

## Molecular Weight Distributions in Continuous Linear Addition Polymerizations

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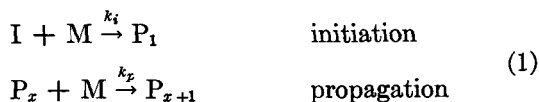
### Synopsis

Molecular weight distributions for addition polymerization without termination in continuous vessels were developed and compared with distributions for batch, chain polymerization with termination. A correspondence was found to exist between: batch, chain polymerization with termination by disproportionation and continuous polyaddition in one vessel; batch polymerization with termination by combination and continuous polyaddition in two vessels in series; and, finally, Flory's multichain condensation polymerization and continuous polyaddition in any number of vessels in series.

### INTRODUCTION

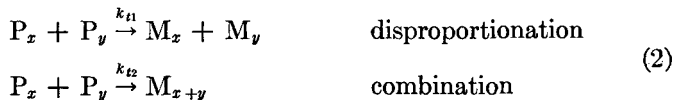
Two well-known linear polymerization mechanisms are chain polymerization with termination and polyaddition without termination.

A kinetic scheme for chain polymerization is:



where I is initiator, M is monomer, and  $P_x$  represents active polymeric intermediates (free radicals or ions) with chain length or degree of polymerization,  $x$  (excluding the initiator fragment).

If termination occurs, but no chain transfer of any kind, the following steps are included in scheme (1) for free radical polymerizations



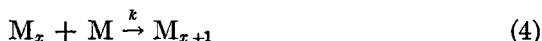
where  $M_x$  represents inactive polymer product,  $x$  units in length.

In the event that termination is absent, the kinetic scheme may more conveniently be written for nonchain polyaddition



where  $x > 1$ . If it is understood that  $x$  includes the initiator molecule as a unit in the chain, this implies that the total concentration of polymer chains is fixed throughout the polymerization and is equal to  $(M_1)_0$ , the initial initiator (or one-mer) concentration.

A special case of eq. (3) is when  $k_t = k_p$ . This leads to a narrow (Poisson) molecular weight distribution (MWD) in batch polymerization and is more simply represented by



for  $x \geq 1$ .

Owing to its chain nature and to the kinetic steady-state assumption, chain polymerization with termination gives polymer product having an integral MWD, at a given conversion, which is the aggregate of all the different MWDs prior to that conversion.<sup>1a</sup> The former MWD is broader than the latter because the probability of propagation varies with conversion.<sup>2</sup> The differential or instantaneous distributions may be derived via statistical arguments.<sup>3</sup>

In the present work, theoretical MWDs for systems obeying kinetic scheme (4), polymerized continuously in well-mixed vessels under steady-state conditions, were investigated. Denbigh<sup>4</sup> has predicted that the MWD will be broader in continuous than in batch polymerization for such systems; also, from general considerations regarding continuous reactor dynamics (cf. Denbigh<sup>5</sup>) more than one vessel in series should reverse this effect and cause a narrowing of the MWD producing, in the limit of many vessels, the same MWD as in the batch case. These predictions were confirmed.

Moreover, the following systems were found to have analogous MWDs: continuous polymerization of kinetic scheme (4) in one vessel and batch polymerization of kinetic scheme (1) with termination by disproportionation; continuous polymerization of kinetic scheme (4) in two vessels in series and batch polymerization of kinetic scheme (1) with termination by combination; and continuous polymerization in any number of vessels and multichain condensation polymerization.

## DISCUSSION

### Batch Chain Polymerization With Termination

In batch polymerizations with kinetic scheme (1), including both types of termination,  $k_{t1}$  and  $k_{t2}$  may be defined in the rate expression

$$d[P_x]/dt = k_p[M]([P_{x-1}] - [P_x]) - k_t[P_x][P] \quad (5)$$

where  $[M]$ ,  $[P_x]$ , and  $[P]$  refer to the concentrations of these respective species,  $k_t \equiv k_{t1} + k_{t2}$  and  $[P] \equiv \sum_{i=1}^{\infty} [P_i]$ .

The probabilities, at some instant in time during polymerization, that an active chain propagates, terminates by disproportionation, or terminates by combination are, respectively,

$$\phi \equiv k_p[M]/(k_p[M] + k_t[P]) \quad (6)$$

$$\psi_1 \equiv k_{d1}[P]/(k_p[M] + k_t[P]) \quad (7)$$

$$\psi_2 \equiv k_{c2}[P]/(k_p[M] + k_t[P]) \quad (8)$$

and all vary with extent of reaction.

If the kinetic steady-state assumption is valid the probability of selecting, at random, active  $x$ -mer from among all the active chains, existing at some instant in time, is given by the most probable distribution<sup>3a</sup>

$$[P_x]/[P] = \phi^{x-1}(1 - \phi) \quad (9)$$

Moreover, given that a termination by combination occurs, the probability that inactive  $x$ -mer is formed is

$$\sum_{i=1}^{x-1} ([P_i]/[P])([P_{x-i}]/[P]) \quad (10)$$

since this termination may produce inactive  $x$ -mer by joining active one-mer and  $(x - 1)$ -mer, active two-mer and  $(x - 2)$ -mer, . . . , or active  $(x - 1)$ -mer and one-mer. This expression (10) may be written, with the aid of equation (9), as<sup>3b</sup>

$$\sum_{i=1}^{x-1} \phi^{i-1}(1 - \phi)\phi^{x-i-1}(1 - \phi) = (x - 1)\phi^{x-2}(1 - \phi)^2 \quad (11)$$

Finally, the probability that any inactive chain is formed from active species via termination by, say, combination, rather than by disproportionation, is

$$(\psi_2/2)/[(\psi_1) + (\psi_2)/2]$$

because two active chains are terminated for each inactive chain formed.

Hence, since inactive  $x$ -mer may be formed from active  $x$ -mer via disproportionation as well as by combination, as described above, the probability of selecting, at random, inactive  $x$ -mer from among all the polymer molecules which are formed at some instant in time is equal to the instantaneous mole fraction of  $x$ -mer formed at that instant. This fraction becomes

$$Y_{xt} = \frac{\psi_1}{\psi_1 + \psi_2/2} \phi^{x-1}(1 - \phi) + \frac{\psi_2/2}{\psi_1 + \psi_2/2} (x - 1)\phi^{x-2}(1 - \phi)^2 \quad (12)$$

If combination is absent, then  $\psi_2 = 0$ , and eq. (12) becomes

$$Y_{xt} = \phi^{x-1}(1 - \phi) \quad (13)$$

On the other hand, if disproportionation is absent, then  $\psi_1 = 0$ , and eq. (12) becomes

$$Y_{xi} = (x - 1)\phi^{x-2}(1 - \phi)^2 \quad (14)$$

If high polymer is formed,  $\phi$  must have a value close to one.

### Continuous Polymerization without Termination

As the continuous reactor, a series of  $n$ , well-mixed, stirred vessels has been chosen for discussion because of its industrial importance as well as its interesting theoretical aspects.

In the treatment which follows it is assumed that: (1) the number of moles of growing chains per unit of reaction volume is constant throughout the system and equal to  $[M_1]_0$ , the initiator (one-mer) concentration entering the first vessel; (2) the probability of propagation is independent of chain length and is, therefore, the same for all polymer chains in any given vessel; (3) the probability of a polymer chain leaving a vessel, at any time, is independent of chain length and the time which it has spent in the vessel because of perfect mixing on a microscopic scale; (4) steady-state conditions obtain and, therefore, all probabilities are independent of time; (5) isothermal conditions prevail and changes in density of the reacting fluid, in which the polymer remains dissolved, may be neglected.

By considering the conservation of monomer in the  $j$ th vessel eq. (15) is obtained

$$-\frac{([M]_j - [M]_{j-1})}{\theta_j} \equiv -\frac{[\Delta M]_j}{\theta_j} = k[M]_j[M_1]_0 \quad (15)$$

where  $j$  may be any integer between 1 and  $n$ ,  $[M]_{j-1}$  and  $[M]_j$  represent monomer concentration entering and leaving the  $j$ th vessel, respectively, and  $\theta_j$  is the mean residence time in the  $j$ th vessel.

The rate at which monomer is added to growing chains, per unit volume, in the  $j$ th vessel is  $k[M]_j[M_1]_0$  and the rate at which polymer chains exit from the vessel, per unit volume, is  $[M_1]_0/\theta_j$ . Hence, the probability,  $\phi_j$ , that any polymer chain adds a monomer unit, in preference to leaving the vessel, is

$$\phi_j = K[M]_j\theta_j/(1 + k[M]_j\theta_j) \quad (16)$$

and the probability that it exits is, of course,  $1 - \phi_j$ .

In the case of one vessel only,  $n = j = 1$  and, if  $\phi_1$  is referred to merely as  $\phi$ , the probability that any polymer molecule in the exit stream, selected at random, is  $x$ -mer ( $x$  includes the initiator molecule) is

$$(Y_x)_1 = \phi^{x-1}(1 - \phi) \quad (17)$$

and is equal to the mole fraction of  $x$ -mer leaving the vessel at any instant in time.

If high polymer is formed,  $\phi$  has a value close to one and the MWD, eq. (17), is analogous to the instantaneous distribution in batch, chain

polymerization with termination by disproportionation, eq. (13), for the same numerical value of  $\phi$ .

If  $n = 2$ , any  $y$ -mer, where  $1 \leq y \leq x$ , entering the second vessel from the first may exit as  $x$ -mer by propagating  $x - y$  times in the second vessel and then leaving that vessel. The probability that this occurs, which is equal to the mole fraction of  $x$ -mer leaving the second vessel, is

$$(Y_x)_2 = \sum_{i=1}^x Y_i \phi_2^{x-i} (1 - \phi_2) \quad (18)$$

or, from eq. (17),

$$(Y_x)_2 = (\phi_2^x - \phi_1^x)(1 - \phi_2)(1 - \phi_1)/(\phi_2 - \phi_1) \quad (19)$$

It is convenient at this point to introduce  $Z_j \equiv k[M]_j \theta_j$ . Clearly, from eq. (15),  $Z_j$  is a measure of the number of moles of monomer which reacts in the  $j$ th vessel, per mole of polymer chains, and has, therefore, precisely the same physical significance as the "eigenzeit transformation" which was introduced<sup>6</sup> in the treatment of linear addition polymerization in order to linearize the infinite set of nonlinear differential equations describing the system. Furthermore, from eq. (16), it is obvious that

$$\phi_j = Z_j / (1 + Z_j) \quad (20)$$

Hence, it may be shown, by extending the above analysis to  $n$  vessels in series, that

$$(Y_x)_n \equiv \frac{[M_x]_n}{[M_1]_0} = \sum_{i=1}^n \frac{Z_i^{n+x-2}}{(1 + Z_i)^x \prod_{\substack{j=1 \\ i \neq j}}^n (Z_i - Z_j)} \quad (21)$$

and that the number-average and weight-average chain lengths leaving the  $n$ th vessel are, respectively,

$$(\bar{x}_N)_n = 1 + \sum_{i=1}^n Z_i \quad (22)$$

$$(\bar{x}_W)_n = \frac{1 + 3 \sum_{i=1}^n Z_i + \sum_{i=1}^n Z_i^2 + \left( \sum_{i=1}^n Z_i \right)^2}{1 + \sum_{i=1}^n Z_i} \quad (23)$$

In the limit, as  $n$  increases to infinity and if  $\theta \equiv \sum_{i=1}^n \theta_i$  remains finite, eq. (21) must take the form of the Poisson distribution

$$Y_x = Z^{x-1} e^{-Z} / (x - 1)! \quad (24)$$

which is the MWD of kinetic scheme (4) in batch polymerization if  $Z = ([M]_0 - [M]) / [M_1]_0$ . This is because the influence of backmixing disappears and the system behaves like a continuous, plug flow or batch polymerization.

A special case of interest is that in which the probability of propagation is equal in all vessels; i.e.,  $\phi_1 = \phi_2 = \dots = \phi_j = \dots = \phi_n \equiv \phi$ . This is not equivalent to the case of vessels of equal size,  $\theta_1 = \theta_2 = \dots = \theta_j = \dots = \theta_n = \theta/n$ , but requires that the vessels increase monotonically in size, with increasing  $j$ ; i.e.,  $\theta_1 < \theta_2 < \dots < \theta_j < \dots < \theta_n$ .

The probability of selecting, at random,  $x$ -mer from the stream emerging from the  $n$ th vessel may, in the case of equal probability of propagation, be compared with the outcome of  $x - 1 + n$  Bernoulli trials,<sup>7a</sup> in which  $x - 1$  are propagations,  $n$  are exits, and where it is permissible to permute only the first  $x - 1 + n - 1$  trials, since the last event must be an exit from tank  $n$ . Hence, it follows immediately that

$$\begin{aligned} (Y_x)_n &= \binom{x+n-2}{x-1} \phi^{x-1} (1-\phi)^n \\ &= \binom{x+n-2}{n-1} \phi^{x-1} (1-\phi)^n \end{aligned} \quad (25)$$

where the terms in parentheses on the right-hand side of eqs. (25) are binomial coefficients.<sup>7b</sup>

The MWD (25) is identical with the negative binomial distribution,<sup>7c</sup> and with Flory's multichain ( $n$ ) distribution for nonlinear condensation polymerization which must be narrower than the monochain distribution.<sup>1b</sup>

For  $n = 2$ , eqs. (25) give

$$(Y_x)_2 = x\phi^{x-1}(1-\phi)^2 \quad (26)$$

If  $x$  were to exclude the initiator molecule, equation (26) would become

$$(Y_x)_2 = (x-1)\phi^{x-2}(1-\phi)^2 \quad (27)$$

At high molecular weights,  $\phi$  has a value of approximately one, and this equation is precisely equivalent to the instantaneous MWD in batch, chain polymerization with termination by combination, eq. (14).

The MWDs in one, two, three, four, and five vessels of equal size (and, therefore, equal residence time) in series are plotted in Figure 1. Conditions were so chosen as to make the conversion 50% in the case of one vessel. The number-average chain length,  $\bar{x}_N$ , in each case is fixed at a value of 101. The MWD is seen to gradually sharpen as the number of vessels increases; it converges to the Poisson distribution with the same  $\bar{x}_N$ .

For comparison, two additional MWDs appear in the figure, namely, those representing the broadest and sharpest distributions possible, at  $\bar{x}_N = 101$ , in batch polymerization with termination by combination.<sup>2</sup> The broadest (integral) MWD was obtained by adjusting parameters in such a way as to give the desired integral value of  $\bar{x}_N = 101$  at complete conversion. The sharpest (instantaneous) MWD was obtained by adjusting parameters in such a way as to give the instantaneous  $\bar{x}_N$ , at zero

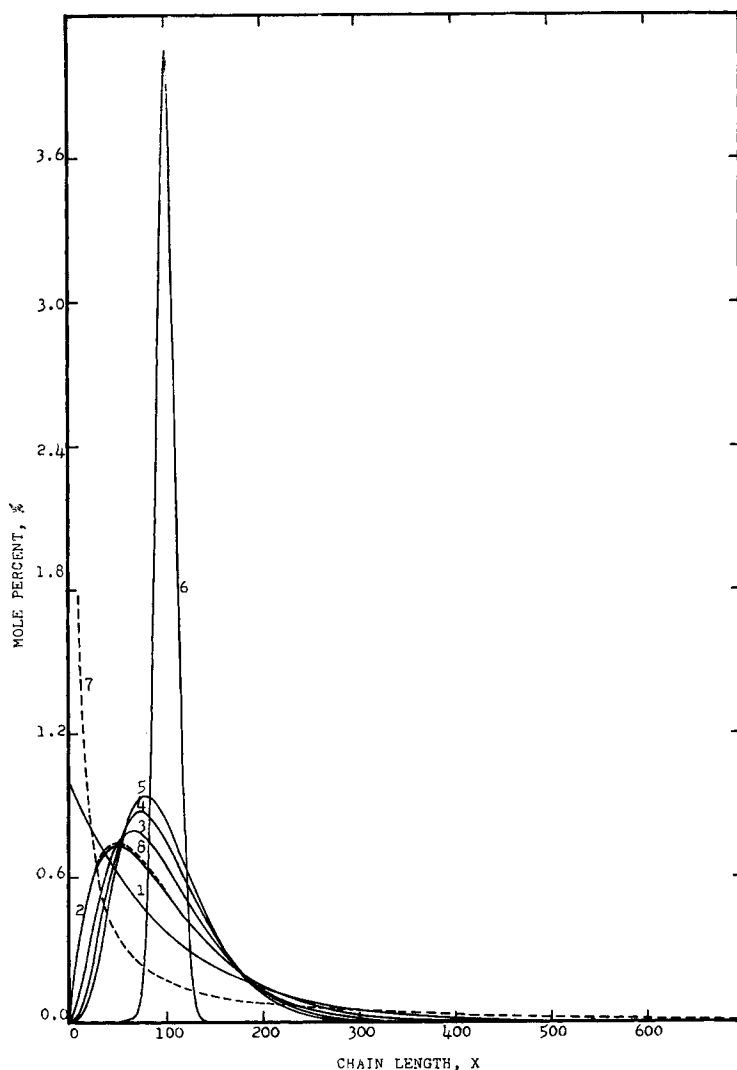


Fig. 1. Molecular weight distributions (MWD) with  $\bar{x}_n = 101$ : (1) MWD in one vessel; (2) MWD in two vessels; (3) MWD in three vessels; (4) MWD in four vessels; (5) MWD in five vessels; (6) Poisson distribution; (7) broadest chain MWD; (8) sharpest chain MWD.

conversion, a value of 101. The latter distribution coincides with the MWD in two vessels, as discussed above.

In conclusion, if a polymerization mechanism conforms to kinetic scheme (4) and leads, therefore, to a Poisson MWD in batch reaction, polymer may be formed via this mechanism in continuous reaction such that its MWD has a relative breadth which lies anywhere between that of the most probable (one vessel) and Poisson (many vessels) distributions.

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### Résumé

Des distributions du poids moléculaire pour la polymérisation par addition sans terminaison, en réacteurs continus, ont été développées et comparées avec des distributions pour des polymérisations discontinues en chaîne avec terminaison. On a trouvé qu'il existe une corrélation en polymérisation discontinue, en chaîne avec terminaison par disproportionnement et polyaddition continue dans un seul réacteur; entre polymérisation discontinue avec terminaison par combinaison et polyaddition continue dans deux réacteurs en série; et enfin, la polymérisation par condensation à chaînes multiples, suivant Flory, et la polyaddition continue dans plusieurs réacteurs en série.

### Zusammenfassung

Die Molekulargewichtsverteilung bei der Additionspolymerisation ohne Abbruch im Fließbetrieb wurde entwickelt und mit den Verteilungen für statische Kettenpolymerisation mit Abbruch verglichen. Korrespondierendes Verhalten wurde gefunden für: statische Kettenpolymerisation mit Abbruch durch Disproportionierung und kontinuierliche Polyaddition in einem Gefäß; statische Polymerisation mit Abbruch durch Kombination und kontinuierliche Polyaddition in zwei Gefässen in Reihe; und schliesslich Vielkettenkondensationspolymerisation nach Flory und kontinuierliche Polyaddition in einer beliebigen Zahl von Gefässen in Reihe.

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