

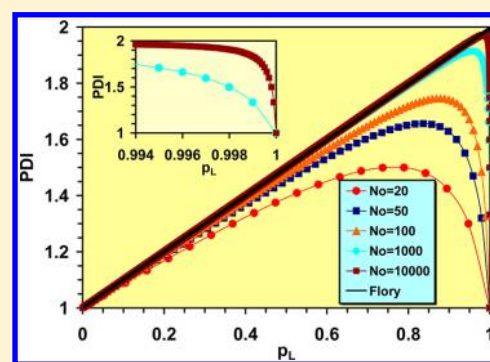
# Theoretical Size Distribution in Linear Step-Growth Polymerization for a Small Number of Reacting Species

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## Supporting Information

**ABSTRACT:** The size distributions for the linear step-growth polymerization containing a relatively small number of molecules (in the range of 20–10000) have been calculated using computer simulations. Contrary to the most probable distribution of Flory, which predicts a continuous linear increase of the polydispersity index (PDI) from the value of 1 to 2, it has been found that the PDI increases up to a certain maximum value followed by a decrease to unity as the extent of conversion ( $p$ ) approaches unity. The maxima of the PDI versus  $p$  curves as well as the sharpness of the decrease of these curves to unity have been found to strongly depend on the number of reacting species. In addition, on the basis of a rigorous statistical treatment, the number and the weight-average size distributions have been derived, which are in perfect agreement with those obtained by computer simulation. Furthermore, the derived distributions can also be applied for the description of reaction products of depolymerization reactions.



## INTRODUCTION

Step-growth polymerization (SGP) is an important class of polymerization reactions from both theoretical and practical points of view. Nearly half of the synthetic polymers produced today are made by SGP. The basic theoretical description of SGP was given by Carothers and Flory.<sup>1–4</sup> Their main results on SGP are summarized in eqs 1–5.

$$\bar{X}_n = \frac{1}{1-p} \quad (1)$$

$$n_x = p^{x-1}(1-p) \quad (2)$$

$$w_x = xp^{x-1}(1-p)^2 \quad (3)$$

$$\frac{\bar{X}_w}{\bar{X}_n} = 1 + p \quad (4)$$

$$p = \frac{n_o - n}{n_o} \quad (5)$$

where  $\bar{X}_n$  and  $\bar{X}_w$  are the number-average and the weight-average degree of polymerization, respectively,  $x$  is the degree of polymerization,  $p$  is the extent of reaction and  $n_o$ , and  $n$  are the numbers of end groups at the beginning and a later time of polymerization.

Equation 1 is also known as the Carothers equation for the linear SGP of A–B and/or the mixture of A–A and B–B type monomers being in equimolar ratio.<sup>5</sup> Equations 2 and 3 represent the most probable distributions of Flory, which are also related to the distributions of reaction products obtained in the Fischer–Tropsch synthesis,<sup>6</sup> which are known as the

Anderson–Schulz–Flory distribution.<sup>7</sup> The Flory distribution functions are well-accepted, and several independent derivations have appeared.<sup>8–16</sup> Alternatively, modifications of the original distributions of Flory to include the considerable formation of cyclic polymers have also been proposed.<sup>17,18</sup> However, as was pointed out by Kricheldorf and co-workers,<sup>18</sup> eq 1 contains inconsistency because in the case of  $p = 1$ , eq 1 predicts the infinite number-average degree of polymerization. The case  $p = 1$  means that all functional end groups have been reacted and the final reaction product should be a giant cyclic polymer with a degree of polymerization equal to the initial number of monomers. However, if we assume the formation of very stiff polymer chains where no ring closure reaction can take place, two end groups still remain unreacted; hence,  $p$  should not be equal to 1 according to the definition by Flory (eq 5). Instead,  $p$  will be smaller than 1, and the final product will be a linear polymer chain with a degree of polymerization identical to the number of monomers initially present in the polymerization system. Moreover, there is another contradiction in relation to eq 4, which, to the best of our knowledge, has never been highlighted. Equation 4 shows that as  $p$  approaches unity, the value of  $\bar{X}_w/\bar{X}_n$ , that is, polydispersity index (PDI), also approaches 2 according to eq 4. This is, however, an incorrect prediction and inherently cannot be true, owing to the following reason: if we assume the case for which eq 4 was derived, that is, only linear polymers are formed during the SGP reaction (no cyclic polymers are formed), the

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final product of the SGP will be *one* linear polymer chain; thus the PDI should not be 2; it would rather be 1. It is now also evident that the value of the PDI for both the initial and the final state should be unity. Furthermore, it can also be surmised that the value of the PDI should increase from 1 to a certain value and then should decrease again to unity at near 100% conversion of the reacting end groups. Considering the contradiction associated with eqs 1–4, the following questions can be raised. (i) What does the PDI versus  $p$  curve look like? (ii) How does it depend on the initial number of species? (iii) What does the most probable distribution of Flory look like for a SGP system containing small number of monomers? (iv) What is the theoretical limitation of using the Flory distribution for the description of SGP systems?

In this report, we attempt to answer these questions using computer simulations. In addition, we have also derived the most probable distribution analytically, which is able to handle a SGP system containing a small number of monomers as well. In the field of nanotechnology and/or in biological systems, for example, in cells, where SGP reactions may proceed with a small number molecules, the derived size distribution functions may find their applications. In this report, we will focus on the linear chain polymer formation by assuming chain length independence of the reactivity of species formed during the SGP.

## EXPERIMENTAL SECTION

**Procedure of the Computer Simulation.** The simulation of the SGP was based on the consecutive random selection of the two reacting species. The process starts with  $N_0$  monomers (length = 1 unit) and ends at the  $(N_0 - 1)$ th step, where only one giant chain (length =  $N_0$  units) with two end groups is present. The number- and weight-average degree of polymerization and the breadth of the molecular weight distribution were determined by averaging the results of  $10^5$  runs of the step-growth procedure for  $N_0 = 1000$  and 10000 and  $10^6$  runs for  $N_0 = 20, 50$ , and 100. The number distribution function for the step polymerization at numerous extents of polymerization was determined by averaging the results of  $10^8$  runs of the step-growth procedure for  $N_0 = 20, 50$  and 100.

## RESULTS AND DISCUSSION

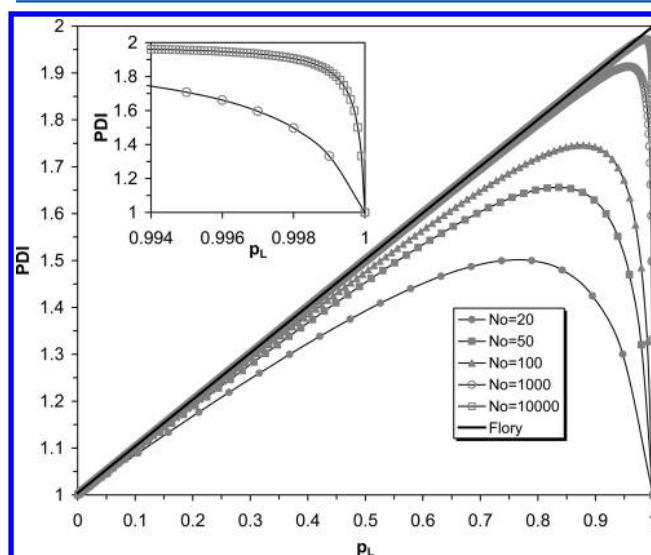
**Size Distribution for the Polymerization System Containing a Small Number of Reacting Species.** In the theoretical treatment of size distributions for the linear SGP to be presented, we will also assume, similarly to the original treatment by Flory,<sup>3</sup> that the reactivity of the end groups of polymers of different sizes is independent of the chain length. Furthermore, we also assume that there is no ring polymer formation either during or at end of polymerization; hence, very stiff linear polymers are formed, which are unable to undergo any ring closure reactions. However, as outlined in the Introduction, in this case, two reactive end groups still remain at the end of the reaction; thus, according to the original definition by Flory,  $p$  can never be equal to 1. Therefore, to eliminate this contradiction, we can give  $p_L$  as

$$p_L = \frac{L}{N_0 - 1} \quad (6)$$

where  $L$  is the total number of linkages and  $N_0$  is the initial number of monomers.

Note that eq 6 is analogous to eq 5, but in some respects, it will be more useful for the further statistical treatment of size distribution for linear SGP. It is also evident that the maximum number of linkages is equal to  $N_0 - 1$ , that is,  $p_L = 1$  means the case when all monomers ( $N_0$ ) are incorporated into a chain with  $N_0 - 1$  links between them.

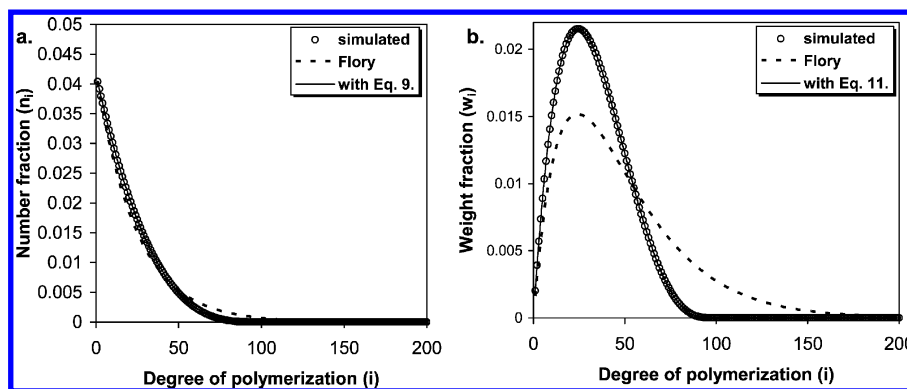
Equation 4, as was pointed out, predicts that as  $p$  (or  $p_L$ ) approaches 1, the values of  $\bar{X}_w/\bar{X}_n$  will be close to 2, and this cannot hold because in the final state of polymerization, that is, when all end groups have been reacted (except the two as discussed before), only one polymer chain with a degree of polymerization  $N_0$  is formed. In order to find out the characteristics of  $\bar{X}_w/\bar{X}_n$  (PDI) versus  $p_L$  curves, computer simulations with different initial numbers of monomers ( $N_0$ ) were performed according to the procedure compiled in the Experimental Section. Figure 1 shows the computer simulated PDI versus  $p_L$  curves with  $N_0 = 20, 50, 100, 1000$ , and 10000.



**Figure 1.** Computer simulated variations of the PDI with the extent of reaction ( $p_L$ ) and the initial numbers of monomers ( $N_0$ ) in the linear SGP. The inset shows the change of PDI at near 100% conversion for  $N_0 = 1000$  and 10000. The solid line from 1 to 2 represents the predicted values by eq 4.

As seen in Figure 1, large deviations from the predicted values by eq 4 can be observed. On the other hand, it can also be recognized that all curves reach a maximum value followed by decreasing to a PDI = 1 value. It is also evident from Figure 1 that the higher the  $N_0$ , the steeper the decrease of PDI to unity. In addition, the higher the initial number of monomers, the higher the maximum values of PDI, and the smaller the deviation of the predicted values by eq 4. For example, as can be seen in the Figure 1 inset in the case of  $N_0 = 10000$ , the PDI approaches the value of 2 at high conversion, and only when  $p_L > 0.998$  does the PDI start to decrease considerably. Therefore, it can also be surmised that with higher  $N_0$ , the values of PDI will be closer to the predicted value of 2. It is important to emphasize that this theoretical calculation does not contradict the experimental results obtained on some SGP systems,<sup>19,20</sup> in which PDIs close to 2 were observed and the experiments were performed evidently with a system containing monomers of several orders of magnitude higher ( $N_0 > 10^{22}$ ).

According to the results of computer simulations obtained at different conversions for various initial numbers of monomers,



**Figure 2.** Computer simulated variations of the number fraction ( $n_i$ ) (a) and weight fraction ( $w_i$ ) (b) with the degree of polymerization ( $i$ ) for the linear SGP system containing  $N_o = 100$  monomer molecules initially ( $p_L = 95/99$ ). Solid lines represent the data calculated by eqs 9 and 11. For comparison, the most probable distributions of Flory are also plotted using dashed lines ( $p_L = 95/99$ ).

as well as based on a rigorous statistical treatment detailed in the Supporting Information for the relative number fraction of two adjacent oligomers, eq 7 can be established.

$$\frac{n_{i+1}}{n_i} = \frac{m-i}{N_o-i-1} \quad (7)$$

where  $n_{i+1}/n_i$  is the relative number fraction of oligomers with degrees of polymerization of  $i+1$  and  $i$ ,  $N_o$  is the initial number of monomers,  $m = p_L(N_o - 1) + 1$ , that is, the maximum degree of polymerization at the extent of reaction  $p_L$ , and  $i$  spans from 1 to  $m-1$ .

For example, if  $N_o = 20$  and  $p_L = 3/19$ , the reaction mixture contains  $L = 3$  linkages (eq 6), and the highest degree of polymerization in this case can be  $m = 4$  (tetramer with three linkages). Thus, the values of the relative number fractions for  $n_2/n_1$ ,  $n_3/n_2$ , and  $n_4/n_3$  are  $3/(N_o - 2) = 3/18$ ,  $2/(N_o - 3) = 2/17$ , and  $1/(N_o - 4) = 1/16$ , respectively (the detailed derivation of the relative number fraction can be found in the Supporting Information).

The number fraction of the  $i$ th oligomer ( $n_i$ ) can be given by eq 8.

$$n_i = \frac{\alpha_{i-1}}{1 + \sum_{j=1}^{i-1} \alpha_j} \quad (8)$$

where  $\alpha_i = \prod_{j=1}^i [(m-j)/(N_o-j-1)] = [(m-1)!(N_o-i-2)!]/[(m-i-1)!(N_o-2)!]$  and  $\alpha_0 = 1$  ( $\alpha_{i-1} = \alpha_0$  when  $i = 1$ ) and  $i \leq m-1$ .

Substituting  $\alpha_i$  into eq 8, the distribution function can take the form of

$$n_i = \frac{(N_o - m)(m-1)!(N_o - i - 1)!}{(N_o - 1)(m-i)!(N_o - 2)!} \quad (9)$$

Similarly, the weight fraction of the  $i$ th oligomer ( $w_i$ ) can be expressed by eq 10.

$$w_i = \frac{\beta_{i-1}}{1 + \sum_{j=1}^{i-1} \beta_j} \quad (10)$$

where  $\beta_i = \prod_{j=1}^i [(j+1)(m-j)]/[j(N_o-j-1)] = (i+1)\{[(m-1)!(N_o-i-2)!]/[(m-i-1)!(N_o-2)!]\}$  and  $\beta_0 = 1$  ( $\beta_{i-1} = \beta_0$  when  $i = 1$ ).

Substitution of  $\beta$  into eq 10, we get the weight fraction distribution function in another form (eq 11)

$$w_i = \frac{i(N_o - m + 1)(N_o - m)(m-1)!(N_o - i - 1)!}{(m-i)!N_o!} \quad (11)$$

Using eqs 8 and 10 and/or eqs 9 and 11, the number-average ( $\bar{X}_n$ ) and the weight-average ( $\bar{X}_w$ ) degree of polymerization then are given by eqs 12 and 13, respectively.

$$\bar{X}_n = \frac{\sum_{i=1}^m i \times n_i}{\sum_{i=1}^m n_i} \quad (12)$$

$$\bar{X}_w = \frac{\sum_{i=1}^m i \times w_i}{\sum_{i=1}^m w_i} \quad (13)$$

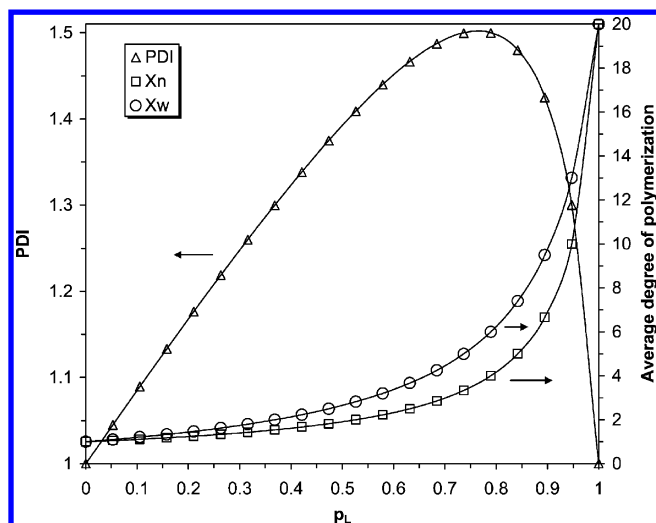
To demonstrate that the derived distributions describe the size distribution of SGP correctly, the computer simulated distributions were compared to those calculated by eqs 8 and 9 and 10 and 11. As representative examples, Figure 2 presents the number fraction and the weight fraction distributions for the case where  $N_o = 100$ , while in Figure 3, the average degrees of polymerization as a function of  $p_L$  are plotted for the case of  $N_o = 20$ .

As it turns out from Figures 2 and 3, the distributions and average degrees of polymerization calculated by eqs 8 and 9 and 10 and 11 fit perfectly to those obtained by computer simulations, supporting the correctness of the derived size distributions. However, large deviations from the Flory distributions can be recognized (Figure 2), and it is evident that the Flory distribution is not capable of describing a polymerization system in the cases when the initial number of the monomer molecules is small and/or at very high conversions, where the number of reacting species is also expected to be rather small. This latter is the reason why eq 4 fails to give correct PDI values at very high conversions.

**Size Distribution for the Polymerization System Containing Large Number of Reacting Species.** In the following, we will examine the relationship between the distribution functions represented by eqs 8–11 and those by Flory. Let  $N_o$  and  $m$  be large. Then, the following relation can be hold for this case

$$\frac{N_2}{N_1} \approx \frac{N_3}{N_2} \approx \frac{N_4}{N_3} \approx \dots \approx \frac{m}{N_o} \approx p_L \approx p \quad (14)$$

Substituting  $p$  into eq 8, eq 15 becomes



**Figure 3.** Comparison of computer simulated and calculated data by eqs 9 and 11 for the number average ( $\bar{X}_n$ ), weight average ( $\bar{X}_w$ ), degree of polymerization, and PDI versus extent of reaction ( $p_L$ ). For the sake of better visualization, the calculated data by eqs 9 and 11 are plotted with solid lines.

$$n_i = \frac{p^{i-1}}{1 + p + p^2 + p^3 + \dots + p^{m-1}} \quad (15)$$

Recognizing that the denominator is a geometric series with the result of  $1/(1-p)$ , we get eq 16, which is identical to the Flory distribution for the number fraction (eq 2).

$$n_i \approx p^{i-1}(1-p) \quad (16)$$

Using a similar line of thought and substituting  $p$  into eq 10, eq 17 is obtained.

$$w_i = \frac{i \times p^{i-1}}{1 + 2p + 3p^2 + 4p^3 + \dots + mp^{m-1}} \quad (17)$$

We can also recognize that the denominator in eq 17 can be approximated by  $1/(1-p)^2$ , and eq 18 is given, which has the same form as that of the Flory weight fraction distribution function.

$$w_i \approx i \times p^{i-1}(1-p)^2 \quad (18)$$

It is now clear from the previous discussion that eqs 8–11 render the most probable distribution of Flory for large  $N_0$  and  $m$  values.

**Size Distribution for the Products of Depolymerization Reactions.** It is also important to emphasize that modification of eqs 9 and 11 can lead to eqs 19 and 20, which are capable of yielding the number and weight fraction distribution functions for the products of depolymerization reactions.

$$n_i = \frac{L(N_0 - L - 1)!(N_0 - i - 1)!}{(N_0 - 1)(N_0 - L - i)!(N_0 - 2)!} \quad (19)$$

$$w_i = \frac{i(L+1)L(N_0 - L - 1)!(N_0 - i - 1)!}{(N_0 - L - i)!N_0!} \quad (20)$$

where  $L$  is the number of the linkages degraded,  $N_0$  now is the initial degree of polymerization of the starting polymer, and  $i$  also represents the degree of the polymerization of the products.

The distribution functions represented by eqs 19 and 20 give identical results to those derived by Mark and Simha for the degradation of long chain molecules.<sup>21</sup>

## CONCLUSIONS

On the basis of the computer simulations and rigorous statistical treatments, the number and weight distribution functions have been derived for the linear SGP systems containing a small number of reacting species (for A–B and/or A–A and B–B monomers in a 1:1 stoichiometric ratio), assuming that the reactivity of the end group is independent of the chain length. The derived distributions seem to be able to give correct PDI values at high conversions and eliminate the contradiction in eq 4. On the basis of the theoretical results, it was shown that the most probable size distributions of Flory are the limiting cases of the distributions defined by eqs 9 and 11, that is, the Flory size distributions are valid only for systems possessing a relatively large number of reacting species. On the other hand, in the cases when the system to be studied contains a small number of species, it may be preferred to use modified distribution functions capable of handling of systems with a small number of reacting species like, for example, those described by eqs 9 and 11. In the field of nanotechnology where SGP reactions may proceed with a small number of molecules, size distribution functions such as eqs 9 and 10 may find their applications.<sup>22,23</sup> In addition, the derived distributions can also be applied for the description of reaction products of depolymerization reactions.

## ASSOCIATED CONTENT

### Supporting Information

Derivation of the size distribution for a small number of monomers. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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