Molecular Weight Distribution Control in a Semibatch Living-Anionic Polymerization. II. Experimental Study

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Synopsis

This work constitutes an indirect verification of a theoretical method that allows the production of polymers with prespecified molecular weight distributions (MWDs), through semibatch living-anionic homopolymerizations. The chemical system consisted of styrene with sec-butyllithium, in a solvent mixture of cyclohexane and tetrahydrofurane (THF). The necessary flow profiles were applied by a pair of computer-controlled pumps, and the produced MWDs were measured by size exclusion chromatography, with correction for nonuniform instrumental spreading. The main difficulty was the estimation of the initial moles of initiator and of the concentration of impurities in the monomer solution. For such estimation, a precalibration experiment was implemented.

INTRODUCTION

Because of its influence on the physical properties, there is an increasing interest in industry in producing polymers with "tailor-made" characteristics from the point of view of molecular structure. In Couso et al.,[1] a theoretical technique is presented that allows the attainment of polymers with any prespecified MWD shape, through living-anionic homopolymerizations carried out in a semibatch reactor. In particular, the so-called "alternative method" is preferable from the point of view of its implementation. The objective of this study is the experimental validation of that method.

Early in the work, it became clear that it is practically impossible to eliminate the impurities present in the monomer solution. For this reason, a rederivation of the mentioned technique will be presented that considers such impurities. This approach has the advantage of simplifying the nomenclature and of producing analytical expressions that are equivalent to those in Ref. 1, but numerically preferable. Thus, we present this work in a self-contained manner.

Assume a chemical system such as that of Figure 1. Very broadly, the semibatch operation consists of the following: (a) the reactor is charged with a volume V^0 of a solution containing N^0 mol of initiator; and (b) a monomer solution feed of molar concentration $[M^0]$ is added with a flow profile $f_M(t)$; and simultaneously, the reactor contents are emptied into a reception vessel with a flow profile $F(t)$. In the reception vessel, the 'living' polymer is

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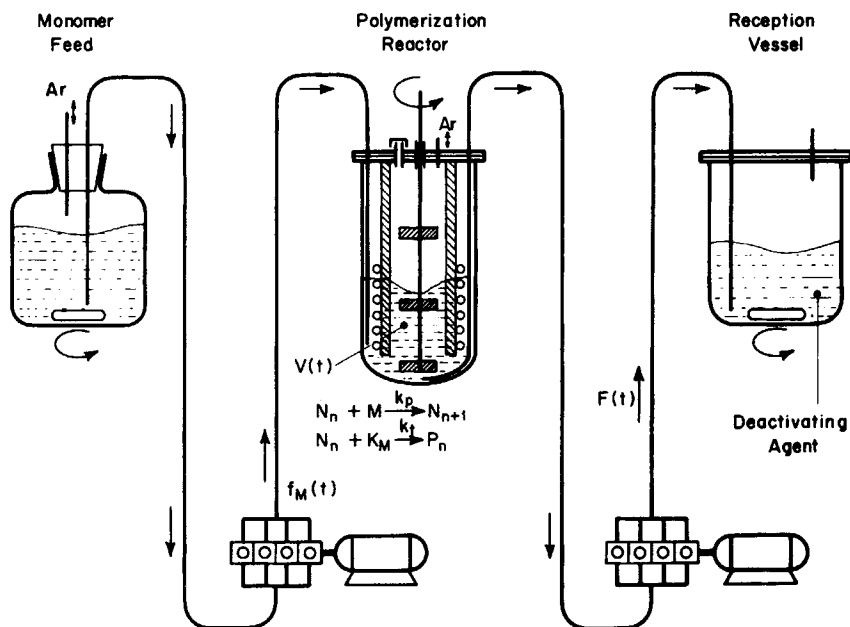
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Fig. 1.   The experimental system.

instantaneously deactivated. The monomer solution is contaminated by an impurity K_M of molar concentration $[K_M^0]$. For this reason, a fraction of the polymer is deactivated in the reactor. At the end of the operation, the reactor is emptied, and the dead polymer accumulated in the reception vessel exhibits the required MWD.

The following are used: $[M(t)]$ and $[K_M(t)]$: the concentrations in the reactor of the monomer and of the impurity (mol/dm^3), respectively. $N_n(n)$ with $(n = 1, 2, \cdots)$: the instantaneous number-chain-length distribution (NCLD) of the living polymer in the reactor (mol vs. chain length). $P_n(n)$ with $(n = 1, 2, \cdots)$: the NCLD of the total deactivated polymer, sum of the dead fractions accumulated in the reactor and in the reception vessel (mol vs. chain length). $V(t)$: the reactor contents volume (dm^3). $N(t)$: the total number of moles of living ends. Superscript 0 indicates feed stock conditions.

The following mass balance equations may be written:

$$\frac{d[M(t)]}{dt} = \frac{f_M(t)}{V(t)}\{[M^0] - [M(t)]\} - \frac{k_p}{V(t)}[M(t)]N(t) - \frac{F(t)}{V(t)}[M(t)]$$

$$\text{(1a)}$$

$$\frac{d[K_M(t)]}{dt} = \frac{f_M(t)}{V(t)}\{[K_M^0] - [K_M(t)]\} - \frac{k_t}{V(t)}[K_M(t)]N(t)$$

$$-\frac{F(t)}{V(t)}[K_M(t)] \qquad\qquad \text{(1b)}$$

$$\frac{dV(t)}{dt} = f_{\mathrm{M}}(t) - F(t) \tag{1c}$$

$$\frac{dN(t)}{dt} = \frac{F(t)}{V(t)} N(t) - k_t [\mathrm{K}_{\mathrm{M}}(t)] N(t) \tag{1d}$$

$$\frac{dN_n(t)}{dt} = -k_p [\mathrm{M}(t)] \{ N_n(t) - N_{n-1}(t) \} - \frac{F(t)}{V(t)} N_n(t) - k_t [\mathrm{K}_{\mathrm{M}}(t)] N_n(t)$$

$$(n = 1, 2, \cdots) \tag{1e}$$

$$\frac{dP_n(t)}{dt} = \frac{F(t)}{V(t)} N_n(t) + k_t [\mathrm{K}_{\mathrm{M}}(t)] N_n(t) \qquad (n = 1, 2, \cdots) \tag{1f}$$

The "stretched variables" are defined as

$$\theta(t) = \int_0^t k_p [\mathrm{M}(\tau)] \, d\tau \tag{2a}$$

$$\Psi(t) = \int_0^t \left[\frac{F(\tau)}{V(\tau)} + k_t [\mathrm{K}_{\mathrm{M}}(\tau)] \right] d\tau \tag{2b}$$

If $[\mathrm{M}(t)]$ is constant throughout the operation, then $\theta(t) \propto t$. If t_f is the period of the semibatch operation and θ_f the corresponding value of θ, then

$$\theta(t) = \frac{\theta_f}{t_f} t \tag{3}$$

From eqs. (2a) and (3), and bearing in mind that at $t = t_f$ the obtained MWD should equal the desired distribution $P_n^d(n)$, then eqs. (1d–f) provide

$$N(t) = N^0 - \int_0^t x(\tau) \, d\tau \tag{4a}$$

$$N_n(t) = N(t) \frac{e^{-\theta(t)} [\theta(t)]^{n-1}}{(n-1)!} \tag{4b}$$

$$P_n^d(n) = \frac{t_f}{\theta_f} \int_0^\infty \left[\frac{e^{-\theta} \theta^{n-1}}{(n-1)!} x\left(\frac{t_f}{\theta_f} \theta \right) \right] d\theta \tag{4c}$$

with

$$x\left(\frac{t_f}{\theta_f} \theta \right) = x(t) = \left[\frac{F(t)}{V(t)} + k_t [\mathrm{K}_{\mathrm{M}}(t)] \right] N(t) \tag{4d}$$

Equation (4b) indicates that the living polymer is Poisson-distributed, with an instantaneous number-average-chain length (NACL) of $(\theta + 1)$. From eq. (4c),

the required MWD may be considered the result of convoluting $x(t)$ with a variable spreading function represented by a set of Poisson distributions. Thus, $x(t)$ may be found by numerical deconvolution. The areas under $P_n^d(n)$ and $x(\theta)$ should be equal to N^0. If a normalized desired NCLD is utilized, then eq. (4c) will provide a normalized $x(t)$ that must be later scaled-up.

Having determined $x(t)$, then $N(t)$ may be obtained through eq. (4a). If k_p and k_t are very large, $[M(t)]$ and $[K_M(t)]$ will adopt very low (and constant) values, and eqs. (1a, b) may be simplified to

$$f_M(t)[M^0] = k_p[M(t)] N(t) \tag{5a}$$

$$f_M(t)[K_M^0] = k_t[K_M(t)] N(t) \tag{5b}$$

Clearly, $[M(t)]$ and $[K_M(t)]$ will remain constant by imposing that $f_M(t) \propto N(t)$. Also, the NACL of the desired polymer μ_n^d must verify:

$$\mu_n^d = \frac{\int_0^{t_l} [M^0] f_M(t) \, dt}{N^0} \tag{6}$$

Thus, the following may be written:

$$f_M(t) = \frac{\mu_n^d N^0 N(t)}{[M^0] \int_0^{t_l} N(t) \, dt} \tag{7}$$

Substituting eq. (5b) into eq. (4d), one can obtain

$$y(t) = \frac{F(t)}{V(t)} = \frac{x(t)}{N(t)} - \frac{f_M(t)[K_M^0]}{N(t)} \tag{8}$$

From the knowledge of $x(t)$, $N(t)$, and $f_M(t)$, the function $y(t)$ may be calculated. Replacing $F(t) = y(t)V(t)$ into eq. (1c), this last equation can be finally solved to yield:

$$F(t) = y(t)\exp\left[-\int_0^t y(\tau) \, d\tau\right]\left[V^0 + \int_0^t f_M(\tau)\exp\left[\int_0^t y(\tau) \, d\tau\right] d\tau\right] \tag{9}$$

Solving eqs. (4c), (3), (4a), and (7)–(9) in that order, the required flow profiles may be calculated. The values of k_p and k_t are not required in the calculation process; the only prerequisite being that they must be both sufficiently high, e.g., $> 10,000$ dm^3/mol min. The concentration of impurities in the monomer solution $[K_M^0]$, and the initial number of moles of living ends N^0, must be *a priori* known.

The limitation of working with impure monomer solutions is that unavoidably, all of the MWDs produced will exhibit low molecular weight tails. To test the theoretical technique, feasible MWDs must be aimed at. For this reason, the desired distributions must be chosen relatively broad and smooth, with low molecular weight tails. Consider, for example, that the polymers with the desired NACLs $P_n^d(n)$ indicated in Figures 2(a) and 3(a) are to be
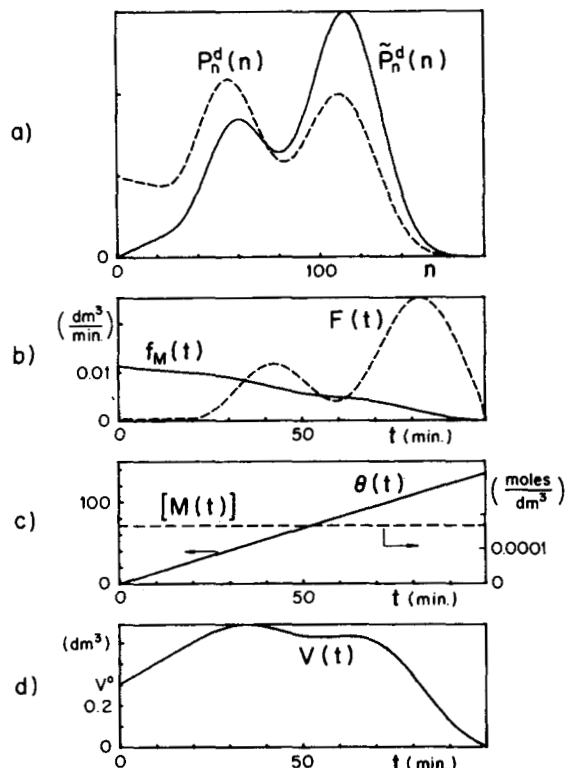
Fig. 2. Polymer A: (a) desired MWD; (b) required flow profiles; (c, d) evolutions of $[M(t)]$, $\theta(t)$, and $V(t)$.

produced. The corresponding weight-chain-length distributions (WCLDs) $\tilde{P}_n(n) = nP_n(n)$, in g vs. chain length, are represented in the same figures. Also, assume the following raw data:

$$[M^0] = 0.485 \text{ mol/dm}^3 \tag{10a}$$

$$V^0 = 0.3 \text{ dm}^3 \tag{10b}$$

$$t_f = 100 \text{ min} \tag{10c}$$

$$[K_M^0] = 0.002 \text{ mol/dm}^3 \tag{10d}$$

$$N^0 = 0.004 \text{ mol} \tag{10e}$$

$$k_p = k_t = 10000 \text{ dm}^3/(\text{mol min}) \tag{10f}$$

For the given specifications, the required flow profiles are illustrated in Figures 2(b) and 3(b). With such profiles and the data of eqs. (10), the model of eqs. (1a–d) and (2)–(4) may be run. In Figures 2(c–d) and 3(c–d), the evolutions of $[M(t)]$, $\theta(t)$, and $V(t)$ are indicated.
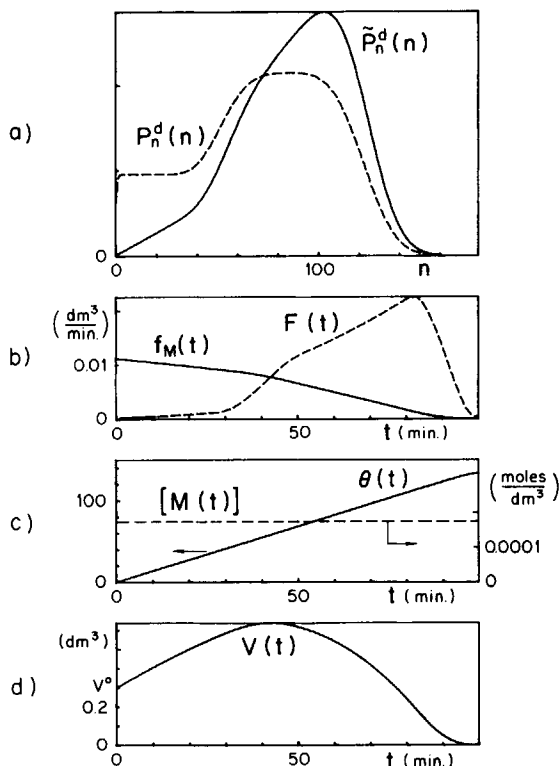
Fig. 3. Polymer B: (a) desired MWD; (b) required flow profiles; (c, d) evolutions of $[M(t)]$, $\theta(t)$, and $V(t)$.

EXPERIMENTAL SETUP

The work involved the polymerization of styrene with sec-butyllithium, in a solvent mixture of cyclohexane and THF in a 80:20 ratio. In the reception vessel, isopropanol was employed as the deactivating agent. For experimental techniques regarding anionic polymerizations, see Refs. 2–4.

The reagent solutions were prepared in a specially constructed glass equipment, operated under an inert gas blanket.

The cyclohexane/THF mixture was first dried with calcium hydride and sodium wire. Then, α-methylstyrene was added. The blood-red solution of the living α-methylstyrene tetramer produced, ensured appropriate conditions for the solvent. Distilled from the tetramer, the solvent was employed in the preparation of the monomer and the initiator solutions.

"Baker" grade styrene from Baker Chemical Co. was utilized, after purification according to the technique recommended in Morton and Fetters.[3] Dibutylmagnesium was used as "scavenger" during the monomer purification, and also added to the final monomer solution in a 1% molar proportion. A 0.485M monomer solution was employed.

A nominal 1.35M Aldrich sec-butyllithium in cyclohexane was used, after measurement of its real concentration according to Gilman and Cartledge.[5] The solution was injected by means of a syringe (previously flushed with

α-methylstyrene tetramer), into the reactor and through a septum. The required amount of pure and dry solvent mixture had previously been charged in the reactor. The final solution was adjusted to contain nominally 0.008 mol of initiator in 0.3 dm^3.

A 2-dm^3 glass reactor with temperature and stirring control was employed. The polymerizations were carried out at room temperature.

The flow profiles were applied by two Milroyal D Milton Roy servo-controlled metering pumps, operated by a pair of Statotrol 6VFW General Electric controllers. The controller set points were adjusted by a Digital MINC-11 process computer. Each pump motor drove four pumping heads of reciprocating action, with a phase difference of 90° between consecutive heads. A pulseless flow was ensured by dividing the feed into each of the heads, and rejoining the outlet flows in parallel fashion. Also, a back pressure valve was installed at the discharge manifold, to allow a correct functioning of the check valves.

Prior to a polymerization, the monomer feed tank, the reactor, the pumping heads, and the 1/4 and 1/8 in. PTFE interconnection tubing were first evacuated and then cleaned under Argon with the red tetramer solution.

The polymer samples were analyzed by a Waters Associates ALC/GPC 244 size exclusion chromatograph fitted with a 254 nm UV detector, and a complete set of μStyragel columns. The chromatograph was linked to the MINC-11 computer for the data acquisition and part of the data treatment. The chromatograms were corrected for nonuniform instrumental broadening in a VAX 11/780 computer. The calibration for such a correction was determined by a recycle technique.[6] MWDs were represented using an abscissa that was linear with respect to chain length.

The nonuniform deconvolutions involved in the calculation of $x(t)$ and in the correction for instrumental spreading were carried out by an inverse Kalman filtering algorithm.[7] When operating with NCLDs, numerical errors are introduced at chain lengths $n \cong 0$. For this reason, it was found preferable to work on a weight basis when performing the deconvolutions and when comparing the measured MWDs. For example, multiplying both sides of eq. (4c) by n, one obtains

$$\tilde{P}_n^d(n) = \frac{t_f}{\theta_f} \int_0^\infty \left[\frac{e^{-\theta}\theta^{n-1}}{(n-1)!} \tilde{x}\left(\frac{t_f}{\theta_f}\theta \right) \right] d\theta \tag{11a}$$

with

$$\tilde{x}(t) = nx(t) \tag{11b}$$

Then, one may find $x(t) = \tilde{x}(t)/n$. To illustrate the accuracy of the deconvolution algorithm, consider Figures 4 and 5, where $x(n)|_{sp}$ are *a priori* specified curves. The desired WCLDs were obtained by convolution of such curves with the set of Poisson distributions. Finally, the curves indicated with $x(n)|_{cal}$ were calculated by deconvolution. The mismatch between $x(n)|_{sp}$ and $x(n)|_{cal}$ is mainly due to the numerical ill-conditioning of the deconvolution operation.
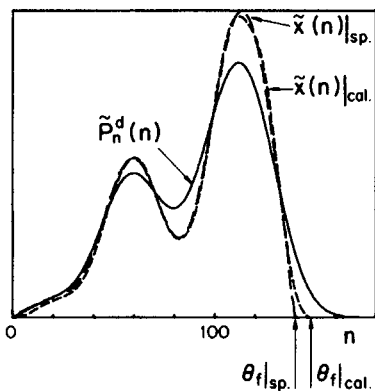
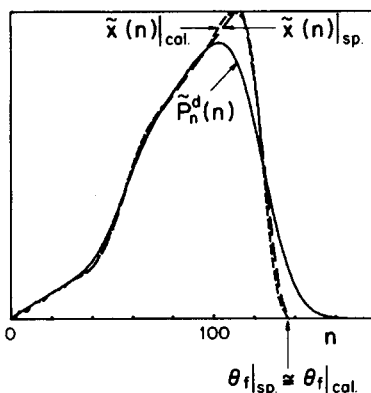Fig. 4. Polymer A: illustration of the deconvolution accuracy.

Fig. 5. Polymer B: illustration of the deconvolution accuracy.

CALIBRATION RUN

The theoretical method requires the MWD of the living polymer to be Poisson-distributed. If this was not verified, some other spreading function might have to be determined to obtain $x(t)$.

The initial moles of living ends N^0 and the concentration of impurities in the monomer solution $[K_M^0]$ must be accurately known for determining the profiles $f_M(t)$ and $F(t)$. To indicate the sensitivity of such parameters on the produced MWDs, consider the simulation of eqs. (1a–c) and (2)–(4), with the flow profiles in Figs. 2(b) and 3(b), and the data of eqs. (10). At $t = t_f$, the accumulated dead polymers exhibit the required MWDs, which are indicated in Figures 6 and 7 by the parameters $N^0 = 0.004$ mol and $[K_M^0] = 0.002 M$. These distributions are compared to the MWDs observed when $\pm 10\%$ variations in the parameters are considered. When (as in the present case), living ends still exist at the end of the operation, then the final NACLs remain essentially unaltered, in spite of variations in $[K_M^0]$.

To check the Poisson hypothesis and to provide a technique for estimating N^0 and $[K_M^0]$, a preliminary calibration run was investigated. The experiment simply consists of adding the monomer solution at a constant rate with no
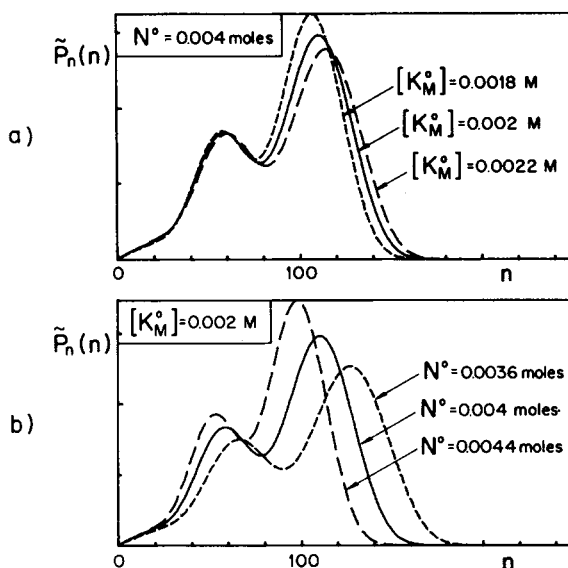
Fig. 6. Polymer A: effect on the WCLD of $\pm 10\%$ variations in $[K_M^0]$ (a) and in N^0 (b).

extraction and analyzing the polymer along the reaction, while a living fraction still exists. (The deactivation of all of the living ends is apparent from the loss of color of the polymerization solution).

Consider a model simulation with the data of eqs. (10), and the following flow rates:

$$F(t) = 0 \tag{12a}$$

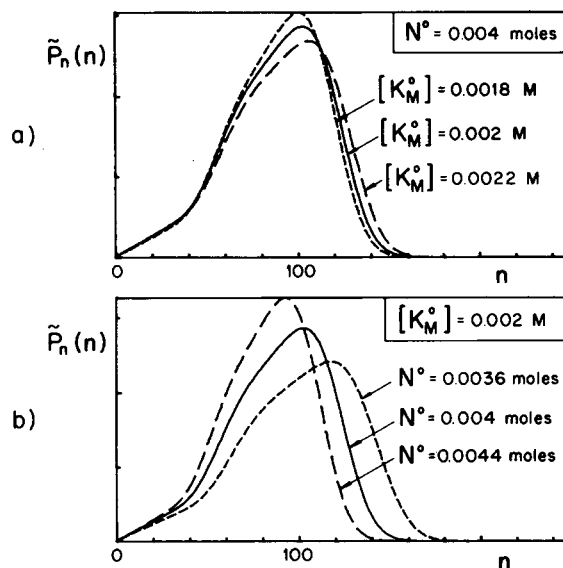$$f_M(t) = 0.0052 \text{ dm}^3/\text{min} \tag{12b}$$

Fig. 7. Polymer B: effect on the WCLD of $\pm 10\%$ variations in $[K_M^0]$ (a) and in N^0 (b).
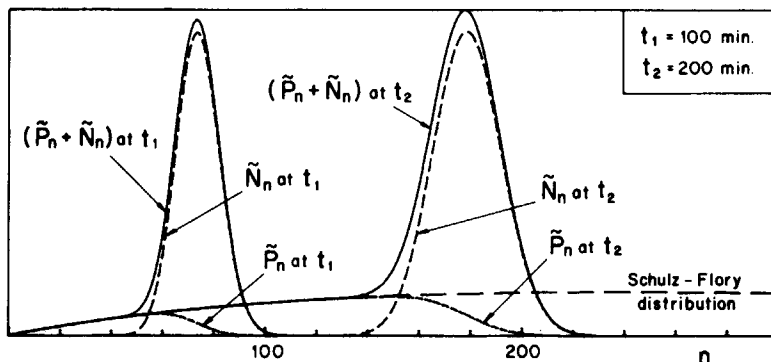
Fig. 8. The calibration run. Predicted distributions at two instants of time.

The WCLDs corresponding to the living and dead fractions at two instants of time, together with their corresponding added curves, are represented in Figure 8. Note the following: (1) The number of moles of the living fraction decays linearly with time, but the corresponding NACL increases nonlinearly with time; (2) when the added monomer solution has deactivated all of the living polymer, then a Schulz–Flory MWD is observed.

The following procedure was found to be the most accurate for the estimation of N^0 and $[K_M^0]$. The instantaneous monomer conversion is very close to unity. Thus, the NACL μ_n of the total polymer should be set equal to the ratio between the total added moles of monomer ($\int_0^{t_i} f_M(t)[M^0]\, dt$) and the initial moles of initiator N^0. Therefore,

$$N^0 = \frac{\int_0^t f_M(\tau)[M^0]\, d\tau}{\mu_n} \tag{13}$$

Having determined N^0, $[K_M^0]$, k_p, and k_t were obtained through a nonlinear least-squares fit involving the mathematical model of eqs. 1(a–c) and (2)–(4). The adjustment was optimal in the sense that the average error between the measured MWD and the total estimated MWD (sum of the dead and living fractions) was minimized. To this effect, an algorithm based on a Marquardt search was employed.[8] Note that, because an analytical expression for the instantaneous MWD is not available, the complete dynamic model must be solved at each iteration.

The calibration run estimates for $[K_M^0]$ and N^0 should be representative of the values of these parameters during the main experiment. For $[K_M^0]$, this is a reasonable assumption, if the same monomer feed stock is employed in both polymerizations. The value for N^0 is more inaccurate, however, because of the uncertain amount of deactivating agent introduced at the clean-up stage, between successive semibatch runs. Consider a typical calibration run, performed under the conditions indicated by eqs. (10a, b) and (12). At $t = 100$ min, a polymer sample was analyzed. The measured chromatogram, and the chromatogram corrected for instrumental broadening, are represented in Figure 9(a). From the observed NACL ($\mu_n = 54$), the moles of initiator was evaluated, yielding $N^0 = 0.005$ mol. In Figure 9(b), the WCLD is represented,
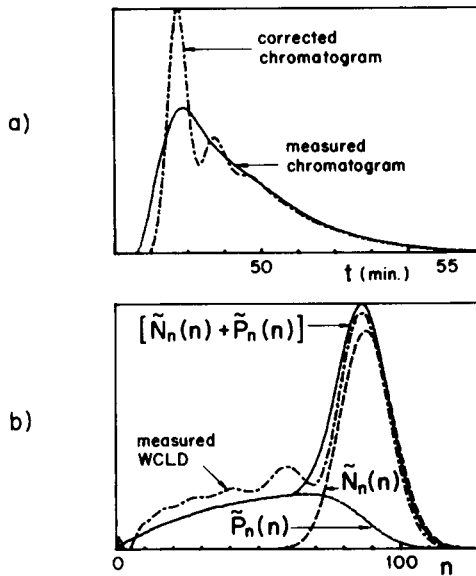
Fig. 9. The calibration run: (a) Measured and corrected chromatograms; (b) fit for the obtention of $[K_M^0]$.

together with the distribution obtained from the optimal fit, which provided $[K_M^0] = 0.0051M$; $k_p = 5813$ dm^3/mol min and $k_t = 18970$ dm^3/mol min. The match between the measured and the theoretical distributions indicates that the mathematical model employed satisfactorily represents the plant, and that the high molecular weight peak of living polymer is well adjusted by a Poisson distribution. Also, "reasonable" values for the rate constants were produced.

MAIN EXPERIMENT

Consider the production of the polymers specified in Figures 2(a) and 3(a), with the values of $[M^0]$, V^0, and t_f indicated in eqs. (10a–c). After a calibration experiment, at least a full day was necessary to estimate the unknown parameters $[K_M^0]$ and N^0, calculate the required flow profiles, and implement these on the computer-controlled pumps. This period proved too long for the parameters to be representative of those in the main experiment. Alternatively, the following experiment was carried out: (a) The feed flows of Figures 2(b) and 3(b) were applied, which involve the "nominal" values of $[K_M^0]$ and N^0 given by eqs. (10c, d); and (b) the calibration run and the two main experiments were performed one immediately after the other, and the polymer analyzed afterwards.

The calibration run provided:

$$N^0 = 0.004 \text{ mol} \tag{14a}$$
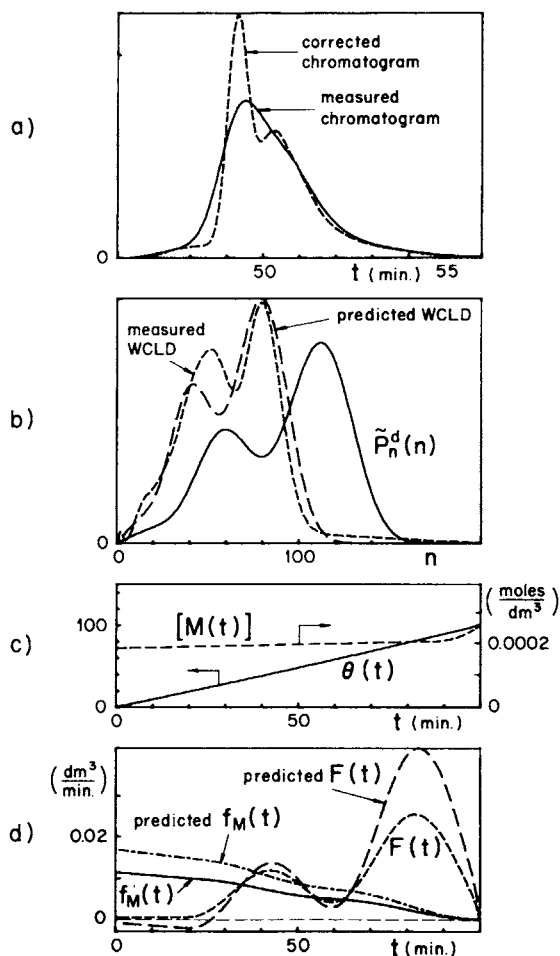
$$[K_M^0] = 0.0035 \text{ mol/dm}^3 \tag{14b}$$

Fig. 10. Polymer A: (a) chromatograms; (b) comparison between measured, desired, and predicted WCLDs; (c) predicted evolution of $\theta(t)$ and [M(t)]; (d) comparison between the applied flow profiles and the *a posteriori* estimated profiles.

For the main experiments, the observed chromatograms are represented in Figures 10(a) and 11(a). The WCLDs of the originally desired and finally observed polymers are shown in Figures 10(b) and 11(b). The match between these curves is clearly not acceptable. From the measured NACLs, the following *a posteriori* estimates of the initial moles of living ends were obtained:

$$\text{for polymer A [Fig. 2(a)]}, \qquad N^0 = 0.0059 \, \text{mol} \qquad (15a)$$

$$\text{for polymer B [Fig. 3(b)]}, \qquad N^0 = 0.0049 \, \text{mol} \qquad (15b)$$

The best *a posteriori* estimates of $[K_M^0]$ and N^0 are provided by the values in eqs. (14b) and (15a, b). With these estimates and the flow profiles of Figures 2(b) and 3(b), the model of eqs. (1a–c) and (2)–(4) was simulated to find the
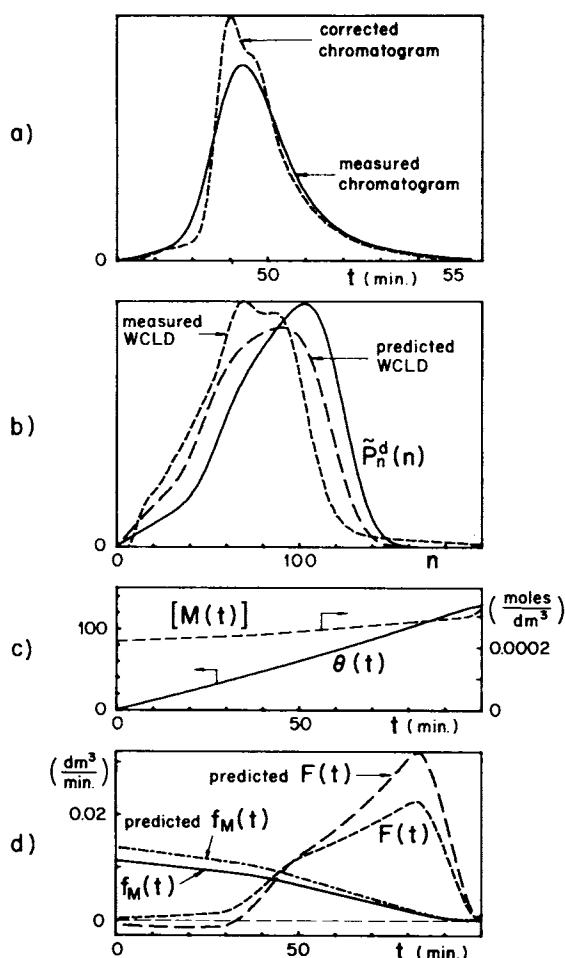
Fig. 11. Polymer B: (a) chromatograms; (b) comparison between measured, desired, and predicted WCLDs; (c) predicted evolution of $\theta(t)$ and $[M(t)]$; (d) comparison between the applied flow profiles and the *a posteriori* estimated profiles.

predicted MWDs. Such distributions are also represented in Figures 10(b) and 11(b) and are reasonably close to the measured curves.

Figures 10(c) and 11(c) illustrate the evolution of $\theta(t)$ and $[M(t)]$, as predicted from the model. The basic hypotheses of a constant $[M(t)]$ and a linear $\theta(t)$ are no longer verified. Finally, in Figures 10(d) and 11(d) the applied flow profiles are compared to the profiles resulting from the best *a posteriori* estimates of $[K_M^0]$ and N^0. The initial negative values of $F(t)$ indicate that the desired MWDs are unobtainable with the final value of $[K_M^0]$.

CONCLUSIONS

The work shows a satisfactory indirect verification of the method proposed in Couso et al.[1] The method was not strictly applied because the concentration of impurities in the monomer solution $[K_M^0]$ and the initial moles of

initiator N^0 were only roughly known when calculating the required feed profiles. However, the match between the observed WCLDs and the curves predicted from *a posteriori* estimates of $[K_M^0]$ and N^0 may be considered acceptable, considering the high sensitivities of these parameters on the final results.

The experiments indicated that the relatively simple mathematical model employed appropriately represents the chosen chemical system. The high molecular weight peaks of living polymer observed in the calibration runs are reasonably well represented by Poisson distributions. This validates the original assumption of an instantaneous initiation and allows a simple calculation of the intermediate function $x(t)$. The correction of chromatograms for instrumental broadening is essential when details of the MWDs are important. If such correction had not been considered in the calibration run chromatograms, for example, then gross errors in the estimation of $[K_M^0]$ would have been produced.

The main experimental limitation was the relatively high concentration of impurities in the monomer solution. If such concentration could be kept sufficiently low, then its accurate estimation would be unimportant, and a greater flexibility in the feasible MWDs could be introduced. The calibration experiment in conjunction with a least squares fit seems a convenient method for estimating the concentration of impurities in the monomer solution. This procedure may also prove useful in other situations involving anionic polymerizations, where the instantaneous monomer conversion is close to 1. In an industrial background, feed stocks for several semibatch operations could be more easily prepared. In this case, the first batches could be used to optimize the operation conditions.

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