Condensation polymerization of ARB type monomers in CSTRs wherein the monomer is *R* times more reactive than other homologues

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Molecular weight distributions (*MWD*s) and their moments for the polycondensations of ARB-type monomers which do not obey the equal reactivity hypothesis, in ideal continuous-flow stirred tank reactors (CSTRs), have been studied. The model assumes that monomers react with monomers and higher homologues at a rate which is *R* times that of all other reactions in the system. It is found that the polydispersity indices are much higher than for the batch reactor. The *MWD* has been found to split into two curves, one for even-ordered homologues and one for odd-ordered ones. For $R < 1$, these curves merge for higher homologues, whereas for $R > 1$, firstly there is a fall in the mass fraction from monomer to the dimer, then a rise to a broad maxima after which they decay slowly. Results are also compared with those for a different kinetic scheme in which the monomer reacts *only* with a monomer at a rate *R* times that characterizing all other species.

INTRODUCTION

Several studies of the rate of polymerization and the *MWD* of condensation polymerizations have been formulated using the equal reactivity hypothesis[1,2]. However, there are several important systems for which monomers do not follow this hypothesis. Examples include the polymerizations of poly(phenylene sulphide)[3], poly(ethylene terephthalate)[4–6], polyimides[7], polyurethanes[8], phenol–formaldehyde[9,10], and the condensation of divinylbenzene with *p*-cresol[11].

Theoretical modelling of the rate of polymerization and *MWD* for systems violating the equal reactivity hypothesis has received attention in the literature[12–23]. In our earlier work, we proposed the following two models to account for unequal reactivity[20–22]:

(a) when monomer reacts with monomer at a different rate compared with other homologues in the reaction mass (model 1);

(b) when the monomer reacts with all the species at a different rate compared with the reaction rate among the latter (model 2).

Results for batch reactors were investigated for these models[20–22].

Studies of polycondensations in ideal, continuous-flow stirred tank reactors (CSTRs) have received less attention, in spite of their theoretical and industrial importance[24–28].

In our previous paper[28], CSTR results for model 1 were presented. In this paper a similar study is made for model 2. Basic equations have been established and solved using the computer. The *MWDs* are found to split for odd and even *n* with subsequent asymptotic merger at high values of *n*. Polydispersity indices have been calculated and are found to be much larger than those for batch reactors.

FORMULATION

Polycondensation reactions for bifunctional monomers can be represented schematically by the following infinite set of reactions:

$$P_m + P_n \xrightarrow{k_{p,mn}} P_{m+n} + \text{Condensation product}$$

$$m, n = 1, 2, 3, \ldots \tag{1}$$

with P_m representing the *m*th oligomer. $k_{p,mn}$ has been modelled[22] in terms of two parameters, k_{11} and k_p, to simplify study of such reactions as:

$$\begin{aligned} k_{p,11} &= k_{11}/2 & & \\ k_{p,1n} &= k_{11} & & n = 2, 3 \\ k_{p,mn} &= k_p = k_p & & m \neq n;\ m, n > 1 \\ &= k_p/2 & & m = n;\ m > 1 \end{aligned} \tag{2}$$

In equation (2), the factor of one-half for reactions between two identical molecules has been included to prevent counting of molecular collisions twice[2]. Equation (2) represents the assumption that $k_{p,1n}$ is governed primarily by the monomer which has intrinsic reactivity, k_{11}, different from that of higher monomers.

Mass balance equations for an ideal CSTR can be written, assuming a feed of pure monomer having molar concentration $[P_1]_0$:

$$\frac{[P_1] - [P_1]_0}{\theta} = -k_{11}[P_1][P] \tag{3a}$$

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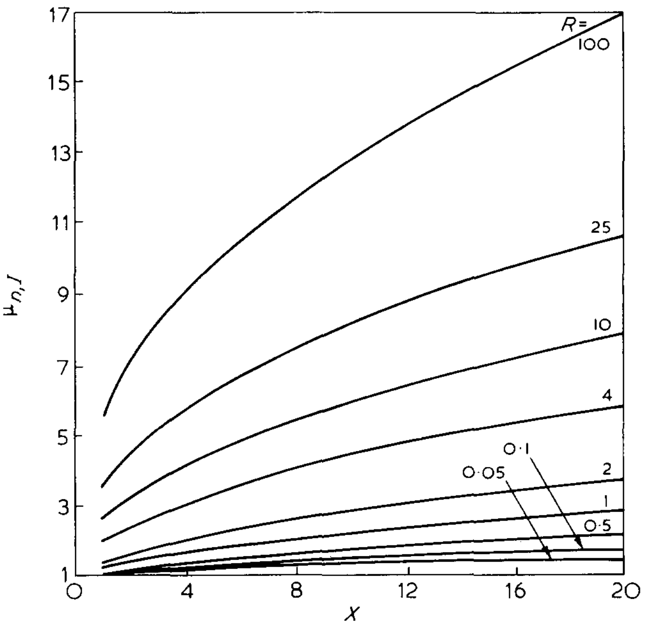

Figure 1 $\mu_{n,I}$ vs X for different R

$$\frac{[P_2]}{\theta}=\frac{1}{2}k_{11}[P_1]^2-(k_{11}-k_p)[P_1][P_2]-k_p[P_2][P] \tag{3b}$$

$$\frac{[P_n]}{\theta}=(k_{11}-k_p)[P_1][P_{n-1}]-(k_{11}-k_p)[P_1][P_n]+\frac{1}{2}k_p\sum_{m=1}^{n-1}[P_m][P_{n-m}]-k_p[P_n][P]; \quad n=3,4,\ldots \tag{3c}$$

$$\frac{[P]-[P_1]_0}{\theta}=\frac{[P_1]+[P_2]+\ldots-[P_1]_0}{\theta}=\tfrac{1}{2}(k_{11}-k_p)[P_1]^2-\tfrac{1}{2}k_p[P]^2-(k_{11}-k_p)[P_1][P] \tag{3d}$$

where the square brackets represent molar concentrations in the exit stream (this is equal to that present inside the ideal CSTR), and θ is the average residence time in the reactor (= volume of reactor contents/flow rate in or out). Equation (3d) has been obtained by summing equations (3a), (3b) and (3c) for all values of n.

Equation (3) may be rewritten in terms of the following dimensionless variables[20-22]:

$$X=k_p[P_1]_0\theta$$

$$Z_n=[P_n]/[P_1]_0; \quad n=1,2,\ldots$$

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

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

to give the following set of coupled algebraic equations to be solved:

$$Z_1-1=-RXYZ_1 \tag{5a}$$

$$Z_2=\tfrac{1}{2}RXZ_1^2-(R-1)XZ_1Z_2-XZ_2Y \tag{5b}$$

$$Z_n=(R-1)XZ_1(Z_{n-1}-Z_n)+\tfrac{1}{2}X\sum_{m=1}^{n-1}Z_mZ_{n-m}-XZ_nY; \quad n=3,4,\ldots \tag{5c}$$

$$Y-1=\tfrac{1}{2}(R-1)XZ_1^2-\tfrac{1}{2}XY^2-(R-1)XZ_1Y \tag{5d}$$

For any R and X, equations (5a) and (5d) must first be solved simultaneously to give Z_1 and Y, and then equations (5b) and (5c) can be solved sequentially to give Z_2, Z_3, Z_4, ..., in that order. These computations have been carried out on a DEC 1090 computer. The solution of Z_1 and Y has been obtained by trial and error involving an assumption of the value of Z_1, computation of Y from equation (5a) and a check of whether equation (5d) is satisfied. Values of Z_1 are then changed by a small increment, which is halved when necessary. The trial and error computations are stopped when Z_1 is within 10^{-7} of the actual solution and Z_2, Z_3, etc. are obtained. Thereafter, the number and weight average chain lengths, $\mu_{n,I}$ and $\mu_{w,I}$ (subscripts I indicates that the monomer is included in the computation of these moments) and the polydispersity index, ρ_I, are computed[20-22].

Two checks are made on the computer program. The first one is to generate results for $R=1$ and compare them with the results of Biesenberger[24]. This was found very satisfactory. The other check was to see how close

$$\sum_{n=1}^{\infty}nZ_n$$

is to the theoretical value of unity and how close

$$\sum_{n=1}^{\infty}Z_n$$

is to the value of Y computed from equation (5d). The former summation was 0.986 in the worst case, and was better than 0.995 in most cases. The latter summation matched with Y at least up to three significant figures.

RESULTS AND DISCUSSION

Figures 1–3 show plots of $\mu_{n,I}$, $\mu_{w,I}$ and ρ_I as functions of X, with the reactivity ratio, R, as a parameter. The larger the value of R, the higher is the conversion ($\equiv 1-\mu_{n,I}^{-1}$) of the functional groups, the number average and the weight-average chain length. When compared to results for a batch reactor[22], it is observed that the spread between the curves for $R>1$ is substantially higher in the CSTR and the spread for $R<1$, lower than in the batch reactor. In fact, in the batch reactor, there is very little difference in the plots for $\mu_{n,I}$ vs. X between $R=25$ and 100, after the initial stages of reaction. This is because in a batch reactor, the rate changes continually with time as the reaction proceeds and, after some time, there is negligible mo-

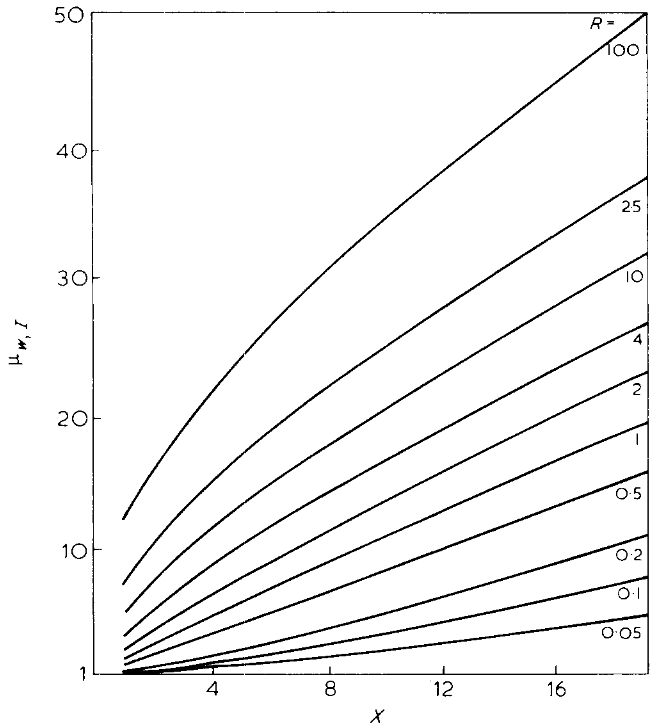

Figure 2 $\mu_{w,I}$ vs X for different R

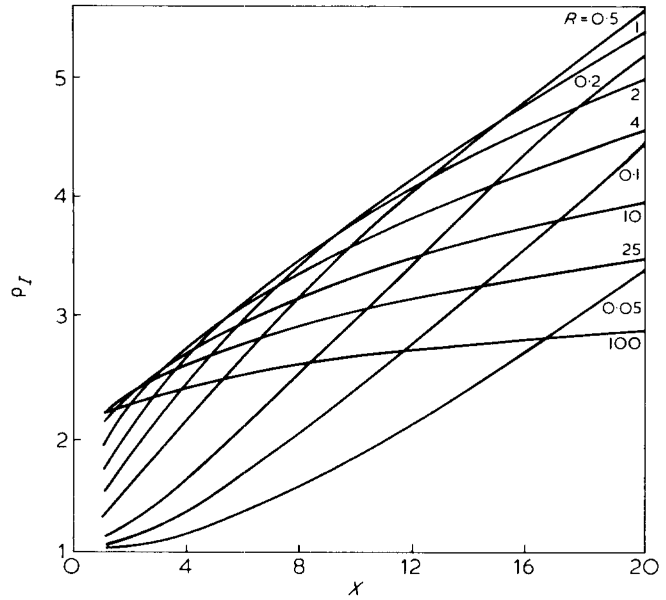

Figure 3 ρ_I vs X for different R

nomer left both for $R=25$ and 100. Therefore after some value of X there is little difference in these two cases. On the other hand, in a CSTR the entire conversion occurs at the exit concentrations and there may still be substantial amounts of monomer present, depending on the value of R. When compared with Model I[28] in a CSTR, it is found that $\mu_{n,I}$ is much higher for $R>1$ in this model, where the reaction between the monomer and all other species is characterized by a higher rate constant than for Model I, where the reaction rate between monomer and monomer only is higher. *Figure* 2 shows similar characteristics for $\mu_{w,I}$ as for $\mu_{n,I}$, for the same reasons. The values of $\mu_{w,I}$ for $R>1$ are substantially higher compared to both batch results for the same kinetic scheme and CSTR results on Model I.

The polydispersity index, ρ_I, is observed (*Figure* 3) to be higher for all values of R, when compared to values obtained in the batch reactor. However, no local peaks are observed for a CSTR, in contrast to results for a batch reactor[22]. This is because the entire reaction takes place at exit concentrations where the monomer concentration is lower. When *Figure* 3 is compared to results for Model I in a CSTR, it is found that the polydispersity index is generally lower for Model II, for all R. Also, the curves are much flatter for the present model.

Figures 4–7 show the *MWD* for several values of the dimensionless time, for $R=0.05$, 0.1, 10 and 100 respectively. As in the case of batch reactors, it is found that

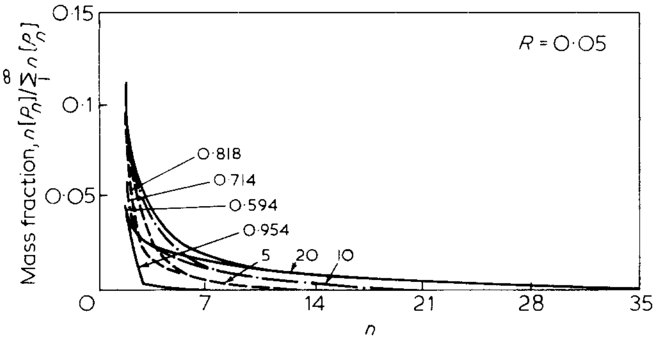

Figure 4 *MWD* for $R=0.05$ for several values of X. Upper curves for any X are for even homologues and lower curves for odd-n. Values on left are mass fractions of monomer

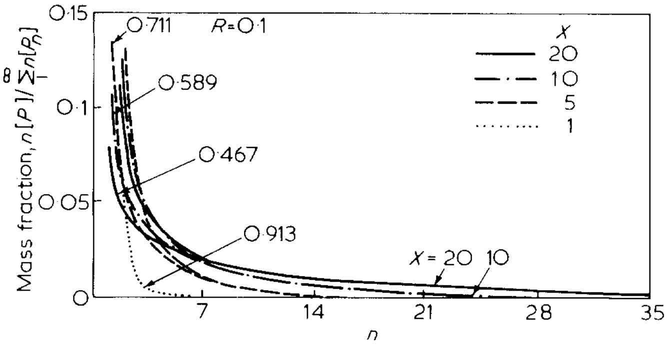

Figure 5 *MWD* for $R=0.1$ for several X. Upper curves are for even-n, lower curves for odd-n. Values on left are mass fractions of monomer

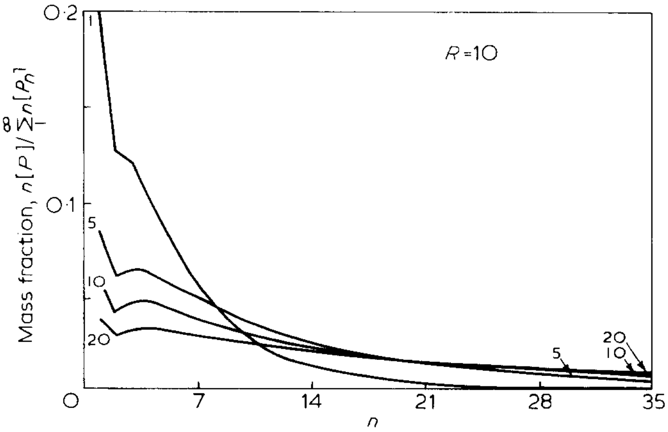

Figure 6 *MWD* for $R=10$ for several X

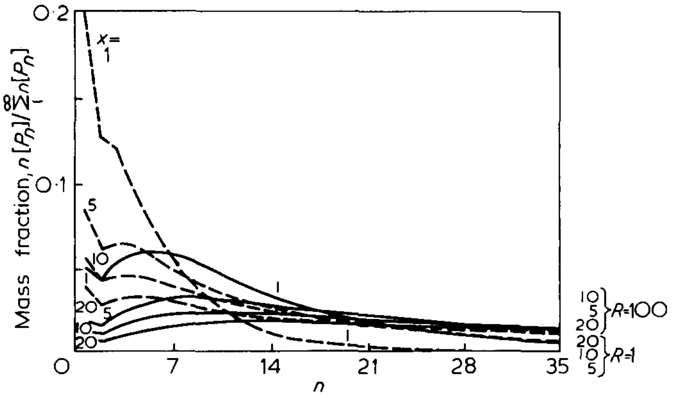

Figure 7 *MWD* for *R* = 100 for several *X*. Dotted lines show results for *R* = 10 for comparison

the split in the *MWD* curves for odd and even-*n* occurs for $R < 1$ for the present kinetic scheme rather than for Model I where the split occurs for $R > 1$. The split persists to higher values of n as X increases, for any R, and the separation between the curves is larger for lower values of R, for any X. The separation between the curves is much less than for Model I because the effect of unequal reactivity is more diffused in the present system. A substantial amount of unreacted monomer is also found for $R < 1$. This phenomenon occurs for values of R greater than unity in Model I. For $R > 1$ (*Figures* 6 and 7), no split in the *MWDs* is observed and a shallow 'hump' appears after the initial drop from the monomer to the dimer. A similar phenomenon occurred for $R < 1$ for Model I, in a CSTR.

In going from Model I to the present model in which more reactions are characterized by k_{11}, the effects which appeared for $R > 1$ now appear only for $R < 1$. The results of these studies[20–22,28] can now be used to predict, intuitively, the *MWDs* for kinetic schemes lying intermediate between the two models, or for kinetic schemes in which the unequal reactivity extends to higher homologues than the monomer.

NOMENCLATURE

k_n, k_p, $k_{p,mn}$	rate constants
n	degree of polymerization
$[P]$	molar concentration of functional groups
$[P_1]_0$	molar concentration of monomer in feed
$[P_m]$	molar concentration of mth homologue in reactor
R	reactivity ratio
X	dimensionless time
Y	dimensionless molar concentration of functional group
Z_n	dimensionless molar concentration of P_n
θ	residence time
ρ_I	polydispersity index
$\mu_{n,I}$	number average chain length
$\mu_{w,I}$	weight average chain length

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