MWD Control in Continuous Free-Radical Polymerizations through Forced Oscillations of the Transfer Agent Feed

L. M. GUGLIOTTA, D. A. COUSO, and G. R. MEIRA*

INTEC (CONICET and Universidad Nacional del Litoral), Guemes 3450, Santa Fe (3000), Argentina

SYNOPSIS

This paper studies the effect of forced-feed oscillations of an intentionally added chain transfer agent on isothermal free-radical polymerizations carried out in continuous stirred-tank reactors (CSTRs). A solution polymerization is first considered. The influence on the molecular weight distribution (MWD) of rectangular waves and impulsive trains of the transfer agent feed is theoretically and experimentally investigated. The main result is that (within certain limits) the average polydispersity can be increased at will with respect to its corresponding steady-state (SS) value, without affecting the average number average chain length or the instantaneous monomer and initiator conversions. This result is extended to an emulsion copolymerization under sinusoidal oscillations of the transfer agent feed, where the "decoupling" between the average molecular polydispersity and other parameters (conversions, number average molecular weight, average number of branches per molecule, and the particle-size distribution) is also produced.

INTRODUCTION

Consider a solution free-radical polymerization carried out in an homogeneous continuous stirred-tank reactor (CSTR) operated in the steady state (SS). Under ideal assumptions and in the case of linear polymers, the observed MWD will exhibit a fixed shape and a polydispersity D_n $(= \mu_w/\mu_n)$ between 1.5 (termination by recombination only with no transfer reactions) and 2 (termination by disproportionation only). In the latter case, a Schulz–Flory distribution is obtained.

The forced periodic operation (PO) of continuous polymerization reactors has shown certain advantages as a means of modifying the MWD of the produced polymers. A review on this subject was published in 1981,[1] and since then, other publications have appeared.[2-6] Forced oscillations in continuous free-radical polymerizations have been studied on several occasions.[7-19] These investigations involved in all cases CSTRs and sinusoidal or square waves. Most works considered the PO of the monomer and/or the initiator. When the average properties of the

polymers obtained under this kind of PO are compared to the properties observed in the SS (with the forced inputs at their time-average values), then the main results of Refs. 7–12 are that (i) the number average chain lengths are similar in both cases and (ii) the polydispersity under PO is always higher than that in the SS. (It is interesting to note that through forced oscillations in continuous "living" anionic polymerizations it is possible to produce polymers with average polydispersities that are lower than in the SS[2,5,6]).

The present work theoretically and experimentally considers the periodic forcing of the transfer agent feed in an isothermal solution free-radical homopolymerization. The objective is to show that under certain conditions it is possible to broaden the average MWD without affecting other properties. The PO of transfer agents had been previously considered in relation to coordination polymerizations,[20,21] but as far as the authors are aware, this is the first application to free-radical mechanisms. Finally, the ideas are extended to a continuous emulsion copolymerization with case II kinetics.[22-24] The closely related problem of natural oscillations under steady-feed conditions were observed, for example, in emulsion polymerizations[25,26] for case I
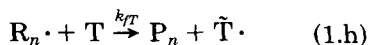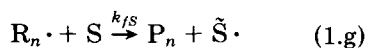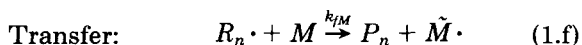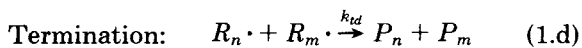
---

kinetics. Forced oscillations in continuous emulsion polymerizations have not been reported so far.

SOLUTION POLYMERIZATION

Theoretical

Consider a solution free-radical homopolymerization carried out in an isothermal and homogeneous CSTR of constant reaction volume V. The reaction mechanism is represented by

Initiation: $\quad I \xrightarrow{k_d} 2R_c \cdot$ (1.a)

$\quad R_c \cdot + M \xrightarrow{k_{pc}} R_1 \cdot$ (1.b)

Propagation: $\quad R_n \cdot + M \xrightarrow{k_p} R_{n+1} \cdot$

$\quad (n \geq 1)$ (1.c)

Termination: $\quad R_n \cdot + R_m \cdot \xrightarrow{k_{td}} P_n + P_m$ (1.d)

$\quad R_n \cdot + R_m \cdot \xrightarrow{k_{tc}} P_{n+m}$ (1.e)

Transfer: $\quad R_n \cdot + M \xrightarrow{k_{fM}} P_n + \tilde{M} \cdot$ (1.f)

$\quad R_n \cdot + S \xrightarrow{k_{fS}} P_n + \tilde{S} \cdot$ (1.g)

$\quad R_n \cdot + T \xrightarrow{k_{fT}} P_n + \tilde{T} \cdot$ (1.h)
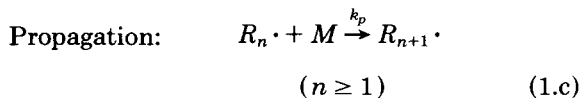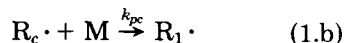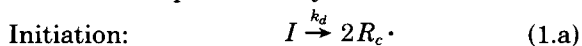
where $I, M, T, S, P_n,$ and R_n, respectively, represent the initiator, the monomer, the intentionally added transfer agent, the solvent, the "dead" polymer, and the growing chain. Assume the following extra hypotheses: (i) secondary radicals $\tilde{M} \cdot$, $\tilde{T} \cdot$ and $\tilde{S} \cdot$ have the same reactivity as does $R_1 \cdot$; (ii) all polymer chains have the same density; (iii) negligible "gel effect"; (iv) the rate constants are independent of chain length; (v) first-order kinetics in each reagent; and (vi) the pseudo-SS hypothesis is applied to the primary initiator $R_c \cdot$. From the mass balances for all intervening species, and by application of the generating function technique for the polymer chains,[27] the dynamic model presented in the Appendix may be obtained.[28]

The quality of a polymer obtained under PO is represented by the average properties under periodicity conditions of the accumulated effluent over an integer number of periods of oscillation T_p. We shall indicate these properties by the superscript *. Call λ_n and ω_n (n = 0, 1, 2), the MWD moments corresponding to the active and the inactive polymer, respectively. For example, the average moments of the active polymer are calculated from:

$$\lambda_n^* = \frac{\displaystyle\int_t^{t+T_p} F(\tau)\lambda_n(\tau)\, d\tau}{\displaystyle\int_t^{t+T_p} F_o(\tau)\, d\tau} \quad (n = 0, 1, 2) \quad (2)$$

where F_o is the total outlet flow. The average values of the number average chain length μ_n and of the polydispersity D_n are calculated through

$$\mu_n^* = \frac{[\lambda_1^* + \omega_1^*]}{[\lambda_0^* + \omega_0^*]} \quad (3)$$

$$D_n^* = \frac{[\lambda_0^* + \omega_0^*][\lambda_2^* + \omega_2^*]}{[\lambda_1^* + \omega_1^*]^2} \quad (4)$$

Other important properties are the average conversions of the initiator η_I and the monomer η_M. For example, η_I is obtained through

$$\eta_I^* = 1 - \frac{\displaystyle\int_t^{t+T_p} F_o(\tau)[I(\tau)]\, d\tau}{\displaystyle\int_t^{t+T_p} f_I(\tau)[I^f]\, d\tau} \quad (5)$$

where f_I is the initiator solution flow rate, the square brackets indicate molar composition, and superscript f indicates feed conditions.

The polymerization of methyl methacrylate in toluene at 80°C with benzoyl peroxide as initiator and benzenethiol as transfer agent was simulated on a VAX 11/780 computer through eqs. (A.1)–(A.14). The computer programs were written in FORTRAN 77, and one of Gear's integration routines was employed.

Consider the POs represented in the upper section of Figure 1, the kinetic data of Table I (taken from Ref. 29), and the input parameters of Table II. The transfer agent feed flow $f_T(t)$ was oscillated as rectangular pulses (Rectangular PO) and as a train of impulses (Impulsive PO). The flows of initiator and of the monomer solutions (f_I and f_M, respectively), were maintained at a steady value of 7.5 mL/min. For the two POs considered, the time-average value of $f_T(t)$ is 0.012 mL/min. Therefore, both POs may be referred to a common SS condition, indicated by superscript s. The SS results are also shown in Table II. Because a pure transfer agent feed is employed, the oscillations of the total outlet flow F_o are negligible under Rectangular PO. Under Impulsive PO, the instantaneous total flow is constant, except when the impulses are applied.

The simulation results are presented in the lower section of Figure 1, in the form of frequency-response graphs. A wide range of frequencies ω (= $2\pi/T_p$) was investigated. The low-frequency limit corresponds to a period T_p = 60 θ (where θ is the instantaneous mean residence time); whereas periods of T_p = $\theta/15$ were adopted at the high-frequency
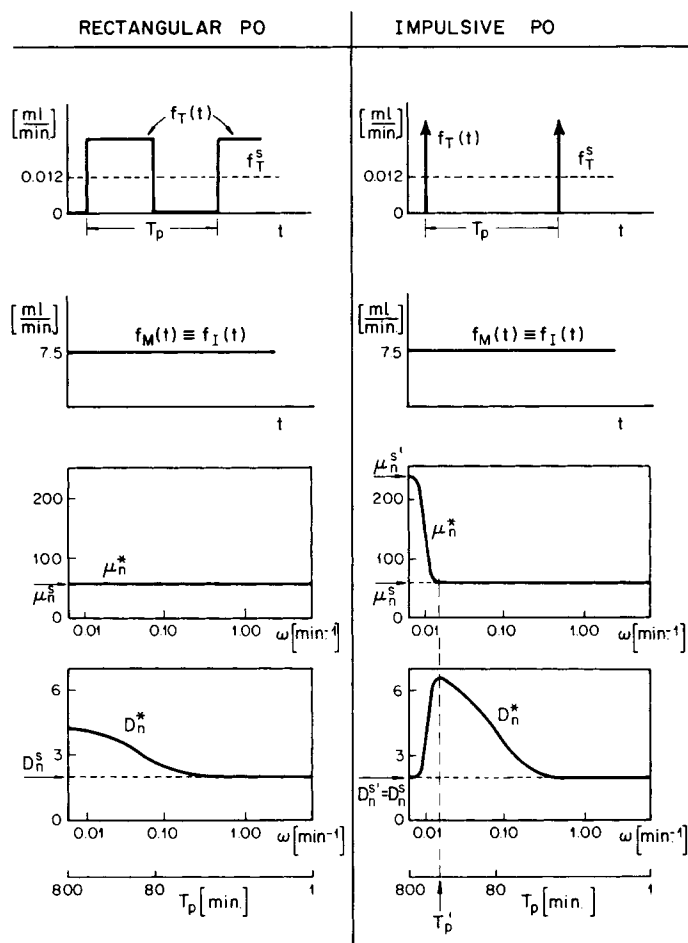
Figure 1 The investigated POs, with simulation results. In the Impulsive PO, the transfer agent volume (mL) associated to each impulse is $[0.012 \text{ mL/min} \times T_p(\text{min})]$.

limit. The average values of η_I and η_M under periodicity conditions are also represented and compared to the SS values. The steady oscillations of the output variables for a typical Rectangular PO are illustrated in Figure 2. The following components can be made:

1. Under PO, the instantaneous values of η_I and η_M (and consequently η_I^* and η_M^*), remain constant at their corresponding SS values. The initiator and monomer mass balances are unaffected by the transfer agent oscillations because (a) the operation is carried out at

Table I Kinetic Data

$$k_d = 1.8182 \times 10^{-3} \text{ dm}^3/\text{mol min}$$
$$k_p = 57{,}434 \text{ dm}^3/\text{mol min}$$
$$k_{fM} = k_{tc} = 0 \text{ dm}^3/\text{mol min}$$
$$k_{fS} = 4.509 \text{ dm}^3/\text{mol min}$$
$$k_{fT} = 79{,}658 \text{ dm}^3/\text{mol min}$$
$$k_{td} = 1.797 \text{ dm}^3/\text{mol min}$$
$$f = 0.9$$
$$\rho_M = 909 \text{ g/dm}^3$$
$$\rho_p = 1059 \text{ g/dm}^3$$

Table II Input Parameters and Common SS Results

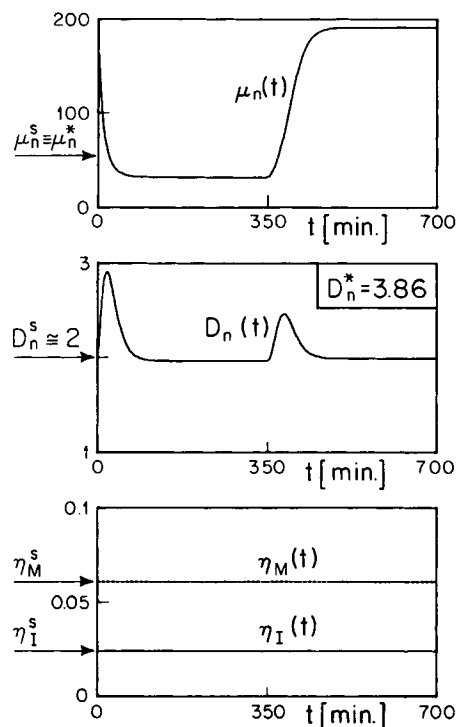| Input Parameters	SS Results
$f_I^s = f_M^s = 0.0075 \text{ dm}^3/\text{min}$	$\mu_n^s = 56.8$
$f_T^s = 0.000012 \text{ dm}^3/\text{min}$	$D_n^s = 1.98$
$F_I^s = 0.015012 \text{ dm}^3/\text{min}$	$\eta_M^s = 0.0693$
$[I^f] = 0.00834 \text{ mol/dm}^3$	$\eta_I^s = 0.024$
$[M^f] = 1.559535 \text{ mol/dm}^3$	
$[T^f] = 9.7386 \text{ mol/dm}^3$	
$V = 0.225 \text{ dm}^3$	

Figure 2 Oscillations of a Rectangular PO simulation with $T_p = 700$ min and corresponding SS values.

constant temperature and (b) the instantaneous mean residence time is practically constant. With $\eta_M(t)$ being constant, the instantaneous rate of polymerization is constant, and, therefore, the PO does not induce perturbations in the reaction temperature.

2. At all frequencies in Rectangular POs, and for periods lower than T'_p for Impulsive POs, μ_n^* is maintained at its SS value. For long periods of oscillation, the transfer agent impulses influence the average μ_n during small fractions of the period, and as $T_p \rightarrow \infty$, a new SS condition corresponding to absence of transfer agent (indicated by superscript s') is reached.

3. The average polydispersity under PO increases with respect to the SS value. Under Rectangular PO, the largest deviations are observed as $T_p \rightarrow \infty$ and at T'_p under Impulsive PO. With very fast cycling, all outputs tend to their SS values because the reactor completely filters out the oscillations. Impulsive PO is useless for very long periods, because the same polymer quality is more easily obtained in the SS. However, for $T_p \leq T'_p$, the impulse forcing is preferable because (a) the same increase in D_n^* may be

obtained at smaller periods and (b) the largest deviation is produced at a finite period. (The lower the period of oscillation, the better, because the volume of the collecting tank required to average the reactor effluent is reduced.)

4. By increasing the total amount of added transfer agent, D_n^* may be further increased, but at the cost of lowering μ_n^*. For example, if under Rectangular PO the transfer agent feed is doubled, the maximum of D_n^* varies from 4.26 to 6.7, but μ_n^* drops from 56.7 to 32.6.

In summary, Impulsive POs seem preferable to Rectangular POs because they are more easy to implement in practice, while simultaneously providing a greater flexibility in D_n^*. A potential disadvantage of intentionally feeding a transfer agent is that it may be difficult to produce high molecular weight material.

Experimental

The work involved the previously simulated chemical system, but with the data of Table III and dodecanethiol (instead of benzenethiol) as transfer agent. The objective was to validate theoretical predictions regarding the behavior of a CSTR under Impulsive PO of the transfer agent feed.

Figure 3 schematically represents the experimental setup. The polymerization was carried out at 80°C in a 300 mL Parr 4561 stainless steel reactor with stirring and ON/OFF temperature control. A septum was adapted in the reactor lid, to allow the transfer agent injection by means of a syringe.

The storage tanks for the initiator and the monomer solutions consisted of two 10 L stainless steel vessels with graduated glass gauges and facilities for inert gas blankets.

The feed flows were applied by two Milroyal D Milton Roy servo-controlled metering pumps, operated by a pair of Statotrol GVFW General Electric controllers. Each pump motor drove two pumping heads of reciprocating action, with a phase difference

Table III   Experimental Data

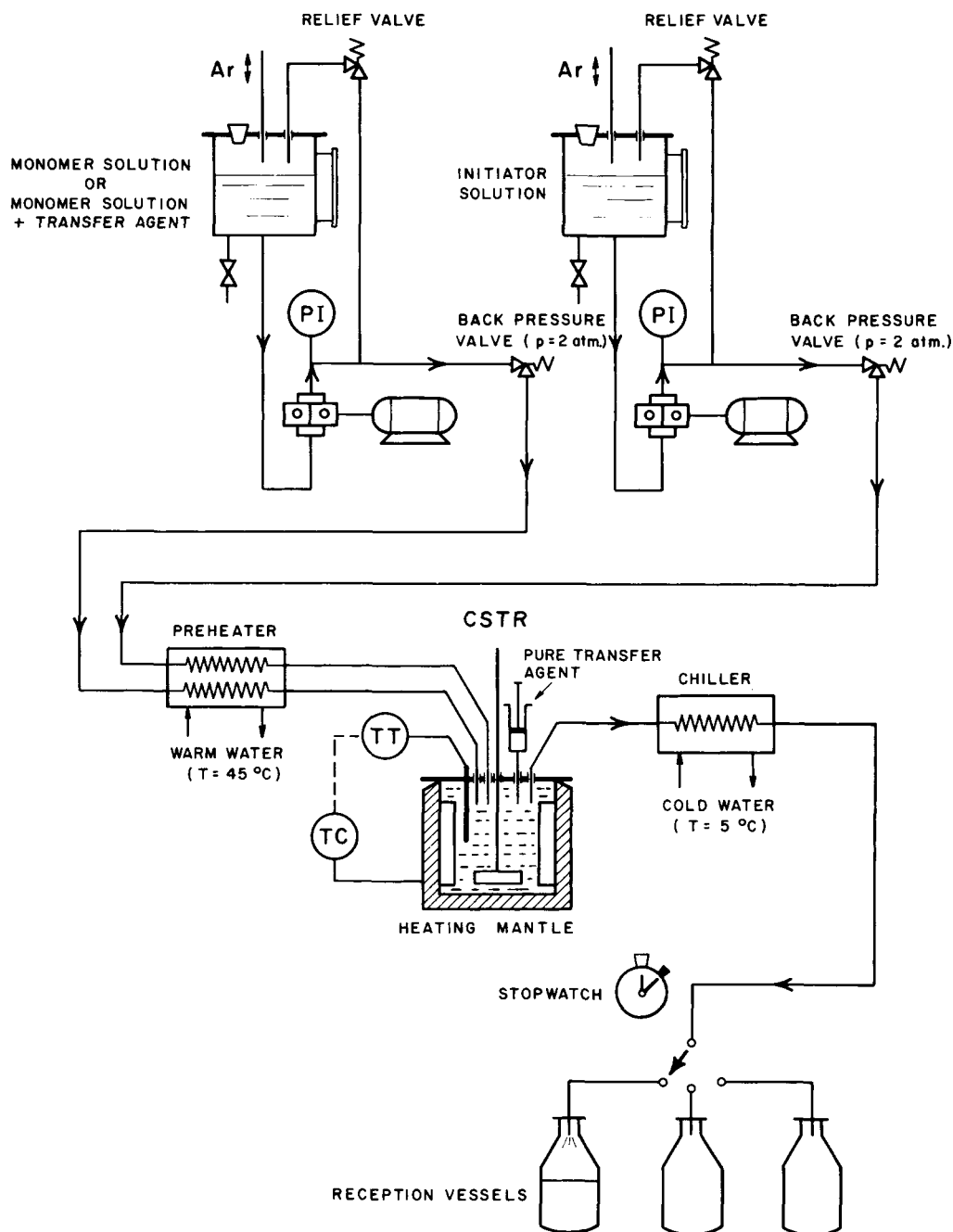| |
| --- |
| $F_i = 0.015$ dm^3/min |
| $V = 0.3$ dm^3 |
| $T = 353.12$ K |
| $[I^f] = 0.01333$ mol/dm^3 |
| $[M^f] = 1.565$ mol/dm^3 |

Figure 3 The experimental rig.

of 180°. A pulseless flow was provided by dividing the feeds into each pumping head and rejoining the outlet flows in a parallel fashion. Also, a back-pressure valve was installed at the discharge manifold, to allow a correct operation of the check valves. The feed flows were preheated to 40°C before entering the reactor, and its effluent was immediately cooled, to deactivate further polymerization.

Representative polymer samples were collected in 5 L glass reception flasks containing hydroquinone as inhibitor. The polymer samples were analyzed by a Waters ALC/GPC 244 size-exclusion chromatograph fitted with an R401 refractive index detector and a complete set of μ-Styragel columns. The chromatograph was linked to a MINC-II computer for the data acquisition and part of the data treatment. The chromatograms were corrected for instrumental broadening (30), in a VAX 11/780

computer. The observed MWDs were represented with linear molecular weight axes. The monomer conversion was gravimetrically determined. To this effect, the solvent was evaporated and the solid product dried under vacuum (all at room temperature).

The reagents were prepared as follows: Toluene, Aldrich 17, 996-5 (99%), was utilized, after distillation under vacuum. Dodecanethiol (lauryl mercaptan), Fluka 44230, was used, without purification. Benzoyl peroxide, Carlo Erba 427345 (77.5 ± 2.5%), was employed, after verification of its purity.[31] Methyl methacrylate, Fluka 64200, was used, after first washing the inhibitor with water and a 5% NaOH solution and then drying the monomer with $CaCl_2$ and CaH_2.[32] After preparation, the initiator and monomer solutions were ultrasonically degassed, to eliminate dissolved O_2. Ice was added into the bath to avoid initiator decomposition.

Figure 4 indicates the stages in which the experiment may be subdivided. Stage I corrresponds to an SS condition without transfer agent feed (indicated by superscript s'). This is equivalent to the situation when $T_p \to \infty$ in the Impulsive PO. Stage II corresponds to the impulsive operation, imple-

mented by two manual injections of 1.68 mL of pure transfer agent into the polymerization reactor. The period of oscillation was 2 h, and the average residence time 20 min. For this reason, the polymer accumulated in the second period could be taken as representative of the PO. In Stage III, the SS corresponding to the impulsive operation (indicated by superscript s) was implemented. To this effect, pure transfer agent was incorporated into the monomer solution tank and the mixture added at flow rate $f_{M,T}$. A transfer agent concentration of 0.0039 mol/dm^3 ensured that in a period of 2 h an equivalent to 1.68 mL of the pure reagent was added.

Experimental conditions slightly differed from those in the Theoretical section. For dodecanethiol at the intended polymerization temperature, k_{fT} = 43,100 dm^3/mol min.[29] With the kinetic data of Table I (except for k_{fT}), the information in Table III, and an impulse area of $[0.014$ mL/min $\times T_p$ (min)$]$, the response to an Impulsive PO similar to that of Figure 1 was simulated. The corresponding results are shown in Figure 5, while the left-hand side of Table IV indicates the predicted output variables under SS' (Stage I), the PO (Stage II), and the SS to which the PO should be compared (Stage III). Note that (a) an increase of over 50% is observed in the number average chain length, when comparing SS with SS', and (b) the PO provides a moderate increase in D_n^*.

From characterization of the samples representative of Stages I–III, the experimental results of Figure 6 and the right-hand side of Table IV were produced. Note that as expected (a) μ_n^* practically coincides with μ_n^s, and η_M^* is very similar to η_M^s; (b) the MWD under PO is broadened with respect to the SS; and (c) the polymer obtained under steady operation without transfer agent feed exhibits a higher number average chain length than with the transfer agent addition.

In Table IV, the following is observed: (a) the experimental values of the μ_n's are considerably lower than are the corresponding theoretical predictions, while (b) the predictions for the D_n's and the η_M's are close the measured values. The discrepancy in the number average chain lengths may be justified by (a) the presence of impurities acting as termination or unwanted transfer agents and/or (b) errors in the kinetic parameters that were directly taken from the literature.
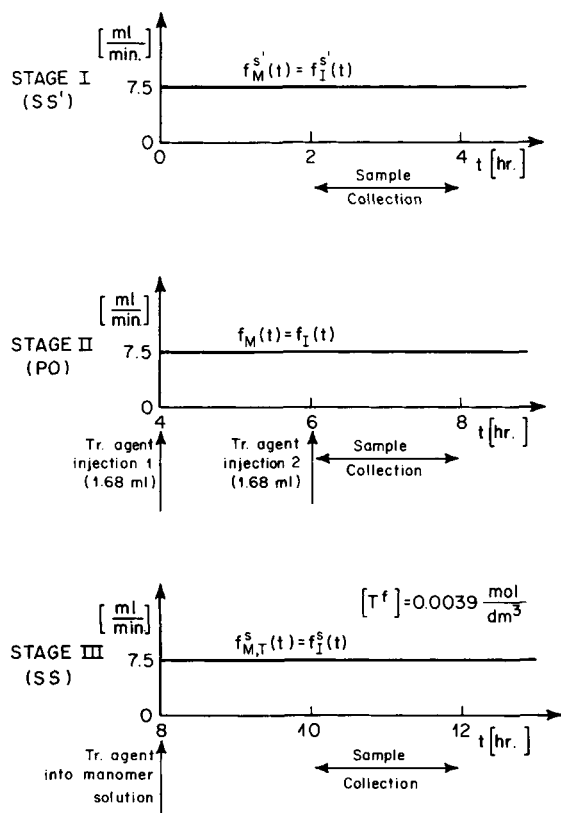

Figure 4 Stages of the experimental run.

EMULSION POLYMERIZATION

In the industrial production of styrene–butadiene rubber (SBR), it is a common practice to adjust the
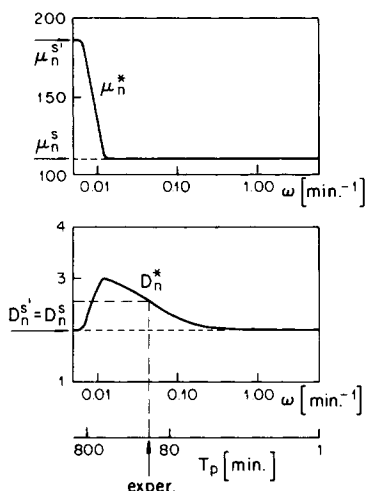
Figure 5 Simulated results for the sought experimental conditions.

observed average molecular weights by appropriate chain transfer agent (modifier) addition. Through a direct extension of the ideas in the previous section, it is here theoretically shown that sinusoidal oscillations of the said reagent also allows a controlled broadening of the MWD, without affecting other parameters.

Consider the emulsion polymerization of styrene and butadiene in a CSTR at 5°C with p-menthane hydroperoxide as initiator, heptahydrated ferrous sulphate with sodium formaldehyde sulfoxylate as redox couple, sodium dodecyl sulphate as emulsifier, and t-dodecyl mercaptan as transfer agent.

A mathematical model of this process due to Broadhead et al.[33,34] was utilized. It is based on a kinetic mechanism consisting of a redox initiation in the aqueous phase and the following reactions in the polymer phase: propagations with the monomer and the polymer; transfers to the monomer, to the polymer, and to a transfer agent; and termination. The main hypotheses in the simulated example are (a) micellar nucleation of the polymer particles[35]; (b) uniform polymer density, irrespective of chain length; (c) reactivity of macrorradicals only dependent on the nature of the terminal monomer; (d) molecular weights determined by transfer reactions (i.e., negligible termination); (e) equilibrium distribution of the molecular species between the phases; (f) monomer concentration in the particles independent of particle size; (g) pseudo-SS for the free radicals and the Fe^{2+} and Fe^{3+} ions; (h) negligible particle agglomeration; and (i) particles of the same generation are monodisperse in size and the PSD only results from the continuous nucleation process. Furthermore, for the given model and at the investigated conversions, the termination reactions may be assumed instantaneous and therefore there is absence of gel effect. Under these conditions, the average number of radicals per particle is equal to 0.5, leading to a case II emulsion polymerization kinetics.

The instantaneous values of the following variables are predicted: (a) number average molecular weight $\bar{M}_n$ and polydispersity D_n; (b) average molar fraction of styrene in the copolymer x_S; (c) number average values of the tri- and tetrafunctional number of branches per polymer molecule B_3 and B_4, respectively; (d) monomer conversion η_M; (e) number of polymer particles per unit volume N_p; and (f) differential number distribution of polymer particle volumes $n(v)$, and from it, the number average volume $\bar{v}_n$ and the polydispersity $Q_n = \bar{v}_w/\bar{v}_n$.

As before, the average properties under PO are of interest. Some of such properties are calculated as follows:

(a) Average MWD moments of the inactive polymer:

$$\omega_n^* = \frac{\displaystyle\int_t^{t+T_p} v_p(\tau)\omega_n(\tau)\,d\tau}{\displaystyle\int_t^{t+T_p} v_p(\tau)} \quad (n = 0, 1, 2) \quad (6)$$

Table IV Simulation vs. Experimental Results

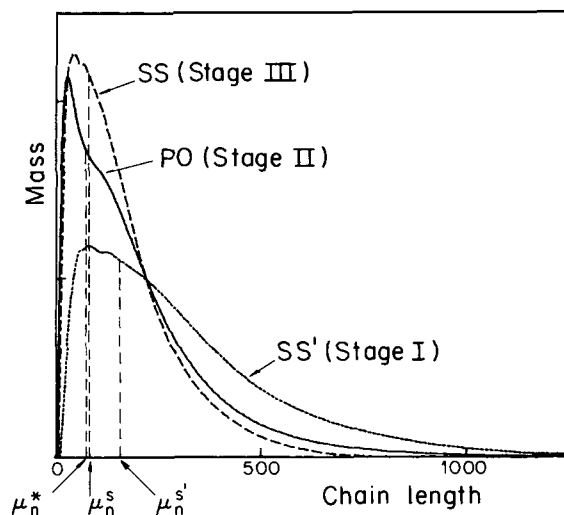|	Simulation Results			Experimental Results		
	SS'	PO with T_p = 2 h	SS	SS'	PO with T_p = 2 h	SS
μ_n	185.89	109.18	109.18	154	77.2	82.0
D_n	1.99	2.59	1.99	2.01	2.58	2.00
η_M	0.111	0.111	0.111	0.104	0.101	0.106
η_I	0.0317	0.0317	0.0317	—	—	—

Figure 6 The measured MWDs.

where v_p is the volumetric polymer phase flow in the reactor effluent.

(b) Average monomer conversion:

$$\eta_M^* = \frac{\int_t^{t+T_p}\left[M_S P_S(\tau)\,\frac{v_p(\tau)}{V_p(\tau)} + M_B P_B(\tau)\,\frac{v_p(\tau)}{V_p(\tau)} \right]d\tau}{\int_t^{t+T_p}\left[M_S\left(P_S(\tau)\,\frac{v_p(\tau)}{V_p(\tau)} + F_S(\tau)\right) + M_B\left(P_B(\tau)\,\frac{v_p(\tau)}{V_p(\tau)} + F_B(\tau)\right)\right]d\tau}$$

(7)

where F_S and F_B are the molar flows of styrene (S) and butadiene (B) in the reactor effluent; M_S and M_B are the molecular weights of the comonomers; P_S and P_B are the moles of styrene and butadiene converted into polymer; and V_p the polymer phase volume in the reactor.

(c) Average of the average number of branches per molecule:

$$B_i^* = \frac{\int_t^{t+T_p}\omega_0(\tau)B_i(\tau)v_p(\tau)\,d\tau}{\int_t^{t+T_p}\omega_0(\tau)v_p(\tau)\,d\tau} \qquad (i = 3, 4) \quad (8)$$

(d) Average number PSD (volume), number average value, and polydispersity:

$$n^*(v) = \frac{\int_t^{t+T_p} N_p(\tau)n(v,\tau)\,F_o(\tau)\,d\tau}{\int_t^{t+T_p} N_p(\tau)\,F_o(\tau)\,d\tau} \qquad (9)$$

$$\bar{v}_n^* = \frac{\int_0^\infty vn^*(v)\,dv}{\int_0^\infty n^*(v)\,dv} \qquad (10)$$

$$\bar{v}_w^* = \frac{\int_0^\infty v^2 n^*(v)\,dv}{\int_0^\infty vn^*(v)\,dv} \qquad (11)$$

$$Q_n^* = \frac{\bar{v}_w^*}{\bar{v}_n^*} \qquad (12)$$

Consider the following sinusoidal oscillation of a pure transfer agent feed:

$$f_T(t) = f_T^s\left[1 + A_m\sin\left(\frac{2\pi t}{T_p}\right)\right] \qquad (13)$$

where A_m is a dimensionless amplitude, defined as the ratio between the maximum and the time-average flow. The other input variables are indicated in Table V. Note that f_T is negligible with respect to the total feed flow, and, therefore, the instantaneous mean residence time remains practically constant. The kinetic parameters, equilibrium constants, emulsifier data, etc., were taken from Ref. 33. The calculated SS condition is presented in Table VI.

Through a sinusoidal forcing with $A_m = 0.5$ and 0.65 [Fig. 7(a)], the results represented in Figure 7(b) are obtained. The PO broadens the MWD without affecting the average values of the number average molecular weight, the branching properties, the reagents conversion, or the PSD. Furthermore,

Table V   The Simulation Data

Reaction volume = 3709.6 dm³
Water feed = 104.6 dm³/min
Styrene feed = 15.6 dm³/min
Butadiene feed = 65.2 dm³/min
Initiator feed = 34.4 g/min
FeSO₄·7H₂O feed = 7.44 g/min
Reduction agent feed = 27.5 g/min
Emulsifier feed = 2439.7 g/min
SS modifier feed (f_T^s) = 0.07636 dm³/min

the instantaneous monomer conversion remains constant at the SS value. The deviations in D_n^* are greater as the amplitude A_m and the frequency of oscillation T_p are increased. Through an appropriate selection of these parameters, polymers with average polydispersities between 3.09 (SS) and 24 (PO) may be obtained.

In solution polymerizations, a sigmoidal function $D_n^*(\omega)$ was observed. In the emulsion case, the curves do not exhibit inflexion points, but also tend to finite average polydispersities as $T_p \rightarrow \infty$. The increased broadening at high T_p's may be due to the branching reactions in emulsion kinetics.

CONCLUDING REMARKS

When free-radical polymerizations are carried out in CSTRs, the sustained periodic forcing of a pure transfer agent feed seems to offer an advantage with respect to the SS operation: The average polydispersity may be broadened without affecting the average values of other parameters. This conclusion is valid for the relatively simple kinetics of a linear solution homopolymerization of MMA and for the much more complex process of a styrene/butadiene emulsion copolymerization.

Apart from the investigated POs, decoupling between D_n^* and other parameters was also observed through rectangular oscillations of the monomer feed 180° out of phase with a pure solvent feed, to ensure a constant mean residence time. Alternatively, a transfer agent solution may replace the pure solvent, with enhanced results from the point of view of D_n^*. However, in such cases, the instantaneous monomer concentration is not constant, thus inducing oscillations in the reaction temperature.

Pure transfer agent forcing is easy to implement and does not affect the total effluent flow. Rectan-
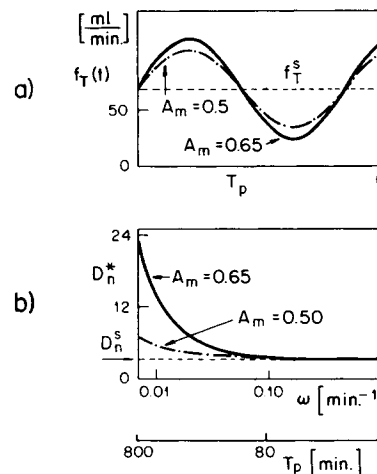
Table VI   SS Results

$$\bar{M}_n^s = 74{,}309 \text{ g/gmol}$$
$$x_S^s = 0.111$$
$$D_n^s = 3.09$$
$$\eta_M^s = 0.105$$
$$B_3^s = 0.233$$
$$B_4^s = 0.026$$
$$\bar{v}_n^s = 2439 \text{ nm}^3$$
$$Q_n^s = 1.79$$
$$N_p^s = 2.723 \times 10^{18} \text{ particle/dm}^3$$

Figure 7   PO of a continuous emulsion polymerization: (a) sinusoidal transfer agent feed flow; (b) corresponding PO results.

gular, sinusoidal, and impulsive POs were investigated. For equal values of the amplitude A_m and the period T_p, rectangular waves produce larger deviations in D_n^* than do sinusoids. Also, impulse trains at intermediate periods of oscillation provide better results than do rectangular oscillations with longer periods. For moderate increases in D_n^*, either sinusoidal, rectangular, or impulsive POs may be employed to produce the same average polymer quality. However, impulsive POs are preferable because they require the shortest period of oscillation, and, therefore, the size of the reception vessel required to average the reactor oscillations is reduced.

REFERENCES

1. G. R. Meira, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C20**, 207 (1981).
2. D. A. Couso and G. R. Meira, *Polym. Eng. Sci.*, **6**, 391 (1984).
3. R. Thiele, *Dynamic Behaviour and Stability of Continuous Reactors for Bulk Polymerization*, Institution of Chemical Engineers Symp. Ser. No. 87, *Chemical Reaction Engineering*, Pergamon Press, Elmsford, NY, 1984.
4. G. L. Frontini, G. E. Eliçabe, D. A. Couso, and G. R. Meira, *J. Appl. Polym. Sci.*, **31**, 1019 (1986).
5. G. L. Frontini, G. E. Eliçabe, and G. R. Meira, *J. Appl. Polym. Sci.*, **33**, 2165 (1987).

6. L. M. Alassia, G. L. Frontini, J. R. Vega, and G. R. Meira, *J. Polym. Sci. Polym. Lett. Ed. C*, **26**, 201 (1988).

7. W. H. Ray, *Ind. Eng. Chem. Proc. Des. Dev.*, **7**, 422 (1968).

8. R. L. Laurence and G. Vasudevan, *Ind. Eng. Chem. Proc. Des. Dev.*, **7**, 427 (1968).

9. C. K. Lee and J. E. Bayley, *AIChE J.*, **20**, 74 (1974).

10. D. Konopnicki and J. L. Kuester, *J. Macromol. Sci. Chem.*, **A8**(5), 887 (1974).

11. J. J. Spitz, R. L. Laurence, and D. C. Chappelear, *AIChE Symp. Ser. 160*, 86 (1976).

12. G. R. Meira, A. F. Johnson, and J. Ramsay, *ACS Symp. Ser. 104*, 253 (1979).

13. F. C. L. Yu, M.Sc. Thesis, University of Massachusetts (1969).

14. M. N. Bhawe, Ph.D. Thesis, Northwestern University (1972).

15. W. Kawakami and S. Machi, *AIChE J.*, **19**(1), 94 (1973).

16. S. Hashimoto and W. Kawakami, *Ind. Eng. Chem. Proc. Des. Dev.*, **15**, 244 (1976).

17. S. Hashimoto and W. Kawakami, *Ind. Eng. Chem. Proc. Des. Dev.*, **4**, 546 (1976).

18. G. Crone and A. Renken, *Chem. Eng. Tech.*, **51**(1), 42 (1979).

19. H. T. Chen, C. N. Kwan, and P. A. Chartier, *AIChE J.*, **26**, 672 (1980).

20. B. E. Claybaugh, J. R. Griffon, and A. T. Watson, U. S. Pat. 3,472,829 (1969).

21. C. K. Lee and J. E. Bailey, *AIChE J.*, **20**, 74 (1974).

22. W. V. Smith and R. H. Ewart, *J. Chem. Phys.*, **16**, 592 (1948).

23. J. T. O'Toole, *J. Appl. Polym. Sci.*, **9**, 1291 (1965).

24. J. Ugelstad, P. C. Mork, and J. E. Aasen, *J. Polym. Sci. A*, **1**, 5, 2281 (1967).

25. R. K. Greene, A. R. Gonzalez, and G. W. Poehlein, in *Emulsion Polymerization*, I. Piirma and J. L. Gardon, Eds., *ACS Symp. Ser. 24*, 341 (1976).

26. C. Kiparissides, Ph.D. Thesis, MacMaster University, Canada (1978).

27. W. H. Ray, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C8**(1), 1 (1960).

28. D. A. Couso, Ph.D. Thesis, Universidad Nacional del Litoral, Santa Fe, Argentina (1986).

29. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1975.

30. L. M. Gugliotta, D. Alba, and G. R. Meira, in *Detection and Data Analysis in Size Exclusion Chromatography*, T. Provder, Ed., *ACS Symp. Ser. No. 352*, 287 (1987).

31. A. Vogel, *Textbook of Practical Organic Chemistry*, Longman, 1986.

32. D. D. Perrin, W. L. F. Armarenego, and D. R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, Elmsford, NY, 1980.

33. T. O. Broadhead, Master Thesis, McMaster University, Hamilton, Canada (1984).

34. T. O. Broadhead, A. E. Hamielec, and J. F. Mac Gregor, *Makromol. Chem.* [*Suppl.*] **10/11**, 105 (1985).

35. W. D. Harkins, *J. Am. Chem. Soc.*, **69**, 1428 (1947).

APPENDIX: DYNAMIC MODEL FOR THE NMA SOLUTION POLYMERIZATION

$$\frac{d[I(t)]}{dt} = \frac{f_I(t)}{V}[I^f] - \frac{1}{\theta(t)}[I(t)] - fk_d[I(t)] \quad (A.1)$$

$$\frac{d[M(t)]}{dt} = \frac{f_M(t)}{V}[M^f] - \frac{1}{\theta(t)}[M(t)]$$
$$- 2fk_d[I(t)] - k_p[M(t)]\lambda_0(t)$$
$$- k_{fM}[M(t)]\{\lambda_0(t) - [R_1\cdot(t)]\} \quad (A.2)$$

$$\frac{d[T(t)]}{dt} = \frac{f_T(t)}{V}[T^f] - \frac{1}{\theta(t)}[T(t)]$$
$$- k_{fT}[T(t)]\{\lambda_0(t) - [R_1\cdot(t)]\} \quad (A.3)$$

$$\frac{d[S(t)]}{dt} = \frac{F_i(t)}{V}[S^f] - \frac{f_I(t)}{V}[I^f]\frac{W_I}{W_S}$$
$$- \frac{f_T(t)}{V}[T^f]\frac{W_T}{W_S} - \frac{f_M(t)}{V}[M^f]\frac{W_M}{W_S}$$

$$- \frac{1}{\theta(t)}[S(t)] - k_{fS}[S(t)]$$
$$\times \{\lambda_0(t) - [R_1\cdot(t)]\} \quad (A.4)$$

$$\frac{d[R_1\cdot(t)]}{dt} = 2fk_d[I(t)] + k_{fM}[M(t)]$$
$$\times \{\lambda_0(t) - [R_1\cdot(t)]\} + k_{fS}[S(t)]$$
$$\times \{\lambda_0(t) - [R_1\cdot(t)]\} + k_{fT}[T(t)]$$
$$\times \{\lambda_0(t) - [R_1\cdot(t)]\} - \{k_p[M(t)]$$
$$+ (k_{tc} + k_{td})\lambda_0(t)\}[R_1\cdot(t)]$$

$$- \frac{1}{\theta(t)}[R_1\cdot(t)] \quad (A.5)$$

$$\frac{d\lambda_0(t)}{dt} = 2fk_d[I(t)]$$

$$- (k_{tc} + k_{td})\lambda_0^2(t) - \frac{1}{\theta(t)}\lambda_0(t) \quad (A.6)$$

$$\frac{d\lambda_n(t)}{dt} = 2fk_d[I(t)] + \{k_{fM}[M(t)] + k_{fS}[S(t)]$$

$$+ k_{fT}[T(t)]\} \lambda_0(t) - k_p[M(t)]$$

$$\times \left\{ [\phi(t) + \beta(t)] \lambda_n(t) - \sum_{i=1}^{n} \binom{n}{i} \lambda_{n-i} \right\}$$

$$- \frac{1}{\theta(t)} \lambda_n(t) \quad (n = 1, 2) \quad (A.7)$$

$$\frac{d\omega_0(t)}{dt} = k_p[M(t)]\phi(t)\lambda_0(t)$$

$$+ \frac{1}{2} k_{tc} \lambda_0^2(t) - \frac{1}{\theta(t)} \omega_0(t) \quad (A.8)$$

$$\frac{d\omega_n(t)}{dt} = k_p[M(t)]\phi(t)\lambda_n(t) + \frac{1}{2} k_{tc} \sum_{i=0}^{n} \binom{n}{i} \lambda_{n-i} \lambda_i$$

$$- \frac{1}{\theta(t)} \omega_n(t) \quad (n = 1, 2) \quad (A.9)$$

with

$$\frac{1}{\theta(t)} = \frac{F_i(t)}{V} + \alpha k_p[M(t)]\lambda_0(t) = \frac{F_o(t)}{V} \quad (A.10)$$

$$F_i(t) = f_I(t) + f_M(t) + f_T(t) + f_S(t) \quad (A.11)$$

$$\alpha = W_M \left(\frac{1}{\rho_p} - \frac{1}{\rho_M} \right) \quad (A.12)$$

$$\phi(t) = \frac{k_{fM}[M(t)] + k_{fS}[S(t)] + k_{fT}[T(t)] + k_{td}\lambda_0(t)}{k_p[M(t)]}$$

$$(A.13)$$

$$\beta(t) = \frac{k_{tc}\lambda_0(t)}{k_p[M(t)]} \quad (A.14)$$

where [ ] indicates molar concentration; $f_I, f_M, f_T,$ and f_S are the feed flow rates of the initiator solution, the monomer solution, the transfer agent, and the pure solvent, respectively; F_i, F_o are the reactor inlet and outlet total flows; superscript f indicates feed stock condition; f is the initiator efficiency; θ is the instantaneous mean residence time; $\lambda_n = \Sigma j^n[R_j \cdot],$ $(n = 0, 1, 2)$ are the nth order moments of the number chain length distribution (NCLD) of the active polymer $[R_j \cdot]$ vs. j; $\omega_n = \Sigma j^n[P_j],$ $(n = 0, 1, 2)$ are the nth order moments of the NCLD of the deactivated polymer $[P_j]$ vs. j; α is the contraction coefficient; W_M, W_I, W_S and W_T are the molecular weights of the monomer, initiator, solvent, and transfer agent, respectively; ρ_p and ρ_M are the densities of the polymer and of the monomer, respectively; and $1/(1 + \phi + \beta)$: is the propagation probability.