

# Molecular Weight Distribution Control in a Semibatch "Living" Anionic Polymerization. I. Theoretical Study

D. A. COUSO, L. M. ALASSIA, and G. R. MEIRA, *INTEC (CONICET and Universidad Nacional del Litoral, Casilla de Correo No. 91, Santa Fe (3000), Argentina*

## Synopsis

A method to produce homopolymers of preestablished molecular weight distribution (MWD), through "living" anionic polymerizations carried out in homogeneous semibatch reactors is proposed and theoretically justified. In the direct form of the technique, very fast reactions are assumed, and the monomer and "killing" agent feed flows are obtained from the knowledge of the desired MWD, the system spreading function, the total reaction time, the initial reaction volume, and the reagent concentrations. Alternatively, by controlling a reactor outlet flow instead of the "killing" agent feed, an external deactivation of the "living" ends can be implemented. The method can be extended to slow reactions, to more elaborated mechanisms, and to take into account the unwanted deactivation of "living" ends by impurities in the monomer solution feed.

## INTRODUCTION

The control of MWDs in polymers is important from the point of view of the influence of this characteristic on the processability and final properties of these materials.

Nonterminated anionic polymerizations with fast initiation with respect to propagation carried out in batch, semibatch, or tubular reactors provide, in principle, the best possible system for controlling MWDs. The reasons are: (a) the number average chain length can be easily altered through the monomer to initiator concentration ratio; (b) the instantaneous MWDs produced tend to be very narrow and in the ideal limit, Poisson-distributed.

The deactivation of the polymer "living" ends during polymerization by impurities such as water, oxygen, acids, etc. tends to broaden the MWD produced, and has been studied in several publications.<sup>1-6</sup> For example, if an impure monomer solution is added to a "living" polymer, and it is assumed that the propagation to termination probability ratio remains constant throughout the reaction, a Schulz-Flory distribution is obtained when the last "living" molecule is deactivated.<sup>1,4</sup>

The periodic operation of continuous "living" polymerizations has been proposed in several opportunities as a means of producing polymers with MWDs different than those produced in the steady state.<sup>7</sup> As far as the authors are aware, there is only one work<sup>8</sup> that has attempted the pro-

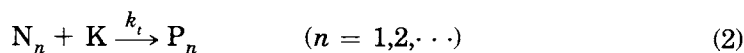
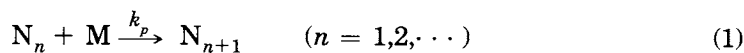
\* To whom correspondence should be sent.

duction of polymers of any prespecified MWD shape, instead of controlling only the first moments of the distribution. In that work, and through a crude hypothesis of monodisperse instantaneous MWDs, a method is proposed by which the desired MWD can be obtained in a plug-flow tubular reactor when the monomer feed is periodically cycled.

The present work studies the way of producing polymers of predetermined MWDs through nonterminated anionic polymerizations carried out in a semibatch reactor. The semibatch operation is performed by adding a monomer solution in a controlled fashion into an initiator solution, while simultaneously deactivating active centers. This deactivation can take place either in the reactor itself by addition of a "killing" agent (direct method) or outside it by manipulating an outlet flow (alternative method). The desired MWD is obtained at the end of the operation. Theoretical limitations for the feasible MWDs are given, and the technique is extended to other nonideal cases.

### AN IDEAL SYSTEM MODEL

Consider the case of solution anionic polymerizations with the following assumptions: monofunctional initiator, instantaneous initiation, isothermal conditions, irreversible reactions, and perfect mixing. The reactor is first loaded with  $N^0$  mol of initiator of volume  $V^0$ . Then, the following reagents are added: monomer solution of concentration  $[M^0]$  at a flow rate  $f_M(t)$ , and "killing" agent solution of concentration  $[K^0]$  at a flow rate  $f_K(t)$ . The following very simple reaction scheme is adopted:



where  $N_n$  and  $P_n$ , respectively, represent the number of moles of the "living" and dead polymer chains, of length  $n$ . The corresponding mass balances are

$$\frac{d[M(t)]}{dt} = \frac{f_M(t) [M^0]}{V(t)} - \frac{f_M(t) + f_K(t)}{V(t)} \times [M(t)] - \frac{k_p}{V(t)} [M(t)] N(t) \quad (3)$$

$$\frac{d[K(t)]}{dt} = \frac{f_K(t) [K^0]}{V(t)} - \frac{f_M(t) + f_K(t)}{V(t)} \times [K(t)] - \frac{k_t}{V(t)} [K(t)] N(t) \quad (4)$$

$$\begin{aligned} \frac{dN_n(t)}{dt} = & -k_p [M(t)] [(N_n(t) - N_{n-1}(t))] - k_t \\ & \times [K(t)] N_n(t) \quad (n = 1, 2, \dots) \end{aligned} \quad (5)$$

$$\frac{dP_n(t)}{dt} = k_t [K(t)] N_n(t) \quad (n = 1, 2, \dots) \quad (6)$$

$$\frac{dN(t)}{dt} = - k_t[K(t)] N(t) \tag{7}$$

$$P(t) = N^0 - N(t) \tag{8}$$

where  $V(t)$  is the reaction volume,  $N(t) = \sum_n N_n(t)$  and  $P(t) = \sum_n P_n(t)$  are the total instantaneous number of moles of “living” and dead polymer, respectively.

The reagents concentration inside the reactor may be, in general, evaluated through eqs. (3) and (4); but, when both  $k_p$  and  $k_t$  are very large, these values reduce to

$$[M(t)] = \frac{f_M(t) [M^0]}{k_p N(t)} \tag{9}$$

$$[K(t)] = \frac{f_K(t)[K^0]}{k_t N(t)} \tag{10}$$

Defining the following “stretched variables,”<sup>4</sup>

$$\theta(t) = \int_0^t k_p [M(\nu)] d\nu \tag{11}$$

$$\psi(t) = \int_0^t k_t [K(\nu)] d\nu \tag{12}$$

where  $\nu$  is a dummy variable, eqs. (5)–(7) may be solved in a general fashion to give:

$$N_n(t) = N(t) \frac{e^{-\theta(t)} \theta^{n-1}(t)}{(n-1)!} \quad (n = 1, 2, \dots) \tag{13}$$

$$P_n(t) = \int_0^t \frac{e^{-\theta(\tau)} \theta^{n-1}(\tau)}{(n-1)!} \{k_t [K(\tau)] N(\tau)\} d\tau \quad (n = 1, 2, \dots) \tag{14}$$

$$N(t) = N^0 e^{-\psi(t)} \tag{15}$$

Equation (13) indicates that at any given time, the “living” polymer is Poisson-distributed of area  $N$ , and with an instantaneous number average chain length of  $(\theta + 1)$ .

If one assumes that at the end of the semi-batch operation (when  $t = t_f$ ) the last polymer molecule is deactivated, then  $P_n(t_f)$  with  $(n = 1, 2, \dots)$  represents the final number chain length distribution. For simplicity, we shall call this distribution.  $[P_n(n)]_f$ . At  $t = t_f$ , eqs. (14) may be written:

$$[P_n(n)]_f = \int_0^{t_f} g[\theta(\tau), n] x'(\tau) d\tau \tag{16a}$$

with

$$g[\theta(t), n] = \frac{e^{-\theta(t)} \theta^{n-1}(t)}{(n-1)!} \quad (16b)$$

and

$$x'(t) = k_t[\mathbf{K}(t)] N(t) \quad (16c)$$

The definition of  $\theta(t)$  indicates that this function is strictly positive and satisfies the conditions for the existence of  $t(\theta)$ . Therefore, a change of variables from  $t$  to  $\theta$  can be performed in eqs. (16) to give

$$[P_n(n)]_f = \int_0^\infty g(\theta, n) x(\theta) d\theta \quad (17)$$

Equation (17) indicates that the final MWD can be considered to be the output of a linear filter with a fictitious input  $x(\theta)$  and a varying impulse response  $g(\theta, n)$  given by the Poisson distribution:

$$g(\theta, n) = \frac{e^{-\theta} \theta^{n-1}}{(n-1)!} \quad (18)$$

Figure 1 illustrates this function, for several values of  $\theta$ . Note that according to eq. (18), when the given ideal model is verified, then the MWD produced will be always broader than the input  $x(\theta)$ . In a real situation, when any of the hypothesis given at the beginning of this section is not verified, the spreading function  $g(\theta, n)$  will be broader than that of eq. (18), and, consequently, the same will happen to  $[P_n(n)]_f$ . Equation (17) provides the clue for the theoretical limits that can be expected in a synthesized MWD: The normalized desired MWD cannot have variations which are more abrupt than those of the normalized impulse response  $g(\theta, n)$ . In the frequency domain, this implies that the cutoff frequency of the transformed desired distribution must be always below that of the transformed impulse response.

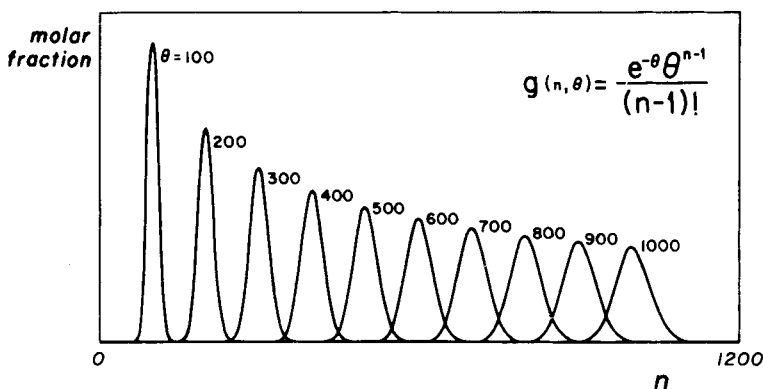


Fig. 1. Poisson spreading function for several values of  $\theta$ .

THE DIRECT METHOD

Assume first that eqs. (9) and (10) are valid. Replacing eq. (9) in eqs. (16), one obtains

$$[P_n(n)]_f = \int_0^{t_f} \frac{e^{-\theta(\tau)} \theta^{n-1}(\tau)}{(n-1)!} \{[K^0] f_K(\tau)\} d\tau \tag{19}$$

Equation (19) is impossible to solve for  $f_K(t)$  unless a simple relationship between  $t$  and  $\theta$  can be established. According to eq. (11), such a relationship will be linear, i.e.,

$$t = c\theta \tag{20}$$

if  $[M(t)]$  is kept steady throughout the operation; and this is achieved by maintaining the ratio  $f_M(t)/N(t)$  constant [eq. (9)]. When this is the case, and by making  $[P_n(n)]_f = P_n^d(n)$  where  $P_n^d(n)$  represents the desired number chain length distribution satisfying

$$\int_0^\infty P_n^d(n) dn = N^0 \tag{21}$$

then, one can write

$$P_n^d(n) = \int_0^\infty \frac{e^{-\theta} \theta^{n-1}}{(n-1)!} \{c[K^0] f_K(c\theta)\} d\theta \tag{22}$$

Calling

$$x_1(c\theta) = c[K^0] f_K(c\theta) \tag{23}$$

this function can be evaluated from eq. (22) by an operation normally known as inverse filtering or input estimation. This operation is totally equivalent to the correction of size exclusion chromatograms for nonuniform instrumental spreading through Tung's integral formula.<sup>9,10</sup> Note that since each  $g(n)$  has unity area, then the area under  $x_1$  will also be  $N^0$ . Calling  $\theta_f$  the highest value of  $\theta$  with nonzero value of  $x_1$ , then the proportionality between  $t$  and  $\theta$  is given by

$$c = \frac{t_f}{\theta_f} \tag{24}$$

From eqs. (20), (23), and (24),

$$f_K(t) = \frac{\theta_f}{t_f [K^0]} x_1(t) \tag{25}$$

Replacing eq. (10) in eq. (7) and solving, we have

$$N(t) = N^0 - \int_0^t [K^0] f_K(\tau) d\tau \quad (26)$$

With total reagents conversions, the desired number average chain length  $\mu_n^d$  is obtained from the ratio between the total added number of moles of the monomer to those of the initiator. Therefore,

$$\int_0^{t_f} f_M(\tau) d\tau = \frac{\mu_n^d N^0}{[M^0]} \quad (27)$$

and

$$f_M(t) = \left[ \frac{\mu_n^d N^0}{[M^0] \int_0^{t_f} N(t) dt} \right] N(t) \quad (28)$$

In summary, the method may be stated as follows: (a) solve for  $f_K(t)$  through eqs. (22)–(25); (b) find  $N(t)$  through eq. (26); and (c) find  $f_M(t)$  through eq. (28).

In the first two columns of Figure 2, the direct method is illustrated by three examples. The required number chain length distributions are rep-

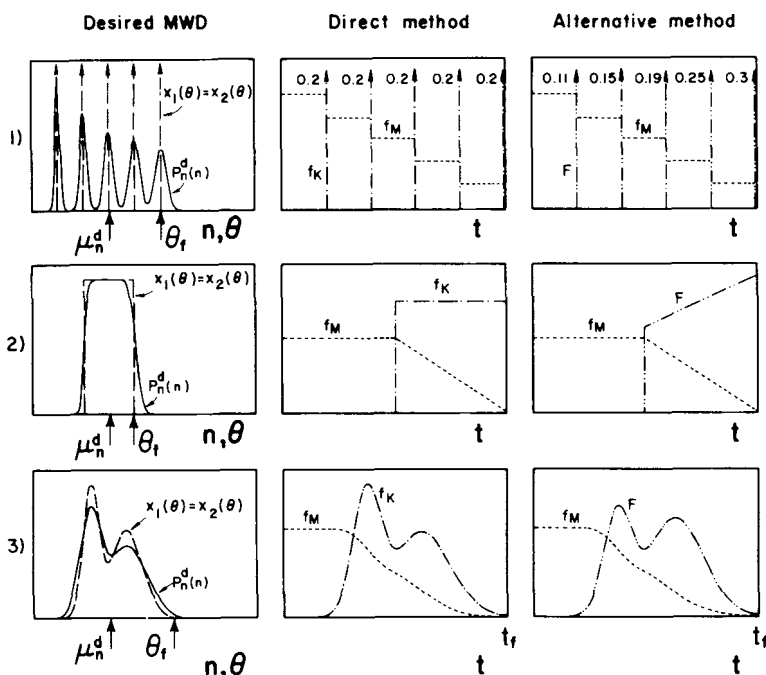


Fig. 2. Three illustrative examples of the proposed method. The numbers by the delta functions represent their corresponding intensity.

resented in the first column together with the corresponding values of  $x_1(\theta)$ . In the second column, the necessary feed profiles are shown. Note that whereas  $f_K(t)$  is proportional to  $x_1(\theta)$ , the monomer flow is a decreasing function that insures a steady growth of the "living" polymer average chain length.

### THE ALTERNATIVE METHOD

In the previous section, the "living" ends were deactivated through the addition of a "killing" agent. Alternatively, one can think of simply deactivating a reactor outlet in a controlled fashion. This procedure has the advantage that the "killing" agent does not need to be prepared nor its concentration adjusted, which may be experimentally difficult to perform. Furthermore, the prerequisite of a high value for  $k_i$  is now relaxed. A possible disadvantage is that the semibatch reactor must now work efficiently throughout the entire reaction volume range.

Calling  $F(t)$  the reactor outlet flow rate and  $V(t)$  the reaction volume, the system model becomes

$$\frac{d[M(t)]}{dt} = \frac{f_M(t)[M^0]}{V(t)} - \frac{f_M(t)[M(t)]}{V(t)} - \frac{k_p[M(t)]N(t)}{V(t)} \quad (29)$$

$$\frac{dV(t)}{dt} = f_M(t) - F(t) \quad (30)$$

$$\frac{dN_n(t)}{dt} = k_p[M(t)] [N_n(t) - N_{n-1}(t)] - \frac{F(t)}{V(t)}N_n(t) \quad (n = 1, 2, \dots) \quad (31)$$

$$\frac{dP_n(t)}{dt} = \frac{F(t)}{V(t)}N_n(t) \quad (n = 1, 2, \dots) \quad (32)$$

$$\frac{dN(t)}{dt} = -\frac{F(t)}{V(t)}N(t) \quad (33)$$

$$P(t) = N^0 - N(t) \quad (34)$$

As before, with  $k_p$  very large, eq. (9) is valid;  $\theta(t)$  is defined as in eq. (11), but  $\psi(t)$  is now

$$\psi(t) = \int_0^t \frac{F(v)}{V(v)} dv \quad (35)$$

The solutions for  $N_n(t)$  and  $N(t)$  are again those of eqs. (13) and (15), respectively; but eq. (14) becomes

$$P_n(t) = \int_0^t \frac{e^{-\theta(\tau)}\theta^{n-1}(\tau)}{(n-1)!} \left\{ \frac{F(\tau) N(\tau)}{V(\tau)} \right\} d\tau \quad (n = 1, 2, \dots) \quad (36)$$

If as in the direct method  $f_M(t)/N(t)$  is maintained constant, then eqs. (20) and (28) are valid, and eq. (36) yields for  $t = t_f$  and  $P_n^d(n)$ :

$$P_n^d(n) = \int_0^\infty \frac{e^{-\theta} \theta^{n-1}}{(n-1)!} \left\{ c \frac{F(c\theta) N(c\theta)}{V(c\theta)} \right\} d\theta \quad (37)$$

Call

$$x_2(c\theta) = c \frac{F(c\theta) N(c\theta)}{V(c\theta)} \quad (38)$$

$x_2(c\theta)$  can be obtained from eq. (37) and then

$$\frac{F(t) N(t)}{V(t)} = \frac{x_2(t)}{c} \quad (39)$$

with  $c$  given by eq. (24).

From eq. (33),  $N(t)$  can be evaluated:

$$N(t) = N^0 - \int_0^t \frac{F(\tau) N(\tau)}{V(\tau)} d\tau \quad (40)$$

and therefore  $f_M(t)$  found through eq. (28).

Consider finally the obtention of  $F(t)$ . Through Eqs. (30) and (33), and defining

$$\alpha(t) = -\frac{1}{N(t)} \frac{dN(t)}{dt} \quad (41)$$

one can arrive at

$$\frac{dF(t)}{dt} + \beta(t)F(t) = \alpha(t)f_M(t) \quad (42a)$$

where

$$\beta(t) = \alpha(t) - \frac{1}{\alpha(t)} \frac{d\alpha(t)}{dt} \quad (42b)$$

The general solution to eqs. (42) is

$$F(t) = \exp \left[ - \int_0^t \beta(\tau) d\tau \right] \times \left\{ \int_0^t \alpha(\tau) f_M(\tau) \exp \left[ \int_0^\tau \beta(\nu) d\nu \right] d\tau + c_1 \right\} \quad (43)$$



From eq. (42b),

$$-\int_0^t \beta(\tau) d\tau = \ln \frac{-dN(t)/dt}{F(0)N^0/V} \quad (44)$$

Therefore,

$$\exp\left[-\int_0^t \beta(\tau) d\tau\right] = \frac{V^0}{F(0)N^0} \left[-\frac{dN(t)}{dt}\right] \quad (45)$$

Replacing eq. (45) into eq. (43) and bearing in mind eq. (28), one can finally obtain

$$F(t) = -\frac{dN(t)}{dt} \left[ \frac{\mu_n^d N^0}{[M^0] \int_0^{t_f} N(t) dt} t + \frac{V^0}{N^0} \right] \quad (46)$$

Thus, the alternative method may be implemented as follows: (a) solve for  $F(t) N(t)/V(t)$  through eqs. (37)–(39); (b) calculate  $N(t)$  by eq. (40); (c) find  $f_M(t)$  through eq. (28); and (d) find  $F(t)$  through eq. (46).

The first and third columns of Figure 2 illustrate the alternative method. Whereas the monomer solution profiles are proportional to those of the direct method, the outlet flow shapes increase more rapidly than the corresponding "killing" agents flows in the direct method, due to the dilution effect by the monomer feed.

### EXTENSIONS OF THE METHOD

As described so far, the proposed method was justified for instantaneous propagation and termination reactions, and no knowledge of the real values of the corresponding kinetic constants was required. With the object of studying the magnitude of  $k_t$  and  $k_p$  above which such conditions are virtually justified, consider the example of Figure 3. Figure 3(a) indicates the desired number chain length distribution together with other initial data, and the  $x_1(\theta) = x_2(\theta)$  function that results from the inverse filtering procedure. The required feed flows are represented in Figure 3(b). With these inputs, the dynamic model of eqs. (3), (4), and (11)–(14) was numerically solved for the four combinations of  $k_t$  and  $k_p$ , which are indicated in the table of Figure 3(c). The curves of Figures 3(c) and (d), respectively, represent the final MWDs produced and the instantaneous monomer concentration along the semibatch operation. Note that only when both  $k_t$  and  $k_p$  are high, the required results are produced. Furthermore, it can be also verified that above  $k_p = k_t = 10^4$  L/mol·min, the ideal solution is always obtained, irrespective of the  $k_p/k_t$  ratio. When  $k_p$  is small, the instantaneous monomer concentration is high, and the final  $\mu_n$  is smaller than required. If, on the other hand,  $k_t$  is small, a Poisson-distributed "living" polymer still remains at the end of the operation.

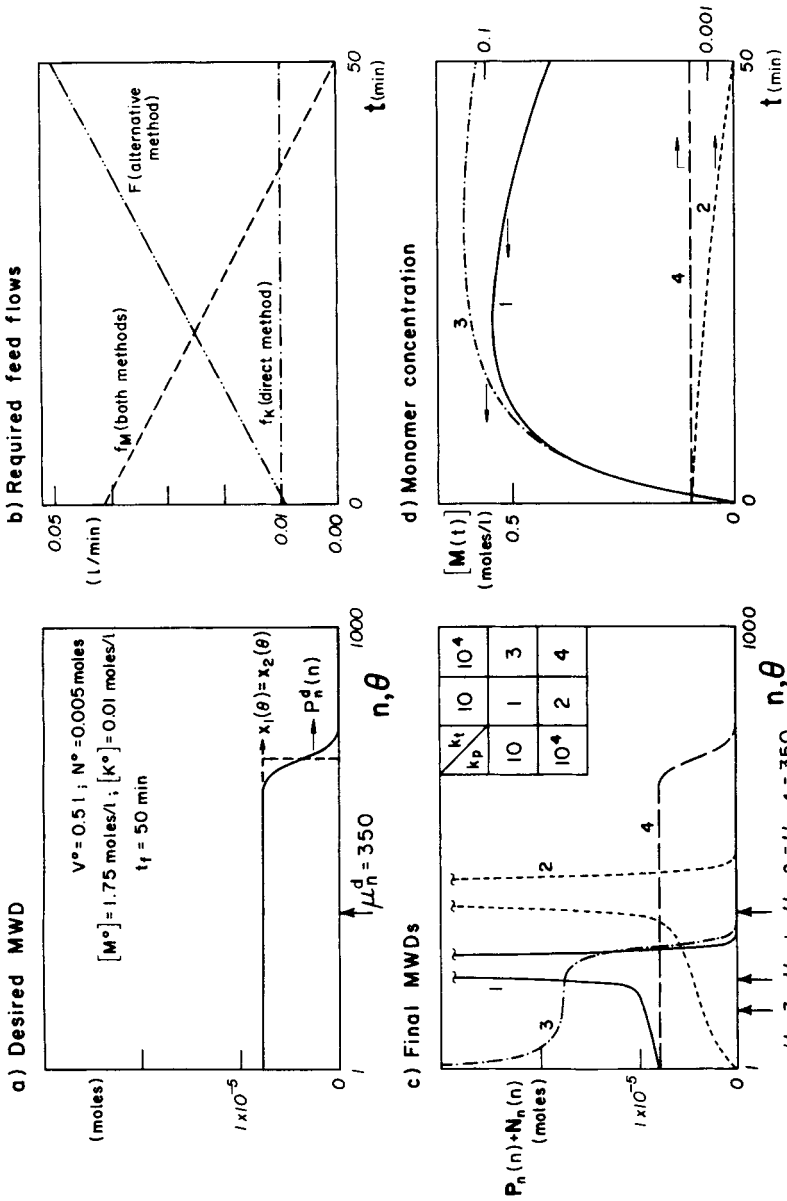


Fig. 3. Example that illustrates the validity of the method for different combinations of  $k_p$  and  $k_t$ :

$k_p$	$k_t$
10	10
$10^4$	$10^4$
10	10
1	1
2	2
4	4
3	3
4	4

In what follows, some extensions of the proposed method will be considered.

### Slow Propagation with Fast Termination

The case of a small (but known)  $k_p$  with a high (and unknown)  $k_t$  is relatively simple. The clue in this case is again to maintain  $[M(t)]$  at a constant level  $[M]$ , which may be calculated [from eq. (11)] through

$$[M] = \frac{\theta_f}{k_p t_f} \quad (47)$$

In the direct version of the method and from eq. (3), one may obtain a more general expression for the required monomer flow as follows:

$$f'_M(t) = \frac{\{f_K(t) + k_p N(t)\} [M]}{[M^0] - [M]} \quad (48)$$

Equation (48) replaces eq. (28), but  $f_K(t)$  and  $N(t)$  are calculated as before.

In the alternative method, eq. (48) reduces to

$$f'_M(t) = \frac{k_p N(t) [M]}{[M^0] - [M]} \quad (49)$$

and the profiles of  $f'_M(t)$  depend now on whether the direct or the alternative method is employed.  $F'(t)$  may be obtained from eqs. (43), (45), and (49):

$$F'(t) = \frac{dN(t)}{dt} \left[ \frac{k_p [M]}{[M^0] - [M]} t + \frac{V^0}{N^0} \right] \quad (50)$$

Consider again the case of  $k_p = 10$  and  $k_t = 10^4$  in the example of Figure 3, where the produced MWD was curve 3 of Figure 3(c) instead of the desired distribution shown in Figure 3(a). The desired MWD may still be produced in the same period of time  $t_f$  if the flows are modified as illustrated in Figure 4. Compared to the profiles of Figure 3(b), note that the values of the corrected monomer flow rates are in both method versions higher than with fast propagation. Consequently,  $F'(t)$  is also larger. The reason for these increases is the 1000-fold increase in  $[M]$  that is predicted by eq. (47). Accordingly, the monomer conversion (that reached 99.84% when  $k_p = 10^4$ ), drops now to 8.57% in the direct method and to 12% in the alternative method. Clearly, by increasing  $t_f$ , this effect could also be compensated.

### Slow Termination

If  $k_t$  is small, it can be shown that the problem still has a theoretical solution when  $x_1(\theta)$  or  $x_2(\theta)$  have no discontinuities. This situation will not be analyzed, however, for the following reasons: (a) in practice, it is generally easy to find deactivating agents which are sufficiently fast; and (b) even

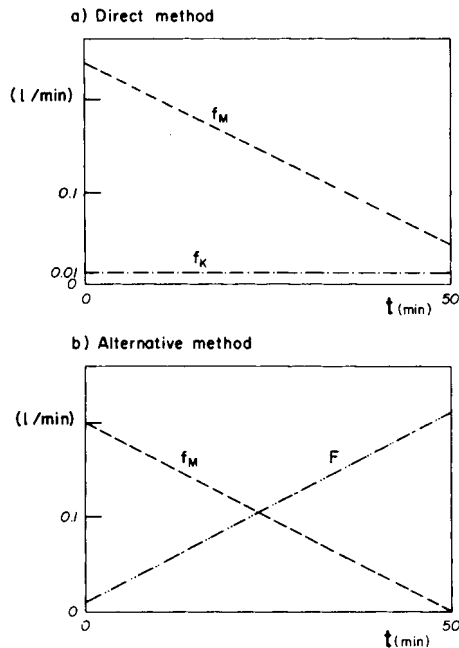


Fig. 4. Flows required to compensate for slow propagation ( $k_p = 10$ ,  $k_t = 10^4$ ), in relation to the example of Figure 3.

with a low  $k_t$ , the alternative method can be utilized, which permits the use of excess of "killing" agent outside the reactor.

### Deactivation by the Monomer Solution

A practical experimental problem that is normally encountered when dealing with anionic polymerizations refers to the unwanted deactivation of "living" ends due to impurities in the monomer solution. When this occurs, and calling  $[K_M]$  the "killing" agent concentration in the monomer solution, the expressions for  $[P_n(n)]_f$  are modified as follows:

(a) *direct method*:

$$[P_n(n)]_f = \int_0^{t_f} \{g[\theta(t), n] [f_K(t) [K^0] + f_M(t) [K_M]]\} dt \quad (51)$$

(b) *alternative method*:

$$[P_n(n)]_f = \int_0^{t_f} \left\{ g[\theta(t), n] \left[ \frac{F(t) N(t)}{V(t)} + f_M(t) [K_M] \right] \right\} dt \quad (52)$$

Note that, in both cases, the net result is the addition of a term that distorts the produced distribution. Furthermore, the number average chain length will be lower than required, because the polymer is completely deactivated before the end of the semibatch operation.

Maintaining  $f_M(t)$  as if the problem did not exist, the unwanted effect may be totally or partially compensated by reducing the original flow  $f_K(t)$  and  $F(t)$  to  $f'_K(t)$  and  $F'(t)$  as indicated below. It is easy to show that the compensation can be complete only if  $[K_M]$  is relatively low and if the functions  $x_1(\theta)$  or  $x_2(\theta)$  have nonzero values up to  $\theta_f$ . Otherwise, a distortion in the final MWD will be produced. Let us now investigate the determination of  $f'_K(t)$  and  $F'(t)$  from the knowledge of  $f_M(t)$ ,  $N(t)$ ,  $f_K(t)$ , and  $F(t)$ , assuming fast deactivation by the monomer solution impurities.

Consider first the direct form of the method. This case is very simple because it is enough to subtract from  $f_K(t)$  the contribution by the monomer solution, i.e.,

$$f'_K(t) = f_K(t) - f_M(t) \frac{[K_M]}{[K^0]} \quad (53)$$

The solution for the alternative method is more elaborate, however. In order to maintain  $f_M(t)$ ,  $N(t)$  and the rate of deactivation of "living" ends  $[F(t)N(t)/V(t)]$  unaltered, it is necessary to change  $F(t)$  and  $V(t)$  to  $F'(t)$  and  $V'(t)$  as follows:

$$\frac{F(t)N(t)}{V(t)} = \frac{F'(t)N(t)}{V'(t)} + f_M(t) [K_M] \quad (54)$$

This can be transformed to

$$F'(t) = \gamma(t)V'(t) \quad (55a)$$

with

$$\gamma(t) = \frac{F(t)}{V(t)} - \frac{f_M(t)}{N(t)} [K_M] = \frac{F(t)}{V(t)} - c_2 \quad (55b)$$

Note that  $\gamma(t)$  is known and that  $c_2$  is a constant. Equation (30) is substituted by

$$\frac{dV'(t)}{dt} = f_M(t) - F'(t) \quad (56)$$

Replacing (55a) in (56), and taking into account eq. (33), one may arrive at

$$V'(t) = \frac{f_M(t)}{c_2} e^{c_2 t} (1 - e^{c_2 t}) + \frac{V^0}{N^0} N(t) e^{c_2 t} \quad (57)$$

Substituting now (57) into (55a), one finally obtains

$$F'(t) = \frac{1}{[K_M]} \left[ e^{c_2 t} \left( 1 + [K_M] \frac{V^0}{N^0} \right) - 1 \right] \left[ \frac{F(t)}{V(t)} N(t) - f_M(t) [K_M] \right] \quad (58a)$$

with

$$c_2 = \frac{f_M(t)}{N(t)}[K_M] \quad (58b)$$

Clearly, negative values for  $f'_K(t)$  or  $F'(t)$  cannot be implemented. When this occurs, zero values for those flows must be adopted, and the compensation will not be complete.

Figure 5(a) illustrates the required corrected flow rates for the example in Figure 3 with  $k_p = k_t = 10^4$ , when  $[K_M] = 0.0005$  mol/L. With this concentration, 10% of the "living" ends are deactivated by the spurious agents at the end of the operation. As shown in Figure 5(b), it is possible in the case to exactly compensate the unwanted effect and produce a MWD which coincides with that required. For comparison, the MWD obtained if the correction was not taken into account is also represented.

### Extension to More Elaborate Reaction Mechanisms

The function  $x'(t)$  of eqs. (16a) and (16c) depends solely on the termination mechanism. Therefore, if the reaction kinetics is further elaborated with the restriction of limiting the termination stage to that of eq. (2); it is, in principle always possible to write an expression in the format of eqs. (16), with the spreading function depending only on the initiation and propa-

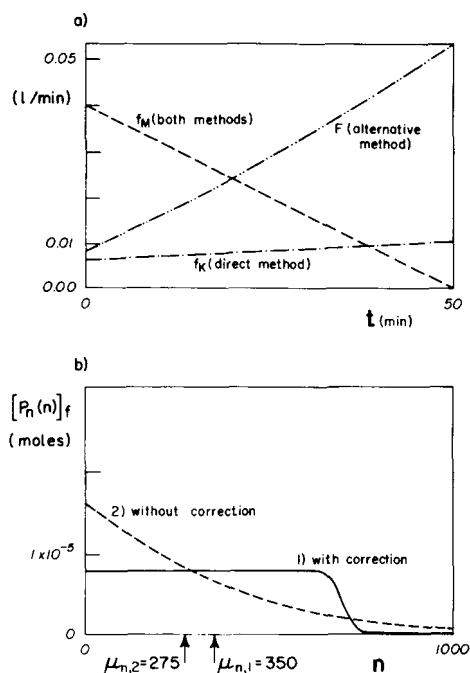


Fig. 5. (a) Flows required to compensate for deactivated by the monomer solution when  $[K_M] = 0.0005$  mol/L; (b) final MWDs with and without the appropriate correction.

gation stages. For example, consider a mechanism where the two following reactions are added to eqs. (1) and (2):



where I and P<sub>0</sub> represent the active and inactive initiator, respectively. Assuming also I<sup>0</sup> moles of initiator at the start of the operation, then it can be shown that eq. (14) is replaced by

$$P_n(t) = \int_0^t \frac{k_i/k_p}{(1 - k_i/k_p)^n} \frac{e^{-\theta(\tau)}}{(n-1)!} \sum_{s=n}^{\infty} \frac{[(1 - k_i/k_p)\theta(\tau)]^s}{s!} \{k_i[K(\tau)](N(\tau) + I(\tau))\} d\tau \tag{61}$$

(n = 1, 2, ...)

with

$$I(t) = I^0 e^{-(k_i/k_p)\theta(t) + \psi(t)} \tag{62}$$

$$N(t) = I^0 e^{-\psi(t)} [1 - e^{-k_i/k_p\theta(t)}] \tag{63}$$

and  $\theta(t)$  and  $\psi(t)$  defines as in eqs. (11) and (12), respectively.

The spreading function is now wider than that of eq. (16b) and is represented by the first factors of the integrand, before the large key. It can also be proved that in this case the proposed method can be employed through: (a) inverse filtering eq. (61), assuming linearity between  $t$  and  $\theta$ ; and (b) considering the total amount of active centers  $[N(t) + I(t)]$  instead of just  $N(t)$ , when calculating the required flow profiles.

### CONCLUSIONS

Based on a very idealized kinetic mechanism, and within certain limitations, this work has theoretically proved that the intentional deactivation of "living" ends in anionic polymerizations carried out in semibatch reactors may be an interesting way of producing homopolymers of any prespecified MWD.

Very broadly, the direct method may be stated as follows: (a) The "killing" agent flow profile is proportional to the result of an inverse filtering operation involving the desired MWD and the system spreading function, and (b) along the operation, the monomer solution must be added in order to insure a constant monomer concentration and a steady growth of the number average chain length of the remaining "living" polymer. In the alternative form of the technique (which may be more attractive from a practical standpoint), the determination of the required outlet flow is not as straightforward as before, and with the same basic conditions the monomer solution flow profile is identical to that of the direct case. The method was also

extended to compensate for slow reactions, deactivation by the monomer solution and more complex reaction mechanisms.

A key point in this work is that of the integral functions of eqs. (16) and (36). These expressions indicate that the desired MWD can be obtained by processing a function of the termination mechanism only, through a time-varying filter that depends on the remaining kinetic stages. The seeming generality of this expression with different reaction mechanisms, indicates that the method could be experimentally applied as follows:

(a) Find the true experimental spreading function by performing a semi-batch experiment with steady addition of the monomer solution only, and measuring the instantaneous MWDs produced. Note that, in case of unwanted deactivation by the monomer solution, the relative areas under the number chain length distribution curve corresponding to the "living" and the "dead" polymer provides also a measurement of the impurities composition.

(b) Find  $x_i(\theta)$  ( $i = 1, 2$ ) by inverse filtering eq. (17) or eq. (37).

(c) Apply the method with the necessary corrections, assuming linearity between  $t$  and  $\theta$ . Alternatively, if the instantaneous number average chain length of the "living" polymer peak could be measured on-line, then the required deactivation could be exactly known.

Finally, consider the extrapolation of the proposed method to improved the technique given in Ref. 8. In that work, the required periodic monomer flow profile to produce the desired MWD through anionic polymerizations in a plug-flow tubular reactor was obtained directly from the desired cumulative MWD, the basic assumption being instantaneous monodisperse polymers. By taking into consideration a relationship similar to eq. (17), the procedure could include a previous inverse filtering of the desired MWD through the experimental spreading function.

At present, the experimental validity of the methods is being investigated, and this will be the subject of a future communication.

#### APPENDIX: NOMENCLATURE

$f_K(t)$	"killing" agent flow rate (L/min)
$f_M(t)$	monomer solution flow rate (L/min)
$F(t)$	outlet flow rate (L/min)
$g(n, \theta)$	system spreading function
$[K(t)]$	"killing" agent concentration (mol/L)
$[K_M]$	spurious "killing" agent concentration in the monomer solution (mol/L)
$k_p$	propagation rate constant (L/mol · min)
$k_t$	termination rate constant (L/mol · min)
$[M(t)]$	monomer concentration (mol/L)
$n$	chain length
$N(t)$	total "living" polymer (mol)
$N_n(t)$	"living" polymer of chain length $n$ (mol)
$N_n(n)$	number chain length distribution of the "living" polymer
$P(t)$	total dead polymer (mol)



$P_n(n)$	number chain length distribution of the dead polymer
$t$	time (min)
$V$	reaction volume (L)
$x'(t)$	defined by eq. (16c)
$x(\theta)$	appears in eq. (17) and it is easy to see that $x(\theta) = x'[t(\theta)][d\theta/dt]$
$x_1, x_2$	defined by eqs. (23) and (38)
$\psi$	defined by eq. (12)
$\theta$	defined by eq. (11)
$\mu_n$	number average chain length
superscript 0	indicates initial or feedstock values
superscript $d$	indicates desired values
subscript $f$	indicates final values
primed flows	indicate corrections with regard to the original method

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