

On the Molecular Weight Distribution Polydispersity of Continuous Living-Radical Polymerization

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ABSTRACT: Batch living-radical polymerization techniques were used to produce polymers with molecular weight distributions approaching the narrowness of truly living (ionic) systems. Continuous reactors may offer some advantages for living polymerization in copolymer morphology, but continuous polymerization with any level of backmixing will broaden the molecular weight distribution. This study used simple moment techniques to demonstrate

that idealized living-radical polymerization in a single stirred tank reactor will have a polydispersity of 2. This is also the theoretical minimum polydispersity for a truly living polymerization. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 539–542, 2004

Key words: living polymerization; mixing; modeling; molecular weight distribution; morphology

INTRODUCTION

Continuous reactors have been used extensively in free-radical polymerization. These reactors, once operating at steady state, will produce a consistent product at a low manufacturing cost. As long as steady state can be maintained, the polymer produced will be consistent over long periods of time. In general, continuous stirred tank reactors (CSTRs) are preferred over plug flow reactors (PFRs) because of the vulnerability of tubular reactors to plugging. However, unlike a PFR in which all of the reactants experience the same residence time in the reactor, a CSTR exhibits a residence time distribution (RTD). If the lifetime of a growing chain is on the order of the average residence time, the molecular weight distribution (MWD) will be affected by the RTD. For conventional free-radical polymerization, this is not an issue, given that the lifetime of a single radical is approximately 1 s, and the residence time of a single CSTR is on the order of magnitude of 1 h. For nonterminating polymerizations [i.e., condensation, some ionic, and living free radical (LRP)] the life of the chain is exactly its residence time in the reactor, and so it is strongly affected by the RTD. For instance, if a condensation polymerization is run in a single CSTR, the polydispersity of the MWD goes to infinity as the molecular weight increases to commercially important levels.¹ For truly living (ionic)

polymerization, the polydispersity approaches 2 rather than 1 as for a batch reaction.

Very little has been published on continuous LRP. In part, the lack of information on continuous LRP is attributed to the newness of the field, but it may also be attributed to the fact that research in LRP has treated narrow MWD as the primary goal of LRP. If one is concerned only with a narrow MWD, any amount of backmixing will cause the polydispersity to increase above the theoretical limit of 1 (for truly living, batch polymerization). Kim and Nauman² calculated the polydispersity for truly living (ionic) polymerization in various reactor configurations. The results can be summarized as follows:

1. Batch (or PFR) with rapid initiation: Polydispersity approaches 1 (under ideal conditions)
2. Single CSTR: Polydispersity approaches 2
3. CSTRs in series: Polydispersity < 2
4. Single segregated CSTR: Polydispersity > 2

These results were derived for an ideal ionic living polymerization. This report shows that conclusions (2) and (4) hold for LRP as well. Conclusion (1) for LRP has been proven elsewhere, and conclusion (3) follows logically from conclusions (1) and (2). Zhang and Ray³ confirmed conclusions (2) and (4) with a rigorous simulation model of continuous-solution LRP. This report shows that conclusions (2), (3), and (4) for LRP systems can be determined with a minimum of calculations.

In the mechanisms considered below, termination is not considered. This is done for two reasons: (1) including termination would substantially increase the complexity of the derivation, and (2) more important,

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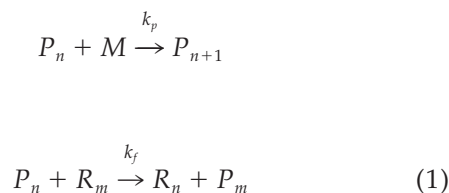
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these derivations are meant to complement those for other types of polymerization in a CSTR. In other words: What is the minimum polydispersity attainable under the very most favorable conditions? Quantitatively, it is easy to see that the existence of any termination would broaden the MWD beyond the minimum described here.

KINETIC MECHANISMS

Polydispersity of an ideal reversible addition-fragmentation transfer (RAFT) polymerization carried out in a single homogeneous CSTR

If one considers solution RAFT polymerization in a single CSTR where initiation is considered to be instantaneous, and chain transfer (through the RAFT agent) is assumed to be fast relative to propagation, the following kinetic steps must be considered:



where P_n is a live chain of length n monomer units, R_m is a dormant chain of length m monomer units, and M is monomer. Balances on P_n and R_n can be written as

$$\frac{dP_n}{dt} = \frac{Q}{V} (P_{ni} - P_n) + k_p M (P_{n-1} - P_n) - k_f R P_n + k_f P R_n$$

$$\frac{dR_n}{dt} = \frac{Q}{V} (R_{ni} - R_n) + k_f R P_n - k_f P R_n$$

$$P \equiv \sum_{n=1}^{\infty} P_n; \quad R \equiv \sum_{n=1}^{\infty} R_n \quad (2)$$

where Q is the volumetric flow rate; V is the reactor volume; k_p and k_f are the rate constants for propagation and transfer, respectively; and the subscript i indicates an inlet condition. The average residence time θ is defined as V/Q . The inlet conditions are assumed to be

$$P_{ni} = \begin{cases} P_{1i} & n = 1 \\ 0 & n > 1 \end{cases}$$

$$R_{ni} = \begin{cases} R_{1i} & n = 1 \\ 0 & n > 1 \end{cases} \quad (3)$$

If steady state is assumed, one can take the z -transform of the first of the resulting algebraic equations:

$$0 = \frac{1}{\theta} [z^{-1}P_{1i} - F_p(z)] - k_p M F_p(z) [1 - z^{-1}] - k_f R F_p + k_f P F_r(z)$$

$$F_p(z) \equiv \sum_{n=1}^{\infty} P_n z^{-n}; \quad F_r(z) \equiv \sum_{n=1}^{\infty} R_n z^{-n} \quad (4)$$

If transfer is rapid with respect to propagation, the chain length distributions of the live and dormant chains will be identical:

$$\frac{F_p(z)}{P} = \frac{F_r(z)}{R} \quad (5)$$

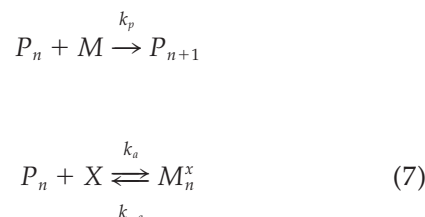
Substituting eq. (5) into eq. (4) gives

$$0 = \frac{1}{\theta} [z^{-1}P_{1i} - F_p(z)] - k_p M F_p(z) [1 - z^{-1}] - k_f R F_p + k_f P R \frac{F_p(z)}{P} \quad (6)$$

Noting that the last two terms will cancel, eq. (6) is exactly the equation for living (ionic) polymerization in a single CSTR.^{1,2} Equation (6) can be solved to give the Flory distribution with a polydispersity that approaches 2 for large residence times.

Polydispersity of an ideal reversible termination polymerization carried out in a single homogeneous CSTR

If one considers solution atom transfer radical polymerization (ATRP) or nitroxide-mediated controlled radical polymerization (both examples of reversible termination living polymerization) in a single CSTR where initiation is considered to be instantaneous, and reversible termination is assumed to be fast relative to propagation, the following kinetic steps must be considered:



where P_n is a live chain of length n monomer units, M_n^x is a dormant chain of length n monomer units, X is

the control agent, and M is monomer. Balances on P_n and M_n^x can be written as

$$\begin{aligned} \frac{dP_n}{dt} &= \frac{Q}{V} (P_{ni} - P_n) + k_p M (P_{n-1} - P_n) \\ &\quad - k_a X P_n + k_{-a} M_n^x \\ \frac{dM_n^x}{dt} &= \frac{Q}{V} (M_{ni}^x - M_n^x) + k_a X P_n - k_{-a} M_n^x \\ P &\equiv \sum_{n=1}^{\infty} P_n; \quad M^x \equiv \sum_{n=1}^{\infty} M_n^x \end{aligned} \quad (8)$$

where k_a and k_{-a} are the rate constants for the forward and reverse termination reactions, respectively, and the subscript i indicates an inlet condition. All other variables are as above. The inlet conditions are assumed to be

$$\begin{aligned} P_{ni} &= \begin{cases} P_{1i} & n = 1 \\ 0 & n > 1 \end{cases} \\ M_{n1}^x &= 0 \quad n > 0 \end{aligned} \quad (9)$$

To give the limiting case, all kinetic steps leading up to the formation of a monomeric living chain were considered to occur instantaneously; any variance from this could only broaden the MWD. If steady state is assumed, one can take the z -transform of the first of the resulting algebraic equations:

$$\begin{aligned} 0 &= \frac{1}{\theta} [z^{-1} P_{1i} - F_p(z)] - k_p M F_p(z) [1 - z^{-1}] \\ &\quad - k_a X F_p + k_{-a} F_m(z) \\ F_p(z) &\equiv \sum_{n=1}^{\infty} P_n z^{-n}; \quad F_m(z) \equiv \sum_{n=1}^{\infty} M_n^x z^{-n} \end{aligned} \quad (10)$$

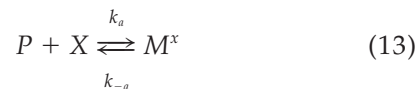
If transfer is rapid with respect to propagation, the chain length distributions of the live and dormant chains will be identical:

$$\frac{F_p(z)}{P} = \frac{F_m(z)}{M^x} \quad (11)$$

Substituting eq. (11) into eq. (10) gives

$$\begin{aligned} 0 &= \frac{1}{\theta} [z^{-1} P_{1i} - F_p(z)] - k_p M F_p(z) [1 - z^{-1}] \\ &\quad + F_p(z) \left(k_{-a} \frac{M^x}{P} - k_a X \right) \end{aligned} \quad (12)$$

To simplify eq. (12), note that



Assuming equilibrium for this reaction

$$K_a = \frac{k_a}{k_{-a}} = \frac{M^x}{PX} \quad (14)$$

or

$$\frac{M^x}{P} = K_a X \quad (15)$$

Substituting eq. (14) into eq. (12) gives

$$0 = \frac{1}{\theta} [z^{-1} P_{1i} - F_p(z)] - k_p M F_p(z) [1 - z^{-1}] + F_p(z) \left(k_{-a} \frac{k_a X}{k_{-a}} - k_a X \right) \quad (16)$$

Noting that the last two terms will cancel, eq. (15) is exactly the equation for living (ionic) polymerization in a single CSTR.^{1,2} Equation (15) can be solved to give the Flory distribution with a polydispersity that approaches 2 for large residence times.

Both of the two types of living-radical polymerization in a single CSTR, under the simplifying assumptions above, give the Flory distribution.¹ For this distribution, the number-average chain length is given as

$$\mu_n = \frac{1}{1 - \phi} \quad (17)$$

where

$$\phi = \frac{\theta k_p M}{1 + \theta k_p M} \quad (18)$$

The polydispersity is given as

$$D = 1 + \phi \quad (19)$$

which, for large residence times, approaches 2. The fact that the level of control agent is absent from the polydispersity equation is a consequence of the simplifying assumptions: because termination has been neglected, a build up of control agent in the reversible termination, which would impact the MWD, was not considered. Again, this is a limiting result giving the minimum possible polydispersity; any build up of control agent can only broaden the MWD.

Polydispersity of an ideal living-radical polymerization carried out in a CSTR train

Having shown that either of the mechanisms for living-radical polymerization gives a polydispersity of 2 (exactly what is found for a truly living polymerization²), when polymerization occurs in a single CSTR, one can generalize and simplify the problem. In a living polymerization, the chain length is a function of residence time. Because the monomer concentration in a CSTR is constant, the rate of propagation for any living chain is constant; therefore the distribution of chain lengths should just follow the RTD of the reactor. Froment and Bischoff⁴ derived the RTD for a series of equal-sized CSTRs. Their results indicate that both the zeroth and first moments of the RTD are unity, and that the variance of the distribution is given as $1/n$, where n is the number of reactors in the train. These results can easily be used to express the polydispersity of the residence time distribution as

$$D_{\text{RTD}} = 1 + \frac{1}{n} \quad (20)$$

Because the chain length distribution will follow the RTD, the polydispersity of the chain length distribution for living polymerization in a series of CSTRs can be written as

$$D = 1 + \frac{1}{n} \quad (21)$$

Not surprisingly, for $n = 1$, $D = 2$.

Continuous living-radical polymerization in a segregated CSTR

Many living-radical polymerizations are carried out in miniemulsion. In an idealized miniemulsion, there is no mixing of material from one monomer droplet/polymer particle to another. Under these conditions, either type of living-radical polymerization treated above may be considered as taking place in a segregated CSTR. Under these conditions, the MWD can be calculated from the results for living-radical polymerization in an infinite series of batch reactors,¹ where the batch time for each is the residence time of that element of fluid. The chain length distribution of the CSTR, then, is the integral of the chain length distribution of the batch reactor weighted with the residence time distribution of the CSTR.

The chain length distribution for a batch living polymerization¹ is given by

$$P_n(t) = P_{10} \exp(-\tau) \frac{(\tau)^{n-1}}{(n-1)!} \quad (22)$$

where

$$\tau = \int_0^t k_p M(t') dt' \quad (23)$$

The residence time distribution for a CSTR is given as

$$E(t) = \frac{1}{\theta} \exp\left(\frac{-t}{\theta}\right) \quad (24)$$

and the chain length distribution for the segregated CSTR is

$$P_n^{\text{CSTR}} = \int_0^\infty P_n(t) E(t) dt \quad (25)$$

Unfortunately, a closed-form solution is not obvious, although the polydispersity will be greater than that of the Flory distribution (homogeneous CSTR), that is, greater than 2.¹

CONCLUSIONS

Using the techniques of z-transforms, it is possible to conclude the following:

- For both reversible transfer and reversible termination living-radical polymerization in a single CSTR, in the most ideal case, the MWD reverts to that expected for true living-radical polymerization.
- For a homogeneous CSTR, the MWD polydispersity approaches 2, rather than the value of unity predicted for a batch reaction.
- For a CSTR train, the MWD polydispersity decreases from 2 with an increase in the number of reactors.
- For the segregated CSTR, the MWD must be calculated numerically, but the polydispersity will always exceed the theoretical limit of 2 for the homogeneous CSTR.

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