The Continuous Synthesis of Addition Polymers with a Precisely Controlled Average Molecular Weight and Minimum Polydispersity

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Synopsis

A novel technique for the control of continuous synthesis of addition polymers with precisely controlled average molecular weight and minimum polydispersity has been developed.   A control system adjusts the concentration of chain-transfer agent in the reactor feed to compensate for all other upsets in the reactor inputs: initiator and monomer concentrations, temperature and feed rate.   The technique has been evaluated quantitatively on a digital computer using a kinetic model of a homogeneous, free-radical solution polymerization.   In computational tests, the modeled control system generally held the instantaneous number-average chain length within 1%, and quickly returned it to the desired value in response to a wide variety of upsets.   By generalizing the Schulz distributions to include termination by disproportionation, combination and chain-transfer, it is shown that changes in the molecular-weight distribution resulting from the action of the control system are minor.

INTRODUCTION

The mechanical properties of a polymer depend strongly on its average molecular weight, and to a lesser degree on the molecular weight distribution.   If a polymer having consistent properties is to be produced commercially, control of molecular weight is essential.

In an addition polymerization, a distribution of chain lengths is obtained because of the inherently random nature of the reaction on a microscopic level and because changes in reactor temperature and concentrations with time cause a variation in the average chain length being produced in the reactor at any instant.   The former is beyond control in most cases, but it is possible to apply process-control techniques to minimize the variation in instantaneous average chain length with time, thereby controlling the average chain length of the product at a desired value and also minimizing the spread of the product's molecular weight distribution.

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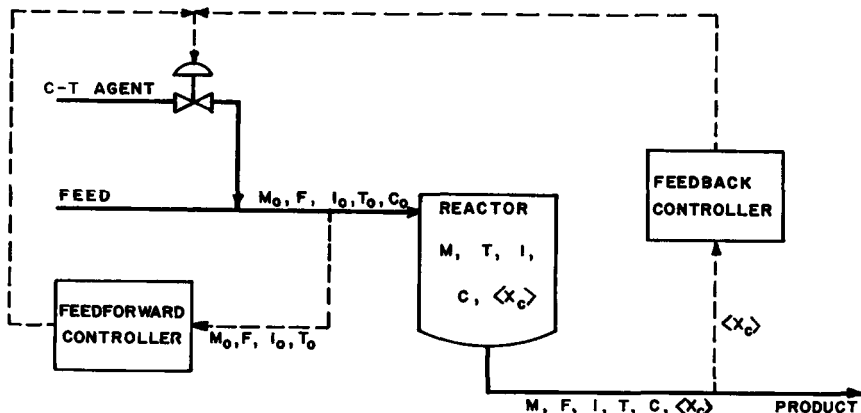
Fig. 1. Schematic diagram of reactor and control systems.

In an ideal continuous stirred-tank reactor, all reactor conditions are time invariant. However, in any actual reactor, upsets to the system give rise to deviations in average molecular weight and broadening of the distribution. The dynamic response of a free-radical solution polymerization carried out in such a reactor has been studied previously.[1] The present work develops a control system for a continuous stirred-tank polymerization reactor. This system is based on the premise that it is control of the molecular weight which is important; slight variations in conversion can be tolerated. It takes advantage of the fact that a chain-transfer agent affects only the molecular weight of the polymer. If a chain-transfer agent is used to achieve the desired steady-state average molecular weight, an increase or decrease in its rate of addition to the reactor can be used to compensate for all other upsets to the system without producing complicating interactions, and without requiring the complexity and expense of precise control of all individual input variables.

The use of feedforward control is particularly beneficial in this application. By monitoring upsets in the feed stream and taking immediate corrective action, much better control can be obtained than with feedback control alone, where relatively large amounts of off-specification material are produced before a controller monitoring the product stream can take appropriate corrective measures. Some feedback control must be employed, however, to eliminate offsets inherent to linearized feedforward controllers, and to correct for nonmeasured feed upsets, such as dissolved oxygen and/or other impurities. The reactor and associated control systems are shown schematically in Figure 1.

Theory

The design of a control system to maintain constant the number-average chain length, X_c, of the polymer being formed in the reactor at any instant proceeds as follows:

1. A process model consisting of the kinetic rate expressions and dynamic material and energy balances is developed. These equations relate conditions in the reactor (and product stream) to feed variables.

2. To make the results more generally appliable and reduce the number of specific parameters required to describe the system, the equations are put in a dimensionless form.

3. The feedforward controller is derived by linearizing the dynamic equations about the desired steady-state operating point, giving expressions which completely describe the response of the linearized system to measured changes in inlet conditions. By setting changes in the instantaneous average chain length equal to zero, the ideal controller, which adjusts the rate of addition of chain transfer agent to compensate for the measured upsets, is obtained.

4. The feedback controller is based on linearized equations relating the effect of chain-transfer agent feed concentration to the measured overall average chain length in the reactor product stream. It further adjusts the rate of chain transfer addition to maintain $\langle X_c \rangle$ at the desired value.

The process model treated here is an addition polymerization carried out in a perfectly stirred continuous reactor. The initial equations are developed in a general form to allow application to a variety of polymerization reactions. Specifically, equations are presented, and the control system is quantitatively analyzed for the case of classical, homogeneous, free-radical addition kinetics.[2] As has been done previously, Arrhenius temperature dependency of the rate constants has been applied, and the usual assumptions made.[1] Here, chain transfer

$$M \cdot_x + C \xrightarrow{k_c} M_x + C \cdot \tag{1}$$

$$C \cdot + M \xrightarrow{k_{ca}} M \cdot_1 \tag{2}$$
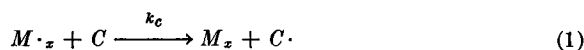
$$r_c = k_c[M \cdot][C] \tag{3}$$

is added, with the assumption that the rate of reaction (2) is of the same order as that of the propagation step, and thus that chain transfer has no significant effect on the rate of polymerization. Underlying the entire development is the assumption that the time required for the growth of a polymer chain is much less than the average reactor residence time, which is perfectly valid for most addition polymerizations.

Rate of Initiator Removal by Reaction:

$$r_d = r_d(T, [I]) = A_d[I] \exp\left(-\frac{E_d}{RT}\right) \tag{4}$$

Rate of initiation = Rate of termination:

$$r_i = r_t = r_i(T, [I]) = 2fA_d[I] \exp\left(-\frac{E_d}{RT}\right) \tag{5}$$

Rate of chain propagation:

$$r_p = (T, [M], [I])$$

$$= A_p[M] \left(\frac{fA_d[I]}{A_t}\right)^{1/2} \exp\left(-\frac{2E_p + E_d - E_t}{2RT}\right) \tag{6}$$

Rate of chain transfer

$$r_c = r_c(T, [I], [C]) = A_c[C] \left(\frac{fA_d[I]}{A_t}\right)^{1/2} \exp\left(-\frac{2E_p + E_d - E_t}{2RT}\right) \tag{7}$$

The number-average chain length in the absence of chain transfer is

$$X = \frac{r_p}{\frac{\eta}{2} r_t} \tag{8}$$

and with chain transfer is

$$X_c = \frac{r_p}{\frac{\eta}{2} r_t + r_c} \tag{9}$$

where η, the number of dead chains produced per termination reaction is given by

$$\eta = \frac{r_{tc} + 2r_{td}}{r_{tc} + r_{td}}; \quad (r_t = r_{tc} + r_{td}) \tag{10}$$

The volume, density, heat capacity, and heat of chain propagation are assumed constant. The other heats of reaction are neglected, and the heat of propagation is removed only in the outlet stream. This manner of heat removal is practically feasible for polymer concentrations up to about 20%, where, in addition, the viscosity is low enough to justify the assumption of perfect mixing and classical kinetics.

Dynamic material and energy balances are shown in Table I. They completely describe the operation of the system.

To make the results more generally applicable and reduce the number of parameters required to describe the system, the equations in Table I are put into dimensionless form in terms of a steady-state operating point, with steady-state values denoted by a bar above the symbol.

The dimensionless constants of the system are given in Table II. The dimensionless variables, I', M', etc., except for time, are expressed as fractional deviations from the steady-state, e.g.,

$$I' = \frac{[I] - \bar{I}}{\bar{I}}$$

TABLE I
Dynamic Material and Energy Balances

Energy Balance

$$\frac{dT}{dt} = \frac{F}{V}(T_0 - T) + \frac{(-\Delta H_p)}{\rho C_p} r_p$$

Monomer Balance

$$\frac{d[M]}{dt} = \frac{F}{V}([M_0] - [M]) - r_p$$

Initiator Balance

$$\frac{d[I]}{dt} = \frac{F}{V}([I_0] - [I]) - r_d$$

Chain Tr. Agent Balance

$$\frac{d[C]}{dt} = \frac{F}{V}([C_0] - [C]) - r_c$$

Polymerized Monomer Balance

$$\frac{d[M_p]}{dt} = -\frac{F}{V}[M_p] + r_p$$

Dead Polymer Balance (Without Transfer)

$$\frac{d[P]}{dt} = -\frac{F}{V}[P] + \frac{\eta}{2} r_t$$

Dead Polymer Balance (With Transfer)

$$\frac{d[P_c]}{dt} = -\frac{F}{V}[P_c] + \frac{\eta}{2} r_t + r_c$$

Outlet Chain Lengths

$$\langle X_c \rangle = \frac{[M_p]}{[P]}$$

$$\langle X_c \rangle = \frac{[M_p]}{[P_c]}$$

and the dimensionless time is $\theta = \bar{F}t/V$. These dimensionless constants and variables are substituted into the equations in Table I to yield the dimensionless equations in Table III. The dimensionless instantaneous chain lengths for the assumed kinetic scheme are: without transfer,

$$X' = \frac{(M' + 1)}{(I' + 1)^{1/2}} \exp\left[(E_2 - E_1)\frac{T'}{T' + 1}\right] - 1 \qquad (11)$$

TABLE II
Steady-State Dimensionless Constants

$$E_1 = \frac{E_d}{R\bar{T}}; \quad E_2 = \frac{2E_p + E_d - E_t}{2R\bar{T}}; \quad E_3 = \frac{2E_c + E_d - E_t}{2R\bar{T}}$$

$$\frac{\bar{T}_0}{\bar{T}} = 1 - \frac{(-\Delta H_p)}{\rho C_p \bar{T}} \frac{V}{F} \quad r_p = 1 - \frac{\bar{M}(-\Delta H_p)}{\bar{T}\rho C_p} \frac{VA_p}{F} \left(\frac{fA_d\bar{I}}{A_t}\right)^{1/2} \exp(-E_2)$$

$$\frac{\bar{M}_0}{\bar{M}} = 1 + \frac{V}{F} \frac{r_p}{\bar{M}} = 1 + \frac{VA_p}{F} \left(\frac{fA_d\bar{I}}{A_t}\right)^{1/2} \exp(-E_2)$$

$$\frac{\bar{I}_0}{\bar{I}} = 1 + \frac{V}{F} \frac{r_d}{\bar{I}} = 1 + \frac{VA_d}{F} \exp(-E_1)$$

$$\frac{\bar{C}_0}{\bar{C}} = 1 + \frac{V}{F} \frac{r_d}{\bar{C}} = 1 + \frac{VA_c}{F} \left(\frac{fA_d\bar{I}}{A_t}\right)^{1/2} \exp(-E_3)$$

$$\frac{\bar{X}_c}{\bar{X}} = \frac{(\eta/2)r_t}{(\eta/2)r_t + r_c} = \frac{1}{1 + [(A_c\bar{C})/\eta(fA_dA_t\bar{I})^{1/2}] \exp(E_1 - E_3)}$$

$$\frac{\bar{M}_p}{\bar{M}} = \frac{\bar{M}_0}{\bar{M}} - 1; \quad \frac{\bar{P}}{\bar{I}} = \eta f \left(\frac{\bar{I}_0}{\bar{I}} - 1\right)$$

$$\frac{\bar{P}_c}{\bar{C}} = \frac{(\bar{C}_0/\bar{C}) - 1}{1 - (\bar{X}_c/\bar{X})}; \quad \frac{\bar{P}}{\bar{P}_c} = \frac{\bar{X}_c}{\bar{X}}$$

with transfer,

$$X'_c =$$

$$\frac{(M' + 1) \exp[(E_2 - E_1)(T'/T' + 1)]}{(\bar{X}_c/\bar{X})(I' + 1)^{1/2} + [1 - (\bar{X}_c/\bar{X})](C' + 1) \exp[(E_3 - E_1)(T'/T' + 1)]}$$
$$- 1 \quad (12)$$

The dimensionless outlet chain lengths are: without transfer,

$$\langle X' \rangle = \frac{M' + 1}{P' + 1} - 1 \tag{13}$$

with transfer,

$$\langle X'_c \rangle = \frac{M' + 1}{P'_c + 1} - 1 \tag{14}$$

These dimensionless number-average chain lengths are expressed as fractional deviations from the steady state. In addition homopolymerization, where the molecular weight is directly proportional to the chain length, the fractional deviation in number-average molecular weight is equal to that for number-average chain length, and the terms may be used interchangeably.

In deriving the dimensionless equations, it is implicitly assumed that the parameter η is constant. This assumption poses no problem when either

TABLE III
Dimensionless Material and Energy Balances

Energy Balance

$$\frac{dT'}{d\theta} = f_1(T'_0, F', T', M', I') = \left[(T'_0 + 1)\frac{\bar{T}_0}{\bar{T}} - (T' + 1) \right] (F' + 1)$$

$$+ \left(1 - \frac{\bar{T}_0}{\bar{T}}\right) (I' + 1)^{1/2} (M' + 1) \exp\left(E_2 \frac{T'}{T' + 1} \right)$$

Monomer Balance

$$\frac{dM'}{d\theta} = f_2(M'_0, F', T', M', I') = \left[(M'_0 + 1)\frac{\bar{M}_0}{\bar{M}} - (M' + 1) \right] (F' + 1)$$

$$+ \left(1 - \frac{\bar{M}_0}{\bar{M}}\right) (I' + 1)^{1/2}(M' + 1) \exp\left(E_2 \frac{T'}{T' + 1} \right)$$

Initiator Balance

$$\frac{dI'}{d\theta} = f_3(I'_0, F', T', I') = \left[(I'_0 + 1)\frac{\bar{I}_0}{\bar{I}} - (I' + 1) \right] (F' + 1)$$

$$+ \left(1 - \frac{\bar{I}_0}{\bar{I}}\right) (I' + 1) \exp\left(E_1 \frac{T'}{T' + 1} \right)$$

Chain-Transfer Agent Balance

$$\frac{dC'}{d\theta} = f_4(C'_0, F', T', C', I') = \left[(C'_0 + 1)\frac{\bar{C}_0}{\bar{C}} - (C' + 1) \right] (F' + 1)$$

$$+ \left(1 - \frac{\bar{C}_0}{\bar{C}}\right) (I' + 1)^{1/2} (C' + 1) \exp\left(E_3 \frac{T'}{T' + 1} \right)$$

Polymerized Monomer Balance

$$\frac{dM'_p}{d\theta} = f_5(M'_p, F', T', M', I') = (I' + 1)^{1/2}(M' + 1) \exp\left(E_2 \frac{T'}{T' + 1} \right)$$

$$- (M_p' + 1)(F' + 1)$$

Dead Polymer Balance Without Transfer

$$\frac{dP'}{d\theta} = f_6(P', F', T', I') = (I' + 1) \exp\left(E_1 \frac{T'}{T' + 1} \right) - (P' + 1)(F' + 1)$$

Dead Polymer Balance With Transfer

$$\frac{dP'_c}{d\theta} = f_7(P'_c, F', T', C', I') = \frac{\bar{X}_c}{\bar{X}} (I' + 1) \exp\left(E_1 \frac{T'}{T' + 1} \right)$$

$$- (P'_c + 1)(F' + 1) + \left(1 - \frac{\bar{X}_c}{\bar{X}}\right) (I' + 1)^{1/2}(C' + 1) \exp\left(E_3 \frac{T'}{T' + 1} \right)$$

combination or disproportionation predominates, but η must be independent of temperature if the mechanisms are competitive, i.e., both reactions must have the same energy of activation.

To derive the feedforward controller, the system model is linearized about the steady-state operating point. Linearization of the first four

TABLE IV
Linearized Dimensionless Equations[a]

Energy Balance

$$\frac{dT'}{d\theta} = \left(\frac{\partial f_1}{\partial T'_0}\right)_{ss} T'_0 + \left(\frac{\partial f_1}{\partial F'}\right)_{ss} F' + \left(\frac{\partial f_1}{\partial T'}\right)_{ss} T' + \left(\frac{\partial f_1}{\partial M'}\right)_{ss} M' + \left(\frac{\partial f_1}{\partial I'}\right)_{ss} I'$$

Monomer Balance

$$\frac{dM'}{d\theta} = \left(\frac{\partial f_2}{\partial M'_0}\right)_{ss} M_0' + \left(\frac{\partial f_2}{\partial F'}\right)_{ss} F' + \left(\frac{\partial f_2}{\partial T'}\right)_{ss} T' + \left(\frac{\partial f_2}{\partial M'}\right)_{ss} M' + \left(\frac{\partial f_2}{\partial I'}\right)_{ss} I'$$

Initiator Balance

$$\frac{dI'}{d\theta} = \left(\frac{\partial f_3}{\partial I'_0}\right)_{ss} I'_0 + \left(\frac{\partial f_3}{\partial F'}\right)_{ss} F' + \left(\frac{\partial f_3}{\partial T'}\right)_{ss} T' + \left(\frac{\partial f_3}{\partial I'}\right)_{ss} I'$$

Chain Tr. Balance

$$\frac{dC'}{d\theta} = \left(\frac{\partial f_4}{\partial C'_0}\right)_{ss} C'_0 + \left(\frac{\partial f_4}{\partial F'}\right)_{ss} F' + \left(\frac{\partial f_4}{\partial T'}\right)_{ss} T' - \left(\frac{\partial f_4}{\partial C'}\right)_{ss} C' + \left(\frac{\partial f_4}{\partial I'}\right)_{ss} I'$$

Number-Average Chain Length

$$X_c' = \left(\frac{\partial X'_c}{\partial T'}\right)_{ss} T' + \left(\frac{\partial X'_c}{\partial M'}\right)_{ss} M' + \left(\frac{\partial C'_c}{\partial I'}\right)_{ss} I' + \left(\frac{\partial X'_c}{\partial C'}\right)_{ss} C'$$

[a] The relations are shown here in functional form for generality. Explicit equations for the assumed kinetic scheme are available.[3]

equations in Table III and use of eq. (12) results in the equations in Table IV. It is then necessary to take Laplace Transforms of the linearized equations. When these transformed equations are solved simultaneously, the solution may be expressed as a plant matrix of transfer functions, which completely describes the response of the linearized system to any change in inlet conditions. (Transformed variables are underlined.)

$$\begin{bmatrix} \underline{T'} \\ \underline{M'} \\ \underline{I'} \\ \underline{C'} \end{bmatrix} = \begin{bmatrix} P_{1,1} & P_{1,2} & P_{1,3} & P_{1,4} & 0 \\ P_{2,1} & P_{2,2} & P_{2,3} & P_{2,4} & 0 \\ P_{3,1} & P_{3,2} & P_{3,3} & P_{3,4} & 0 \\ P_{4,1} & P_{4,2} & P_{4,3} & P_{4,4} & P_{4,5} \end{bmatrix} \begin{bmatrix} \underline{T'_0} \\ \underline{M'_0} \\ \underline{I'_0} \\ \underline{F'} \\ \underline{C'_0} \end{bmatrix} \tag{15}$$

The effect of reactor conditions on instantaneous chain length may be expressed as

$$\underline{X'_c} = [X_1 X_2 X_3 X_4] \begin{bmatrix} \underline{T'} \\ \underline{M'} \\ \underline{I'} \\ \underline{C'} \end{bmatrix} \tag{16}$$

Combining eqs. (15) and (16)

$$\underline{X'_c} = [X_1 X_2 X_3 X_4][P_{(4 \times 5)}] \begin{bmatrix} T_0' \\ \underline{M'_0} \\ \underline{I'_0} \\ \underline{F'} \\ \underline{C'_0} \end{bmatrix} \quad (17)$$

Since $P_{1,5}$, $P_{2,5}$ and $P_{3,5}$ are all zero, $P_{4,5}$ may be separated to yield a four-by-four matrix and a separate term for $\underline{C'_0}$. This, of course, reflects the appearance of $[C]$ only in the chain transfer rate equation. The separability of $\underline{C'_0}$ makes it an ideal manipulative variable, as it affects only the variable to be controlled. The ideal feedforward controller, which perfectly controls the linearized system is derived by setting $\underline{X'_c} = 0$ and solving for $\underline{C'_0}$.

$$C'_0 = \frac{-1}{X_4 P_{4,5}} [X_1 X_2 X_3 X_4][P_{(4 \times 4)}] \begin{bmatrix} T_0' \\ \underline{M_0'} \\ \underline{I'_0} \\ \underline{F'} \end{bmatrix} \quad (18)$$

An alternate expression for the controller may be written in terms of a transfer function for each input.

$$\underline{C'_0} = F_1 T'_0 + F_2 \underline{M'_0} + F_3 \underline{I'_0} + F_4 \underline{F'} \quad (19)$$

The transfer functions are of the form

$$F_n = \frac{A_n s^2 + B_n s + C_n}{s^2 + \alpha s + \beta} \quad (20)$$

where all the terms are constants based on the steady-state operating point (explicit expressions are available).[3]

A system of this complexity would obviously require on-line computer control. However, a simplification has been developed which could be obtained with standard controllers.

$$F_n = \frac{A_n s + \left(\dfrac{C_n}{\beta}\right) \beta^\lambda}{s + \beta^{\lambda_n}} \quad (21)$$

where λ_n is a parameter which is adjusted to equalize the area under the ideal and simplified amplitude-ratio curves.[3]

$$\lambda_n = 1 + \frac{\ln[(A_n^2 + 1)/(C_n^2 + \beta^2)] + \{[(1/(A_n^2 + 1) + (\beta^2/C_n^2 + \beta^2) - (2(\alpha^2 - 2\beta)/b)]/[(1/A_n^2 + 1) - (\beta^2/C_n^2 + \beta^2)]\}}{4 \ln \beta}$$

$$\times f(b,q) \quad (22)$$

where

$$f(b,q) = 0 \qquad \qquad \text{If } q = 0$$

$$f(b,q) = \frac{b}{\sqrt{q}}\left[\pi - 2\tan^{-1}\frac{b}{\sqrt{q}}\right] \quad \text{If } q > 0$$

$$f(b,q) = \frac{b}{\sqrt{-q}} \ln \frac{b + \sqrt{-q}}{b - \sqrt{-q}} \quad \text{If } q < 0$$

and

$$b = (B_n{}^2 - 2A_nC_n) + (\alpha^2 - 2\beta)$$

$$q = 4(A_n{}^2 + 1)(C_n{}^2 + \beta^2) - b^2$$

For systems with large frequency peaks, this calculated λ_n may lie outside the range from zero to one. When this happens, the simplification will never closely approximate the ideal system, and it is therefore advisable to use the ideal controller.

The feedback controller also uses chain transfer agent as a means of controlling molecular weight. Linearized equations are formulated to give the effect of C'_0 on X'_c. These equations are then transformed, giving a transfer function relating inlet chain-transfer agent to average outlet chain length.

$$\langle X'_c \rangle = \frac{-\partial f_7/\partial C'}{[s/(\partial f_4/\partial C'_0) + 1](s + 1)} \quad \underline{C_0'} \qquad (23)$$

A sample-data feedback system is used here because of practical difficulties involved in obtaining a continuous analysis of average molecular weight in a reactor where temperature and polymer concentration are varying also. The dimensionless time between samplings is τ_s. The
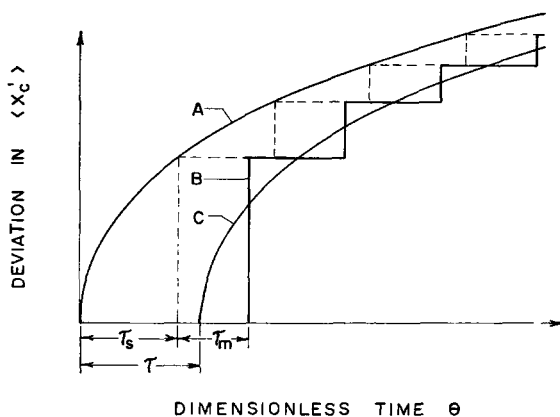

Fig. 2. Design of feedback sampling system. Curve A = reactor output, B = controller input; C = input for which controller is designed.
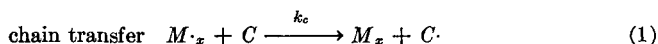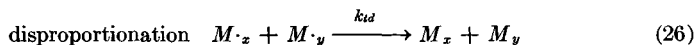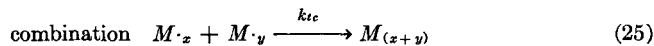
length of time between the instant a sample is taken and the instant the feedback controller takes action on the new information is τ_m. Figure 2 shows how this sample-data system may be approximated by a single transportation lag, τ.

$$\tau = \tau_m + \frac{\tau_s}{2} \tag{24}$$

In Figure 2, Curve A is the actual reactor output and the dotted lines show the points at which samples are taken. The series of steps in Curve B shows the actual input to the controller. The controller is designed as if its input were Curve C, which is an approximation to the Curve B using the transportation lag in eq. (24).

A proportional-integral controller is used, and its parameters are obtained by applying the Ziegler-Nichols criteria.[4] Measurement lags of 0.05, 0.10 and 0.20 $V/\bar{F}$ and sampling times from 0 (continuous) to 0.5 $V/\bar{F}$ were investigated.[3] Representative results are shown here for $\tau_m = 0.10$ $V/\bar{F}$ and $\tau_s = 0.20$ $V/\bar{F}$. Surprisingly, continuous feedback does not improve control much.

In a classical, free-radical addition polymerization, a growing chain radical may be terminated by one of three reactions:

$$\text{combination} \quad M\cdot_x + M\cdot_y \xrightarrow{k_{tc}} M_{(x+y)} \tag{25}$$

$$\text{disproportionation} \quad M\cdot_x + M\cdot_y \xrightarrow{k_{td}} M_x + M_y \tag{26}$$

$$\text{chain transfer} \quad M\cdot_x + C \xrightarrow{k_c} M_x + C\cdot \tag{1}$$

Statistically, disproportionation and chain transfer are identical; a growing chain is converted to a dead chain, undergoing no change in length in the process. Hence, it may be concluded initially that in a polymerization system which inherently (in the absence of any chain-transfer agent) terminates exclusively by disproportionation, the addition of chain-transfer agent in any proportion will not alter the molecular weight distribution. The combination reaction, on the average, halves the number of chains and doubles their length. The resulting distribution is therefore different than that produced by transfer or disproportionation, and if the polymerizing system terminates inherently at least partially by combination, varying the concentration of chain-transfer agent will alter the distribution, even though the number average is held constant.

For a system in which all three termination mechanisms are present, the overall distribution must account for the relative proportion of polymers formed by each. These proportions are number (mole) fractions in the case of the number distribution, and weight fractions for the weight distributions. Since disproportionation and transfer yield the same distribution function, they may be combined, making it necessary only to separate that fraction of the polymer formed by combination.

The well-known Schulz distribution[5] has been adopted here to describe molecular-weight distributions quantitatively because it is based on essentially the same assumptions involved in the control-system analysis, and has been shown to agree well with experimental results.[6]

The overall rate for termination by combination and disproportionation is the sum of the individual rates, i.e.,

$$r_t = r_{tc} + r_{td}; \quad k_t = k_{tc} + k_{td} \tag{27}$$

The ratio

$$\frac{X_c}{X} = \frac{(\eta/2)\, r_t}{(\eta/2)r_t + r_c} \tag{28}$$

represents the number (mole) fraction of polymer molecules produced by combination and/or disproportionation. Of the molecules resulting from disproportionation and/or combination reactions, the fraction produced by combination alone is $(2/\eta - 1)$. Therefore, the overall number (mole) fraction of *all* molecules produced by combination, Ψ, is

$$\Psi = \left(\frac{2}{\eta} - 1\right)\left[\frac{(\eta/2)r_t}{(\eta/2)r_t + r_c}\right] = \left(\frac{2}{\eta} - 1\right)\left(\frac{X_c}{X}\right) \tag{29}$$

It is conceptually useful at this point to introduce the "growing chain length" X_g. This is defined as the number-average length of growing chain radicals immediately prior to termination, i.e.,

$$X_g = \frac{r_p}{r_t + r_c} = \frac{X_c}{1 + (X_c/X)\left(\dfrac{2}{\eta} - 1\right)} = \frac{X_c}{1 + \Psi} \tag{30}$$

The number-average length of dead polymer chains produced by transfer or disproportionation is equal to X_g, while that of chains terminated by combination is twice X_g.

In an ensemble of N polymer molecules, ΨN of them will have been formed by combination. Since the number-average chain length of these chains formed by combination is $2X_g$, the total number of monomer units involved in chains formed by combination is $2X_g\Psi N$. There will be $(1 - \Psi)N$ molecules formed by transfer and/or disproportionation, and the number-average length of these is X_g. Therefore, there are $X_g(1 - \Psi)N$ monomer units tied up in these chains. The weight fraction of all molecules produced by combination is then $2X_g\Psi N/[2X_g\Psi N + X_g(1 - \Psi)N]$ or $2\Psi/(\Psi + 1)$.

The overall distributions are obtained by weighting the individual Schulz distributions for combination and transfer and/or disproportionation by the fractions defined above (number fractions for the number distributions and weight fractions for the weight distributions). When put in dimensionless form, the distributions $X_c N(x/X_c)$ and $X_c W(x/X_c)$ given in Table V depend only on Ψ, and in this form are particularly useful for

TABLE V

Dimensionless Overall Distributions

$$X_c N(x/X_c) = \left[\Psi(\Psi + 1)^2 \left(\frac{x}{X_c}\right) + (1 + \Psi^2) \right] \exp \left[-(\Psi + 1) \left(\frac{x}{X_c}\right) \right]$$

$$X_c W(x/X_c) = \left[\Psi(\Psi + 1)^2 \left(\frac{x}{X_c}\right) + (1 - \Psi^2) \right] \frac{x}{X_c} \exp \left[-(\Psi + 1) \left(\frac{x}{X_c}\right) \right]$$

$$\frac{X_w}{X_c} = \frac{4\Psi + 2}{(\Psi + 1)^2}$$

observing the effects of the control system which varies Ψ through X_c/X to maintain X_c constant.

Results

The control system developed here has been evaluated on a digital computer over a wide range of parameters typical of common free-radical addition systems. Transient responses have been calculated for step changes of various sizes in all four inlet variables. The root-mean-square time average deviation in instantaneous chain length over the first two reactor hold times after a step change is used as a measure of control system effectiveness. These deviations are presented in Table VI for the reference case where

$$\bar{T}_0/\bar{T} = 0.90 \qquad\qquad E_1 = 35$$
$$\bar{M}_0/\bar{M} = 4 \qquad\qquad E_2 = 25$$
$$\bar{I}_0/\bar{I} = 4 \qquad\qquad E_3 = 40$$
$$\bar{C}_0/\bar{C} = 4 \qquad\qquad \bar{X}_c/\bar{X} = 0.50$$

The values of $\bar{M}_0/\bar{M} = \bar{I}_0/\bar{I} = \bar{C}_0/\bar{C} = 4$ represent 75% reaction of the monomer, initiator and chain-transfer agent, respectively, in the reactor at steady-state. Since monomer conversion and temperature rise are related by

$$(\bar{T}_0 - \bar{T}) = \frac{\Delta H_p}{\rho C_p} (\bar{M}_0 - \bar{M}) \qquad\qquad (31)$$

specific values for $\bar{T}_0/\bar{T}$ are determined by the heat of polymerization and the thermal properties of the reaction mass, as well as the monomer conversion. The value of 0.9 illustrated is representative of the steady-state temperature rise resulting from the polymerization of a room temperature, 10 to 20% monomer feed solution at the above conversion. The values for the dimensionless activation energies E_1, E_2 and E_3 (defined in Table II) are chosen to be representative of common initiators, monomers and chain-transfer agents. The effects of varying these parameters were investigated, and the effects of inlet step changes in temperature, monomer concentration, initiator concentration, and flow rate were studied for six different control systems. Complete data are available.[3]

TABLE VI
Per Cent Root-Mean-Square Deviation in X'_c

Inlet step change	Uncon-trolled	Feedback only	Simplified feed-forward	Simplified Feed-forward with feedback	Ideal feed-forward	Ideal Feed-forward with feedback
Temperature						
+1%	4.4296	2.1354	0.8871	0.3255	1.0319	0.4014
−1%	6.6716	2.6388	1.3995	0.5925	1.2525	0.5223
Monomer						
+10%	4.3006	1.7581	0.4057	0.3855	0.5456	0.3729
−10%	3.9474	3.5885	0.7250	0.5732	0.5366	0.4573
Initiator						
+10%	4.4612	2.0774	0.1169	0.1830	0.0942	0.0479
−10%	5.0508	2.2774	0.2948	0.2695	0.1168	0.0583
Flow Rate						
+10%	2.1376	1.5944	0.0967	0.0886	0.1035	0.1044
−10%	1.9352	1.6155	0.2878	0.2769	0.1010	0.1091

To illustrate typical transient response, the effect of a 10% step increase
in inlet monomer concentration is shown.   Figure 3 shows the transient
response of the uncontrolled system.   Immediately after the step change,
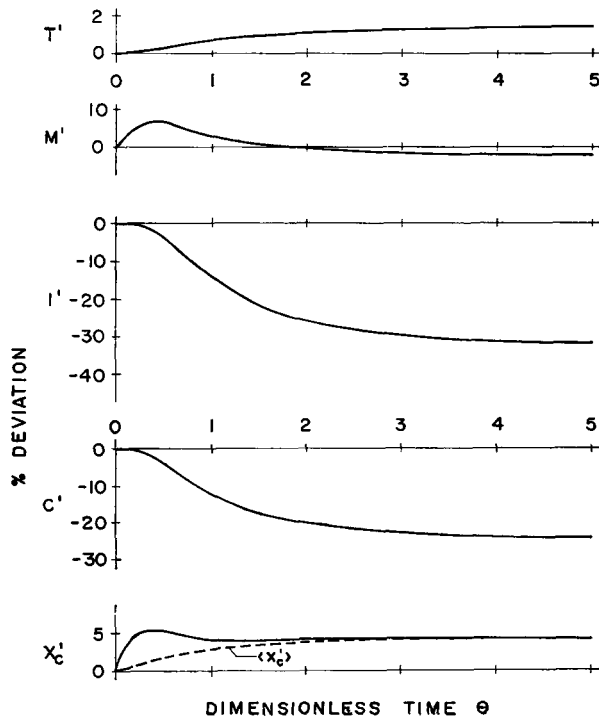

DIMENSIONLESS TIME Θ
Fig. 3. Uncontrolled response to a 10% step increase in monomer feed concentration.
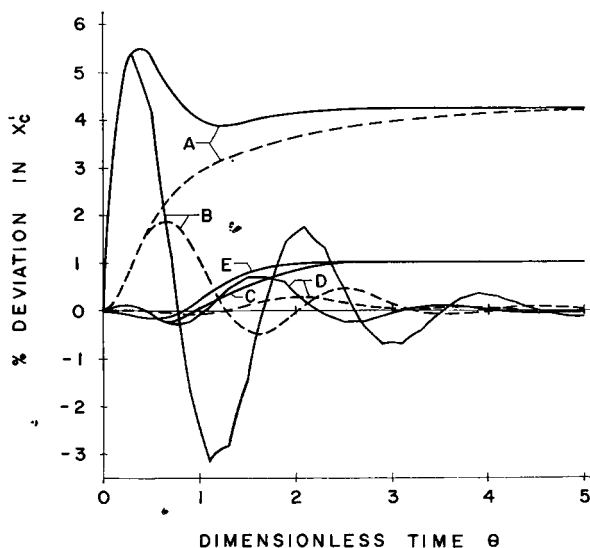
Fig. 4. Dynamic response of chain length to a 10% step increase in monomer feed concentration.   Curves A = uncontrolled response; B = sample-data feedback control; C = simplified feedforward control; D = simplified feedforward with feedback; E = ideal feedforward. ———— X'_c, --------- $<X'_c>$

the monomer concentration, and thus the reaction rate and chain length, shows an initial increase.   The faster reaction rate causes a temperature rise which further increases the rate until the monomer concentration drops below its initial steady-state value and causes the chain length to drop.   This self-regulating effect is discussed in greater detail in the preliminary study of the uncontrolled system.[1]   The transient responses of chain length to the step change are shown for various controllers in Figure 4. Table VI summarizes the effects of the control systems in response to various feed upsets.

Consider the reactor operating at the steady-state reference point with $\overline{\Psi} = 0.5$, $\eta = 1$ (i.e., half the product molecules resulting from combination, the exclusive inherent termination mode, with the remainder terminated by chain transfer).   When an upset occurs, the control system takes action to restore the number-average molecular weight to its steady-state value, ultimately establishing a new steady state.   As long as some of the chains are inherently terminated by combination, the new steady-state will have an altered distribution and a different weight-average molecular weight than the original.

The solid curves in Figure 5 show the initial steady-state distributions, $\overline{\Psi} = 0.5$.   To compensate for a 10% increase in initiator concentration to the reactor, $\overline{\Psi}$ is increased to 0.549, giving the dashed curves, with a resulting decrease in X_w of 1.63%.   Similarly, a 1% increase in temperature increases Ψ to 0.530.   Graphically, the altered distribution is similar to that for the +10% initiator step change shown in Figure 5.   The weight-
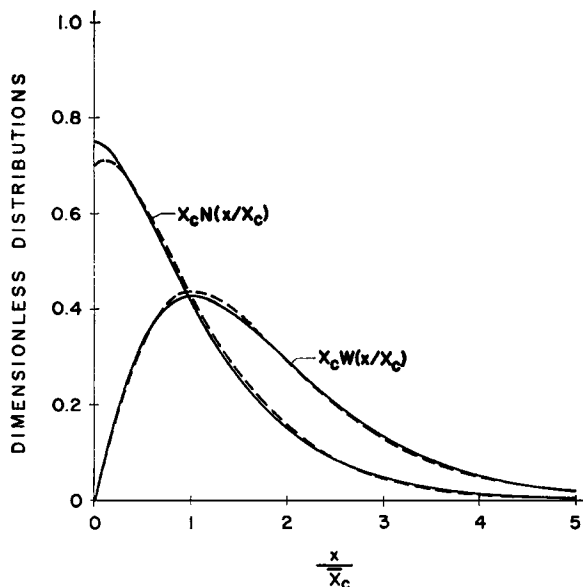
Fig. 5. The effect of a 10% step increase in initiator feed concentration on the distributions. ————— Initial steady state, Ψ = 0.5. — — — New steady state, Ψ = 0.549.

average molecular weight is decreased 1%. Ten percent changes in monomer concentration and flow rate do not shift the distributions enough to warrant graphical presentation. Table VII summarizes the effects of some upsets on X_w. These results are representative of those obtained for similar upsets to systems with a variety of initial steady-state operating conditions. In general, it was found that higher initial steady-state concentrations of chain-transfer agent, i.e., lower $\bar{X}_c/\bar{X}$ resulted in slightly better control and a smaller offset in X_w.[3] This study was limited to 1% (absolute) temperature upsets because previous work has demonstrated the advisability of maintaining feed temperature within these limits ($\pm 3^\circ$C, or so) for effective control of X_c.

TABLE VII
Deviations of Weight-average Chain Length in Controlled System
From Steady-State Reference Point

Upset	Ψ New steady-state	Offset in X_w
+1% temperature	0.530	−1.00%
−1% temperature	0.454	−1.53%
+10% monomer	0.485	+0.500%
−10% monomer	0.501	−0.020%
+10% initiator	0.549	−1.63%
−10% initiator	0.451	+1.63%
+10% flow rate	0.488	+0.400%
−10% flow rate	0.511	−0.350%

Conclusions

The control system developed here provides excellent control of number-average chain length for systems which follow the assumed model. To follow this model, a system must be low enough in polymer concentration for ideal stirring, follow approximately the classical kinetic scheme, have an η that is essentially constant, and use a chain transfer agent that does not act as an inhibitor.

As was shown in previous work,[1] independent control of the inlet temperature would be beneficial, since the nonlinearity of the system with respect to temperature causes some control problems.

The use of feedforward control in conjunction with feedback control combines the excellent transient control of the feedforward system and the lack of a final offset of the feedback system. It eliminates the offset of feedforward alone and the poor initial response of feedback alone.

The control system provides excellent control over a wide range of parameters, but certain parameters have important effects on controller performance. Control is better when T_0/T is closer to unity, as the system exhibits less nonlinearity. Higher energies of activation create larger temperature effects thus causing greater nonlinearity and poorer control. Both high chain-transfer agent conversion and low initiator conversion can make the simplified controller a poor approximation to the ideal controller. Finally, a low $\bar{X}_c/\bar{X}$, attained by the use of more chain-transfer agent, results in better transient control. In any actual system, the monomer, desired product properties and economic considerations will set practical limits on these parameters.

The action of the control system results in very minor changes in the distribution and weight-average molecular weight while holding the number average constant. The control system should, where the assumptions of the analysis are valid, provide a polymer product approaching the narrowest possible distribution, with a precisely controlled average molecular weight.

Nomenclature

A	= Arrhenius constant, sec^{-1} or moles/liter/sec
A_n, B_n, C_n	= feedforward transfer function terms
C_p	= heat capacity of reaction mass, cal/mole/°C
C	= chain-transfer agent and its concentration, moles/liter
E	= energy of activation, cal/mole
F	= volumetric flow rate, liters/sec
F_n	= feedforward controller transfer function
I	= initiator and its concentration, moles/liter
M	= monomer and its concentration, moles/liter
M_p	= concentration of polymerized monomer molecules, moles/liter
M_x	= dead polymer chain of x monomer units
$M \cdot_x$	= growing chain radical and its concentration, moles/liter

$N(x)$ = number (mole) fraction of polymer molecules with chain length x
P = concentration of dead polymer molecules, moles/liter
$P_{i,j}$ = plant matrix terms
R = gas constant, cal/mole/°K
T = absolute temperature, °K
V = reactor volume, liters
$X(x)$ = weight fraction of polymer molecules with chain length x
X = instantaneous number-average chain length in the absence of transfer
X_c = instantaneous number-average chain length with transfer
X_g = instantaneous growing chain length, the number-average length of growing radical chains prior to termination
X_w = weight-average chain length
$\langle X_c \rangle$ = overall number-average chain length of reactor product.
X_t = matrix terms relating X_c to reactor conditions
b = parameter for λ_n solution
f = reactivity fraction for free radicals
k = reaction rate constant, $\sec^{-1}$ or moles/liter/sec
q = parameter for λ_n solution
r = reaction rate, moles/liter/sec
s = Laplace transform variable
t = time, sec
x = number of units per chain

Greek Letters

α, β = feedforward transfer function terms
η = average number of polymer molecules formed per inherent (disproportionation and combination) termination reaction
θ = dimensionless time
λ = parameter in simplified controller
ρ = density of reaction mass, grams/liter
τ = dimensionless controller lag time
τ_m = dimensionless measurement time
τ_s = dimensionless time between samples
Ψ = number fraction of polymer molecules produced by combination

Subscripts, superscripts, etc.

c = chain-transfer reaction
d = decomposition of initiator
i = initiation process
o = inlet value of variable
p = propagation reaction

t = termination reaction
tc = termination by combination
td = termination by disproportionation
—   = (overbar) steady-state value of variable
—   = (underline) Laplace transformed variable

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