# On-Line Molecular Weight Distribution Estimation and Control in Batch Polymerization

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*A molecular weight distribution (MWD) estimator for batch methyl methacrylate solution polymerization is implemented experimentally for on-line control and estimation of the MWD. The estimator is based on an extended Kalman filter and provides current estimates of the entire MWD, reaction temperature, monomer conversion, and initiator conversion. It uses a detailed polymerization model, on-line monomer conversion measurements, temperature measurements, and periodic, time-delayed measurements of the MWD from an on-line size-exclusion chromatograph. The estimator is shown to perform well with several on-line MWD estimation experiments. Real-time feedback control of the molecular weight is presented by utilizing the on-line MWD information. Temperature, monomer-addition, and simultaneous temperature and monomer-addition control are investigated experimentally to achieve a specific constant weight-average molecular weight. The on-line feedback control is effective in rejecting realistic disturbances which deteriorate molecular weight control.*

## Introduction

The molecular weight distribution (MWD) is a fundamental polymer property that directly influences end-use polymer characteristics. The MWD affects processing through the polymer melting point and the flow properties of the melted polymer. It also determines many of the mechanical properties of the processed product, such as strength and impact resistance. Several other important polymer characteristics, which are governed by the molecular weight distribution, are described by Martin et al. (1972), Nunes et al. (1982), Ray (1983), Tirrell (1984), and Graessley (1974). It is apparent that there is a strong incentive to control the molecular weight distribution accurately during polymerization.

Molecular weight distribution control is difficult with online measurement being the primary obstacle. Without measurement, feedback control of the MWD is not possible. Common industrial methods for molecular weight control have been to perform polymerizations in an open-loop fashion with measurement after the product is already made. The process is operated according to a predetermined recipe (such as temperature profile and feed addition rate) which has been found to produce product with the desired properties. The recipe is usually determined by trial-and-error experience, experimental design, intuition, or a combination of these. A less common industrial approach for determining feedforward control profiles is through the use of polymerization models along with optimal control methodologies (Denn, 1969; Bryson and Ho, 1975; Ray, 1981). The obvious difficulty in these instances is that it is not possible to compensate for unexpected disturbances which can adversely affect MWD control and, thus, the end-use polymer characteristics.

In certain cases, coarse on-line process correction is possible based on infrequent, cumbersome and time-delayed measurements from analytical laboratory measuring devices. The time

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delays involved can introduce instability. Also, it is difficult to incorporate the measurement information into an automated feedback control scheme because human intervention is necessary to take samples, prepare the samples for analysis, perform the test, interpret the results, and make the appropriate control decisions, increasing the risk of process variability.

Recently, commercial on-line size-exclusion chromatographs (SEC), devices which can provide direct measurements of the MWD, have become available. However, the measurements from these devices are periodic, time-delayed (10–40 min or more), and can be corrupted by noise. This can obviously deteriorate feedback controller performance.

The two-time-scale MWD estimation algorithm by Ellis et al. (1988a) was developed to incorporate the periodic, time-delayed molecular weight measurements from an on-line size exclusion chromatograph, as well as the relatively simple and more rapid on-line measurements of temperature and monomer conversion. A detailed polymerization model, capable of predicting the entire shape of the MWD, was used in combination with an extended Kalman filter (EKF) to provide current estimates of the MWD, monomer conversion, initiator conversion, and reaction temperature. Ellis et al. (1988a) demonstrated the feasibility of the MWD estimator with simulation studies, and off-line experimental measurements which were fed to a simulated estimator in the manner that they would be available if the experimental equipment was functioning in real time.

There were two primary objectives of the work presented in this article. The first intent was to implement the MWD estimator of Ellis et al. (1988a) and experimentally test it for a variety of polymerization conditions which are likely to be encountered in an industrial setting. The second aim was to use the on-line MWD information available from the estimator for experimental feedback control of the molecular weight.

The chemical system chosen for the study was the batch polymerization of methyl methacrylate (MMA) because its kinetics are relatively well known and the rate constant data are documented in the literature. The solvent selected for the polymerization was ethyl acetate, since MMA and polymethylacrylate (PMMA) are soluble in it and it is a common solvent for solution polymerizations. The thermal initiator azobisisobutyronitrile (Vazo-64; AIBN) was chosen as it is a common initiator used for free-radical polymerization.

The background references prior to 1988 relating to estimation in polymerization systems are provided by Ellis et al. (1988a). More recently, Adebekun and Schork (1989) developed a Kalman filtering technique for state estimation of the leading moments of the MWD in the polymerization of methyl methacrylate in a continuous stirred tank reactor. The technique was tested in a simulation study, and the robustness of the filter was demonstrated for poor initialization. They also dealt with the important consideration of incorporating the estimator in a simulated closed-loop control scheme and found it feasible to control molecular weight, even in cases where the desired equilibrium point is open-loop unstable.

Dimitratos et al. (1989) have developed a Kalman filtering technique for estimation of the copolymer composition in a semibatch emulsion polymerization reactor. The extended Kalman filtering routine used in their study adaptively computed the error covariance matrices rather than the standard approach for assuming them constant. Further, a limited-memory version of the extended Kalman filter was investigated. Preliminary simulated estimation results demonstrated implementation of the approach and its feasibility. In a follow-up study, Dimitratos et al. (1991) demonstrated the experimental application of the technique using a laboratory-scale reaction system.

Extended Kalman filtering for tracking the states of continuous emulsion polymerization was investigated by Gagnon and MacGregor (1991). Simulated emulsion styrene/butadiene copolymerization was used for estimation case studies. The importance of introducing nonstationary disturbance and/or model mismatch states for removing bias in the state estimates was highlighted. Also a procedure for selecting optimal combinations of on-line sensors was presented.

Kozub and MacGregor (1992b) investigated three approaches for state estimation in semibatch emulsion polymerization, using free-radical emulsion copolymerization of styrene/butadiene as a case study. Two variations of the extended Kalman filter (EKF) and an on-line optimization procedure for state estimation were compared in simulated polymerizations. A recursive variation of the EKF, capable of estimating the initial states, was found to be the most suitable for the semibatch polymerization problem. Finally, their work reinforced the benefits of incorporating nonstationary disturbance states for preventing bias in the state estimates.

With the recent availability of on-line SEC devices and other advances in on-line polymer property measurement, some researchers have directed their attention to investigating feedback control algorithms for polymer property control. However, most works have been simulation studies which assume that desired polymer properties are measurable. For example, in the work of Kiparissides et al. (1981), the suboptimal feedback control algorithm developed for control of a continuous latex reactor was investigated through simulation studies. Ponnuswamy et al. (1987) have investigated optimal closed-loop control of methyl methacrylate polymerization in a simulated batch reactor. Houston and Schork (1987) have presented an adaptive-predictive controller for controlling conversion and molecular weight in a simulated batch reactor. The optimal feedback control of methyl methacrylate polymerization in a continuous reactor was investigated using simulation studies by Adebekun and Schork (1989). Congalidis et al. (1989) presented a combined feedforward/feedback control scheme for control of molecular weight and copolymer composition in solution polymerization performed in a continuous stirred tank reactor. This control algorithm was also tested using simulation studies. Tzouanas and Shah (1989) compared an adaptive pole-placement controller, a generalized minimum variance adaptive controller, and a fixed-gain PID controller for control of weight-average molecular weight and conversion in batch polymerization of methylmethacrylate. Conversion control cases were experimental, but molecular weight control cases were simulation studies. Kozub and MacGregor (1992a) proposed a feedback control strategy for on-line control of copolymer properties in a semibatch polymerization. The control strategy contains a nonlinear estimator (Kozub and MacGregor, 1992b), an on-line implementation of optimal open-loop operating policies, and a feedback controller to correct for errors in the recomputed optimal trajectories. Simulation studies were used to demonstrate the application of the feedback control strategy on semibatch styrene/butadiene emulsion polymerization.

The on-line molecular weight control cases involve the industrially important case of controlling to achieve and maintain a constant, specified weight-average molecular weight, $M_w$. Several other control objectives could have been selected, but this one illustrates many of the features and potential benefits of on-line feedback control of molecular weight. Maintaining $M_w$ constant during polymerization has the effect of minimizing the breadth of the MWD. A narrow distribution is desired because it improves elongational properties and produces higher tensile strength of the polymer product (Hoffman et al., 1964). In a review article, Martin et al. (1972) cite several references indicating that stress-strain properties, thermal properties, impact resistance and stress crack resistance of many polymer systems were improved by narrowing the MWD. Apart from obtaining a narrow MWD, obtaining a specific weight-average molecular weight may be desirable because the melt and concentrated-solution viscosities are directly related to $M_w$ (Graessley, 1974).

A simple proportional-integral-derivative (PID) controller was used to adjust the reactor temperature setpoint, monomer addition setpoint, or simultaneous monomer addition and temperature control to maintain $M_w$ at its desired value. The results show that the on-line MWD information enables correction of the molecular weight for severe disturbances in polymerization conditions and reduces the batch-to-batch variability. This article, to the best of our knowledge, is one of the first illustrations of on-line feedback control of molecular weight in the literature.

## Polymerization Model

The emphasis in developing the model was to predict as accurately as possible the MWD between the periodic SEC measurements and forward in time until the next time-delayed measurement is available. Since a primary objective of this work was to use the estimates of molecular weight for feedback control, the performance of the control scheme depends on the accuracy of the underlying polymerization model.

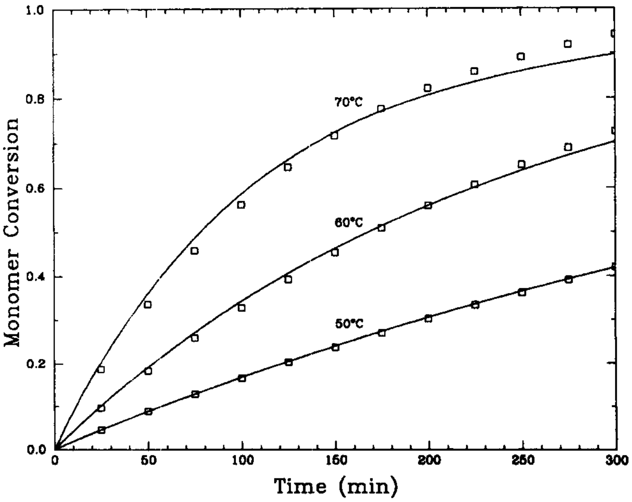

**Figure 1a. Comparison of experimental observations with model-predicted conversions obtained using literature parameters.**

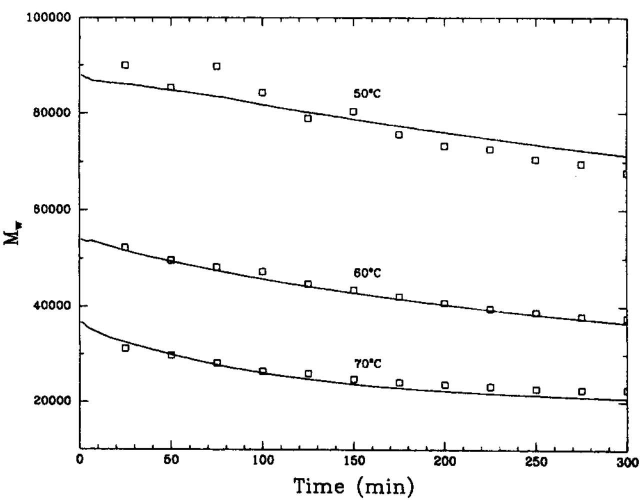

**Figure 1b. Comparison of experimental observations with model-predicted weight-average molecular weights obtained using optimized parameters.**

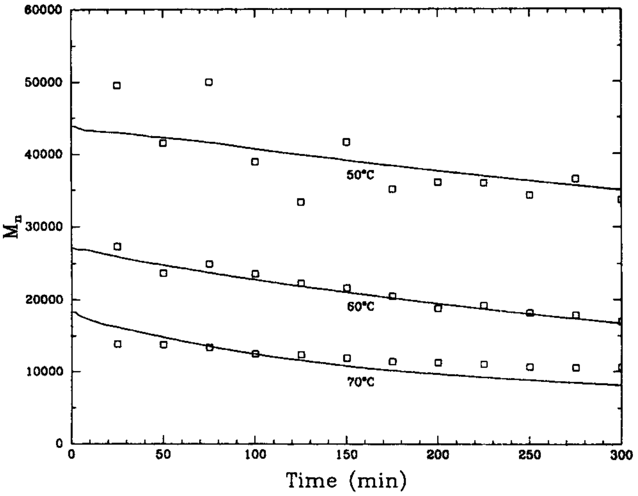

**Figure 1c. Comparison of experimental observations with model-predicted number-average molecular weights obtained using optimized parameters.**

The polymerization model and the numerical solution and discretization of the rate equations for the discrete extended Kalman filter have been detailed by Ellis et al. (1988a) and Ellis (1990).

To validate the predictions from the polymerization model in the range of conditions used for the estimation and control case studies, a series of polymerizations were performed in the temperature range 323 to 343 K with 25% MMA by weight (2,842 mL ethyl acetate charged), and 0.05 molar in AIBN. Model predictions made using the values for the kinetic constants by Ellis et al. (1988a) provided very good agreement with the experimental values of monomer conversion obtained (see Figure 1a). The values for weight-average and number-average molecular weight did not agree as well ($M_w$ and $M_n$ were both predicted about 40% too high). As described by Ellis (1990), a nonlinear least-squares routine (Levenberg-Marquardt method available in the IMSL library, ZXSSQ) was used to simultaneously optimize, in a least-squares fashion, the activation energies in the Arrhenius expressions for the transfer reactions to solvent and monomer, $E_{\mathrm{trs}}$ and $E_{\mathrm{trm}}$. The objective function, $J(E_{\mathrm{trm}}, E_{\mathrm{trs}})$, was the sum of the squares of the difference between predicted and measured molecular weights:

$$J(E_{\mathrm{trm}}, E_{\mathrm{trs}}) = \sum_{i=1}^{N} (M_{w_{\mathrm{exp},i}} - M_{w_{\mathrm{pred},i}})^2 \qquad (1)$$

Here, the $M_w$ values with the exp subscript denote the experimentally measured weight-average molecular weight values, and the $M_w$ values with the pred subscript are the corresponding model-predicted weight-average molecular weights evaluated at a certain set of $E_{\mathrm{trm}}$ and $E_{\mathrm{trs}}$ values. The values of $E_{\mathrm{trm}}$ and $E_{\mathrm{trs}}$ sought were those which minimize $J(E_{\mathrm{trm}}, E_{\mathrm{trs}})$. The weight-average molecular weight was selected for parameter fitting because it was relatively insensitive to baseline drift, whereas $M_n$, number-average molecular weight, showed more noise in the values obtained from the on-line SEC.

The values $E_{\mathrm{trm}} = 75{,}508$ kJ·kmol$^{-1}$ and $E_{\mathrm{trs}} = 59{,}690$ kJ·kmol$^{-1}$ resulted from applying this procedure. The optimized values for $E_{\mathrm{trm}}$ and $E_{\mathrm{trs}}$ changed by less than 10% from the starting literature values and therefore were decided to be physically reasonable. Figures 1b and 1c show that the molecular weight predictions obtained using these parameters agree very well with the experimental values—within the reproducibility of the experiments (the noise in the number-average molecular weights for the 323 K polymerization was due to the higher significance of SEC baseline drift for the lower monomer conversion and consequently smaller SEC peaks obtained).

## Experimental System

A schematic diagram of the experimental apparatus is provided in Figure 2. The reactor was a 0.005-m$^3$ stainless-steel jacketed cylindrical vessel with a 0.00635-m (1/4-in.) drain centered at the bottom. The reactor's contents were mixed by a 0.0889-m-dia. four-blade turbine agitator at 250 rpm during the polymerizations. A 0.00635-m stainless-steel tube was inserted through one of the reactor head ports and extended into the reaction mixture. This was used to bubble nitrogen (Linde, oxygen-free grade) through the reaction mixture before and during experiments to keep oxygen (a reaction inhibitor) out of the system. A 0.2286-m straight-tube condenser was attached to another port. Its function was to provide an exit for the nitrogen purge while condensing any solvent and monomer which were in the escaping nitrogen. Tap water (roughly 283 K) was used as the coolant on the shell side of the condenser.

The reactor batch temperature was controlled by a cascade control loop. An RTD was inserted through a fitting in another port on the reactor head and measured the batch temperature. The measured batch temperature was compared to the batch setpoint and the error signal was sent to the primary controller, a PID control algorithm. The output of the primary controller served as the setpoint for the jacket temperature control loop, another PID controller. The output of this controller (0–100%) was split-ranged, with heating ranging from 0–100% as the controller output ranges from 45 to 100%, and cooling ranges from 100 to 0% as the controller output ranges from 0 to 55%.

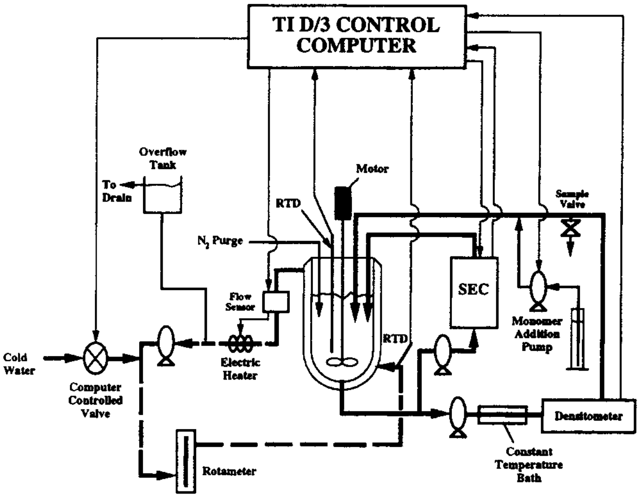

Figure 2. Experimental reactor and measurement system.

The cascade controller algorithm was a modification of standard batch-reactor cascade controller (Davidson, 1989). The central idea of this algorithm is to turn off the integral control action of the batch controller and reinitialize it in a prescribed way to reduce overshoots and "integral windup." The algorithm was found to perform well for exothermic reaction conditions and reached startup temperatures rapidly with little overshoot or oscillation.

The reactor temperature control recycle loop was composed of sections of 0.00953-m (3/8-in.) copper and 0.00953-m flexible poly-flow tubing, insulated with wrap-on insulating cloth. A Universal Electric pump (model ABZR049N) circulated water through the loop and jacket at a constant flow rate of approximately 0.001 m$^3$/min. The water in the loop was heated with a 1,500 W Chromalox electric heater (P/N 058144 001). A 4- to 20-mA signal from the process control computer (a Texas Instruments D/3 industrial control system) caused the output from the heater to vary linearly from 0 to 1,500 W. If cooling was necessary, cold tap-water (roughly 283 K) was introduced into the temperature control loop through a Versa solenoid valve. The water pressure of the inlet line is adjusted using a regulator to force the existing water in the jacket loop out to the overflow tank. The elevation of the overflow tank maintains a constant positive pressure in the jacket line. The Versa solenoid valve was cycled open and closed time-proportionally at a rate calculated linearly based on the percent cooling desired (ranging from closed continuously for no cooling to open constantly for full cooling).

There were two measurement loops associated with the reactor system. Both loops were fed from a T-fitting connected to the drain at the bottom of the reactor. They were constructed of flexible teflon tubing, reinforced by braided stainless steel, with stainless steel fittings on the ends. This tubing was chosen because it could handle the pressures generated from pumping the reaction mixture at high viscosities through the loops.

The first measurement loop pumped the reaction mixture through an on-line densitometer, used for determining monomer conversion during polymerizations (described in more detail below). A Zenith gear pump (model 1471-15) was used to pump the reaction mixture through this loop at roughly 0.00162 $m^3$/min. To reduce heat losses from the reaction mixture while in this recirculation loop, a tube-in-tube heat exchanger was included in the loop. After passing through the recirculation loop, the reaction mixture entered the reactor through a 0.254-m piece of 0.00635-m stainless-steel tubing inserted through a fitting in a port in the reactor head. The stainless-steel tubing extended into the reaction mixture to prevent bubbles from forming as the reaction mixture reentered the reactor's contents. This loop also contained a small valve connected to a T-fitting for sampling the reactor's contents for off-line measurements.

The second measurement loop was used to pump the reaction mixture through an on-line size-exclusion chromatograph. As described below, this device was used to obtain measurements of the molecular weight distribution of the polymer in the reaction mixture. A Viking pump (model #0432) was used to pump the reaction mixture at roughly $4.3\times10^{-4}$ $m^3$/min through the loop. The tubing for this measurement loop was wrapped with electrical heating tape to reduce the heat losses. After passing through this loop, the reaction mixture reentered the reactor through a 0.254-m piece of 0.00635-m stainless-steel tubing inserted through a fitting in a separate head port in the same manner as the densitometer loop.

For monomer-addition polymerizations, a computer-controlled metering pump (Scientific Systems, Inc. liquid chromatography pump, model #200) was used to add monomer to the reactor. The monomer was pumped from a nitrogen-purged graduated cylinder into the densitometer recirculation loop, just before the loop entered the reactor through the final 0.254-m piece of 0.00635-m stainless tubing. This method of introducing monomer provided rapid heating of the monomer and mixed it vigorously into the reaction mixture; it was implemented as opposed to simply dripping the monomer directly into the reactor because of the superior mixing.

### *On-line monomer conversion measurements*

Since the density of polymer is higher than the density of the monomer for this polymerization system, the density of the polymerization mixture increases during the course of polymerization. Thus, density measurement was a convenient means to monitor the conversion of monomer during polymerization. On-line density measurement was chosen because it is simple and has been reported to work very well for homopolymerizations (Schork and Ray, 1983; Ponnuswamy, 1984). For this purpose, an Anton-Paar (Austria) DPR XE 4112 on-line densitometer was used.

From the density measurement of the process fluid, the monomer conversion was calculated using the following mass-balance relation:

$$x_m=\frac{(w_{\text{total}}/\rho-w_s/\rho_s-w_i/\rho_i-w_m/\rho_m)}{(w_m/\rho_p-w_m/\rho_m)} \tag{2}$$

Here, $\rho$ is the measured density of the reaction mixture. The subscripts $s$, $i$, $m$, and $p$ denote solvent, initiator, monomer, and polymer, respectively. The densities of monomer, solvent, and polymer were calculated from temperature-density correlations used by Ellis et al. (1988a). The density of dissolved initiator was approximated to be 1.14 g/mL (roughly determined by observing the volume change when a known weight of AIBN was dissolved in ethyl acetate). $w$ denotes the known weight of the components charged to the reactor. This relation assumes ideal mixing of the components.

The on-line density measurements along with Eq. 1 provided very accurate indications of the monomer conversion. An independent check of the results with gravimetric conversion analysis showed excellent agreement, well within the accuracy possible in gravimetric analysis (Ellis, 1990).

### *On-line molecular weight measurements*

An Optichrom Advance liquid chromatograph, supplied by Applied Automation, was used for on-line molecular weight measurements. A refractive-index detector, supplied with the device, was used for measuring polymer concentration in the carrier stream as it eluted from the separation columns (two DuPont Zorbax PSM 60-S and PSM 1000-S, 6.2 mm × 25 cm, in series). The carrier solvent for separation was tetrahydrofuran (THF) and regulated to a flow rate of $1\times10^{-6}$ $m^3$/min. The chromatograph was calibrated by injecting a mixture of narrow MWD PMMA calibration standards (Polymer Laboratories) along with ethyl acetate, mixed in THF (0.1 g of each sample per 100 mL of THF and 1 mL ethyl acetate per 100 mL of THF). The ethyl acetate was used as an internal standard in comparison to the ethyl acetate peak from the process fluid. This enabled correction of the retention times for the process fluid to adjust for variations in the flow rate of the carrier THF. The on-line SEC device was found to have a stable calibration and operate consistently, over a period of several months, during the control and estimation experiments.

The chromatograph contained an automatic sampling and dilution system for periodically sampling the process stream, diluting it, and directing the diluted process fluid to the sampling valve. The dilution system was programmed to dilute the process stream to roughly 0.1 g polymer per 100 mL of THF (this is an average concentration since the polymer concentration increased as polymer accumulated in the reaction mixture, causing a proportional increase in the concentration entering the columns). Although the volume of THF added to the process stream was small during dilution, any process fluid which was diluted with THF was not sent back to the reactor; it was automatically sent to a waste stream from the chromatograph. The sample valve injected 170 $\mu$L of the diluted polymer into the columns. The sampling system, in combination with the size of the sampling lines and Viking pump used, was capable of properly diluting the process stream, while the polymer concentration was less than 35 wt. % for the polymerization conditions presented below. Above this concentration, the solution viscosity became prohibitively high.

The time between SEC measurements was 25 min. This was the time necessary for sample dilution, polymer elusion through the separation columns used, communication of the chromatogram from the SEC to the process control computers, and chromatogram analysis. Peak elusion time was the major contributor.

The molecular weight measurement results from the on-line SEC were compared to those from a laboratory analytical SEC,

**Table 1. Check of On-Line SEC Accuracy**

| | Waters 150-C ALC/GPC | On-Line SEC | % Difference |
|---|---|---|---|
| *PMMA Sample #1* | | | |
| $M_n$ | 19,756 | 18,254 | 7.6 |
| $M_w$ | 34,550 | 34,820 | −0.78 |
| *PMMA Sample #2* | | | |
| $M_n$ | 46,353 | 47,075 | −1.56 |
| $M_w$ | 84,510 | 82,743 | 2.0 |

a Waters 150-C ALC/GPC laboratory size-exclusion chromatograph with a refractive index detector. Three PL-Gel columns in series ($10^3$, $10^4$ and $10^5$ Å) supplied by Polymer Laboratories were used in the Waters chromatograph. Molecular weights for two unimodal PMMA samples with molecular weights that spanned the range encountered in the control and estimation experiments, Table 1, agree very well. In contrast, the on-line SEC did not have the proper resolution to reproduce accurately a bimodal MWD. Because of this, all experimental results obtained with the on-line SEC involve polymer with unimodal molecular weight distributions.

The reproducibility of measurements from the on-line SEC was found to be very good. In sampling the same PMMA sample ($M_n = 20{,}328$ and $M_w = 43{,}356$) 11 times, standard deviations of 665 and 646 were obtained for $M_n$ and $M_w$, respectively.

### *Computer interfacing*

A DPR 2000 serial interface (Anton-Paar) was used to send the measurement signals from the densitometer over a RS-232 serial line to the TI process control computer. The chromatograph also communicated with the control computer over a RS-232 serial line. At the appropriate times, the control computer instructed the SEC to begin sampling and then polled the device until the chromatogram was ready to be sent. Chromatogram points were collected every half second, and roughly 500 points were required to traverse a polymer peak.

An Apollo DN3000 Workstation was interfaced with the control computer to handle computationally intensive tasks. Chromatogram analysis was performed by the Apollo computer. A procedure was developed to automatically truncate the leading and trailing baseline of the chromatograms. Further, on-line Kalman filtering calculations were performed using the Apollo computer. Finally, the on-line control setpoints (batch temperature, monomer addition, or simultaneous monomer addition and temperature control) were determined in the Apollo computer.

All communication programs in the TI computer, the Apollo computer, and the SEC's microprocessor were user-written.

### *Raw materials*

Methyl methacrylate was obtained from Rohm and Haas inhibited with 10-ppm hydroquinone. Prior to polymerizations, the hydroquinone was removed by passing the MMA through Rohm and Haas A-27 synthetic ion-exchange resin. As a further purification step, the monomer was purified by vacuum distillation. The initiator used was 2,2′ azobisisobutyronitrile (Vazo-64; AIBN) supplied by Dupont. The solvent was ethyl acetate supplied by EM Science (GR anhydrous). The solvent was used without any further purification. The solvent used for the carrier solvent in SEC measurements was EM Science unstabilized tetrahydrofuran.

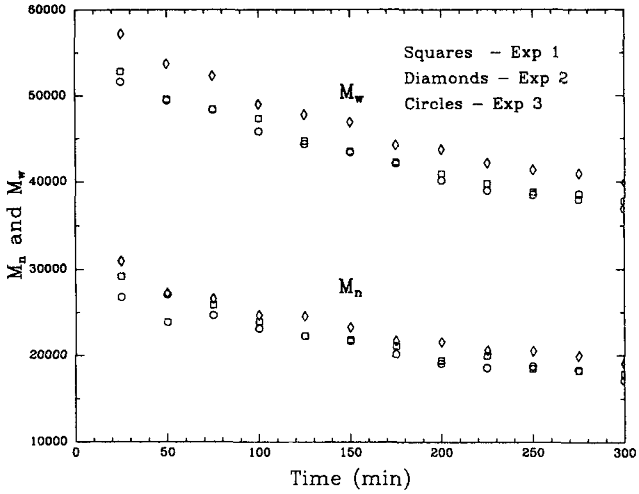

**Figure 3a. Experiment reproducibility: molecular weight.**

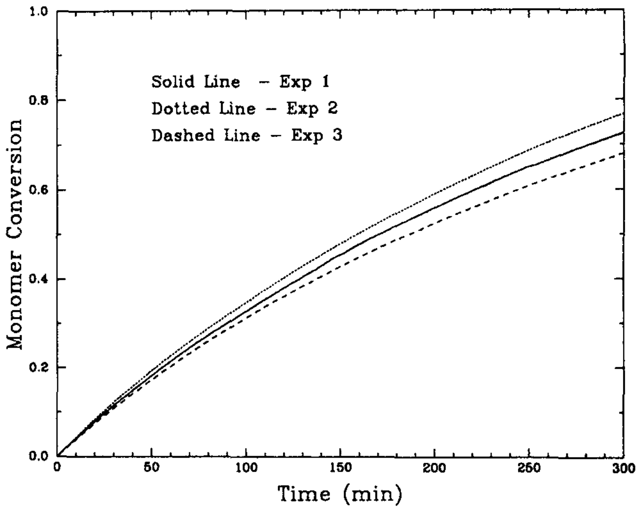

**Figure 3b. Experiment reproducibility: monomer conversion.**

### *Experiment reproducibility*

Over a period of several months, the same polymerization was reproduced three times (333 K, 25% MMA by weight, 2,842 mL ethyl acetate charged, and 0.05 molar AIBN). Resulting plots of molecular weight in Figure 3a and corresponding monomer conversions in Figure 3b show that there was noticeable variability in the molecular weight and conversion, even with the use of purified monomer, accurate reactor charging, and precise reactor temperature control. The cause of the variability was not determined (possibly because the ethyl acetate was not distilled, the AIBN was not recrystallized, slight AIBN decomposition with time, trace impurities remaining in the reactor, variations in the monomer from the supplier, and so on). Nevertheless, polymerization conditions were probably better controlled than the majority of industrial polymerizations where inhibitor in the monomer is not frequently removed before polymerization, the solvent is generally less pure, and reactor charging and control often are not so meticulous, and so on. It is shown below that with on-line MWD control the variability was reduced significantly (from 10 to 2% run-to-run variability in weight-average molecular weight).

## On-Line Molecular Weight Estimation

Kalman filtering equations and assumed error statistics were implemented the same as described by Ellis et al. (1988a), except for the measurement error statistics from the on-line size-exclusion chromatograph. It was found that the molecular weight measurements were subject to higher errors during the beginning of a polymerization, before a significant amount of polymer had accumulated in the reaction mixture. This was because the peaks obtained in the SEC analysis were small relative to the inherent baseline drift on the on-line SEC chromatograms during the start of a polymerization. A procedure adopted to address this was to have $r_{X_D}$ (defined in Ellis et al., 1988a) large when small chromatogram peaks were obtained, and then decrease the value for larger peaks. $r_{X_D}$ was chosen to be $1.0 \times 10^{-2}$ kmol/m$^3$ until the area under the peaks reached 20,000 (units [=] refractive index detector deflection units·seconds). This usually occurred when the polymer weight fraction in the reaction mixture was near 0.05. When the peak was found larger than this value, $r_{X_D}$ was then set to be $1.0 \times 10^{-4}$ kmol/m$^3$. Typically, during a polymerization for the conditions used in the studies presented below, the peak area ranged from 0 to 70,000 (the magnitude of peak area will vary depending on the chromatograph manufacturer and detector used). When the peak area was below 4,000, the SEC measurement was rejected because of the unreliability in the molecular weight results from the chromatogram analysis. For most cases investigated, this simply was the chromatogram obtained at the start of each polymerization. The subsequent measurement (at 25 min into the polymerization) usually had a peak large enough to analyze reliably.

### *Estimation during isothermal polymerization*

In Figure 4a, the results from an on-line estimation of the molecular weight are presented (333 K, 25% MMA by weight, 2,842 mL ethyl acetate charged, and 0.05 molar AIBN). The solid curves show the on-line estimates of weight- and number-average molecular weights obtained as the polymerization proceeded. The squares are the molecular weight measurements from the on-line SEC. As depicted in the figure, the estimates tracked the actual measurement data very well. Further, the filter provided some smoothing of the noise in the MWD measurements. More importantly, the estimates were essentially continuous, rather than the relatively infrequent, time-delayed measurements from the on-line size-exclusion chromatograph. This is important for on-line feedback control of molecular weight. The estimated and measured monomer conversions, along with the estimated initiator conversion, are presented in Figure 4b. The measured and estimated monomer conversions essentially coincided (appearing as a single solid curve in Figure 4b). This is a desirable result because of the accuracy expected in monomer conversion measurement; the error covariance matrices were selected to have high confidence in this measurement. The initiator conversion in the figure is an unmeasurable state, inferred based on other measurements using the polymerization model. Knowledge of this quantity may be desirable for certain on-line control schemes where initiator concentration is a control variable.

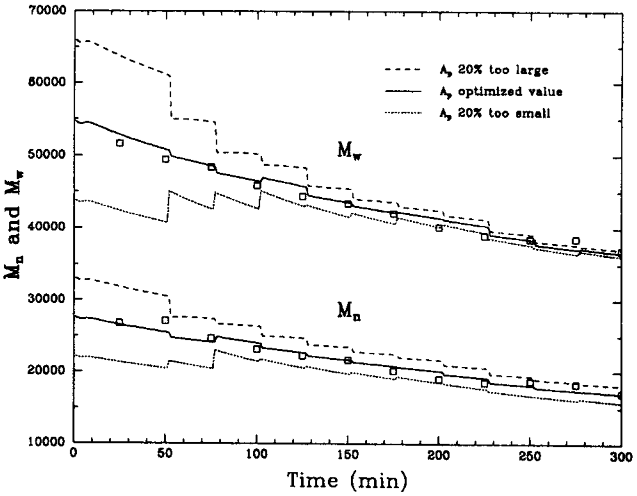

**Figure 4a. Average molecular weights from estimator.**

□, SEC measurements; —, literature $A_p$ value; ····, $A_p$ 20% low; ----, $A_p$ 20% too high.

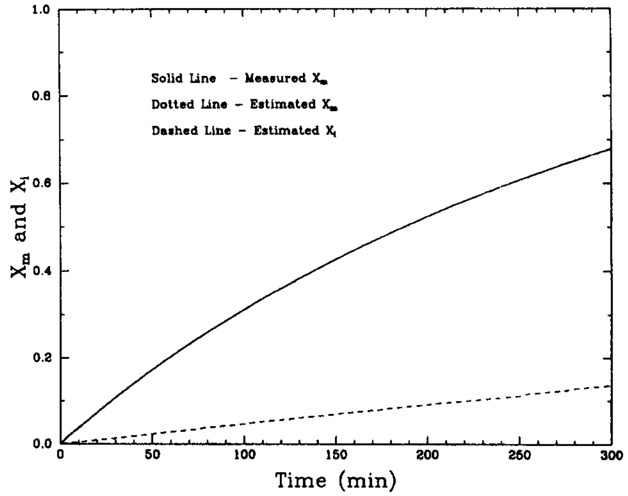

**Figure 4b. Measured and estimated monomer conversions as well as estimated initiator conversion for cases in Figure 4a.**

The solid and dotted curves coincide to appear as one solid curve.

These results may be somewhat better than what could be encountered in an industrial setting, since the model was able to predict the polymerization results so well. Conditions as carefully maintained as this laboratory study are often difficult to obtain in a plant setting (such as varying feedstock purity and operator changes). To test the estimator under conditions of model parameter error, two estimations were performed where the preexponential factor for the propagation reaction constant was first 20% above the value presented in Ellis et al. (1988a) and then 20% below that value. For consistency, the estimation was applied to the measurement data collected in the previous example and estimated off-line. The propagation reaction constant was selected because it strongly influences the predicted molecular weights; a variation of ±20% in the propagation rate constant is significant.

The estimated molecular weight values are presented in Figure 4a as the dashed and dotted curves ($A_p$ 20% high and $A_p$ 20% low, respectively). Initial estimates for both cases were poor. At that point, the estimates were based solely on model predictions. However, as SEC molecular weight measurement data became available, the estimates progressively became better to converge near the actual measured data. At 50 min of reaction time, an on-line feedback control scheme would be able to begin correcting for the unexpected deviation in the model parameter. For these cases, the plot of monomer conversion appeared essentially the same as that of Figure 4b. This occurred because, as described above, high confidence in the monomer measurement was assumed in selecting the measurement error covariance matrices. The initiator conversion was also similar to that shown in Figure 4b because the temperature measurement for both cases was identical.

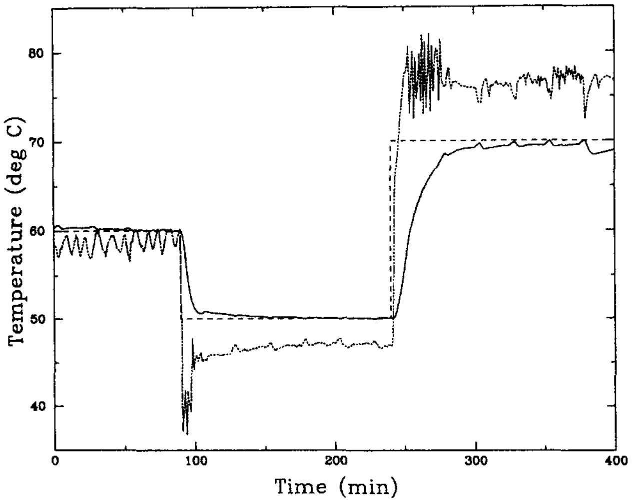

**Figure 5a. Temperature data from an estimation involving nonisothermal conditions.**

—, reactor temperature; ----, setpoint; ••••, jacket temperature.

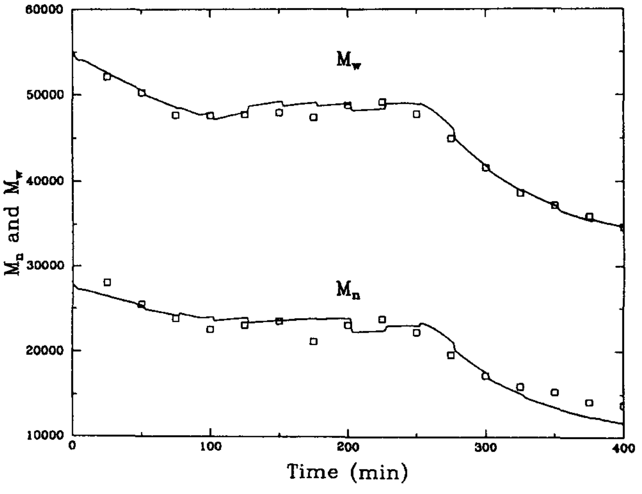

**Figure 5b. Average molecular weight data for an estimation involving nonisothermal conditions.**

□, SEC measurements; —, on-line estimates.

### *Estimation during nonisothermal polymerization*

The estimation routine was evaluated for a nonisothermal polymerization (25% MMA by weight, 2,842 mL ethyl acetate charged, 0.05 molar AIBN). The temperature profile for this study is presented in Figure 5a, which included actual batch and jacket temperatures required to maintain the batch temperature. This temperature profile is highly nonisothermal and was a good test of the temperature controller for the batch reactor. The batch temperature controller did a good job in tracking the setpoint temperature profile.

It is interesting to note that the jacket temperature was lower than that for the batch during the first two temperature steps, indicating the exothermic load. For the last temperature range, the jacket temperature was significantly higher than the batch temperature to compensate for heat losses in the measurement loops. The periodic bumps in the batch temperature occurred when the on-line SEC performed a measurement (every 25 min).

The on-line estimates of the molecular weight and the measured molecular weight values are presented in Figure 5b. The estimator successfully tracked the variations in molecular weight over the course of the polymerization. This indicated that the model properly accounts for the temperature dependence of the polymerization kinetics. Further, the measured molecular weights followed the expected trends for this temperature profile. A decreasing molecular weight profile should be obtained during the first isothermal portion of the polymerization, as was obtained, since monomer is being consumed and the instantaneous degree of polymerization is proportional to the monomer concentration (Allcock and Lampe, 1981). The molecular weights then slightly increased when the temperature dropped and conversely when the temperature rose. This is expected because the instantaneous degree of polymerization decreases with increasing temperature in free-radical polymerization initiated by a thermal initiator.

### *Estimation with measurement bias*

The effects of measurement bias were explored for each measurement device. The case of bias in conversion measurements from the densitometer was studied because of the potential for fouling of this device with polymer scale. The on-line estimation data from the case in Figures 4a and 4b were used in an off-line simulation as a frame of reference but the conversion measurements were multiplied by 0.75, which is a significant error in this measurement considering the accuracy which was normally obtained. As can be expected, the estimated monomer conversion measurement tracked the measured monomer conversion which was in error. However, the estimates of the initiator conversion and molecular weights tracked the actual values very well, as shown in Figure 6. The molecular weight estimates were only slightly high over the course of the polymerization because the estimator consistently used a higher than

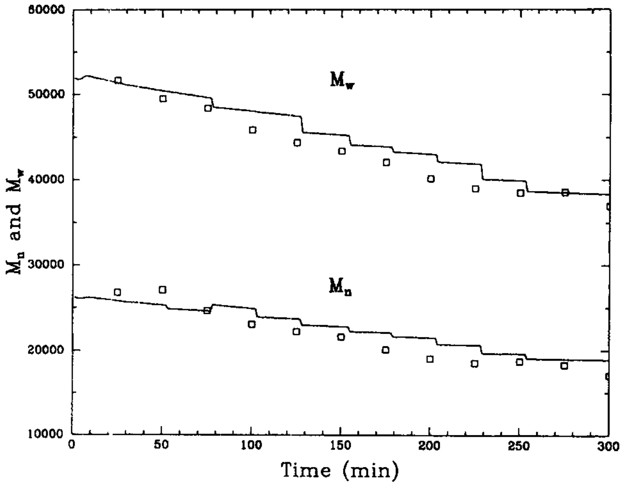

**Figure 6. Average molecular weights for the case of an estimation with a conversion measurement bias.**

□, SEC measurements; —, on-line estimates.

actual amount of monomer in the polymerization mixture to provide the predictions from the polymerization model.

The case of bias in the temperature measurement was investigated because it is possible for the temperature probe to have polymer buildup, corrupting the measurement. A bias of 6 K was added to the measured data from the case of Figures 4a and 4b. As depicted in Figure 7, the response of this estimation was very similar to the cases of kinetic parameter error investigated above. Initially the estimates were in error because only model and incorrect temperature information were used to predict the MWD. As the MWD measurements became available, however, the estimates rapidly converged to the actual data. The monomer conversion estimates were accurate (identical to that in Figure 4b) because of the accuracy assumed for that measurement in the Kalman filter. The initiator conversion, however, was in error and predicted 50% too low at the end of the polymerization. This was because its estimate was based solely on the temperature readings. Unless accurate temperature data are available, the estimates of initiator conversion will not be reliable.

Considering the case of bias in molecular weight measurement, it is intuitive that the estimates will attempt to converge to biased MWD measurements. As implemented here, the online MWD estimation routine is unable to correct for biased molecular weight measurements. To detect bias in MWD measurements, the estimation scheme could incorporate redundant SEC measurements. A different approach may be to incorporate a different secondary measurement for molecular weight into the estimation scheme. A good candidate for an on-line secondary measurement of molecular weight is the solution viscosity (Jo and Bankoff, 1976). This, however, will only provide an estimate of average molecular weight properties, not the entire MWD. Because the calibration of the on-line SEC was frequently checked, bias in molecular weight measurements was not considered to be very likely.

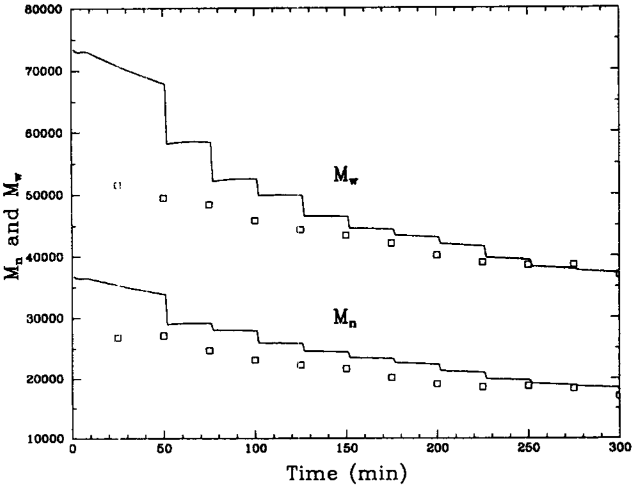

**Figure 7. Average molecular weights for the case of a bias in temperature measurement.**

□, SEC measurements; —, on-line estimates.

## *Bimodal distribution estimation*

The cases presented above were for a polymerization where a unimodal MWD was formed. The estimates could have been obtained with a model which only predicts the leading moments of the distribution, rather than the entire MWD shape. To demonstrate the full capabilities of the estimator, estimation results are presented for a polymerization case for which a bimodal MWD shape occurred, a case where using the leading moments of the MWD would be inadequate to predict the MWD shape.

Figures 8a to 8c show results from an experimental, off-line test of the measurement scheme's ability to estimate bimodal MWDs during a 4-h polymerization. At the start of the polymerization, a small amount of low-molecular-weight PMMA was present in the reactor but unknown to the estimator. This could perhaps occur if the reactor was improperly cleaned after the previous polymerization. It may also be desirable to add prepolymer to the reactor before polymerization to influence the molecular weight of the polymerizing polymer. The reaction conditions were such that high-molecular-weight polymer was to be produced, causing a bimodal MWD to develop. The low-molecular-weight polymer had a number-average molecular weight of 17,400 and a weight-average molecular weight of 32,200. It had a weight fraction of 0.01738 in the reaction fluid, and the MMA had an initial weight fraction of 0.4958. The initial concentration of AIBN was 0.0095 molar, and the polymerization was isothermal at 333 K.

SEC chromatograms were obtained in an off-line manner using a Waters 150-C ALC/GPC. The measurements collected were fed to the estimator in an off-line manner in the form they are available on-line; temperature and conversion measurements were provided to the estimator every minute, and the SEC updates were supplied at 30-min intervals with a 30-min delay. Other details are provided by Ellis et al. (1988b) and Ellis (1990).

Figure 8a shows the estimated, measured and model-predicted monomer conversions. The monomer conversions determined by off-line gravimetric methods, as well as the model-predicted and estimated initiator conversions, are also presented in Figure 8a. The measured conversion trace is obtained

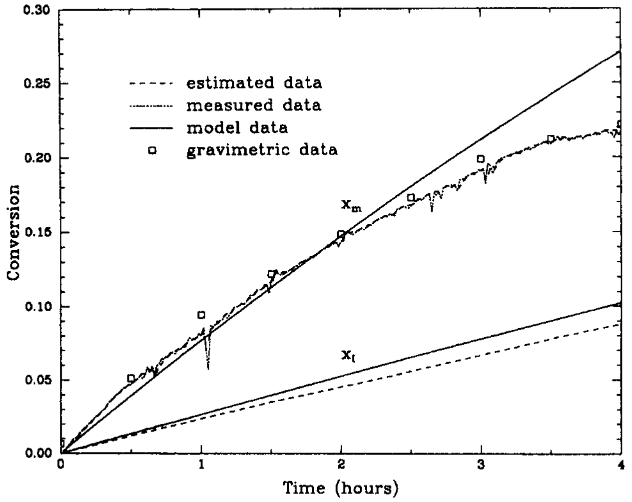

**Figure 8a. Conversion data from an estimation where a bimodal molecular weight distribution formed.**

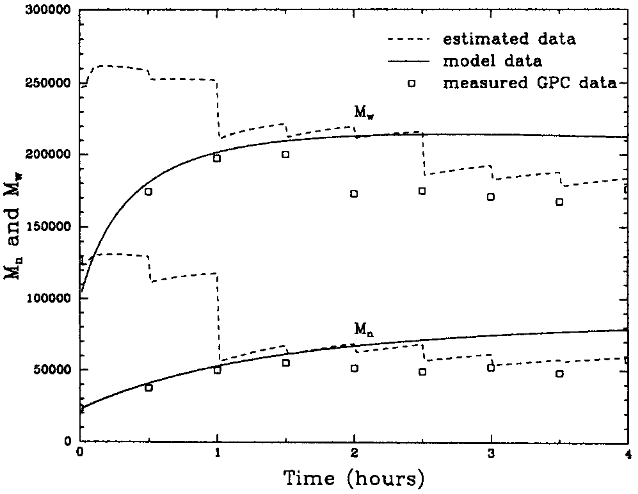

**Figure 8b. Average molecular weight data from an estimation where a bimodal molecular weight distribution formed.**

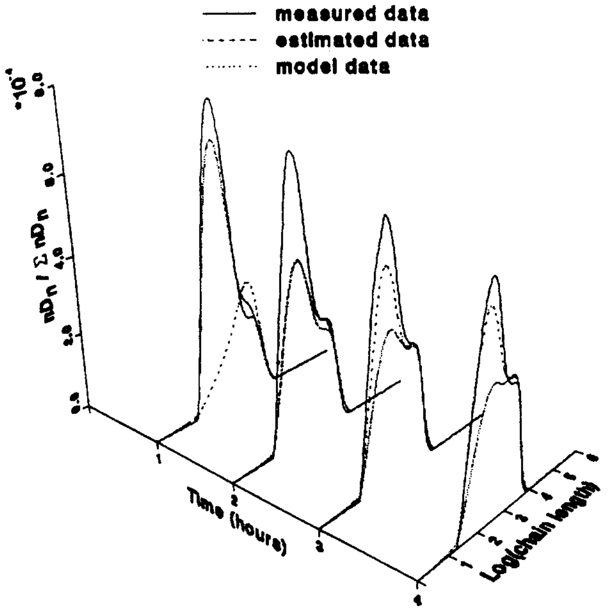

**Figure 8c. Evolution of the MWD during the course of a polymerization where a bimodal MWD formed.**

from the on-line densitometer. The estimated and measured monomer conversions essentially coincided (dashed and dotted curves nearly overlap). The places where they did not overlap were where the estimated monomer conversion (dashed curve) was smoother than the measured conversion (dotted curve), indicating that the estimator was successful in filtering out spikes which occurred because bubbles passed through the densitometer (a problem later resolved by improving the measurement loops). The model-predicted conversion was that obtained by model predictions prior to running the experiment (discussed in more detail below).

Figure 8b shows the estimated, model-predicted and measured average molecular weight values over the course of the polymerization. The estimations quickly approached the measured data. The initial errors occurred since the estimator was not aware of the low-molecular-weight polymer until after 30 min of polymerization when the first SEC measurement became available. In contrast, the model-predicted molecular weights initially matched the measured molecular weights because the amount of low-molecular-weight polymer present at the start of the polymerization was used as an initial condition for off-line prediction of the molecular weight. Considering the estimated molecular weights, this figure shows the estimator's ability to provide current estimates of the MWD, rather than the time-delayed measurements available from a SEC.

The discrepancy between measured and model-predicted values toward the end of the polymerization in Figures 8a to 8c is attributed to oxygen entering the reaction system through a measurement recirculation loop, a problem later solved with improved sampling lines. Nevertheless, even though unexpected inhibitor entered the reactor and unanticipated polymer was present at the start of polymerization, the estimator provided accurate estimates of the MWD, a required feature of a measurement scheme to be used for on-line control of MWD shape.

The measured, estimated and model-predicted MWDs at 1-h intervals are presented in Figure 8c. The estimated MWDs at 2, 3 and 4 hours showed reasonable agreement (improving with time) with the measured data, which had a bimodal character.

## On-Line Molecular Weight Control

As described earlier, a primary objective of this work was to investigate using the on-line MWD estimator for feedback MWD control. Of the numerous control objectives possible, controlling to achieve a specific, constant weight-average molecular weight was selected. It was decided to use a PID controller to adjust the reactor operating conditions based on the comparison of the estimated $M_w$ with the setpoint. The manipulated variables investigated were batch temperature control, monomer-addition control, and simultaneous temperature control, and monomer-addition control.

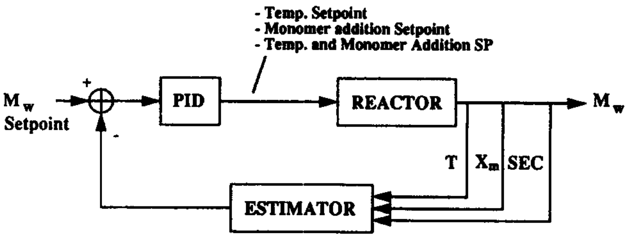

**Figure 9. On-line feedback control scheme.**

The feedback control scheme is illustrated in Figure 9. Although it would have probably been better to use a model-based control algorithm in place of the PID controller, the PID controller functioned reasonably well. The values for the PID controller tuning constants were found by repetitive trial-and-error simulations of feedback control using the polymerization model. The basic criterion for adjusting the control parameters during tuning was to have the molecular weight approach the setpoint as quickly as possible, but also obtain little or no overshoot. The control parameters obtained in this manner are presented in Table 2. These values are not claimed to be the best possible, but produced satisfactory control. The value of $K_C$ for temperature control is negative since the molecular weight decreases with increasing temperature.

These tuning parameters are based on absolute error and are therefore reasonable for molecular weight setpoints near those used in this study. Tuning parameters based on relative errors would be more general and provide better control for significantly different setpoints.

The controller tuning for the case of monomer addition was rather difficult, because the controller needed to be somewhat cautious in its addition of monomer. Since the reactor is batch, if too much monomer were added, it would be "stuck" in the reactor until it reacted away.

### *On-line temperature control, no errors in operating conditions*

The molecular weights from two on-line control experiments are presented in Figure 10a (25% MMA by weight, 2,842 mL ethyl acetate charged, 0.05 molar AIBN). The molecular-weight setpoint for all of the on-line control studies was 40,000. This value was obtained because it was within the range of the calibration of the on-line SEC and the temperature profile required to maintain $M_w$ constant at 40,000 spanned the temperature range of optimization for the kinetic parameters in the polymerization model (323 to 343 K). The initial temperature of 340.1 K was chosen by trial-and-error simulations as the value necessary to produce an $M_w$ equal to 40,000 at the start of polymerization for these reaction conditions.

Figure 10a shows that the on-line control was very good for both cases. The molecular weight did not deviate from the setpoint of 40,000 by more than 2,000 molecular-weight units over the course of the polymerization. This is within the reproducibility of the on-line SEC measurements. Further, the molecular weights at the end of both polymerizations were within 1,000 molecular-weight units from the setpoint (within 2% of setpoint). This is much less than the batch-to-batch variability obtained in performing isothermal polymerizations without feedback control. This is a very encouraging result because it illustrates a benefit of employing on-line molecular weight information for feedback control of molecular weight to improve batch-to-batch reproducibility, even with simple PID control.

**Table 2. PID Control Parameters for Feedback MWD Control**

| | Temperature Control | Monomer-Addition Control |
|---|---|---|
| $K_c$ | $-0.01$ (K)/($M_w$ units) | $10^{-6}$ (mL/min)/($M_w$ units) |
| $\tau_I$ | 500 s | 2,000 s |
| $\tau_D$ | 1 s | 2,500 s |

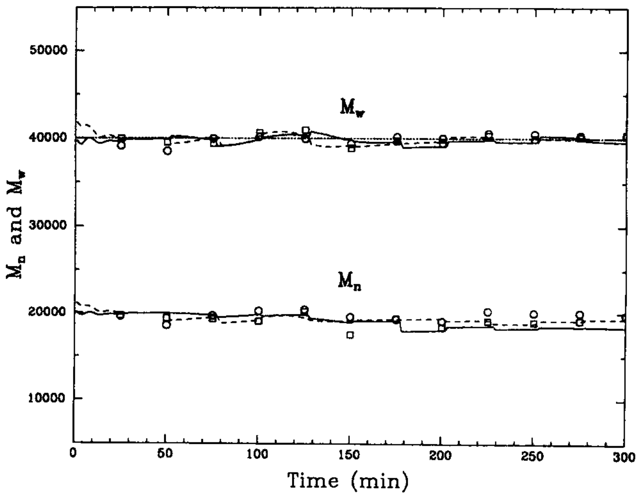

**Figure 10a. Average molecular weights for two on-line temperature control cases.**

□, —, case 1; ○, ----, case 2; ••••, $M_w$ setpoint of 40,000.

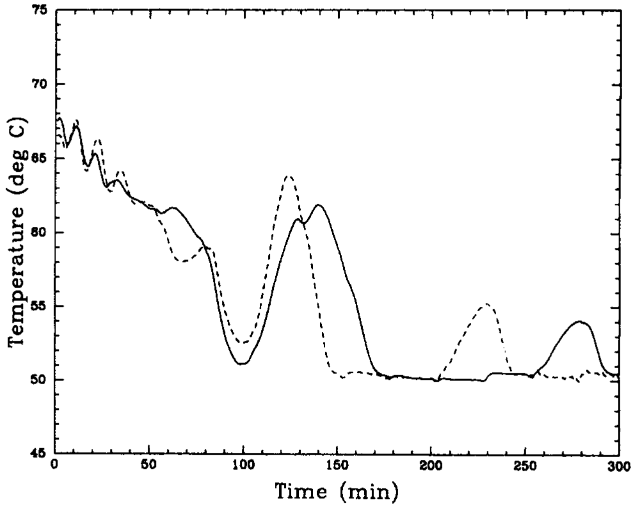

**Figure 10b. Temperatures traversed for two on-line molecular-weight control cases.**

—, case 1; ----, case 2.

The temperature profiles traversed to achieve these molecular-weight control results are presented in Figure 10b. Both profiles followed the same basic trend (an overall decreasing temperature profile), but were not exactly the same indicating that on-line control action was required to maintain the molecular weights at setpoint.

The somewhat irregular shifts in the temperature setpoint are a result of the tuning parameters being somewhat aggressive. In hindsight, less strict controller tuning would probably have reduced some of the fluctuations in temperature setpoints. However, molecular-weight control was good, and the changes in temperature were not unreasonable.

A rate-of-change limit of ±1 K/min was applied to the calculated temperature setpoint so that it would not deviate away from the heating and cooling capabilities of the experimental temperature control system (which are similar to the capabilities of large industrial reactor systems). This constraint was used for all of on-line temperature control investigations presented.

Note that the temperature setpoint from the PID controller was constrained at the lower bound of 323 K. This was required because below 323 K, the polymerization rate became almost zero. Without the constraint, the PID controller would allow the temperature setpoint to continue down and quench the reaction. When the temperature rate-of-change limit was active or the batch setpoint was saturated at its minimum temperature constraint, the bias (integral portion) of the batch PID controller was frozen to prevent "integral windup."

A final point to be made about these cases is that it was necessary to stop the polymerization at 300 min, because at that point the temperature setpoint was saturated at the bottom constraint. If polymerizations were to continue much longer, the molecular weights would have begun to decrease away from the setpoint (resulting in off-specification product and a broadening of the MWD) due to the depletion of monomer and operation at isothermal conditions (the instantaneous degree of polymerization is proportional to the monomer concentration).

The monomer conversions at 300 min were 61-64%. Although 100% conversion is desired to reduce polymer product purification costs, it cannot be achieved using temperature control alone with these polymerization conditions and hold the molecular weight constant during polymerization. The necessary decreasing temperature profile prohibits achieving complete conversion (discussed in more detail below).

### *On-line temperature control, errors in amount of initiator charged*

To introduce uncertainty and simulate the types of disturbances encountered in an industrial setting, predetermined variations in the amount of initiator charged to the reactor were made to simulate errors in initiator charging. The cases studied consisted of a 20% undercharge, a 20% overcharge and a 40% overcharge of AIBN.

The molecular weights obtained during temperature control to counteract a 20% undercharge of AIBN are shown in Figure 11a. Assuming that the undercharge was not known to have occurred, the molecular weight started out unexpectedly high (the first measurement shown had noise due to the low polymer concentration at that point in the polymerization; the relative size of SEC baseline fluctuation can corrupt molecular-weight calculations when the polymer chromatogram peak is small). As shown in Figure 11b, once the estimator detected the discrepancy between the experimental molecular weights being obtained and the desired setpoint, the PID controller raised the temperature setpoint to lower the molecular weight. The polymerization was stopped when the temperature setpoint was saturated at the minimum constraint and the weight-average molecular weight obtained was at the setpoint of 40,000. At this point, the monomer conversion was 60%.

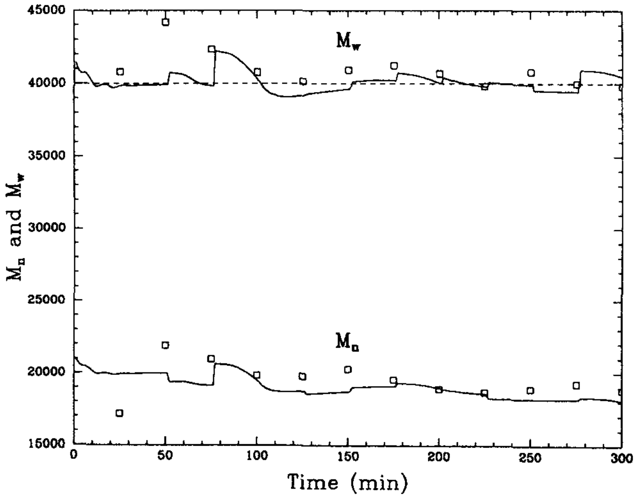

**Figure 11a. Average molecular weights for on-line molecular-weight control by manipulating temperature with a 20% undercharge of initiator.**

□, SEC measurements; —, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

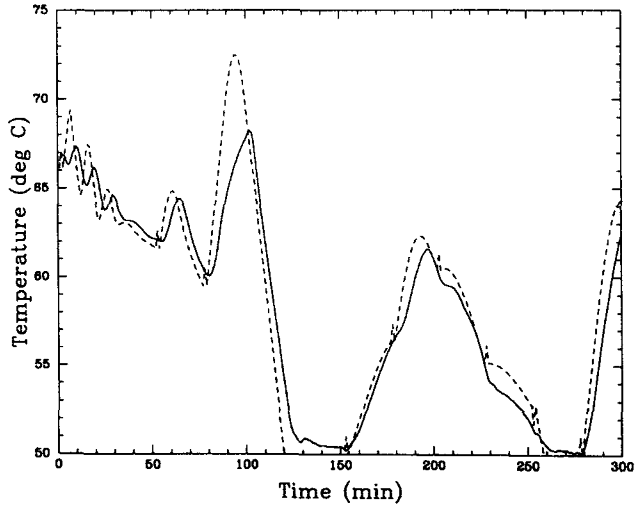

**Figure 11b. Temperature profile for Figure 11a.**

----, batch setpoint; —, batch temperature.

The polydispersity ($M_w/M_n$) rose to about 2.2 for this case, indicating a slightly broader distribution than the minimum obtainable (a value of 2 indicates a distribution as narrow as possible for this polymerization system, Ray, 1972). The broadening occurred because initially polymer of the wrong molecular weight was being formed. The controller first adjusted the temperature to lower the molecular weight producing some polymer below the setpoint to counteract the molecular

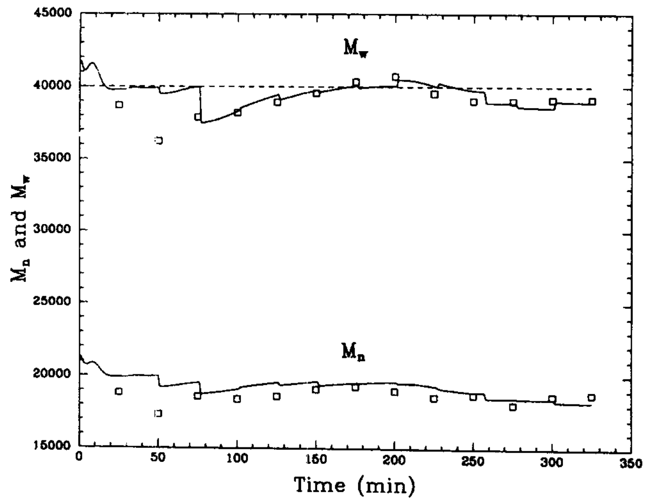

**Figure 12a. Average molecular weights for on-line molecular-weight control by manipulating temperature with a 20% overcharge of initiator.**

□, SEC measurements; —, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

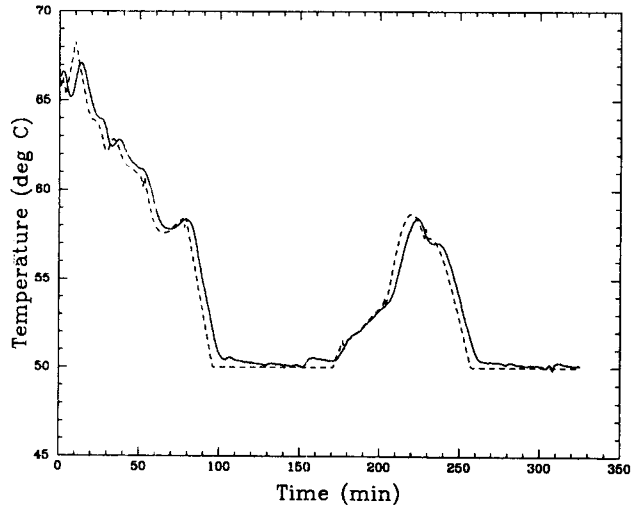

**Figure 12b. Temperature profile for Figure 12a.**

----, batch setpoint; —, batch temperature.

weight of polymer already present. Then, the controller adjusted the temperature to maintain polymer from then onward to have $M_w$ of 40,000.

For the case of a 20% overcharge of AIBN in Figure 12a, the controller was able to adjust the molecular weights relatively close to the setpoint (within 3%). However, it was difficult to pull the molecular weight up because the natural tendency is to have the molecular weight decrease due to monomer depletion for isothermal polymerization (without significant gel effect). The underlying chemistry made molecular-weight control more difficult than for the case above. The temperature profile for this case is shown in Figure 12b. Once again, polymerization was stopped when the temperature setpoint was saturated at the minimum constraint and the molecular weight began to fall below the setpoint.

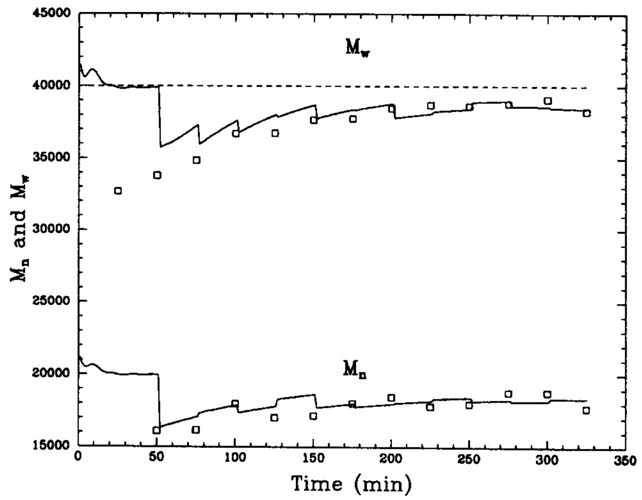

**Figure 13a. Average molecular weights for on-line molecular-weight control by manipulating temperature with a 40% overcharge of initiator.**

□, SEC measurements; —, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

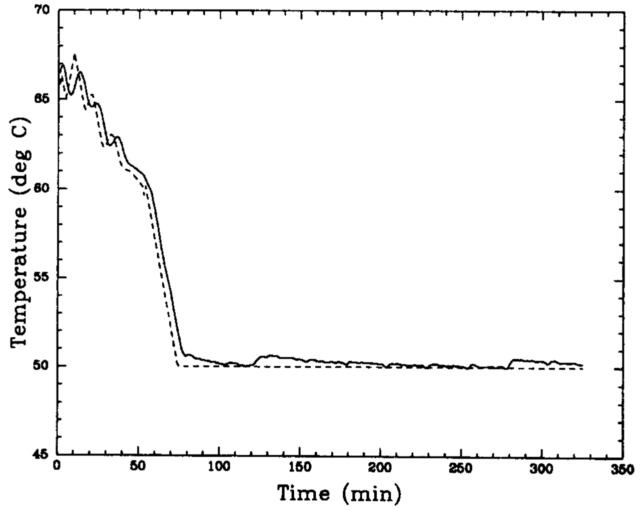

**Figure 13b. Temperature profile for Figure 13a.**

----, batch setpoint; —, batch temperature.

In the extreme case of a 40% overcharge of AIBN in Figure 13a, the molecular weight was adjusted significantly closer to the setpoint (benefiting from the on-line control), but not pulled all the way to it. As shown in Figure 13b, once the estimator discovered the discrepancy, the PID controller dropped the batch temperature setpoint to the minimum constraint and remained there for the duration of the polymerization. The polymerization was stopped when the molecular weights began to decrease away from the setpoint after roughly 300 min of polymerization. The final monomer conversions for these three cases were in the range 63–65%.

This series of control experiments illustrates the limitations of using only temperature control to manipulate molecular weight. For this thermally-initiated free-radical polymerization system, molecular weight is relatively easily reduced by raising temperature. However, it is difficult to raise molecular weight significantly by adjusting temperature because it is necessary to lower the temperature causing polymer production to decrease. The decrease in polymer production is counter to the desire to produce as much product as possible in a given batch. For cases where only temperature control is practical (monomer addition is not an option), the improvement in molecular-weight control comes at the expense of less polymer product. The economic gains from improved polymer properties by having a narrow MWD and a specific weight-average molecular weight must be balanced with the higher separation cost in removing unreacted monomer at the end of the polymerization. For a specialty polymer with relatively high profit margin, this potentially can be justifiable.

Should the sampling systems have been capable of handling higher viscosities, sufficiently increasing the monomer fraction would have caused the polymerization to enter the region where the "gel" effect or Trommsdorff effect becomes significant at higher monomer conversion. When the gel effect is significant, the natural tendency is to have the conversion accelerate and increase further toward completion, and have molecular weight increase. An increasing temperature profile in this range would then serve to maintain a constant molecular weight. However, the resulting higher solution viscosity can pose heat transfer and mixing problems.

### *On-line monomer-addition control*

For some polymer reactor configurations it may be difficult to vary the reactor temperature enought to effect molecular-weight control. For example, if the thermal mass of the reaction mixture is very large in proportion to the heat-transfer area, vigorous temperature control may be difficult. For this reason, on-line monomer-addition control was investigated.

As described above, during isothermal polymerization, without monomer addition, the natural tendency is for the molecular weight to drop mildly during the course of polymerization due to monomer depletion. Therefore, when monomer addition control is used and the molecular weight is slightly above the setpoint, simply stopping the addition of monomer can cause the molecular weight to drift back to setpoint. Conversely, increasing the monomer addition rate will cause the molecular weight to increase. This will work well when the polymer concentration in the reacting mixture is mild, enabling quick mixing of the added monomer relative to reaction dynamics. For these polymerization conditions, apart from adding monomer or lowering the batch temperature, there is no practical way to increase the molecular weight; most every other control option, such as addition of initiator or chain transfer agents, can only reduce the molecular weight. Initiator addition can be effective for molecular weight control if conditions are such that initiator concentration is declining (dead-end polymerization), causing the molecular weight to drift upward.

An on-line monomer-addition control experiment was performed where the polymerization conditions were 333 K isothermal, initially 25% MMA by weight, 2,842-mL ethyl acetate charged, and 0.05-molar AIBN. For this case, the initial weight-average molecular weight expected at the start of polymerization was 53,000; this was the molecular weight setpoint chosen.

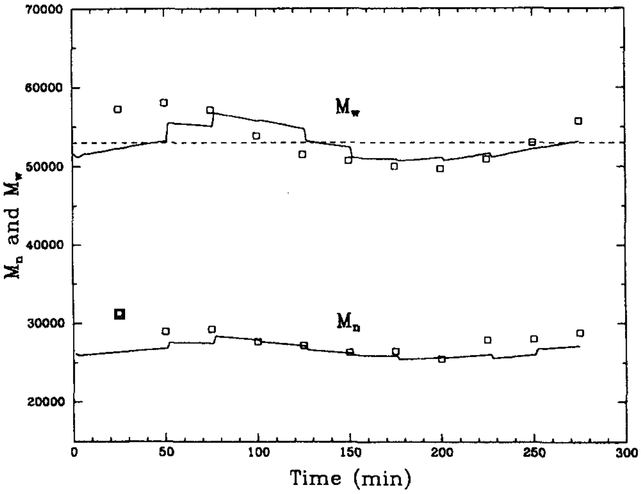

**Figure 14a. Average molecular weights for on-line molecular-weight control by manipulating monomer addition.**

□, SEC measurements; —, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

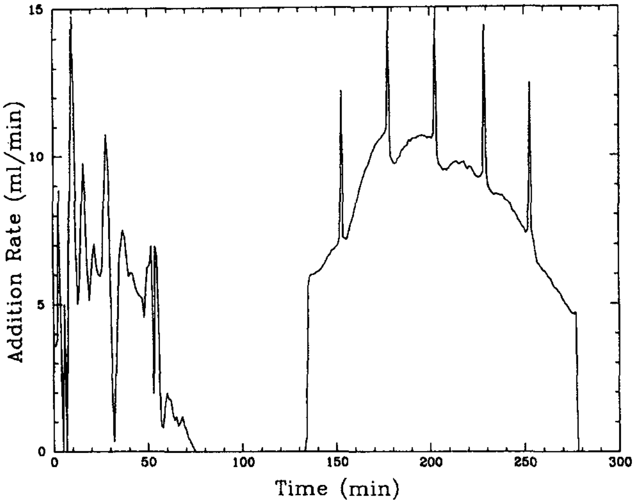

**Figure 14b. Monomer-addition profile for on-line molecular-weight control.**

The molecular weights obtained over the course of the polymerization are presented in Figure 14a. The molecular weight initially obtained was above the setpoint. The controller then stopped monomer addition (Figure 14b) to reduce the molecular weight of polymer being formed. The monomer addition controller was given an initial setpoint of 3.58 mL/min, because trial-and-error simulations showed this to be the value necessary to obtain a constant weight-average molecular weight at 53,000. The PID controller then caused the molecular weight to oscillate slowly about the setpoint as the polymerization progressed. Temperature control during the polymerization was good, holding the batch steady at 333 K.

The spikes on the monomer-addition plot were a result of the derivative control mode of the PID controller at the points where a new SEC update was incorporated in the on-line estimates. This polymerization was terminated when the solution

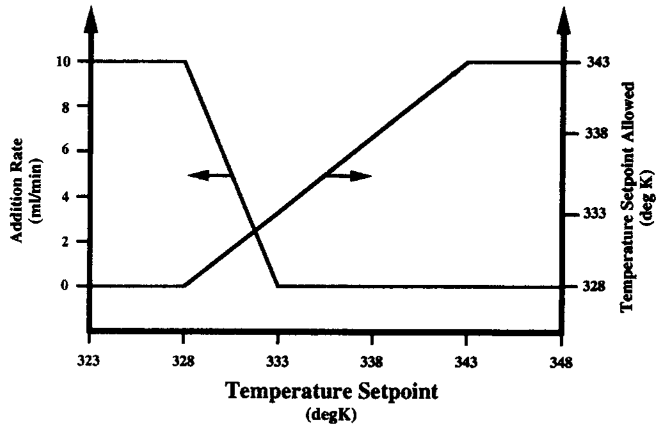

**Figure 15. Split-range temperature/monomer-addition control algorithm.**

viscosity became prohibitively high for the on-line sampling systems. Through monomer addition, the polymer concentration rose to increase the solution viscosity substantially. The terminal monomer conversion reached was 58% (based on the total amount of MMA added).

Rather than allowing the molecular weights to undershoot the setpoint, it would have been desirable to simply approach setpoint and remain there. The somewhat disappointing control can be attributed to the difficult control problem of monomer-addition control. As discussed above, the controller must be cautious in the manipulation of molecular weight. However, the PID parameters could possibly have been adjusted better. A better control approach would make use of on-line monomer conversion measurement and employ the on-line modeling information to adjust the monomer addition rate. Nonetheless, the PID monomer-addition controller did a reasonable job of controlling the molecular weight; the results obtained were within the 10% variability in noncontrolled isothermal polymerizations.

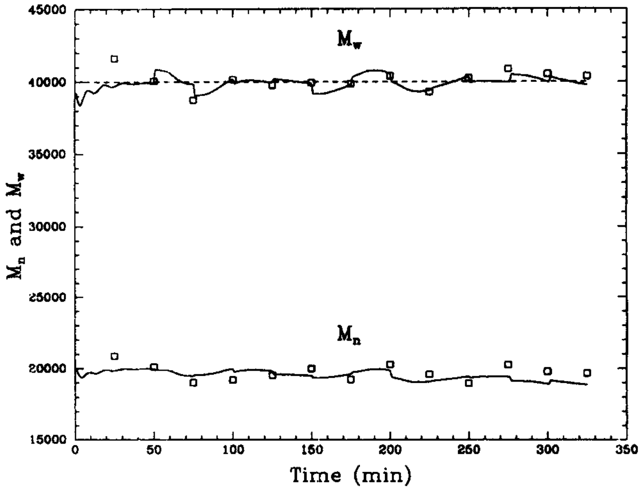

**Figure 16a. Average molecular weights for simultaneous on-line temperature and monomer-addition control of molecular weight.**

□, SEC measurements; ——, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

### *Simultaneous temperature and monomer-addition control*

For polymerization systems where both monomer-addition and temperature control are feasible, it is desirable to take advantage of the benefits obtainable from each approach. Temperature control is capable of lowering molecular weight relatively easily, and monomer addition is able to raise molecular weight much better than solely using temperature control. A simple split-range controller was devised for simultaneous temperature and monomer-addition control. The algorithm is illustrated in Figure 15. As the batch temperature setpoint decreases, a point is reached where monomer addition starts. The monomer addition rate increases linearly until the lower constraint for temperature is reached. The lower-temperature constraint was raised to 328 K, instead of 323 K, as was the

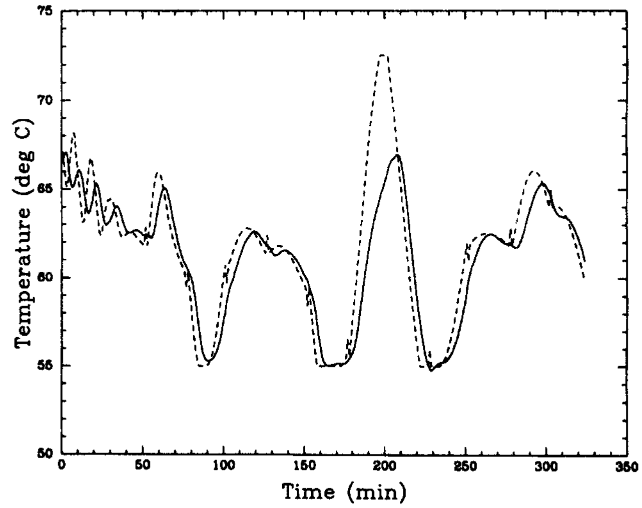

**Figure 16b. On-line molecular-weight control using simultaneous temperature and monomer addition.**

----, batch temperature setpoint; ——, actual temperature.

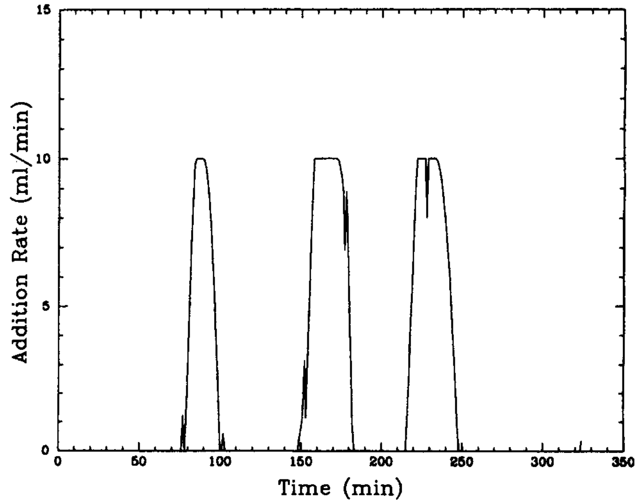

**Figure 16c. Monomer-addition rate for on-line molecular-weight control using simultaneous temperature and monomer addition.**

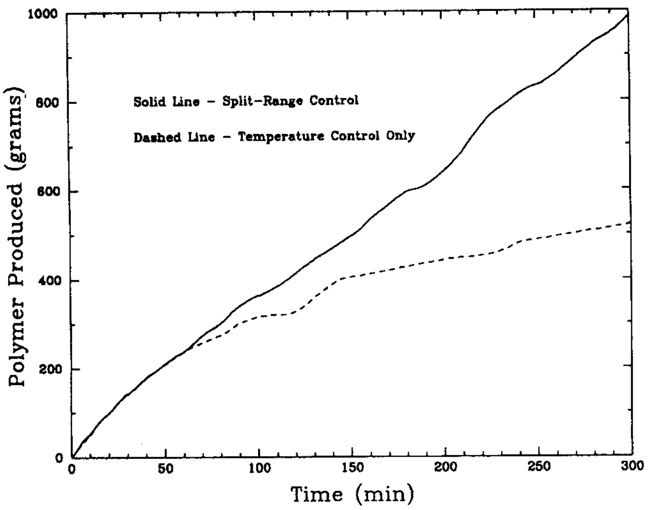

**Figure 16d. Polymer production comparison.**

——, simultaneous temperature/monomer-addition control; ----, temperature control only.

case in sole temperature control, to increase the polymerization rate. The monomer addition counteracts for increasing the lower temperature constraint in the ability to raise molecular weight. The control parameters used for the split-range controller were the same as those for the temperature control scheme (Table 2).

*Case 1: No Errors in Operating Conditions.* The split-range controller was first tested for the cases in Figures 10a and 10b, that of charging the proper amount of initiator along with the other raw materials (initially 25% MMA, 2,842-mL ethyl acetate charged, 0.05-molar AIBN). As shown in Figure 16a, the split-range controller was as successful in controlling the molecular weight as using only temperature control for the same conditions. The corresponding temperature profile and monomer addition rate are presented in Figures 16b and 16c, respectively. Amounts of polymer produced for only temperature control and the split-range control scheme are compared in Figure 16d. The split-range control scheme was able to produce more than twice as much polymer in the same amount of time as sole temperature control because of the additional monomer introduced and the higher minimum temperature constraint, an obvious advantage.

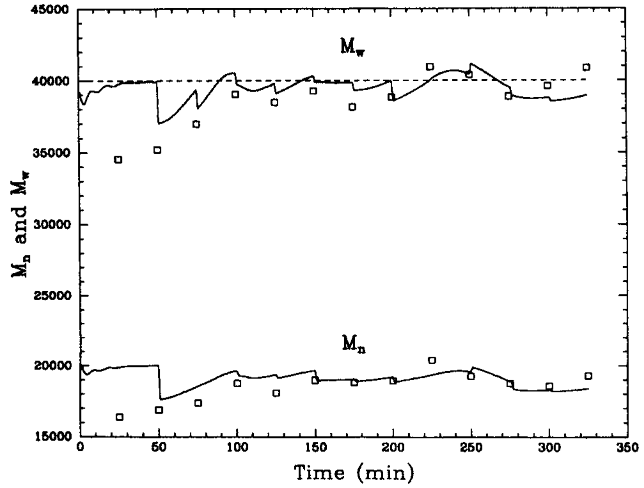

**Figure 17a. Average molecular weights for simultaneous on-line temperature and monomer-addition control of molecular weight with a 40% overcharge of initiator.**

□, SEC measurements; ——, on-line molecular weight estimates; ----, $M_w$ setpoint of 40,000.

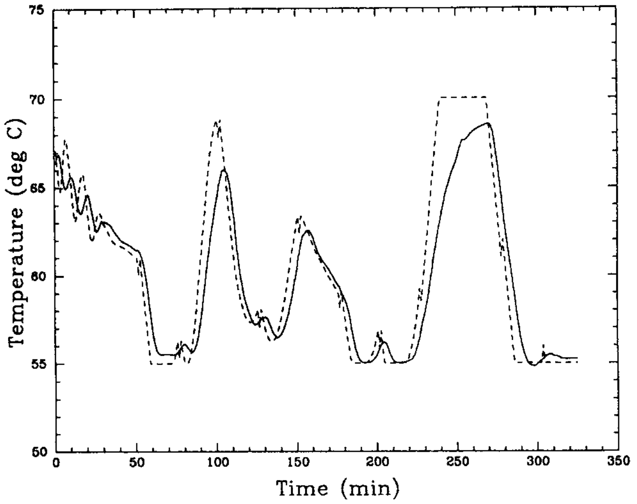

**Figure 17b. On-line molecular-weight control using simultaneous temperature and monomer addition, 40% overcharge of initiator.**

----, batch temperature setpoint; ——, actual temperature.

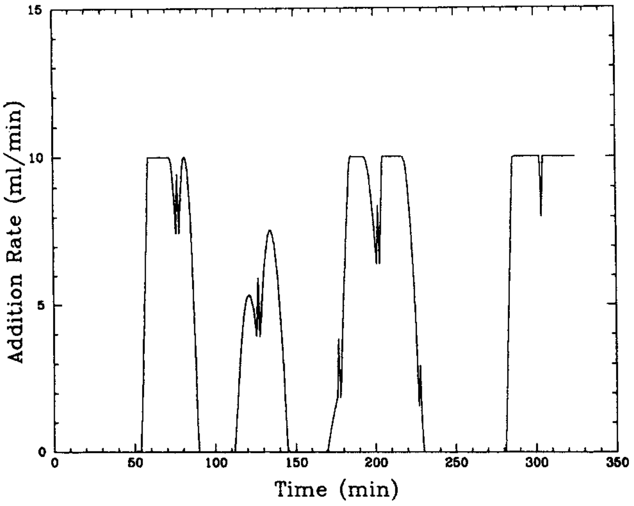

**Figure 17c. Monomer-addition rate for on-line molecular-weight control using simultaneous temperature and monomer addition, 40% overcharge of initiator.**

The limitation prohibiting continuation of the polymerization past 325 min became the high-solution viscosity of the reacting mixture, rather than leveling out at the minimum temperature constraint as was the case for simple temperature control. The monomer conversion at this point was 74% (based on the total amount of MMA charged).

*Case 2: 40% Overcharge of Initiator.* The split-range control scheme was also tested for the case of a 40% overcharge of AIBN (initially 25% MMA by weight, 2,842-mL ethyl acetate charged, 0.07-molar AIBN). The molecular weights obtained are illustrated in Figure 17a. Corresponding temperature and monomer addition profiles are shown in Figures 17b and 17c. The combined estimation and split-range control scheme had little difficulty in adjusting the molecular weight back to the setpoint, whereas temperature control alone was unable to raise the molecular weight because of the underlying chemical limitations. Since the on-line adjustment was rapid, early in the polymerization, and the control was accurate past that point, the polydispersity did not rise appreciably, reaching 2.11 at the end of polymerization. Therefore, the distribution was close to the minimum breadth attainable.

An underlying feature that made control for this case successful was the ability of the estimator to properly reject the error in initiator charged and to converge to the proper molecular weight estimates. This initiator-charging error was equivalent to a model parameter error within the estimator.

Considering the severe mischarge of initiator, this is excellent molecular-weight control. This result can reasonably be thought to encompass other realistic industrial disturbances such as other reactor mischarges, impure raw materials, an improperly cleaned reactor, errors in the structure of the polymerization model, and kinetic parameter inaccuracies.

As was the case for all monomer addition studies, the increasing solution viscosity here became the limiting factor in continuing the polymerization any further. The monomer conversion at the end of the polymerization for this case was 72% (based on the total amount of MMA charged).

## Conclusions

The molecular-weight distribution estimator developed by Ellis et al. (1988a) was fully implemented in an experimental apparatus consisting of a pilot-scale batch reactor, an on-line size exclusion chromatograph, and an on-line density meter. The estimator was shown to perform well for a variety of polymerization cases which could reasonably occur in an industrial setting. Further, the estimator was used as the molecular weight measuring device for a simple feedback control scheme for on-line control of the weight-average molecular weight. Three controlled variables were investigated: temperature control, monomer-addition control, and simultaneous temperature and monomer-addition control. All were shown to be able to reject realistic disturbances and reduce batch-to-batch variability. To the best of our knowledge, this is one of the first articles to document on-line, feedback molecular weight control.

## Acknowledgment

The financial support of the 3M Company is gratefully acknowledged.

## Notation

$A_p$ = preexponential factor for the propagation reaction constant

$E_{\mathrm{trm}}, E_{\mathrm{trs}}$ = activation energies for transfer to monomer and to solvent reactions

$J$ = objective function for parameter optimization

$K_c$ = proportional gain for PID controller

$M_n$ = number-average molecular weight

$M_w$ = weight-average molecular weight

$N$ = total number of experimental observations of weight-average molecular weight for use in nonlinear parameter estimation

$r_{X_D}$ = parameter in Kalman filter measurement noise covariance matrix (Ellis et al., 1988a)

$w_i, w_m, w_s$ = total mass of initiator, monomer, and solvent charged to the reactor

$w_{\mathrm{total}}$ = total combined mass of monomer, solvent, and initiator charged to the reactor

$x_I$ = initiator conversion

$x_m$ = monomer conversion

### Greek letters

$\rho_m, \rho_p, \rho_s$ = densities of monomer, polymer, and solvent

$\tau_I$ = integral time constant for PID controller

$\tau_D$ = derivative time constant for PID controller

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