Simulation of Nonequimolecular Polycondensation in Continuous Flow-Stirred Tank Reactors

CHEN-CHONG LIN and WEN-YEN CHIU, *Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China*

Synopsis

Conversion and molecular weight distribution are computed and compared for uncatalyzed and catalyzed nonequimolecular polycondensation in continuous flow-stirred tank reactors (CSTRs) using two different kinetic schemes proposed by Flory and Lin, respectively. The contrast between the two schemes is also remarkable as found in the batch reactors. The polydispersity indices in the CSTRs are substantially larger than those obtained in the batch reactors. Also, the molecular weight distribution splits into two curves for odd and even homologues regardless of the two different schemes. An extremely long rersidence time is needed to obtain the higher conversion accompanying a large polydispersity index as compared to the batch reactors. The polydispersity can be expressed in CSTR as $\bar{x}_w/\bar{x}_n = 2\sum_{n=1}^{\infty} n^2 N_n (R + 1 - 2P)/(1 + R)^2[A]_0$.

INTRODUCTION

Studies on molecular weight distribution (MWD) for equimolecular condensation in batch reactors exist in the literature (e.g. Refs. 1–3). However, all of these studies were based on Flory's kinetic schemes. The mechanism of nonequimolecular polycondensation does not obey Flory's schemes but Lin's.[4-6] The contrast of behavior between these two schemes in the batch reactors has been demonstrated in our previous work.[7] Very little has been reported on the simulation of nonequimolecular condensation polymerization in continuous-flow stirred tank reactors (CSTRs), in spite of its theoretical and industrial importance. Biesenberger[8] obtained the MWD and the polydispersity index for condensation polymerization and found substantially higher polydispersity indices in the ideal CSTR as compared to the batch reactor. Recently, Gupta et al.[9] obtained MWD and polydispersity indices for condensation polymerization in CSTRs of monomers violating the equal reactivity hypothesis. In this paper, the polycondensation of the two bifunctional species AA and BB in CSTRs has been simulated and discussed according to the two different kinetic schemes proposed by Flory and Lin, respectively.

MODEL DEVELOPMENT

On the basis of the material balance in the CSTR, the following equations can be derived based on Lin's kinetic scheme for batch reactors.

For an uncatalyzed reaction:

When $n = 1$,

$$\frac{[A]_0}{\bar{\theta}} - \frac{[A_1]}{\bar{\theta}} - 2k[A_1][B][B] = 0 \tag{1}$$

CCC 0021-8995/82/010063-07$01.00

$$\frac{[B]_0}{\bar{\theta}} - \frac{[B_1]}{\bar{\theta}} - 2k[B_1][A][B] = 0 \tag{2}$$

When $n = 2x$ (even),

$$\frac{[A_n]}{\bar{\theta}} = k \left\{ \sum_{i=1}^{2x-1} [A_i][B_{n-i}] - [A_n][B] - [B_n][A] \right\}[B] \tag{3}$$

$$[B_n] = [A_n] \tag{4}$$

When $n = 2x - 1$ (odd), $n = 3, 5, 7, \cdots$,

$$\frac{[A_n]}{\bar{\theta}} = 2k \left\{ \sum_{i=1}^{x-1} [A_{2i-1}][B_{n-2i+1}] - [A_n][B] \right\}[B] \tag{5}$$

$$\frac{[B_n]}{\bar{\theta}} = 2k \left[\sum_{i=1}^{x-1} [A_{2i}][B_{n-2i}] - [B_n][A] \right\}[B] \tag{6}$$

The summation of the set of above equations leads to

$$\frac{[A]_0}{\bar{\theta}} - \frac{[A]}{\bar{\theta}} - k[A][B]^2 = 0 \tag{7}$$

$$\frac{[B]_0}{\bar{\theta}} - \frac{[B]}{\bar{\theta}} - k[A][B]^2 = 0 \tag{8}$$

where $[A] = [A]_0(1 - P)$, $[B] = [B]_0 (1 - P/R)$, and $R = [B]_0/[A]_0$

For a catalyzed reaction:

When $n = 1$,

$$\frac{[A]_0}{\bar{\theta}} - \frac{[A_1]}{\bar{\theta}} - 2k'[A_1][A] = 0 \tag{9}$$

$$\frac{[B]_0}{\bar{\theta}} - \frac{[B_1]}{\bar{\theta}} - 2k'[B_1][A]^2/[B] = 0 \tag{10}$$

When $n = 2x$ (even),

$$\frac{[A_n]}{\bar{\theta}} = k' \left\{ \sum_{i=1}^{2x-1} [A_i][B_{n-i}] - [A_n][B] - [B_n][A] \right\}[A]/[B] \tag{11}$$

$$[B_n] = [A_n] \tag{12}$$

When $n = 2x - 1$ (odd), $n = 3, 5, 7, \cdots$,

$$\frac{[A_n]}{\bar{\theta}} = 2k' \left\{ \sum_{i=1}^{x-1} [A_{2i-1}][B_{n-2i+1}] - [A_n][B] \right\}[A]/[B] \tag{13}$$

$$\frac{[B_n]}{\bar{\theta}} = 2k' \left\{ \sum_{i=1}^{x-1} [A_{2i}][B_{n-2i}] - [B_n][A] \right\}[A]/[B] \tag{14}$$

The summation of the set of these equations results in

$$\frac{[A]_0}{\bar{\theta}} - \frac{[A]}{\bar{\theta}} - k'[A]^2 = 0 \tag{15}$$

$$\frac{[B]_0}{\bar{\theta}} - \frac{[B]}{\bar{\theta}} - k'[A]^2 = 0 \tag{16}$$

where $[A] = [A]_0(1 - P)$, $[B] = [B]_0(1 - P/R)$, and $R = [B]_0/[A]_0$

The relationship between conversion in terms of the extent of reaction (P) and

mean residence time (θ) can be derived from the set of above equations as follows:

For an uncatalyzed reaction:

$$\frac{1}{\theta} = \frac{k(1-P)}{P} [B]_0^2 \left(\frac{1-P}{R}\right)^2 \qquad \text{(based on Lin's scheme)} \qquad (17)$$

If one uses Flory's scheme for derivation of this reaction, the following equation results:

$$\frac{1}{\theta} = \frac{k(1-P)^2}{P} [B]_0 \left(\frac{1-P}{R}\right) \qquad \text{(based on Flory's scheme)} \qquad (17')$$

For a catalyzed reaction:

$$\frac{1}{\theta} = \frac{k'[A]_0 (1-P)^2}{P} \qquad \text{(based on Lin's scheme)} \qquad (18)$$

$$\frac{1}{\theta} = \frac{k'[B]_0 (1-P)}{P} \left(\frac{1-P}{R}\right) \qquad \text{(based on Flory's scheme)} \qquad (18')$$

The substitutions of eq. (17) into eqs. (1)–(6) or eq. (17') into the Flory's mechanism, and of eq. (18) into eqs. (9)–(14) or eq. (18') into the Flory's mechanism, lead to the following equations for $[A_n]$ and $[B_n]$ regardless of the two different kinetic schemes, since $[A_n]$ and $[B_n]$ are now expressed in terms of the extent of reaction, P.

When $n = 1$,

$$[A_1] = \frac{[A]_0}{P} \bigg/ \left(\frac{1}{P} + \frac{2}{1-P}\right) \qquad (19)$$

$$[B_1] = \frac{[B]_0}{P} \bigg/ \left(\frac{1}{P} + \frac{2}{R-P}\right) \qquad (20)$$

When $n = 2x$ (even),

$$[A_n] = \frac{\displaystyle\sum_{i=1}^{2x-1} [A_i][B_{n-i}]}{[B](1-P)} \bigg/ \left(\frac{1}{P} + \frac{[B]+[A]}{[B](1-P)}\right) \qquad (21)$$

$$[B_n] = [A_n] \qquad (22)$$

When $n = 2x - 1$ (odd), $n = 3, 5, 7, \cdots$,

$$[A_n] = \frac{2\displaystyle\sum_{i=1}^{x-1} [A_{2i-1}][B_{n-2i+1}]}{[B](1-P)} \bigg/ \left(\frac{1}{P} + \frac{2}{1-P}\right) \qquad (23)$$

$$[B_n] = \frac{2\displaystyle\sum_{i=1}^{x-1} [A_{2i}][B_{n-2i}]}{[B](1-P)} \bigg/ \left(\frac{1}{P} + \frac{2[A]}{(1-P)[B]}\right) \qquad (24)$$

Now, let

$$N_n = \frac{1}{2} \left([A_n] + [B_n]\right)$$

$$N_0 = \frac{1}{2}\left([A]_0 + [B]_0\right) \tag{25}$$

Then the weight fraction and the number average degree of polymerization can be expressed as

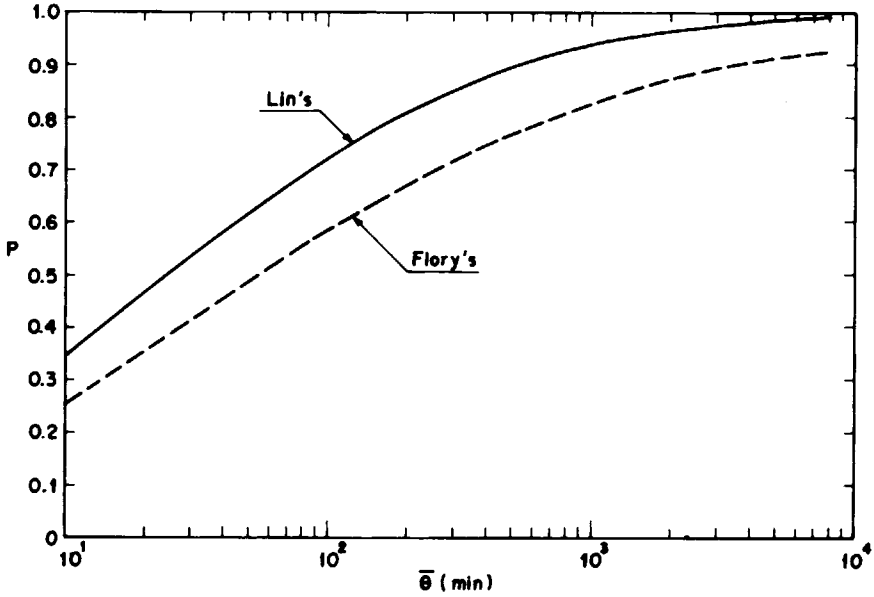$$W_n = \frac{nN_n}{N_0} \tag{26}$$

Fig. 1. Plot of the extent of reaction vs. mean residence time for uncatalyzed polycondensation ($R = 1.6$). (——) Lin's scheme; (- - -) Flory's scheme.
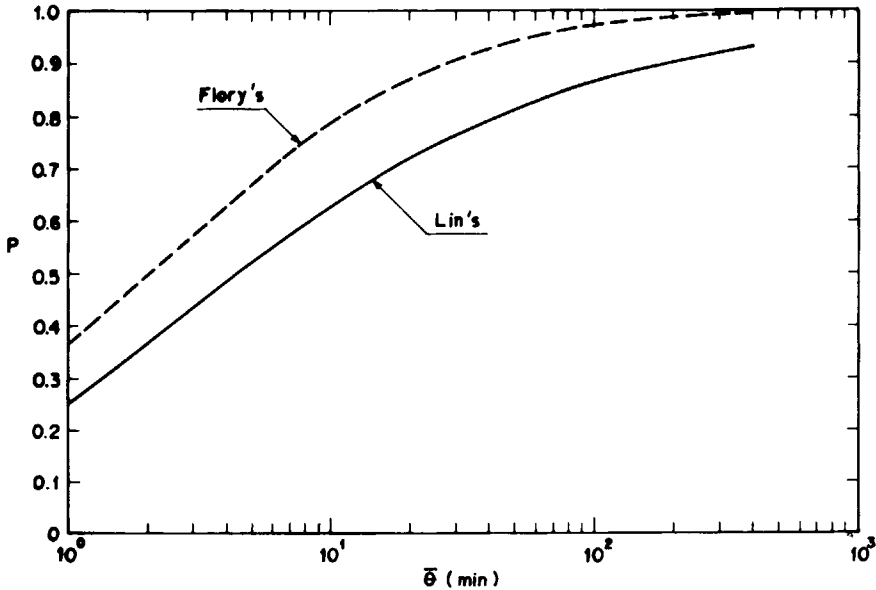

Fig. 2. Plot of the extent of reaction vs. mean residence time for catalyzed polycondensation ($R = 1.6$). (——) Lin's scheme; (- - -) Flory's scheme.
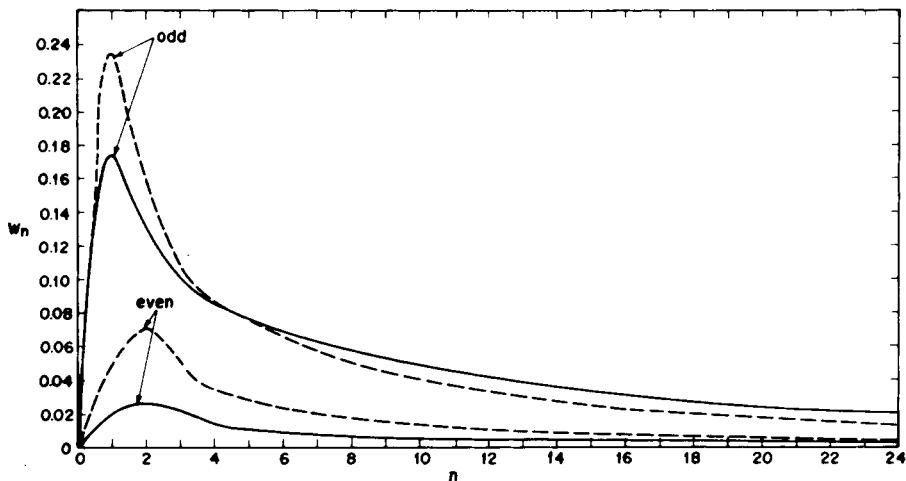
Fig. 3. MWD for uncatalyzed polycondensation ($R = 1.6, \bar{\theta} = 1000$ min). (——) Lin's scheme; (- - -) Flory's scheme.

and

$$\bar{x}_n = \frac{R + 1}{R + 1 - 2P} \tag{27}$$

Similarly, for $\bar{x}_w$

$$\bar{x}_w = \frac{2 \sum\limits_{n=1}^{\infty} n^2 N_n}{[A]_0(1 + R)} \tag{28}$$

Then the polydispersity index is

$$\frac{\bar{x}_w}{\bar{x}_n} = \frac{2 \sum\limits_{n=1}^{\infty} n^2 N_n (R + 1 - 2P)}{[A]_0(1 + R)^2} \tag{29}$$

The above model can now be used to simulate the polycondensation in CSTRs.

RESULTS AND DISCUSSION

The simulation was performed with the succinic acid–ethylene glycol poly-condensation system shown in Table I of our previous paper.[7] Figures 1 and 2 show the calculated examples for the plots of the extent of reaction against the logarithmic mean residence time for uncatalyzed and catalyzed reactions in the CSTRs. The contrast between the two different kinetic schemes is also observed. Moreover, a very long mean residence time is needed to reach a high extent of reaction compared to the batch reactors. It is more serious in the case of un-catalyzed reactions. The reaction proceeds more rapidly by Lin's than by Flory's kinetic scheme in the case of an uncatalyzed reaction. The reaction proceeds more rapidly by Flory's than by Lin's kinetic scheme in the case of the catalyzed reaction scheme. Figures 3 and 4 show that the MWDs in the CSTRs at $\bar{\theta} = 1000$ min for uncatalyzed and $\bar{\theta} = 100$ min for catalyzed reactions, respectively. The
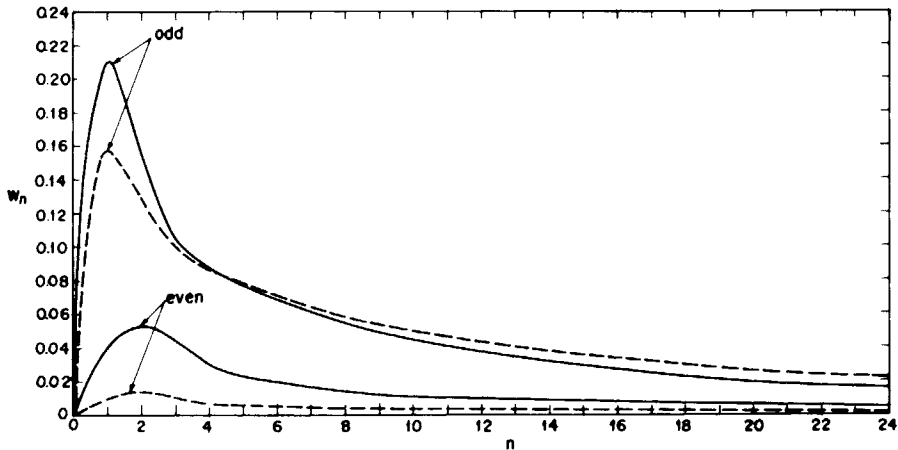
Fig. 4. MWD for catalyzed polycondensation ($R = 1.6, \bar{\theta} = 100$ min). (——) Lin's scheme; (- - -) Flory's scheme.

distribution curves for these kinds of nonequimolecular polycondensations (i.e., $R > 1$) split for odd and even chain lengths regardless of the two different kinetic schemes. Moreover, the MWDs have broad tailing in their shapes when compared with batch reactors. Figures 5 and 6 show the plots of polydispersity indices against logarithmic mean residence time. In general, the polydispersity index including monomer for CSTRs is much higher than that for batch reactors for the same reaction time. In the batch reactors, the polydispersity index has never exceeded 2,[7] but in the CSTRs, it can be as large as 5.
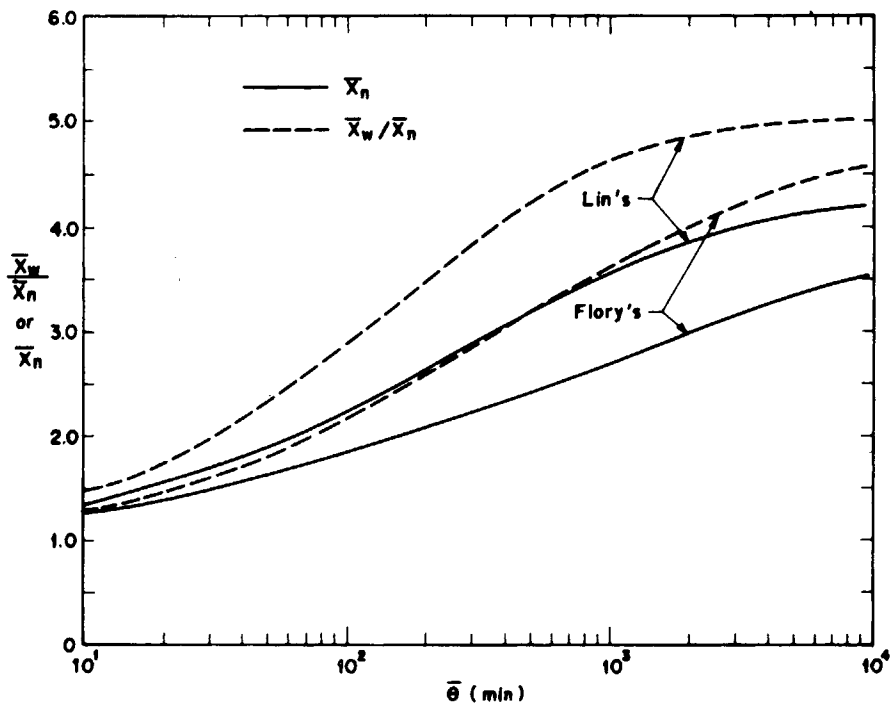

Fig. 5. $\bar{x}_n$ or polydispersity index vs. mean residence time for uncatalyzed polycondensation ($R = 1.6$).
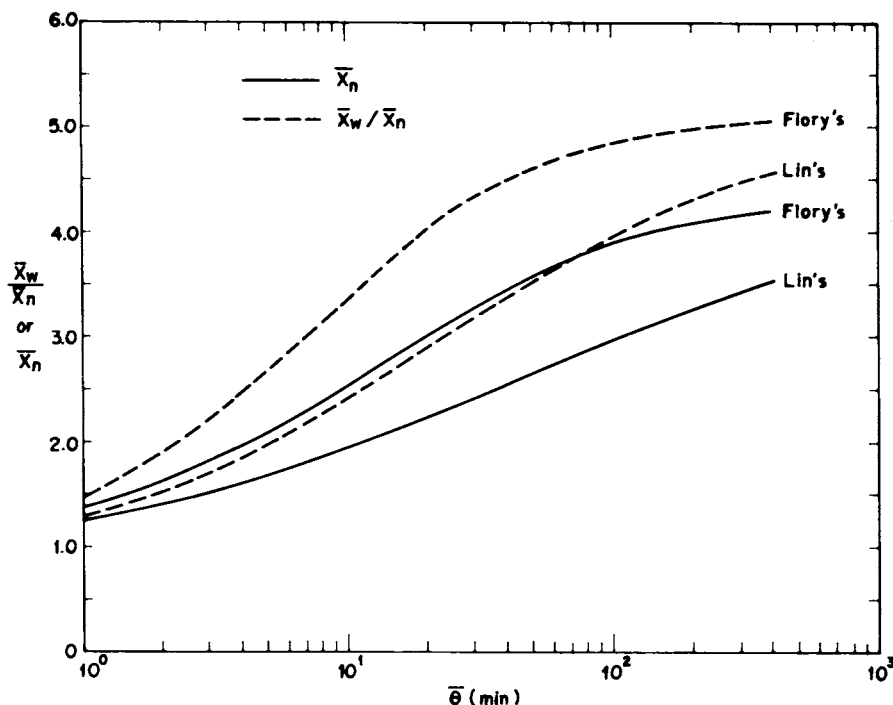
Fig. 6. $\bar{x}_n$ or polydispersity index vs. mean residence time for catalyzed polycondensation ($R = 1.6$).

In conclusion, an extremely long residence time in the CSTRs is necessary to obtain the high conversion accompanying a large polydispersity index when compared with the batch reactors. The polydispersity index at a certain reaction time is always larger by Lin's kinetic scheme than by Flory's for uncatalyzed reactions. In contrast, the value is always larger by Flory's kinetic scheme than by Lin's for catalyzed reactions. The CSTRs are not useful for producing large macromolecules of nonequimolecular polycondensation systems, but they may be applicable for producing reactive oligomers. Network polymers are formed by polymerizing prepolymers or oligomers.

References

1. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, N.Y., 1953.
2. Fred W. Billmeyer, Jr., *Textbook of Polymer Science*, Interscience, New York, 1962.
3. A. Kumar and S. K. Gupta, *Fundamentals of Polymer Science and Engineering*, Tata McGraw-Hill, New Delhi, India, 1978.
4. C. C. Lin and K. H. Hsieh, *J. Appl. Polym. Sci.*, **21**, 2711 (1977).
5. C. C. Lin and P. C. Yu, *J. Polym. Sci., Polym. Chem. Ed.*, **16**, 1005 (1978).
6. C. C. Lin and P. C. Yu, *J. Appl. Polym. Sci.*, **22**, 1797 (1978).
7. C. C. Lin and W. Y. Chiu, *J. Chinese Inst. Chem. Eng.*, **12**, 147 (1981).
8. J. A. Biesenberger, *AIChE J.*, **11**, 369 (1965).
9. S. K. Gupta, A. Kumar, and R. Saraf, *J. Appl. Polym. Sci.*, **25**, 1049 (1980).