output linearizing state feedback. Among these algorithms, model predictive control (MPC) is known as the most successful one. Mutha et al. (1997) proposed a new nonlinear model-based predictive control and illustrated the performance of the algorithm by applying it to the semibatch acrylonitril-butadiene (NBR) emulsion copolymerization process. However, only a few applications have been reported on the implementation of the nonlinear MPC to copolymerization reactors.

In general, semi-batch reactors are known to be effective for the control of copolymer properties (Buruaga et al., 1997; Du et al., 2000). In this type of reactor, the more reactive monomer is chosen as the manipulated variable for the control of copolymer composition, while the chain-transfer agent is selected for the control of molecular weight. For a batch copolymerization reactor, Krishnan and Kosanovich (1998) designed a multiple model-based controller, while Padilla and Alvarez (1997) studied the control of copolymer properties in a continuous copolymerization reactor. On the other hand, Ogunnaike (1994) carried out the control of terpolymer properties in a continuous terpolymerization reactor. Most of the research works on the control of copolymerization reactors have been concerned with the emulsion copolymerization system.

In this study, an online state estimation scheme with the extended Kalman filter (EKF) is developed for a semi-batch methyl methacrylate (MMA)/methyl acrylate (MA) solution copolymerization reactor by using an online densitometer and viscometer. On the basis of these estimated states, an MPC is designed and implemented to the copolymerization reactor for the production of copolymers with uniform composition and desired weight-average molecular weight (M_w).

Semi-batch MMA/MA Solution Copolymerization Reactor

Let us consider a semi-batch reactor for the copolymerization of MMA and MA. The reaction kinetics are assumed to follow the free radical copolymerization mechanism including chain-transfer reactions to both solvent and monomers. To reduce the complexity of the rate expressions, the pseudo-kinetic rate constant method, which was introduced by Hamielec and Xie (1993) and developed further by Yoo et al. (1995a,b) and Hwang et al. (1997), is applied to the present copolymerization system. Only the mass balance equations for individual components are presented here. For more details, it is suggested to refer to Park et al. (2000).

$$\text{Initiator} \quad d(IV)/dt = r_I V \quad (1)$$

$$\text{Monomer 1} \quad d(M_1 V)/dt = q_f M_{1f} + r_{M1} V$$

(more reactive monomer) (2)

$$\text{Monomer 2} \quad d(M_2 V)/dt = r_{M2} V \quad (3)$$

$$\text{Solvent} \quad d(SV)/dt = r_S V \quad (4)$$

in which r_j denotes the rate of formation of species j and $q_f M_{1f}$ represents the rate of input of monomer 1 which is more reactive.

In addition, the model contains the moment equations of the living and dead polymer concentrations defined as follows

$$G_k = \sum_{r=1}^{\infty} r^k \{ [R_{r,1} \cdot] + [R_{r,2} \cdot] \}, \quad H_k = \sum_{r=1}^{\infty} r^k [P_r] \quad (5)$$

where G_k and H_k represent the k^{th} moment of the living and dead polymer concentrations, respectively. Here, $[R_{r,i} \cdot]$ denotes the concentration of living polymer with monomer i as the terminal and r units of monomer. $[P_r]$ is the concentration of dead polymer with r units of monomers. The mass balance equations for the moments are given by

moments of living polymer concentrations

$$d(G_k V)/dt = r_{G_k} V \quad k = 0, 1, 2 \quad (6)$$

moments of dead polymer concentrations

$$d(H_k V)/dt = r_{H_k} V \quad k = 0, 1, 2 \quad (7)$$

Average molecular weights of polymers are determined in the same manner as in homopolymerization, except that the molecular weight of monomer is used in the form of instantaneous average molecular weight $M_{av}(t) = W_{m1} F_1 + W_{m2} F_2$, where F_i and W_j represent the instantaneous copolymer composition (mol fraction of monomer i in the copolymer) and the molecular weight of species j , respectively. Then, the number and weight average molecular weights can be calcu-

lated by using the equations

$$M_n = \int_0^t \left\{ \frac{d(G_1V)}{Vdt} + \frac{d(H_1V)}{Vdt} \right\} M_{av}(t) dt \bigg/ \int_0^t \left\{ \frac{d(G_0V)}{Vdt} + \frac{d(H_0V)}{Vdt} \right\} dt \quad (8)$$

$$M_w = \int_0^t \left\{ \frac{d(G_2V)}{Vdt} + \frac{d(H_2V)}{Vdt} \right\} M_{av}^2(t) dt \bigg/ \int_0^t \left\{ \frac{d(G_1V)}{Vdt} + \frac{d(H_1V)}{Vdt} \right\} M_{av}(t) dt \quad (9)$$

As the monomers are converted to the copolymer, the density of the reaction mixture increases and the volume of the reaction mixture V shrinks. Rearranging the total mass balance equation, one can obtain the following equation that can be used to calculate the change in the volume of the reaction mixture, that is

$$dV_p/dt = - [W_{m_1}r_{M_1}V + W_{m_2}r_{M_2}V + W_s r_s V] / \rho_p \quad (10)$$

$$V_{M_1} = (M_1V) \frac{W_{m_1}}{\rho_{M_1}}, V_{M_2} = (M_2V) \frac{W_{m_2}}{\rho_{M_2}}, V_s = (SV) \frac{W_s}{\rho_s}$$

where V_j and ρ_j denote the volume and density of species j , respectively.

Experimental System

Figure 1 shows diagram the semi-batch MMA/MA solution copolymerization reactor system employed in this study. The system consists of the reaction part and the automatic control part. The reaction part is composed of a polymeriza-

tion reactor, the heat-transfer apparatus, and the stirrer. The automatic control part includes a programmable logic controller (PLC) for input/output process data and a computer for control and data acquisition, and actuators. Heating and cooling of the reaction mixture are performed by the heating-cooling water flowing 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 set point pump is used for pumping the monomers into the reactor. This is a piston-operated metering pump from FMI LAB (Model QVG50). The speed of the pump motor is regulated by the stroke rate controller (Model V200). In order to measure the density and viscosity of the reaction mixture, a circulation line is attached to the reactor. The reaction mixture is circulated by a diaphragm metering pump through the circulation line at a rate of 50 mL/min, in which the online densitometer (Anton Paar, Model DMA401YH) and viscometer (Sofraser, Model MIVI-ADF) are installed.

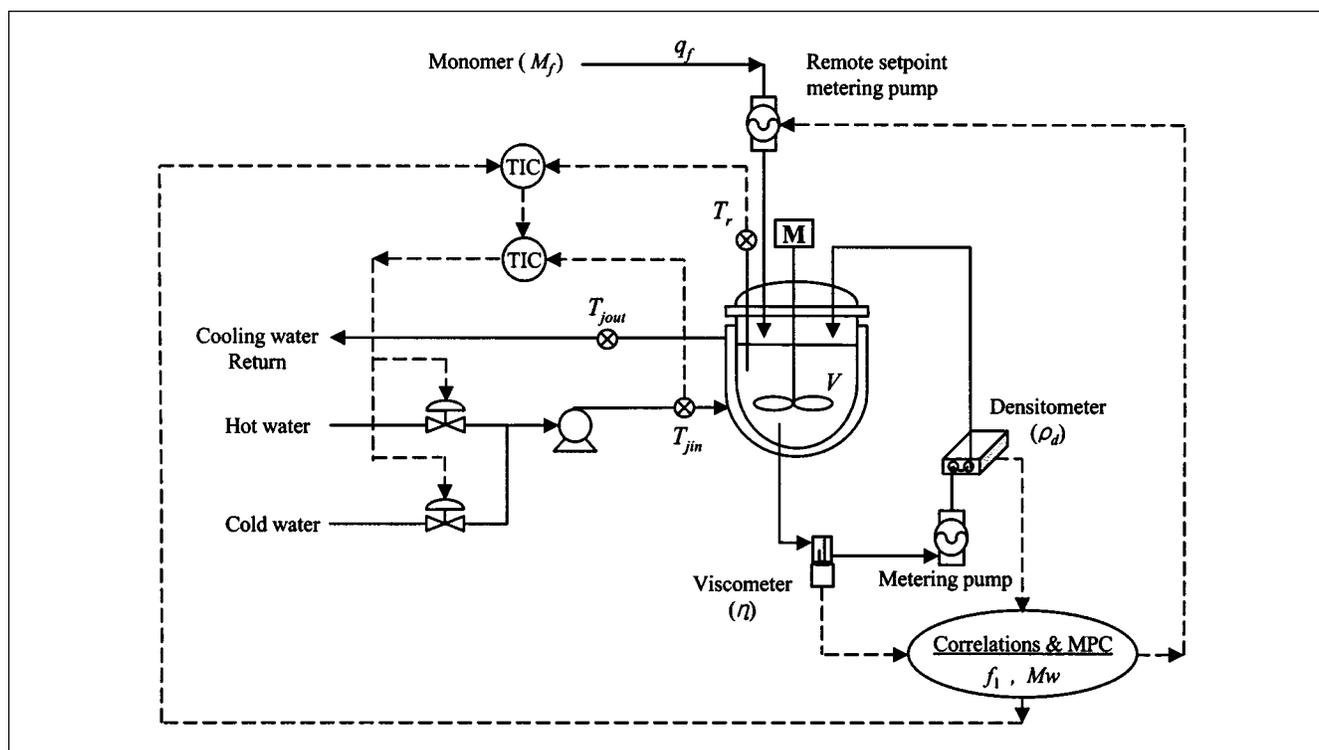


Figure 1. Semi-batch MMA/MA solution copolymerization reactor system.

Online Estimation

The density and the weight-average molecular weight (M_w) of the reaction mixture are measured online to estimate the state of the semi-batch copolymerization reactor by using the extended Kalman filter (Grewal and Andrews, 1993). The density is calculated by the equation

$$\rho = \frac{W}{V}$$

$$= \frac{W}{V_{m1} + V_{m2} + V_s + V_p} = \frac{W}{W_{m1} \frac{M_1 V}{\rho_{m1}} + W_{m2} \frac{M_2 V}{\rho_{m2}} + W_s \frac{SV}{\rho_s} + V_p} \quad (11)$$

where W denotes the total weight of the reaction mixture in the reactor. The volume of copolymer V_p is calculated by Eq. 10, which requires the calculation of copolymer density ρ_p .

In case of homopolymers, the density as a function of temperature is readily available from the literature. However, as the copolymer chains are composed of different types of monomers with variable compositions, it is a rather difficult task to derive an expression for the copolymer density. In this study, the expression for the hydrodynamic volume of a copolymer suggested by Goldwasser and Rudin (1983) is extended to calculate the density of copolymer with an assumption that all the polymers produced during the reaction course have almost the same copolymer composition. The resulting equation is

$$1/\rho_{\text{copolymer}} = \left(w_1 (1/\rho_{p1})^{2/3} + w_2 (1/\rho_{p2})^{2/3} \right)^{3/2} \quad (12)$$

where w_i and ρ_{pi} denote the weight fraction of monomer i in the copolymer chain and the density of homopolymer of monomer i , respectively. Due to the composition drift, however, the assumption of uniform copolymer composition may not be valid, and thus we add an unmeasured disturbance d (Lee and Ricker, 1994) to $\rho_{\text{copolymer}}$ to have

$$\rho_p = \rho_{\text{copolymer}} + d \quad (13)$$

Here, it is assumed that the unmeasured disturbance signal d is generated through the following stochastic difference equation

$$x_k^w = A^w x_{k-1}^w + B^w h_{k-1}$$

$$d_k = C^w x_k^w \quad (14)$$

where h_k is discrete-time white noise with covariance R^w .

For the online measurement of M_w , the following correlation is proposed to describe the relationship between the specific viscosity (η_{sp}) measured by the viscometer and the intrinsic viscosity ($[\eta]$)

$$\eta_{sp} = C^{0.8} [\eta] \exp \frac{k_H [\eta] C^{0.8}}{1 - bC^{0.8}} + (C^{0.8})^2 [\eta]^2 \exp \frac{2k_H [\eta] C^{0.8}}{1 - bC^{0.8}}$$

$$+ (C^{0.8})^3 [\eta]^3 \exp \frac{3k_H [\eta] C^{0.8}}{1 - bC^{0.8}} \quad (15)$$

The parameters k_H and b are specified as 0.58 and 0.8, respectively, when the viscosities are given in the unit of cp (centipoise).

The intrinsic viscosity is used to calculate the weight average molecular weight by the Mark-Houwink equation

$$[\eta] = K(M_w)^a \quad (16)$$

The Mark-Houwink constants are determined as

$$K = 3.35 \times 10^{-5}$$

$$a = 0.92 + 5.0 \times 10^{-5} (\eta - \eta|_{x=0})$$

In Eq. 15, C indicates the mass concentration (g/mL) of copolymer in the reactor that can be obtained by using the online densitometer data, that is, $C = \rho X$, where X denotes the solid content which is defined as the ratio of the weight of copolymer produced to the weight of the total reaction mixture that consists of monomers, solvent, and copolymer. Here, the weight of copolymer is given by the moles of monomers consumed in the copolymerization.

The four parameters k_H , b , K , and a appearing in Eqs. 15 and 16 were determined by applying the trial and error method in such a way that the offline measurement of M_w coincides over a wide range with the values calculated by the correlation equations. At first, the online measurement data for density and viscosity were collected by conducting experiments in an open-loop manner. The variation of solid content X with time was also obtained by analyzing the samples taken successively from the reactor. These measured values were then applied to the pair of Eqs. 15 and 16 to determine the four parameters so as for the calculated values of M_w to match the offline measurement. In carrying out this procedure, the values for K and a were chosen to have the same orders of magnitude as their respective values for the homopolymers reported by Brandrup and Immergut (1989).

The state variables used in the model are IV , M_1V , M_2V , SV , H_0V , H_2V , V_p , and x^w (a variable which is related to the unmeasured disturbance). These are used in normalized dimensionless forms to reduce the differences among the orders of magnitude of individual variables. The conventional EKF has several design variables such as measurement noise covariance matrix, process noise covariance matrix, and initial state error covariance matrix. As the degree of model mismatch is assumed to be weak, we assign larger values to measurement noise covariance than process noise covariance so as to effectively attenuate the measurement noise. We also take into account the fact that a too optimistic (small) value for the process noise covariance matrix makes the filter diverge, although a poor estimate for this value may be easily tolerated. Furthermore, these matrices are used in diagonal form for the sake of convenience, as well as due to lack of information regarding the covariance. Finally, the process noise covariance matrix and the measurement noise covariance matrix are chosen as $1 \times 10^{-4} I_{8 \times 8}$ and $1 \times 10^{-2} I_{2 \times 2}$, respectively. The initial state error covariance matrix is specified as $\text{diag}(1 \times 10^{-3}, 1 \times 10^{-6}, 1 \times 10^{-6}, 1 \times 10^{-3}, 1 \times 10^{-5}, 1 \times 10^{-6}, 1 \times 10^{-4}, 1 \times 10^{-2})$.

In order to corroborate the validity of EKF, experiments were conducted under isothermal condition at 80°C with ini-

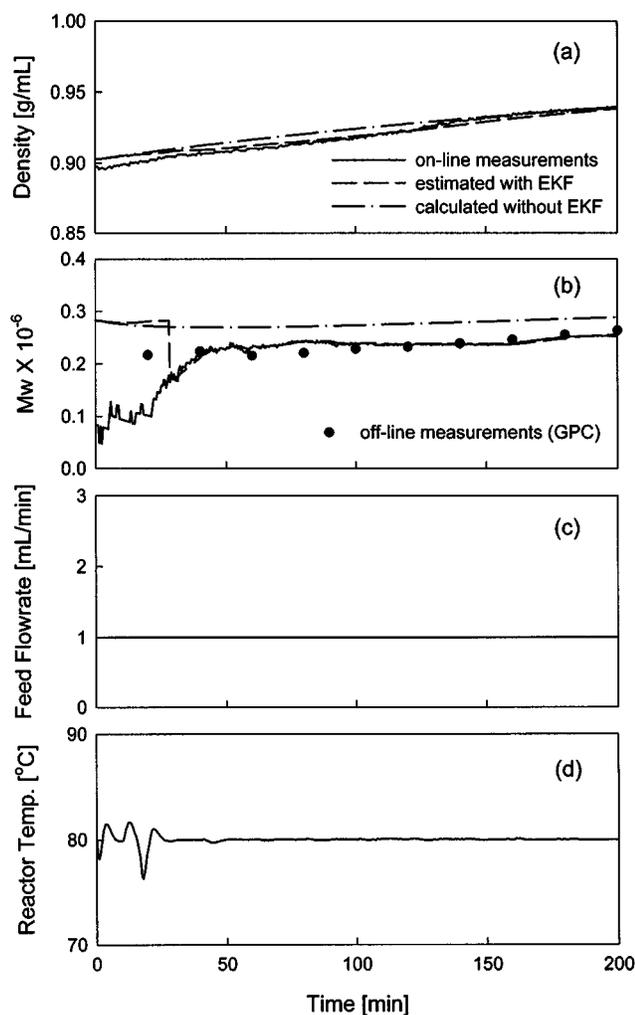


Figure 2. Comparison of estimated outputs for the density and M_w determined by the extended Kalman filter, outputs without EKF, and experimentally determined outputs under isothermal condition at 80°C.

tial charges of 390 mL of MMA, 50 mL of MA, 460 mL of toluene and 0.3 g of AIBN. The feed is injected at a rate of 1 mL/min to prevent a severe composition drift. Figure 2 shows the experimental result of online state estimation with errors in the initial estimates of states. It is assumed that the initial charge of monomer 1 (MMA) is lower than the actual charge by 10% and the initial value of H_2V is 0.1, although the actual value is zero. It should be noticed that the assumption of initial loading error causes the states of the reactor estimated in the earlier part to have deviations from exact ones. This indicates that exact values of solid content needed in the viscosity- M_w correlation are not available in this period. For the initial period of 30 min, therefore, only the density is used in the measurement correction procedure in such a way that the states used in the calculation of solid content may converge to the actual states. In view of the observability, however, all the values are not the optimal estimates during this period because some states such as H_2V are not associated with

density, but with M_w . After 30 min, both the density and M_w obtained by the online measurement are used and all the states are estimated with optimality.

As shown in Figure 2a, the density calculated by using the EKF tracks the online measured value, while the value calculated by the model without using EKF deviates from the actual value. A sluggish convergence of density is observed here, because the density of monomer 1 is not much different from that of monomer 2. If the online value of density is applied to a copolymerization system with two monomers with much different densities, it is expected to obtain more satisfactory estimation performance.

With respect to M_w , Figure 2b shows the convergence of M_w to the online measured value at 30 min. The effectiveness of the viscosity- M_w correlation equation is proven by the comparison between the online measured values and the off-line measured values obtained by gel permeation chromatography (GPC). As shown in the figure, the online and offline measurements essentially coincide after 50 min. However, there exists a discrepancy between the online and offline measurements during the first 50 min, which may be caused by the low viscosity in the earlier period of the reaction course. In other words, Eq. 15 may not provide a good estimate for the intrinsic viscosity $[\eta]$ when the specific viscosity η_{sp} is very low. As the viscosity increases, however, the correlation becomes effective to give better estimates for the intrinsic viscosity.

Figure 3a and Figure 3b present the mol fraction f_1 of MMA in the remaining monomers and the solid content, respectively. The solid circle represents the offline measurement obtained by analyzing samples of about one gram taken from the reactor every 20 min. The mol fraction of MMA was analyzed by using gas chromatography (GC) and the solid content was determined by the gravimetry method. As shown in Figure 3, the value from EKF predicts the offline measure-

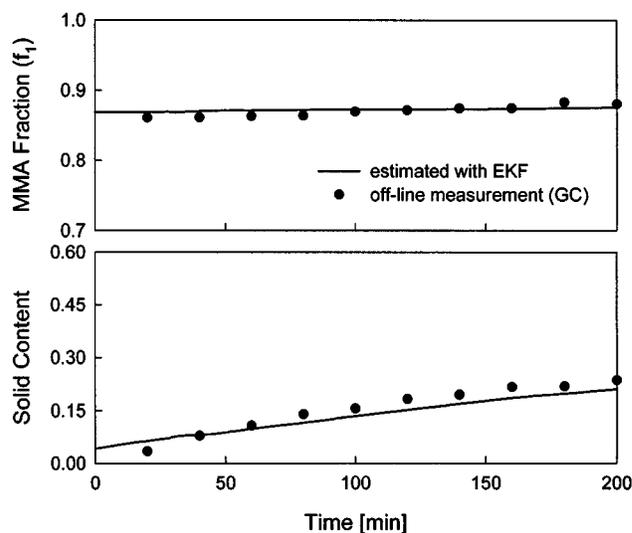


Figure 3. Comparison of estimated outputs for MMA mol fraction and the solid content determined by the extended Kalman filter to the measured outputs by experiment under isothermal condition at 80°C.

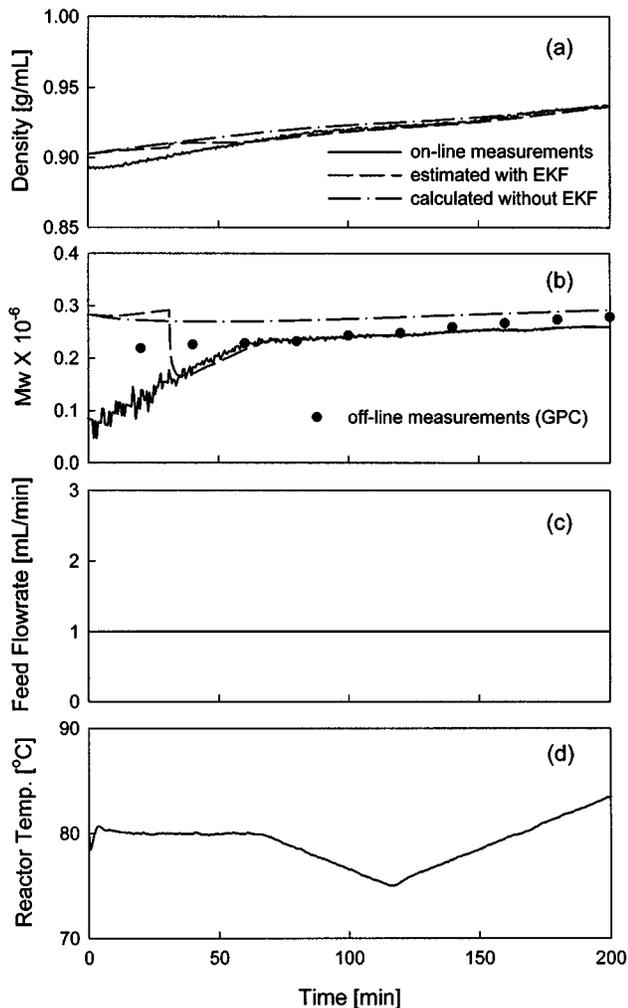


Figure 4. Comparison of estimated outputs for the density and M_w determined by the extended Kalman filter, outputs without EKF, and experimentally determined outputs under non-isothermal condition (Case I).

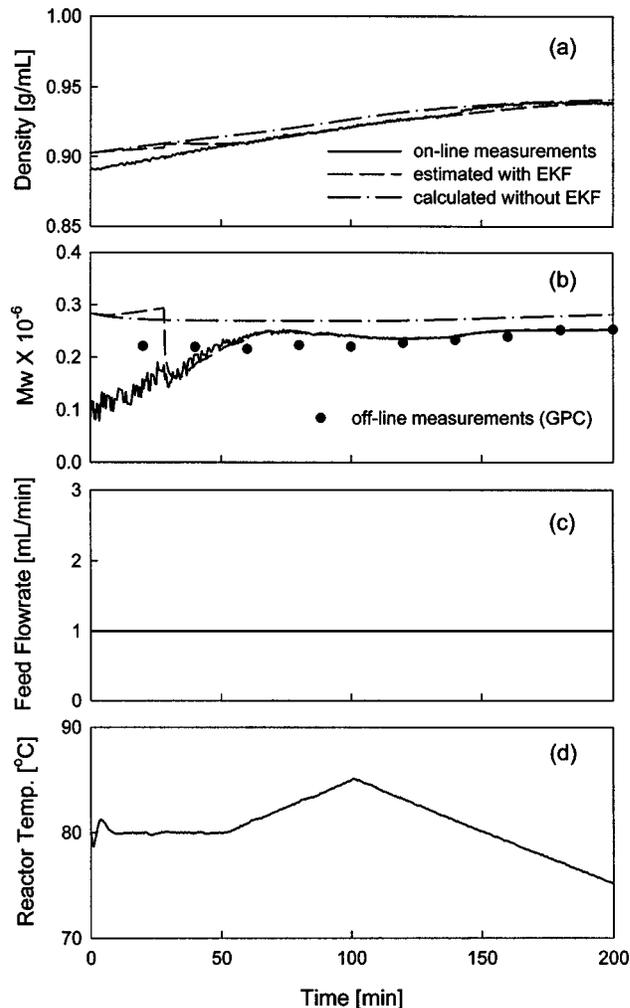


Figure 5. Comparison of estimated outputs for the density and M_w determined by the extended Kalman filter, outputs without EKF, and experimentally determined outputs under non-isothermal condition (Case II).

ment quite well. Since the feed flow rate of MMA is kept constant, MMA is accumulated in the reactor. Accordingly, the mol fraction of MMA increases gradually.

Because the reaction temperature is used as the manipulated variable, the estimation procedure is also evaluated under nonisothermal conditions and the results are shown in Figures 4 and 5. Figures 4d and 5d present the temperature profiles, which are found to cover the entire operating range for the control of the semi-batch reactor.

From the online estimates and measurements of density and M_w shown in Figures 4 and 5, it is noticed that the filter successfully tracks the online measured values during the entire course of polymerization. This indicates that the online estimation may be applied to the copolymerization reactor for the control of polymer properties.

Further analysis of this nonisothermal operation provides important information. As the temperature increases, it is expected that the degree of polymerization decreases in free-radical polymerization system initiated by a thermal initiator.

In the latter part of the reaction course (see Figure 4), however, M_w still gradually increases although the temperature increases. The continuous supplement of monomer appears to be responsible for this phenomenon. Hence, it is expected to be rather difficult to decrease M_w in a semi-batch copolymerization reactor.

Property Control

In most of the control studies, the feed flow rate of more reactive monomer is used for the control of copolymer composition while the chain transfer agent (CTA) is used to obtain polymers with desired M_w . Since the use of CTA is restricted to the case of lowering the molecular weight, instead the reaction temperature is taken as the manipulated variable in this study.

The use of both feed flow rate and reaction temperature brings about difficulties in the calculation of optimal operating conditions, because inputs and outputs are highly corre-

lated with each other. Experimental studies are conducted here to produce copolymers with uniform composition and desired Mw by applying the EKF-based nonlinear model predictive controller suggested by Lee and Ricker (1994) and successfully applied to the continuous polymerization reactor by Ahn et al. (1999).

In the EKF-based nonlinear MPC, a sequence of optimal control moves which minimize the following objective function can be computed

$$\min_{\Delta U_k} \left\| \Lambda^y [Y_{k+1|k} - R_{k+1|k}] \right\|_2^2 + \left\| \Lambda^u \Delta U_k \right\|_2^2 \quad (16)$$

where $Y_{k+1|k}$ and $R_{k+1|k}$ represent the multistep prediction vector and the future reference vector for the controlled outputs, respectively, and ΔU_k denotes a sequence of the rates of the control inputs. It is assumed that copolymer composition in this system obeys the Mayo's equation, that is, copolymer composition is determined by the reactivity ratio and the mol fraction of more reactive monomer in the remaining monomers. The mol fraction f_1 of MMA in remaining monomers and the weight average molecular weight (Mw) are chosen as controlled outputs, while the feed flow rate of MMA and the reaction temperature are taken as the control inputs. Weighting matrices Λ^y and Λ^u are used in diagonal form for convenience and determined by trial-and-error method as follows

Weighting matrix for outputs: $\Lambda^y = \text{diag}(1.2 \quad 1.0)$

Weighting matrix for inputs: $\Lambda^u = \text{diag}(0.01 \quad 0.08)$

The first and the second elements of weighting matrix for outputs are related here to the mol fraction of MMA and Mw , respectively. The first and the second elements of weighting matrix for inputs are related to the feed flow rate and the reaction temperature, respectively. Too low a value for weighting matrix for inputs leads to abrupt changes of inputs which would result in the production of copolymers with poor quality. The sampling time, the prediction horizon, and the control horizon are specified as 1, 20, and 10 min, respectively. In addition, the following constraints are taken into account. It is to be noticed that output constraint, so-called hard constraint, is not considered because it can be violated by disturbance.

Constraints for the magnitude of inputs:

$$0.1 \leq \text{feed flow rate} \leq 20 \text{ [mL/min]}$$

$$70 \leq \text{reaction temperature} \leq 90 \text{ [}^\circ\text{C]}$$

Constraints for the rate of inputs:

$$-0.5 \leq \Delta(\text{feed flow rate}) \leq 0.5 \text{ [mL/min]}$$

$$-2 \leq \Delta(\text{reaction temperature}) \leq 5 \text{ [}^\circ\text{C]}$$

Figure 6 shows the experimental results when the set points of f_1 and Mw are set to be 0.87 and 220,000, respectively. During the initial 50 min, the reactor is operated in an open-loop manner and then the control action is started at 50 min, because the online estimation during the initial 50 min may not provide a proper value for the optimal state of the reactor due to the following reasons:

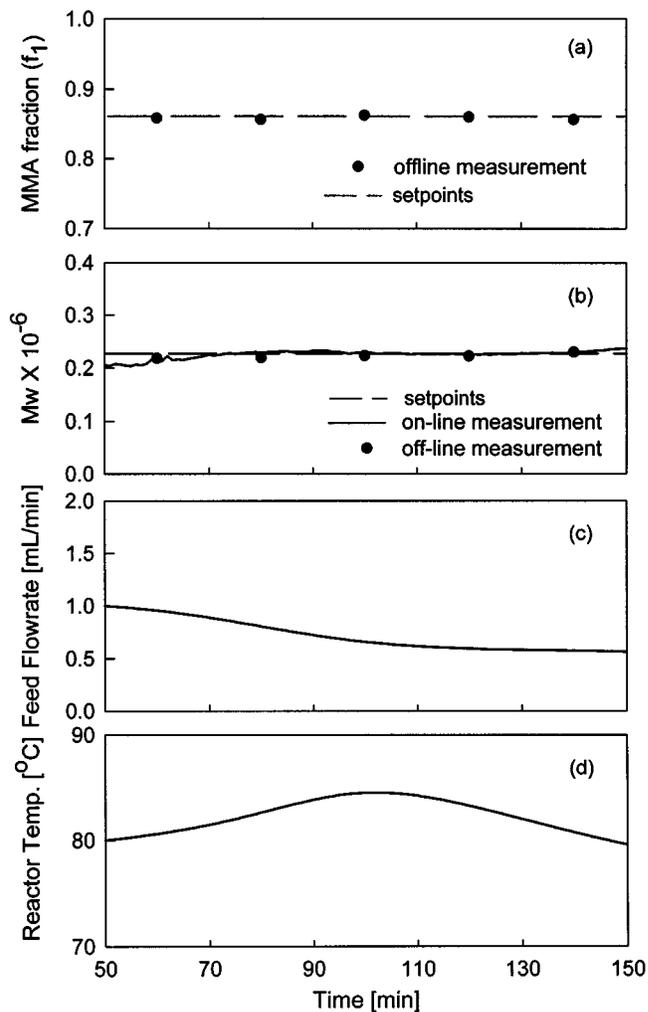


Figure 6. Regulatory performance of the EKF-based nonlinear model predictive control for the mol fraction of MMA in the remaining monomers and the weight average molecular weight.

(1) The correlation may not provide a good estimate for Mw when the viscosity is very low as mentioned in the previous section.

(2) The estimated value of density converges to its online measurement value after about 50 min since the densities of two monomers have similar values in the present system.

As soon as the optimization scheme starts, the controller increases the reaction temperature and simultaneously decreases the feed flow rate. It is worth noting that the feed flow rate tends to decrease continuously to prevent Mw from increasing. As the reaction proceeds, the controller maintains f_1 at its desired value and also drives Mw to its set point. 20 min after the control action was taken, Mw converges to its set point and is maintained there. In most of research works related to the control of Mw in a batch or semi-batch reactor, the aim of the control was to obtain polymers with desired Mw at the final time. In this study, an objective is to maintain Mw during the entire course of polymerization. It has been reported that maintaining Mw constant during

polymerization has the effect of minimizing the breadth of the MWD and a narrow distribution improves elongational properties and produces higher tensile strength of the polymer product (Hoffman et al., 1964). In this regard, the nonlinear MPC proposed in this study certainly demonstrates its applicability to actual processes.

As the viscosity increases much sharply after 140 min, the online measurement correlation tends to give a value larger than the actual one. Consequently, the online measurement may not be applied in this region of high viscosity. Such a difficulty caused by high viscosity has also been reported in the control of polymer properties for batch or semi-batch polymerization reactors (Ellis et al., 1994).

The performance of the EKF-based nonlinear MPC is also tested for the case of equipment failure. We consider the case of circulation pump breakdown during the operation. Figure 7 presents the time evolution of the control inputs and controlled outputs under such a circumstance. Between

80 and 100 min, the circulation pump is stopped by accident and the error caused by the equipment failure is observed in the online measured value of M_w (see Figure 7b). During the period of equipment failure, the controller decreases the feed flow rate more rapidly than in the previous case to compensate for the deviation from the set points. After 100 min when the equipment recovers its function, the feed flow rate tends to decrease slowly again. The more slowly the feed flow rate decreases, the more the monomer is accumulated in the reactor, which results in an increase of M_w . Accordingly, the reaction temperature shows a sudden increase to prevent M_w from increasing. As shown in Figure 7, the controller performs satisfactorily under the existence of equipment failure. As the reaction temperature increases to a higher range than that in Figure 6, the rate of polymerization becomes larger and thus the sharp rise in viscosity appears well before 140 min.

Concluding Remarks

Online state estimation with EKF is applied to the semi-batch MMA/MA solution copolymerization reactor using the online measurement of density and weight average molecular weight. For the calculation of M_w , the viscosity- M_w correlation equation is suggested and its effectiveness is corroborated by conducting experiments under isothermal and non-isothermal conditions. The experimental result shows that EKF can estimate the state of the reactor quite well and that the weight average molecular weight tends to increase regardless of the change in the reaction temperature due to the continuous supplement of MMA.

On the basis of the estimated states, an MPC is designed and implemented experimentally to the semi-batch copolymerization reactor by using the monomer feed rate and the reaction temperature as the manipulated variables. When the control outputs are the copolymer composition and the weight average molecular weight, it is demonstrated that the MPC performs satisfactorily for the production of copolymers with uniform composition and desired M_w even when equipment failure occurs. As the viscosity of reaction mixture becomes large, the viscosity- M_w correlation equation fails to provide a proper estimation of M_w and this feature requires further investigation.

Acknowledgment

The financial aid from the Brain Korea 21 Program supported by the Ministry of Education is gratefully acknowledged.

Notation

- f_i = mol fraction of monomer i in the remaining monomers
- F_i = mol fraction of monomer i in the copolymer chain
- G_k = k th moment of living polymer concentration, mol/L
- H_k = k th moment of dead polymer concentration, mol/L
- I = mol of initiator, mol
- M_1 = mol of monomer 1, mol
- M_2 = mol of monomer 2, mol
- M_{av} = instantaneous average molecular weight, g/mol
- M_n = number-average molecular weight, g/mol
- M_w = weight-average molecular weight, g/mol
- $[P_r]$ = concentration of dead polymer with r units of monomer, mol/L
- q_f = feed flow rate, L/min

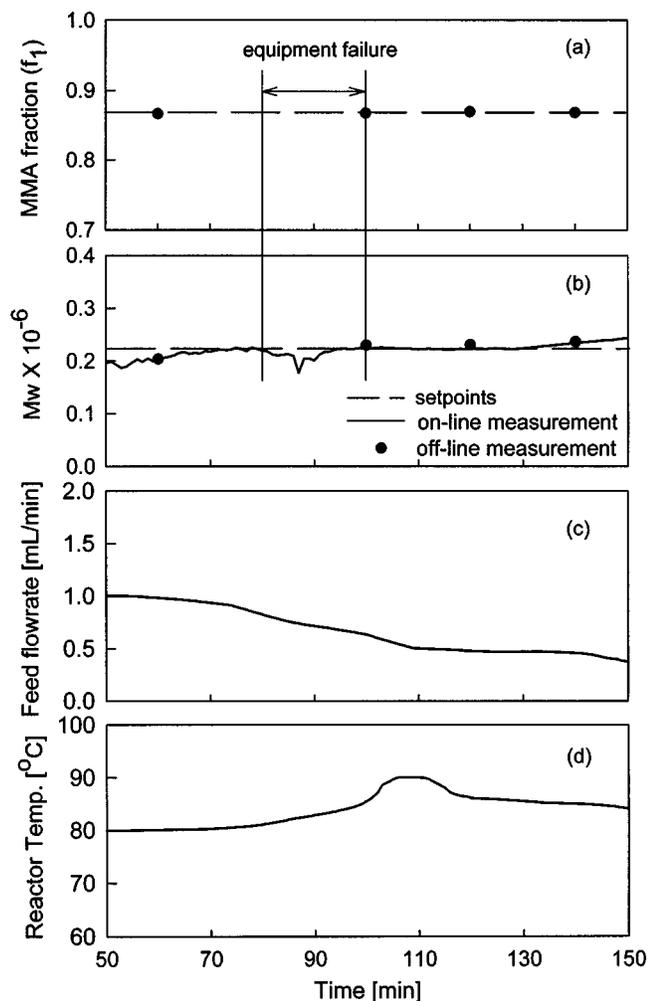


Figure 7. Regulatory performance of the EKF-based nonlinear model predictive control for the mol fraction of MMA in the remaining monomers and the weight average molecular weight with equipment failure between 80 and 100 min.

$[R_{r,i}]$ = concentration of living polymer with monomer i as the terminal and r units of monomer, mol/L
 SV = mol of solvent, mol
 V = volume of reaction mixture, L
 V_i = volume of component i , L
 W_i = molecular weight of component i , g/mol
 x^w = state for unmeasured disturbance
 η_{sp} = specific viscosity
 $[\eta]$ = intrinsic viscosity, mL/g
 ρ_i = density of component i , g/L

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Manuscript received July 24, 2001, and revision received Oct. 24, 2001.