Condensation Polymerizations in Ideal Continuous-Flow-Stirred Tank Reactors of Monomers Violating the Equal Reactivity Hypothesis

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Synopsis

Molecular weight distributions, moments, and the polydispersity indices were computed for AB-type condensation polymerization in an ideal continuous-flow-stirred tank reactor for monomers not following the equal reactivity hypothesis. The model considers the rate of reaction between monomer and monomer to be R times that characterizing the reaction between any other species in the reaction mass. It is found that the polydispersity indices in these reactors are substantially larger than values obtained in batch reactors. Also, the molecular weight distribution splits into two curves—one for odd-order homologs and the other for even-order ones for $R > 1$. For $R < 1$, substantial amounts of unreacted monomer are present in the exit stream, and curve splitting does not occur.

INTRODUCTION

Studies on molecular weight distributions (MWD) for condensation polymerizations in batch reactors assuming the equal reactivity hypothesis exist in the literature.[1,2] However, these studies are extremely idealized because there are several systems of practical interest that do not obey the equal reactivity hypothesis. For example, in the polymerization of phenylene sulfide, the monomer reacts at a lower rate than its higher oligomers, which all react at equal rates.[3] Similar violation of the equal reactivity hypothesis has been observed in the formation of poly(ethylene terephthalate) by the ester interchange mechanism,[4–6] in the formation of polyimides[7] and polyurethanes,[8,9] the condensation of divinylbenzene and *p*-cresol,[10] and the polymerization of phenol formaldehyde.[11,12]

Theoretical modeling of the rates of polymerization and MWDs for such systems has received very little attention. Nanda et al.[13] assumed a linear dependence of the rate constant with the degree of polymerization and obtained the MWD and its first two moments analytically. Gandhi et al.[14] studied the condensation of two bifunctional monomers, one symmetric and one asymmetric, with the latter having functional groups of different reactivities. Miller and Macosko[15] obtained average molecular weights and other average properties for network condensation polymerization with unequal reactivities, using a probabilistic approach. Gupta, Kumar, and co-workers[16–18] studied two idealized,

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limiting models (each associated with two rate constants) for the polymerization of AB-type monomers in batch reactors: in model I, the monomer P_1 reacts with P_1 at a rate which is R times that associated with all the other reactions occurring in the system; and in model II, P_1 reacts with *all* the species in the reaction mass at a rate which is R times that characterizing the reaction between the higher homologs.

Very little has been reported on the simulation of condensation polymerizations in ideal continuous-flow-stirred tank reactors (CSTRs),[19] in spite of its industrial and theoretical importance. Biesenberger[20] obtained the MWD and the polydispersity index for condensation polymerizations characterized by the equal reactivity hypothesis and found substantially higher polydispersity indices in the ideal CSTR as compared to the batch reactor. Hicks et al.[21] studied the polymerization of these monomers in sequences of ideal CSTRs at different temperatures and obtained an optimal control policy. Laurence et al.[22] simulated the more complex polymerization of caprolactam in sequences of ideal CSTRs. In this system, both addition and condensation reactions occur. More recently, Gandhi et al.[23] obtained average molecular weights and polydispersity indices for their model of condensation polymerization of a symmetric and an asymmetric monomer in CSTRs.

In this paper, MWDs and moments have been obtained for the polymerization in ideal CSTRs of AB-type monomers characterized by two rate constants (model I[16,17] as already discussed). The distribution curves for $R > 1$ are found to split for odd and even chain lengths. The polydispersity index excluding monomer for CSTRs is much higher than that for batch reactors for the same reaction time.

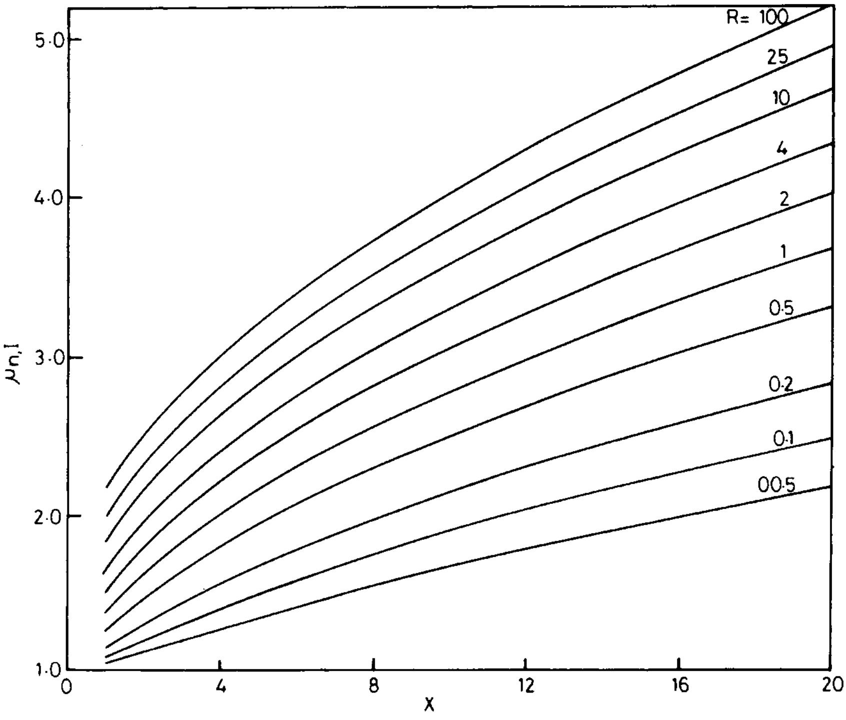

Fig. 1. $\mu_{n,I}$ vs. X for different values of R.

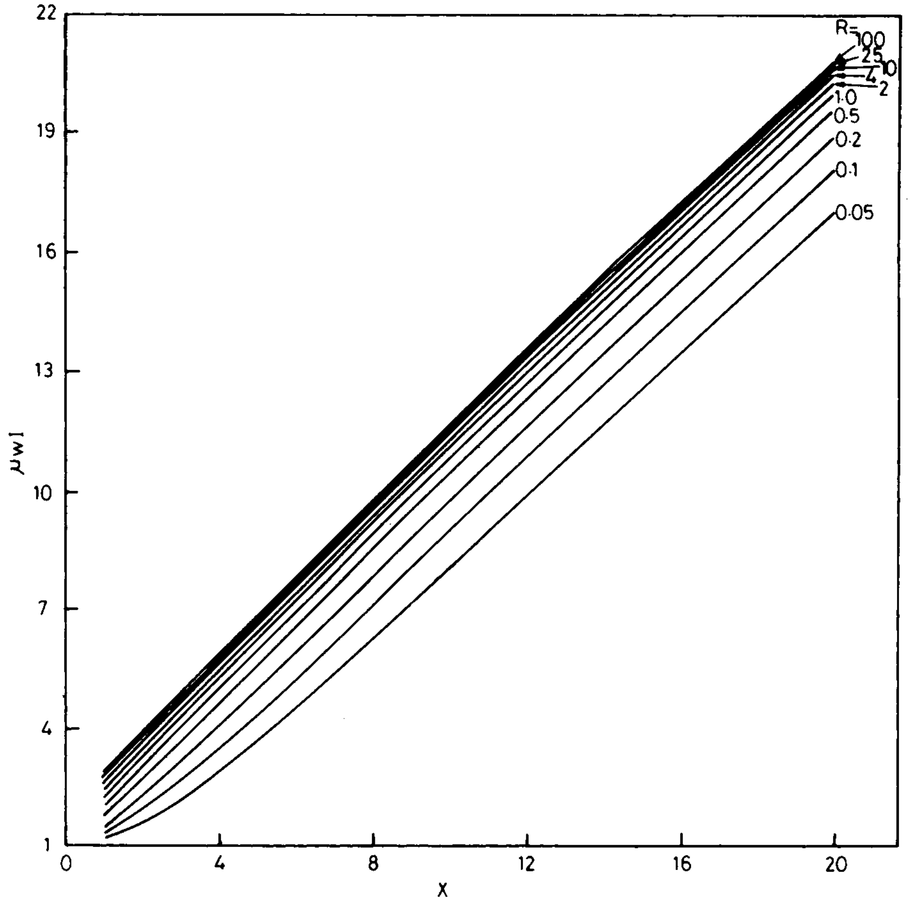

Fig. 2. $\mu_{w,I}$ vs. X for different values of R.

FORMULATION

The kinetic scheme for model I[16,17] is as follows:

$$P_m + P_n \xrightarrow{k_{p,mn}} P_{m+n} + \text{condensation product} \qquad (1)$$

where P_m is a bifunctional A-B type molecule having m repeat units. The rate constant $k_{p,mn}$ is modeled as

$$\begin{aligned} k_{p,11} &= k_{11}/2 \\ k_{p,mn} &= k_p \qquad m \neq n; \quad m,n = 1,2,\ldots \\ &= k_p/2 \qquad m = n; \quad m,n > 1 \end{aligned} \qquad (2)$$

Equation (2) represents the assumption that the rate of reaction between P_1 and P_n is controlled primarily by P_n rather than by P_1. The introduction of a factor of 1/2 for the reaction between similar molecules is necessary in order to give the correct collision frequency.[2] It may be emphasized that the rate constants k_{11} and k_p used in this work characterize the reaction between *molecular species* and are twice the rate constants which characterize the reaction between *functional groups* (as reported, for example, in Flory[1]).

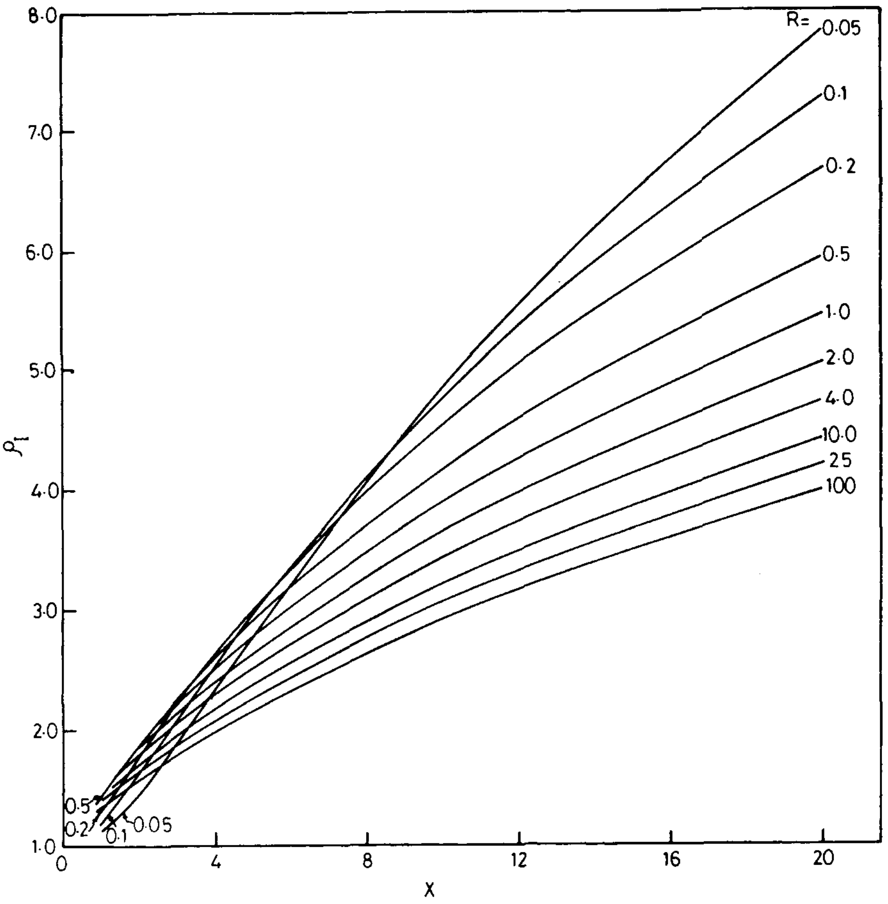

Fig. 3. ρ_I vs. X for different values of R.

Mass balance equations for the ideal CSTR with feed of pure monomer (having concentration $[P_1]_0$) are obtained using the kinetic scheme of eqs. (1) and (2) as

$$\frac{[P_1]_0 - [P_1]}{\theta} = [P_1]^2(k_{11} - k_p) + k_p[P_1][P] \tag{3a}$$

$$-\frac{[P_2]}{\theta} = k_p[P_2][P] - \frac{k_{11}}{2}[P_1]^2 \tag{3b}$$

$$-\frac{[P_n]}{\theta} = k_p[P_n][P] - \frac{k_p}{2}\sum_{m=1}^{n-1}[P_m][P_{n-m}] \qquad n = 3,4,\ldots \tag{3c}$$

where $[P_n]$ represents the molar concentration of molecular species P_n in the well-stirred reactor (which is identical to that in the product stream), $[P]$ is the sum of all $[P_n]$s for n going from 1 to ∞, and θ is the mean residence time (= volume of the contents of the reactor divided by the input or output flow rate). The above equations can easily be rewritten in terms of the following variables[17,18]:

$$Z_n = [P_n]/[P_1]_0 \tag{4a}$$

$$Y = [P]/[P_1]_0 = \sum_{n=1}^{\infty} Z_n \tag{4b}$$

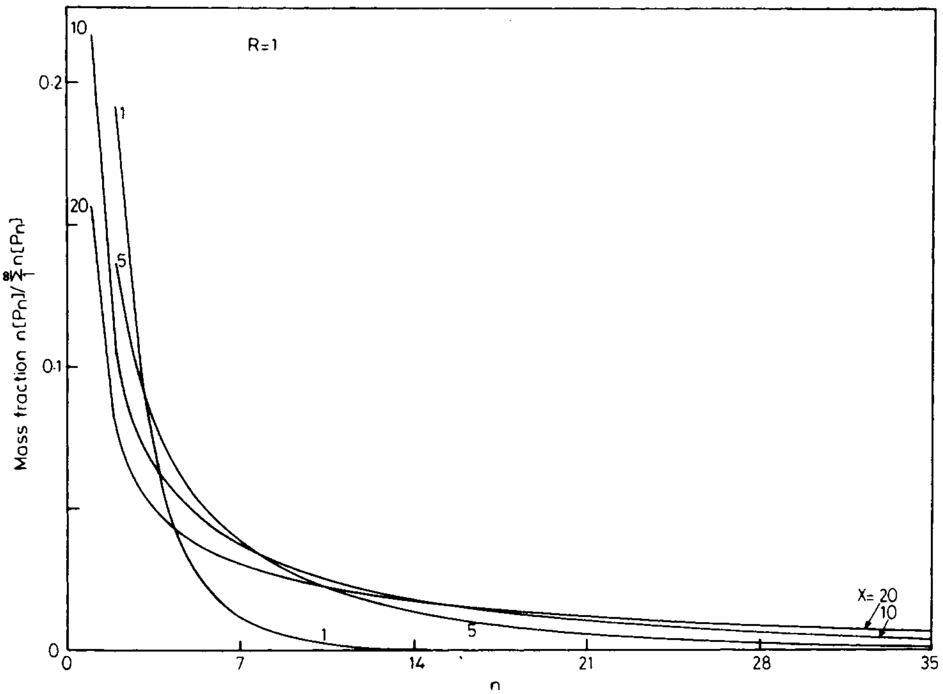

Fig. 4. MWD for $R = 1$. Values of X indicated for each curve.

$$X = k_p[P_1]_0\,\theta \tag{4c}$$

$$R = k_{11}/k_p \tag{4d}$$

In eq. (4), Z_n represents the dimensionless ratio of the concentration of P_n in the reactor to the concentration of the monomer in the feed stream, Y represents the ratio of the concentration of functional groups A or B in the reactor (since $[-A] = \Sigma_{n=1}^{\infty}[P_n] = [-B]$) to the monomer concentration in the feed, X is a dimensionless residence time, and R represents the relative reactivity of P_1 and P_1, with respect to the reactivities of the other molecular species. After some simple mathematical manipulations, eqs. (3) and (4) yield finally

$$Y = \left[(1 - R)Z_1^2 + \frac{1 - Z_1}{X}\right] \Big/ Z_1 \tag{5a}$$

$$0 = (R - 1)\,Z_1^2 + \frac{2(Y - 1)}{X} + Y^2 \tag{5b}$$

$$Z_2 = \frac{1}{2} R Z_1^2 \Big/ \left(\frac{1}{X} + Y\right) \tag{5c}$$

$$Z_n = \frac{1}{2}\sum_{m=1}^{n-1} (Z_m\, Z_{n-m}) \Big/ \left(\frac{1}{X} + Y\right) \qquad n = 3,4,\ldots \tag{5d}$$

Equations (5a) and (5b) are coupled algebraic equations and must be solved simultaneously to give Z_1 and Y for given values of X and R. Thereafter, one can sequentially solve for Z_2, Z_3, ... etc., to obtain the molecular weight distributions for different values of X and R.

The computations have been performed on a DEC 1090 computer for several

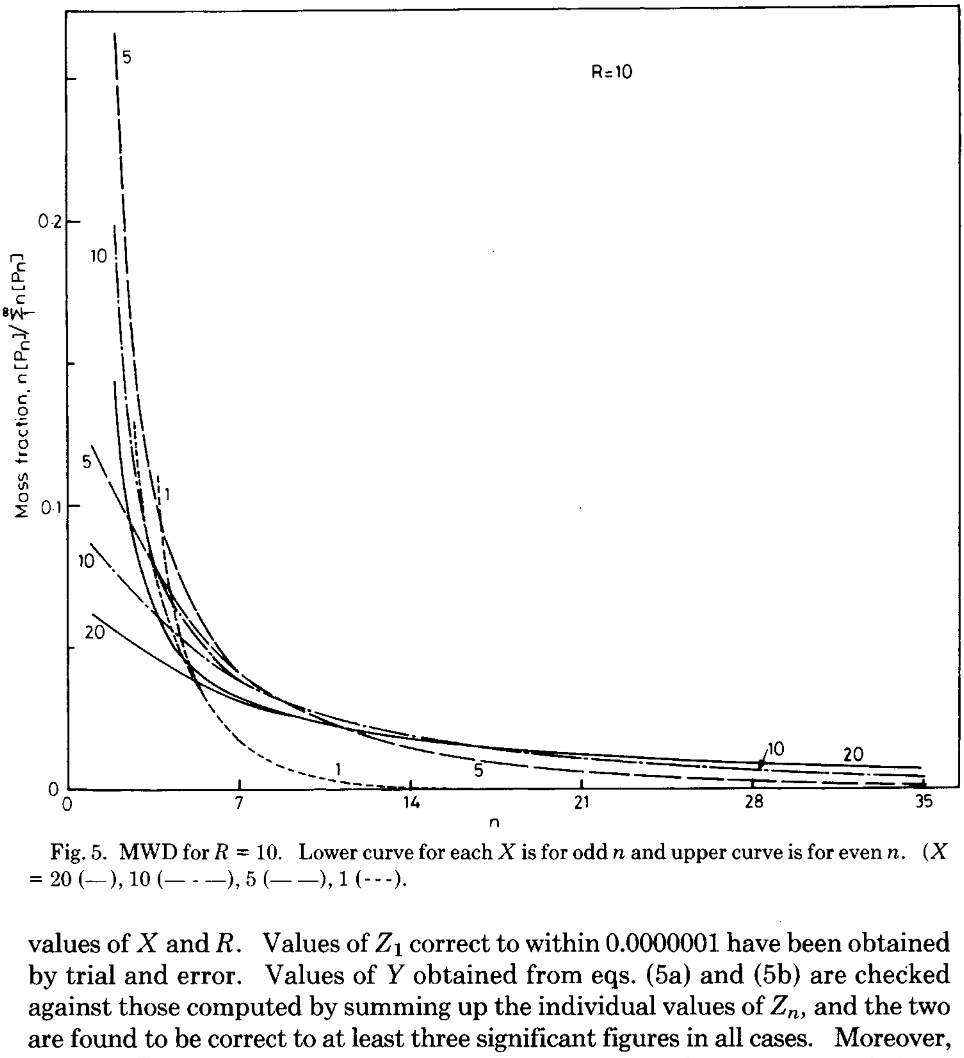

Fig. 5. MWD for $R = 10$. Lower curve for each X is for odd n and upper curve is for even n. (X = 20 (—), 10 (— - —), 5 (— —), 1 (- - -).

values of X and R. Values of Z_1 correct to within 0.0000001 have been obtained by trial and error. Values of Y obtained from eqs. (5a) and (5b) are checked against those computed by summing up the individual values of Z_n, and the two are found to be correct to at least three significant figures in all cases. Moreover, values of $\Sigma_1^\infty (nZ_n)$ obtained by summing up the computed Z_n appropriately have been found to be 0.994 for the worst case and close to 0.9999 in most cases. The moments and polydispersity index were obtained thereafter by appropriate summations of Z_n.

RESULTS AND DISCUSSION

Figures 1–3 show $\mu_{n,I}$, $\mu_{w,I}$, and ρ_I, respectively (the number- and weight-average chain lengths and the polydispersity index; subscript I signifies that the monomer is included in the computation of the moments) as functions of the dimensionless residence time X, with R as a parameter. The general features are similar to the results obtained for batch reactors.[16,17] However, much lower values of $\mu_{n,I}$ are observed for the CSTR as compared to the batch reactor for the same dimensionless times. This is consistent with the fact that in CSTRs the reactions occur at concentrations corresponding to exit conditions, whereas in batch reactions they occur at (usually higher) concentrations which change

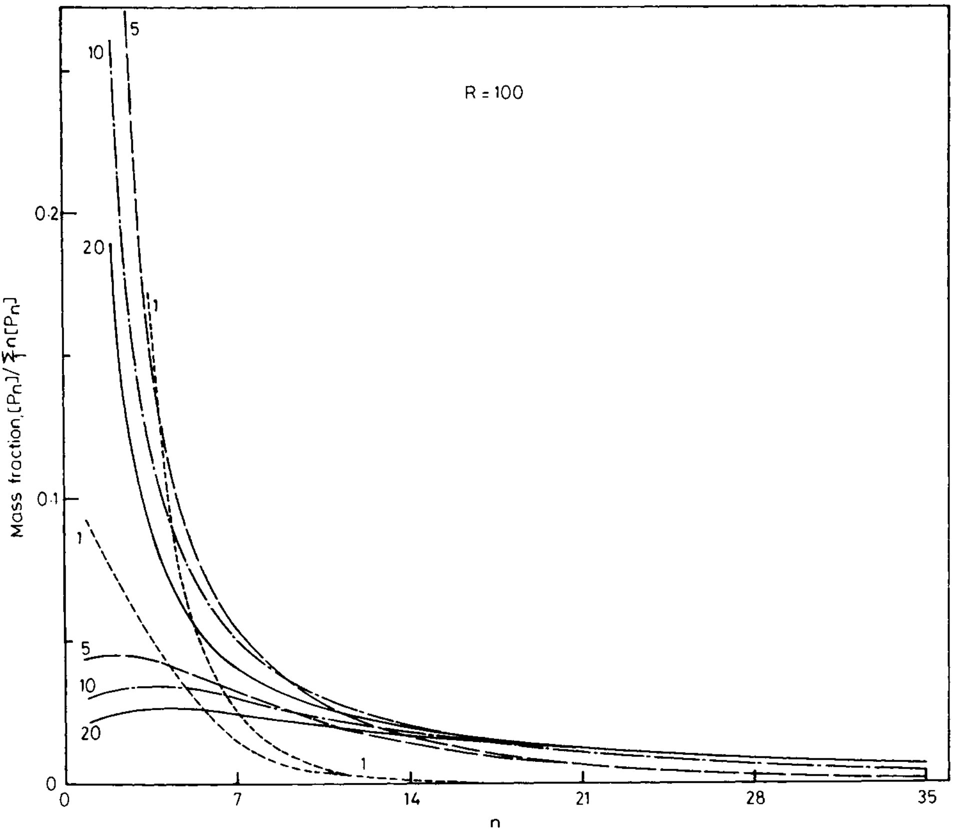

Fig. 6. MWD for $R = 100$. Lower curve for each X is for odd n and upper curve is for even n. See Fig. 5 for legend.

with time. What is surprising, however, is the fact that values of $\mu_{w,I}$ for corresponding values of X are similar for both batch reactors and CSTRs. This suggests that the polydispersity index will be substantially higher in a CSTR, a fact borne out by Figure 3 when compared with batch results.[17] It may be emphasized here that the values of ρ_I are far beyond the value of 2 characterizing batch condensation polymerizations of monomers following the equal reactivity hypothesis. If the monomer is excluded from computations[16–18,24] (designated by subscript II), plots of ρ_{II} vs. X for different Rs do not show any intersections, as was observed for batch polymerization.

Figures 4–6 show the MWD for different values of the dimensionless time X for three values of R, namely, 1, 10, and 100. It may be noted that the curves in Figure 4 ($R = 1$, i.e., with the equal reactivity hypothesis valid) are characterized by a continuous fall in the mass fraction with increasing n, in contrast to the most probable distributions of Flory obtained in batch reactors. Results for $R = 1$ are similar to those reported by Biesenberger.[20] Another important point to be noted in Figure 4 is the large amount of unreacted monomer present, compared to corresponding values for batch reactors.[16] For $R = 10$ and 100, as was found in the case of batch reactors,[16] the MWD curves split into two, the lower one for odd-order homologs and the upper one for the even-order homologs. The separation between the odd-n and even-n curves decreases with increasing

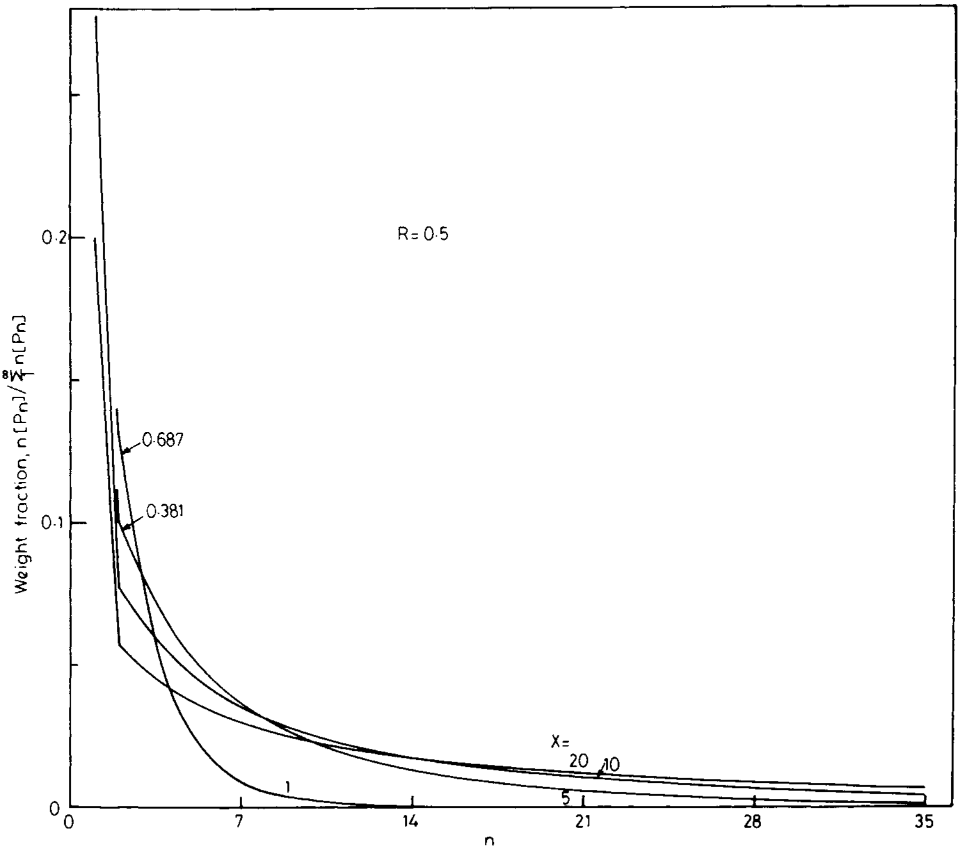

Fig. 7. MWD for $R = 0.5$. Numbers marked on graphs are mass fractions of monomer.

time for a given R. Also, for a given R, the merger of the odd-n and even-n curves occurs at higher and higher values of n as X increases. As R becomes larger, the split in the curves persists till higher values of n. This phenomenon is explained

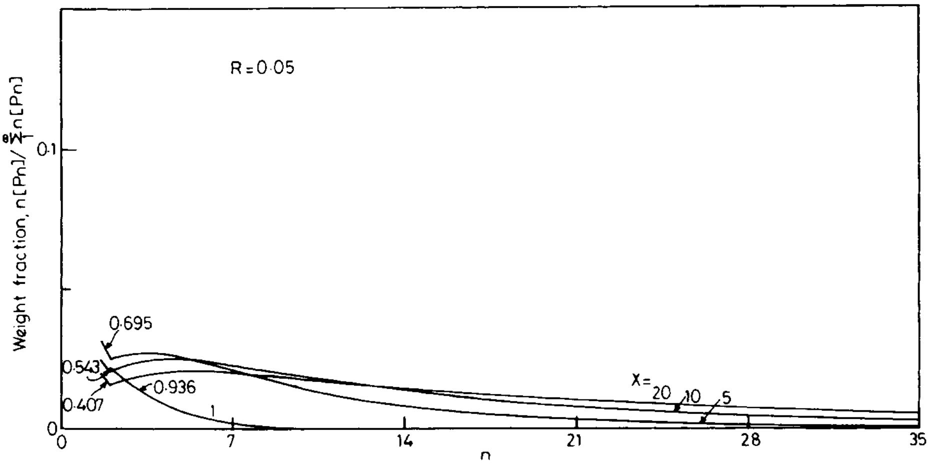

Fig. 8. MWD for $R = 0.05$. Numbers indicated are mass fractions of monomer.

physically as follows. As the value of R increases, the monomer gets depleted faster to form the dimer. However, the dimer does not find sufficient amount of the monomer and tends to react with the already formed dimer, so that more of the four-mer is formed than the trimer. This phenomenon continues and odd-mers are present in lower concentrations compared to even-mers.

Figures 7 and 8 show the MWD for values of R of 0.5 and 0.05, respectively. No split is observed in these plots. The shapes of the curves for $n > 2, R = 0.5$ are similar to those for $R = 1$; however, there is an excess of unreacted monomer in the output stream. For $R = 0.05$, in addition to the excess of monomer present, a shallow "hump" appears in the MWD, a phenomenon which is not observed at higher values of R.

CONCLUSIONS

MWD and moments for a two-parameter AB-type condensation polymerization in ideal CSTRs have been studied. For the reactivity ratio $R > 1$, the MWDs are found to split into two curves corresponding to odd and even values of n, as observed for the case of batch reactors. For $R < 1$, substantial amounts of unreacted monomer are found and a better index of the polydispersity would be the one in which the monomer is excluded from computations. Even though the weight-average chain lengths are similar to values obtained at corresponding values of X in batch reactors, the number-average chain lengths, however, are substantially lower, and polydispersity indices are correspondingly much higher in CSTRs.

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