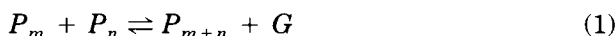# Effect of Reversible and Interchange Reactions on MWD of Condensation Polymers in a CSTR*

K. RAVINDRANATH and R. A. MASHELKAR, *Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune-411 008, India*
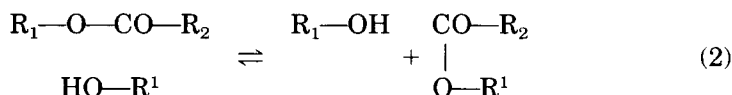
INTRODUCTION

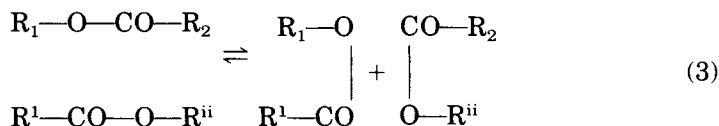Polycondensation reactions are generally represented as

$$P_m + P_n \rightleftharpoons P_{m+n} + G \tag{1}$$

where P_m and P_n are polymer molecules having m and n repeating units and G is the condensation product. The condensation polymer formed through reaction (1) is usually characterized by a distribution of molecular weights. The molecular weight distribution (MWD) depends on the mode of operation of the reactor used, and it is sensitive to the presence of condensation product and to the presence of interchange reactions.[1] In polyesters, two types of interchange reactions are possible,[2] when the chains are terminated only by hydroxyl groups. These are

Intermolecular alcoholysis:

$$
\begin{array}{cc}
R_1\!-\!O\!-\!CO\!-\!R_2 & R_1\!-\!OH \quad CO\!-\!R_2 \\
\rightleftharpoons & + \quad | \\
HO\!-\!R^1 & O\!-\!R^1
\end{array}
\tag{2}
$$

Ester–ester interchange:

$$
\begin{array}{cc}
R_1\!-\!O\!-\!CO\!-\!R_2 & R_1\!-\!O \quad CO\!-\!R_2 \\
\rightleftharpoons & | \; + \; | \\
R^1\!-\!CO\!-\!O\!-\!R^{ii} & R^1\!-\!CO \quad O\!-\!R^{ii}
\end{array}
\tag{3}
$$

Similar type of reactions (e.g., aminolysis and amidolysis) occurs in polyamides,[1] and the analysis given below can be easily applied to polyamides also. For reversible and irreversible condensation reactions, the MWD in a batch reactor is characterized by the most probable distribution generally known as Flory distribution.[3] This is also true in the presence of interchange reactions. Kotliar[4,5] and Ravindranath and Mashelkar[6] examined the process

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of blending of molten PET chips having different molecular weights. Further, Ravindranath and Mashelkar[6] calculated the equilibrium MWD as well as the time required to reach the equilibrium MWD. They showed that, due to interchange and reversible reaction, there is an approach towards the attainment of Flory distribution. It is well known that the condensation polymers prepared in a continuous stirred tank reactor (CSTR) result in a broader MWD than would be obtained in a batch reactor. Kumar et al.[7] showed that interchange reactions play a major role in MWD calculations for CSTR. They showed that if the residence times were to be kept the same in a batch reactor and a CSTR, then the latter gives a lower number average molecular weight as well as lower polydispersity index. However, they did not examine the range of high conversion and high polydispersity index nor did they provide comparison under identical conversion conditions. Kilkson,[8] Biesenberger,[9] and Denbigh[10] found that CSTR gives a higher polydispersity index in comparison to a batch reactor at the same conversion. Szabo and Leathrum[11] developed a model for CSTR taking into account the interchange reactions, but the model results are not provided to ascertain the influence of interchange reactions. The aim of the present work is to fill this important gap that has existed in the literature and examine the influence of reversible and interchange reactions on MWD in a CSTR.

MODEL DEVELOPMENT
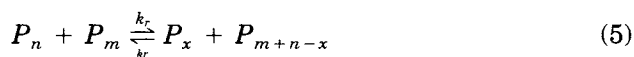
For simplicity, only main reversible polycondensation and intermolecular alcoholysis reaction are considered. It is reported in the open literature[2] that the ester–ester interchange reaction rate (3) is very slow and hence this reaction is excluded:

Polycondensation reaction:

$$P_n + P_m \underset{k'}{\overset{k}{\rightleftharpoons}} P_{n+m} + G \tag{4}$$
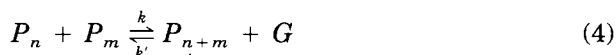
where $m, n = 1, 2, \ldots, \infty$.

Intermolecular alcoholysis:

$$P_n + P_m \underset{kr}{\overset{k_r}{\rightleftharpoons}} P_x + P_{m+n-x} \tag{5}$$

where $m, n = 2, 3, \ldots, \infty$, $x = 1, 2, \ldots, m + n - 1$, $m = 1, n \geq 2$, $n = 1, m \geq 2$. The species balance equations for monomer (P_1) and P_n for a CSTR can be written as

$$P_1 - k\tau\left[-8P_1 \sum_{x=1}^{\infty} P_x + 2A_1 g \sum_{m=2}^{\infty} P_m - 4A_2 P_1 \sum_{x=1}^{\infty} (x-1)P_x \right] = P_1^0 \tag{6}$$

$$P_n - k\tau\left\{ 4\left(\sum_{m=1}^{n-1} P_m P_{n-m} - 2P_n \sum_{x=1}^{\infty} P_x \right) + A_1 g\left[\sum_{m=n+1}^{\infty} 2P_m - (n-1)P_n \right] \right.$$

$$-A_2\left[4P_n\sum_{x=1}^{\infty}(x-1)P_x + 2(n-1)P_n\sum_{x=1}^{\infty}P_x - \sum_{m=1}^{n-1}\sum_{x=1}^{\infty}4P_mP_{n+x-m}\right]\Bigg\} = P_n^0$$

$$n \geq 2 \tag{7}$$

where $A_1 = k'/k$ and $A_2 = k_r/k$. τ is the residence time. P_1^0 and P_n^0 are the concentrations of the species P_1 and P_n in the feed, respectively. Solving the mass balance equations for each species $(P_n, n = 1, 2, \ldots, \infty)$ is cumbersome. Since polymer properties are sensitive to the moments of the distribution, the species balance equations were transformed into moment balance equations. By definition, the zeroth, first, and second moments of the reaction mixture are given as

$$\bar{\bar{P}}^0 = \sum_{n=1}^{\infty}P_n, \qquad \bar{\bar{P}}^1 = \sum_{n=1}^{\infty}nP_n, \qquad \bar{\bar{P}}^2 = \sum_{n=1}^{\infty}n^2P_n \tag{8}$$

Using eq. (8), the moment balance equations can be obtained from eqs. (6) and (7). These are as follows:

$$\bar{\bar{P}}^0 - k\tau\left\{-4(\bar{\bar{P}}^0)^2 + 4A_1g(\bar{\bar{P}}^1 - \bar{\bar{P}}^0)\right\} = \bar{\bar{P}}_0^0 \tag{9}$$

$$\bar{\bar{P}}^1 = \bar{\bar{P}}_0^1 \tag{10}$$

$$\bar{\bar{P}}^2 - k\tau\{8(\bar{\bar{P}}^1)^2 - \tfrac{4}{3}(A_1g + A_2\bar{\bar{P}}^0)(\bar{\bar{P}}^3 - \bar{\bar{P}}^1) + 4A_2\bar{\bar{P}}^1(\bar{\bar{P}}^2 - \bar{\bar{P}}^1)\} = \bar{\bar{P}}_0^2 \tag{11}$$

Here $\bar{\bar{P}}_0^0$, $\bar{\bar{P}}_0^1$, and $\bar{\bar{P}}_0^2$ represent the zeroth, first, and second moments of the feed.

Equation (11) contains third moment terms, showing the coupled nature of the equations. Assuming that Schultz–Zimm distribution is valid, the third moment can be calculated from the knowledge of the zeroth, first, and second moments as shown in[12]

$$\bar{\bar{P}}^3 = \bar{\bar{P}}^2\frac{2\bar{\bar{P}}^2\bar{\bar{P}}^0 - (\bar{\bar{P}}^1)^2}{\bar{\bar{P}}^1\bar{\bar{P}}^0} \tag{12}$$

This approximation is helpful in reducing considerably the mathematical complexity. Please note that Schultz–Zimm distribution is not a good approximation at low fraction of end groups (viz., number average molecular weight is very low). The pertinent averages are given by

$$\frac{x_w}{x_n} = \frac{\bar{\bar{P}}^2\bar{\bar{P}}^0}{(\bar{\bar{P}}^1)^2}, \qquad \frac{x_z}{x_n} = \frac{\bar{\bar{P}}^3\bar{\bar{P}}^0}{\bar{\bar{P}}^2\bar{\bar{P}}^1} \tag{13}$$

where x_n, x_w, and x_z are number average, weight average, and z-average molecular weights. Equations (9)–(13) were solved to obtain x_w/x_n, x_z/x_n as a function of conversion for a set of kinetic parameters. The results are

obtained using the following feed specifications written for the feed containing only monomer:

$$\bar{\bar{P}}_0^0/\bar{\bar{P}}_0^1 = 1, \qquad \bar{\bar{P}}_0^2/\bar{\bar{P}}_0^1 = 1 \tag{14}$$

The concentration of the condensation product ($g^* = g/\bar{\bar{P}}_0^1$) in the reaction mixture depends on the vapor pressure of the condensation product and on the reactor pressure. Therefore, a set of values are used in this work. When very high vacuum is applied, the concentration of the condensation product will be negligible (viz., $g^* = 0$).

RESULTS AND DISCUSSION

To facilitate easy comparison of the calculated performance of a CSTR with that of a batch reactor, the results were obtained as a function of the fractional conversion of the end groups rather than time. This provides a rational basis for comparison. Figure 1 shows the influence of interchange and reversible reactions on x_w/x_n and x_z/x_n. When the MWD is broader (which is true for the condensation polymers prepared in CSTR), the polydispersity
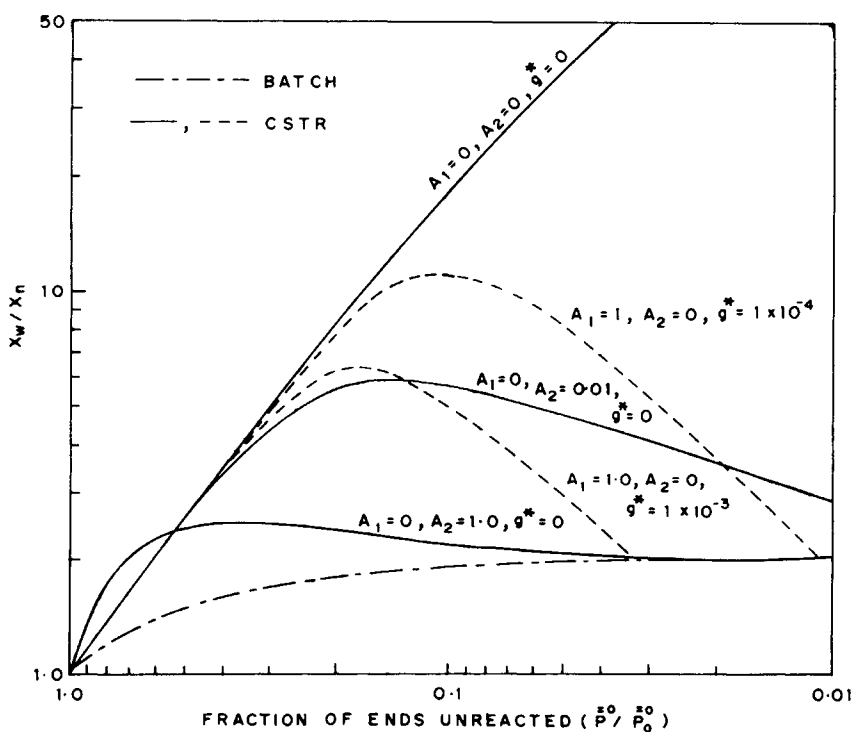

Fig. 1. Effect of interchange (——) and reversible (---) reactions on x_w/x_n in CSTR.

index (x_w/x_n) is very high as shown in Figure 1. In the presence of interchange and reversible reactions, x_w/x_n increases first and then decreases with an increase in conversion. For comparison, the batch reactor results are also shown in Figure 1. At very high conversion, x_w/x_n approaches 2 (please note that, for Flory distribution, x_w/x_n approaches 2). In the presence of reversible reactions, the time required for a fixed conversion will be longer, and, depending on the concentration of volatile products (in the present case G), the final percentage conversion that can be obtained in a CSTR is also fixed (see Fig. 1). At very low conversions, interchange reactions cause an increase in the polydispersity index. Similarly, interchange and reversible reactions help in reducing the x_z/x_n and it finally approaches a value of 3 (the same as in the case of a batch reactor).

CONCLUSIONS

In the foregoing, we have examined the influence of reversible and interchange reactions on MWD of condensation polymers prepared in a CSTR. Our analysis shows that, in the presence of reversible and interchange reactions, the polydispersity decreases and at high conversions the polydispersity index approaches that obtainable in a batch reactor. Our analysis shows the usefulness of a CSTR for preparing condensation polymers having low polydispersity index.

APPENDIX: NOTATION

A_1	k'/k
A_2	k_r/k
g	concentration of the condensation product
g^*	$g/\bar{P}_0^1$
k	polycondensation rate constant
k'	reversible polycondensation reaction rate constant
k_r	intermolecular alcoholysis reaction rate constant
P_n	concentration of polymer molecules having n repeating units
P_n^0	initial concentration of polymer molecules having n repeating units
$\bar{P}^0, \bar{P}^1, \bar{P}^2$	zeroth, first, and second moments as defined in eq. (8) (subscript zero indicates moments of the feed).
x_w/x_n	polydispersity index
x_n, x_w, x_z	number average, weight average, and z-average molecular weights
τ	residence time

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