Reversible polycondensation characterized by unequal reactivities of functional groups

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Molecular weight distributions and moments for reversible condensation polymerizations with unequal reactivities of functional groups both in the forward and reverse steps, have been obtained. Results are qualitatively similar to those obtained for the corresponding irreversible case, i.e., *MWD* curves split into two, one for odd-*n* and one for even values of *n* for *R* (= reactivity of monomer with monomer/reactivity of other oligomers) larger than unity. When *R* is less than one, there is a preponderance of monomer in the reaction mass. However, these effects are considerable reduced due to the reversibility of polymerization. Comparison with Flory's most probable distribution indicates that this function represents the *MWD*s of the polymer for both irreversible and reversible cases only when the functional groups exhibit equal reactivity. For the unequal reactivity case, such a one-parameter (in terms of functional group conversion) characterization of the *MWD*s is unlikely.

Keywords Characterization; condensation; polymerization; molecular weight distribution; functional groups

INTRODUCTION

Molecular weight distributions (*MWD*s) for polycondensations have conventionally been obtained using the assumption of the equal reactivity of functional groups[1-3]. Several systems, however, do not follow the hypothesis, e.g., phenylene sulphide[4], polyimides[5], polyurethanes[6,7], the condensation of divinyl benzene and *p*-cresol[8], of phenol formaldehyde[9-13] and polymerization of polyethylene terephthalate by the ester interchange reaction[14-16]. Theoretical modelling of such polycondensations has started receiving attention only recently, which is surprising in view of the commercial importance of several of these polymers. Gordon and Scantlebury[17] computed the average molecular weight and the chain length distribution for *f*-functional polycondensations having the free energy of activation of forming a bond between an *n*-mer and an *m*-mer proportional to $m+n$. Several workers[18-21] have studied the reactions of polymer chains where the rate of reaction at a site depends on whether the adjacent site has reacted or not. Nanda *et al.*[22] assumed a linear dependence of the rate constant on the degree of polymerization and obtained the *MWD* and the first two moments analytically. Gandhi, *et al.*[23] studied the condensation of two bifunctional monomers A–A and B′–B″ with the functional groups, B′ and B″ on B′–B″ having different reactivities with A. Later, they[24] extended their work to the polycondensation of A′–A″ and B′–B″. Their results on A–A and B′–B″ were confirmed later by Ozizmer and Odian[25]. Miller and Macosko[26] used statistical arguments to obtain average molecular weights for network condensation polymerizations characterized by unequal reactivities of functional groups. Gupta, Kumar and coworkers[27-29] studied two idealized models for the polymerization of ARB type monomers: 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, the monomer reacts with all the species in the reaction mass at a rate which is *R* times that for the reaction between higher homologues. As well as giving fundamental information leading to an insight into polycondensations associated with different reactivities of functional groups, these two models are directly applicable to some systems. For example, model I would give results which are close to the experimental behaviour of polyurethane polymerizations, wherein the reactivity of the –NCO group on a di-isocyanate changes after reaction with an –OH group on a diol whereas model II would apply for the polymerization of polyimides[5]. For other physical systems, these two models would give the two limits between which the results would lie.

Simulations of actual polycondensation reactors in which several other complex phenomena are present in addition to the unequal reactivity of functional groups has received very little attention in the literature. Simulation of such polycondensation reactions in homogeneous[30-32] and segregated[33] continuous-flow, stirred-tank reactors have been carried out recently.

Simulations of reversible polycondensations of nylon-6 have been carried out by Gupta, Kumar and coworkers[34,35] in which the equilibrium constant of the cyclization step is chain-length dependent. Similar simulations of reversible nylon-6,6 polymerizations have been presented by these workers[36,37]. These studies, though of great industrial importance, do not give much insight into the behaviour of reversible polycondensations since the kinetic schemes used incorporate several side reactions. Abraham[38] used an extension of the *Z*-transform method to study reversible polycondensations with equal reactivity of functional groups but he was unable to obtain an analytic solution. Later, Mellichamp[39] obtained *MWD*s and moments for this reversible case with removal of condensation product. Here, reversible condensation polymerizations of ARB type monomers with functional groups exhibiting unequal reactivity are simulated wherein the

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condensation product is not removed from the reaction mass.

FORMULATION

The reversible polycondensation reactions for ARB type monomers can be written in its most general form as follows

$$P_m + P_n \underset{k'_{m+n}}{\overset{k_{p,mn}}{\rightleftharpoons}} P_{m+n} + W \tag{1}$$

where P_m and P_n are molecules having m and n repeat units respectively and W is the condensation product. $k_{p,mn}$ and k'_{m+n} are the rate constants for the forward and reverse reactions between P_m and P_n and in order to write mass balance equations, they must be modelled. In the kinetic scheme proposed in this work, $k_{p,mn}$ has been expressed in terms of two constants which characterize the rate of reaction between functional groups (model I of Ref. 28).

$$k_{p11} = (k_{11}/2)*2 \tag{2a}$$

$$k_{p,mn} = 2k_p;\ m \neq n;\ m,n = 1,2,\ldots \tag{2b}$$

$$= (k_p/2)*2;\ m = n;\ m,n > 1 \tag{2c}$$

The factor of 1/2 in brackets in the above equations for $m = n$ is required to avoid counting of molecular collisions twice and the factor of 2 in each of the equations is to account for the fact that P_m and P_n can react by the reaction of A on P_n with B on P_m and B on P_n with A on P_m.

The reverse reaction between the condensation product W and the reacted group ⟮AB⟯ will depend, in general, on the location of the latter on the molecule of P_{m+n} (see *Figure 1*). However, just as in the case of the forward reaction, it is assumed that the reactivity of the ⟮AB⟯ groups at the end of P_{m+n} is substantially different from that of the other ⟮AB⟯ groups further removed from the ends, whose reactivities are all equal. The rate constants associated with the reaction between W and the end ⟮AB⟯ group is denoted as k'_e and that between an internal ⟮AB⟯ group and W as k'_p.

Mass balance equations for P_1, P_2.... and W for a batch reactor may be written for this kinetic scheme as

$$\frac{d[P_1]}{dt} = -2(k_{11} - k_p)[P_1]^2 - 2k_p[P_1][P] + 2k'_e[W]\sum_{n=2}^{\infty}[P_n] \tag{5a}$$

$$\frac{d[P_2]}{dt} = -2k_p[P_2][P] + k_{11}[P_1]^2 + 2k'_e[P_3][W] + 2k'_p[W]\sum_{n=4}^{\infty}[P_n] - k'_e[P_2][W] \tag{5b}$$

$$\frac{d[P_n]}{dt} = k_p\sum_{m=1}^{n-1}[P_m][P_{n-m}] - 2k_p[P_n][P] + 2k'_e[P_{n+1}][W] + 2k'_p[W]\sum_{m=n+2}^{\infty}[P_m] - 2k'_e[P_n][W] - k'_p(n-3)[P_n][W];\ n = 3,4\ldots \tag{5c}$$

$$d[W] = k_{11}[P_1]^2 + k_p\sum_{n=3}^{\infty}\sum_{m=1}^{n-1}[P_m][P_{n-m}] - k'_e[P_2][W] - \sum_{n=3}^{\infty}\{2k'_e + (n-3)k'_p\}[W][P_n] \tag{5d}$$

where the square brackets represent molar concentrations and [P] is the sum of the concentrations of individual mers, P_1, P_2, P_3....

These mass balance equations must be integrated with the following usually encountered initial conditions:

$$\text{at } t=0:\ [P_1] = [P] = [P_1]_0$$
$$[P_2] = [P_3] = \ldots = 0; \tag{6}$$

The number and weight-average chain lengths are defined conventionally by:

$$\mu_n = \frac{\sum_{n=1}^{\infty} n[P_n]}{\sum_{n=1}^{\infty}[P_n]} \tag{7a}$$

$$\mu_w = \frac{\sum_{n=1}^{\infty} n^2[P_n]}{\sum_{n=1}^{\infty} n[P_n]} \tag{7b}$$

with the polydispersity index, ρ, being the ratio of μ_w and μ_n. In polycondensations characterized by unequal reactivity of functional groups, because of a preponderance of monomer in the reaction mass, it is, at times[23,28,29], appropriate to consider averages defined without including the monomer in the summations as follows

$$\mu_{n,\text{II}} \equiv \frac{\sum_2^{\infty} n[P_n]}{\sum_2^{\infty}[P_n]};$$

$$\mu_{w,\text{II}} \equiv \frac{\sum_{n=2}^{\infty} n^2[P_n]}{\sum_2^{\infty} n[P_n]};\quad \rho_{\text{II}} \equiv \frac{\mu_{w,\text{II}}}{\mu_{n,\text{II}}} \tag{8}$$

The above equations are rewritten in terms of the following dimensionless variables

$$X = k_p[P_1]_0 t \tag{9a}$$

$$Y = [P]/[P_1]_0 \tag{9b}$$

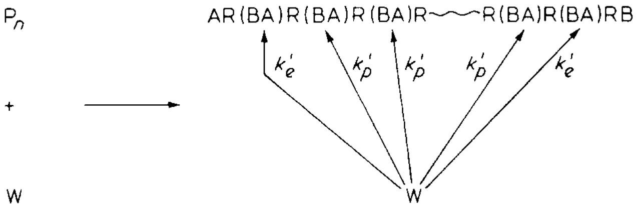

Figure 1 Attack of W on —AB— groups and the associated rate constants

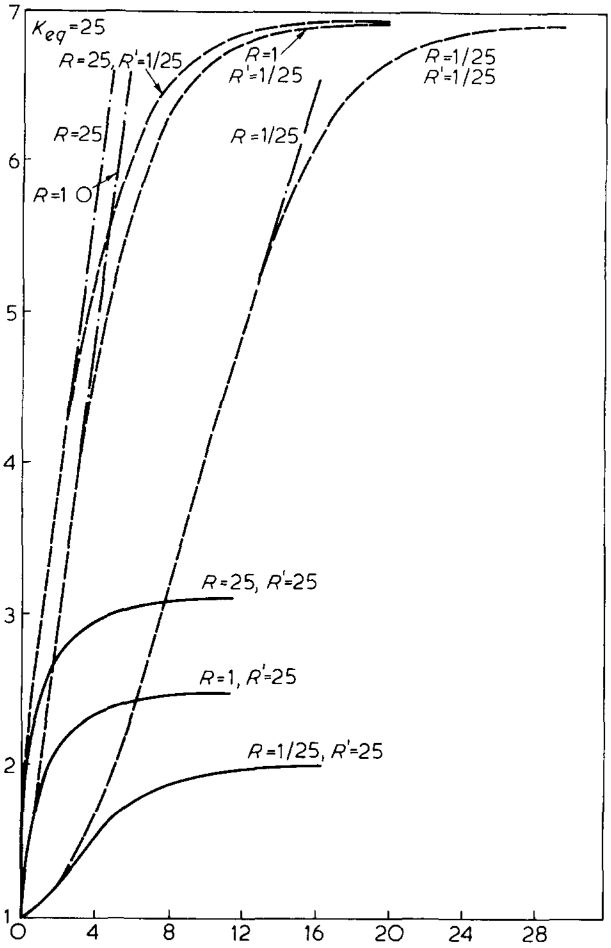

Figure 2 μ_n vs. X for K_{eq} = 25. Results for the irreversible case are shown by (— · —)

$$Z_n=[P_n]/[P_1]_0;\ n=1,2,\ldots \quad (9c)$$

$$C=[W]/[P_1]_0 \quad (9d)$$

$$R=k_{11}/k_p \quad (9e)$$

$$K_{eq}=k_p/k'_p \quad (9f)$$

$$R'=k'_e/k'_p \quad (9g)$$

On taking $R=R'=1$, these equations lead to

$$\frac{d\sum[P_n]}{dt}=-k_p[P]^2+k'_p[W]\sum_{n=1}^{\infty}(n-1)[P_n] \quad (10)$$

which is the same as the one obtained when the equal reactivity hypothesis holds[2].

RESULTS AND DISCUSSION

The set of differential equations are solved simultaneously using the fourth order Runge–Kutta method to obtain Y, Z_n and C as a function of the dimensionless time X. Reduction in the value of ΔX from 0.01 did not lead to any significant changes in the numerical value of molecular weight distribution and therefore results were generated with $\Delta X=0.01$. Equations (7) are then used to compute the various moments and their ratios. The computation time on a DEC 1090 computer for obtaining the *MWD* and moments for any one set of parameters R, R' and K_{eq} for X up to 30 was about 20 min.

Several checks were made on the computer program. Runs were made using $K_{eq}=\infty$ and $R=1$ (i.e. irreversible with equal reactivity) and results were found to match with the most probable Flory[1] distribution. Similarly, on putting $K_{eq}=\infty$ (irreversible), results obtained agreed with earlier results of Gupta *et al.*[28] for different R. The value of $\sum_{1}^{\infty} nZ_n$ obtained by summing up the computed Z_n's was found to be 1.00005 in the worst case, which compares very well with the expected value of unity. A similar check on the value of Y was also made. The computed value of C matched the theoretically expected value of $1-Y$ to the fourth decimal place. Numerical results for $K_{eq}=1$ and $R=1$ matched the analytical solution.

It may be added that, on the computer, the various summations extending to infinity in equation (5) had to be cut-off at some large value of the index n or m. Initially, this cut-off was taken at the index equal to 50 (i.e., the number of equations for Z_n solved simultaneously, was 50) and as soon as the computed value of the last Z_n exceeded 10^{-10}, the number of equations was increased by 25. The total number of equations for Z_n at the end of the longest run was 200.

Results on μ_n and ρ are shown in *Figures 2–7* for several combinations of K_{eq}, R and R'. Plots for the irreversible case ($K_{eq}=\infty$) and for similar values of R are also shown for comparison. It is observed that ρ increases monotonically with the dimensionless time, X, to an asymptotic value in some cases and for some, it attains an asymptotic value after exhibiting a maximum. A study of the *MWDs* shown in *Figures 8–12* indicates that in those cases where a peak is exhibited in the ρ vs. X curves, there is a preponderance of the monomer in the reaction mass. Therefore a plot of the polydispersity index excluding monomer, ρ_{II}, vs. X is expected to vary monotonically with X. This is indeed found to be so and the

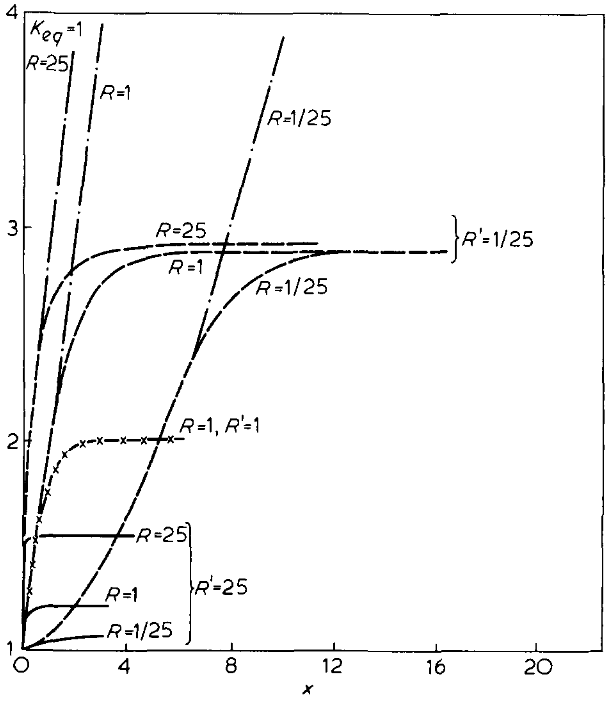

Figure 3 μ_n vs. X for K_{eq} = 1. Results for the irreversible case are shown by (— · —)

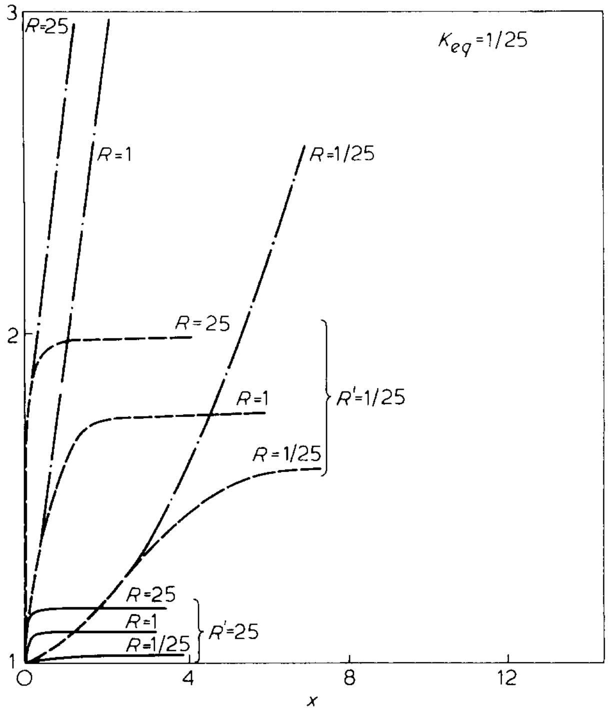

Figure 4 μ_n vs. X for K_{eq} = 1/25. Results for the irreversible case are shown by (— · —)

corresponding curve of ρ_{II} vs. X for $K_{eq}=25$, $R=1/25$, $R'=1/25$ is shown in *Figure 5*. The equilibrium values of both μ_n and ρ increase as K_{eq} increases, i.e. as the rates of the forward reactions increase relatively compared with those of the reverse steps. For any given value of K_{eq}, the number average chain length is found to decrease as R' increases because of the faster rate of attack of W on the end –AB– groups in the polymer chains. It was confirmed that in all the cases, the number average chain length, μ_n, was related to the conversion, p, of functional groups, as

$$\mu_n = \frac{1}{1-p} \tag{13}$$

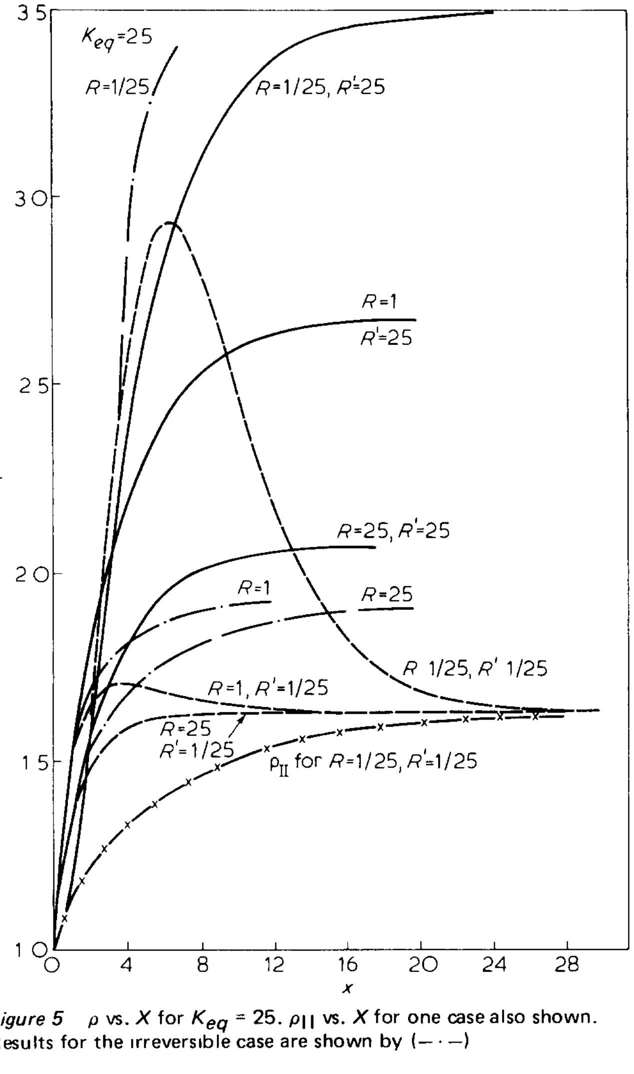

Figure 5 ρ vs. X for K_{eq} = 25. ρ_{II} vs. X for one case also shown. Results for the irreversible case are shown by (— · —)

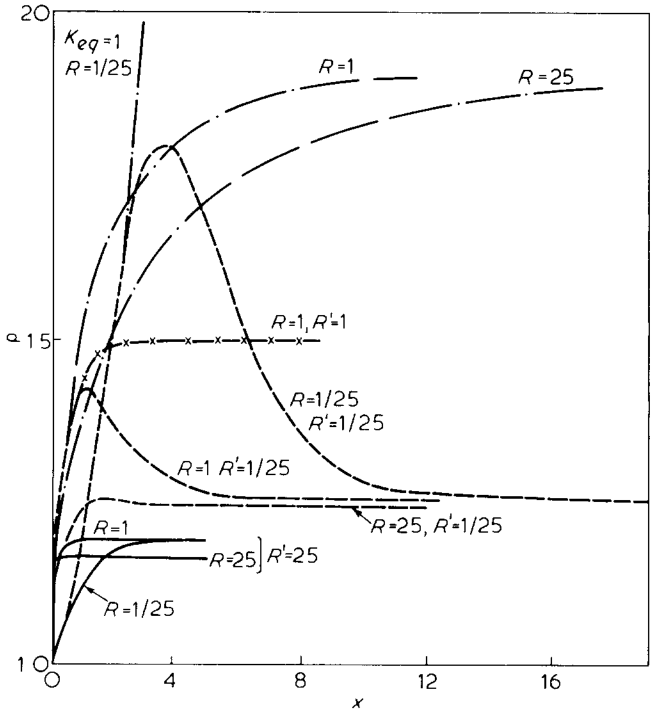

Figure 6 ρ vs. X for K_{eq} = 1. Results for the irreversible case are shown by (— · —)

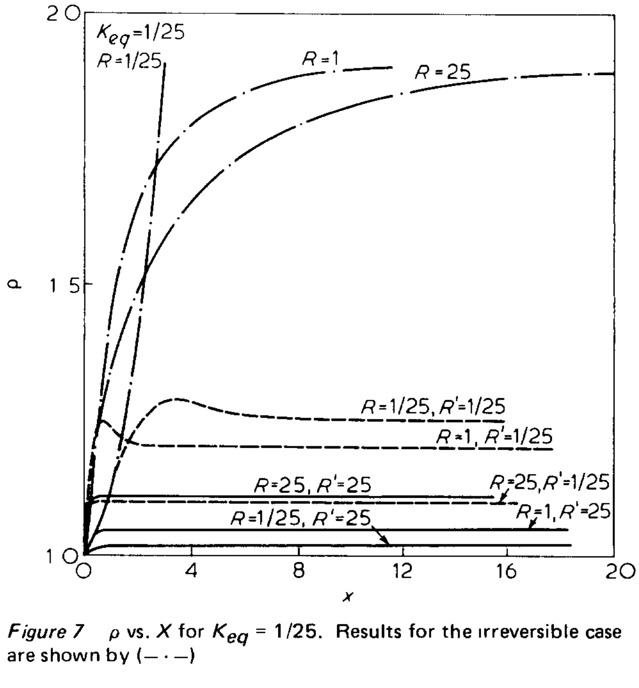

Figure 7 ρ vs. X for K_{eq} = 1/25. Results for the irreversible case are shown by (— · —)

Molecular weight distributions for some combinations of the rate parameters are shown in *Figures 8–12*. For two cases studied, namely, $K_{eq}=25$, $R=25$, $R'=1/25$ (*Figure 8*) and $K_{eq}=1$, $R=25$, $R'=1/25$ (*Figure 11*), the *MWD*s at low reaction times consist of two curves—one for odd

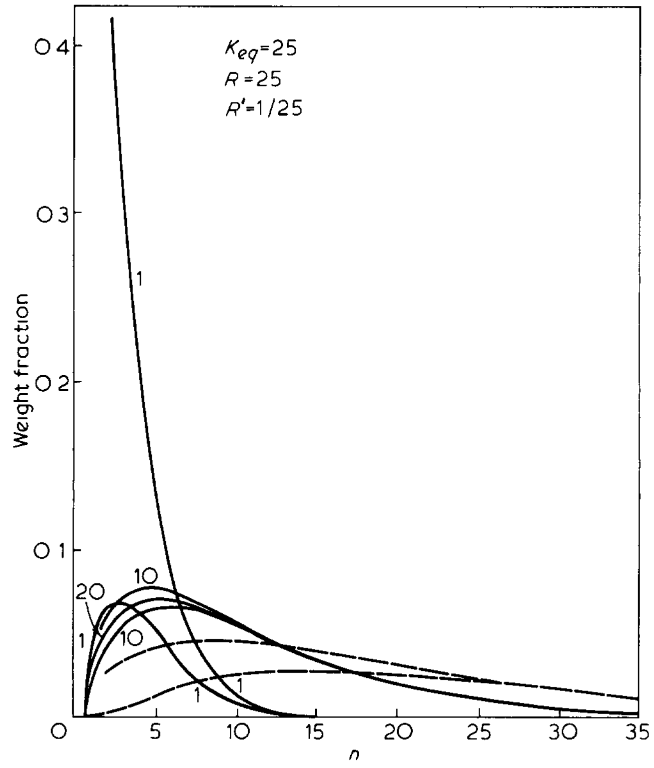

Figure 8 *MWD* for $K_{eq}=25$, $R=25$, $R'=1/25$ for values of X indicated. Lower curves are for odd-n and upper curves are for even n. Irreversible case for $X=10$ shown by broken lines

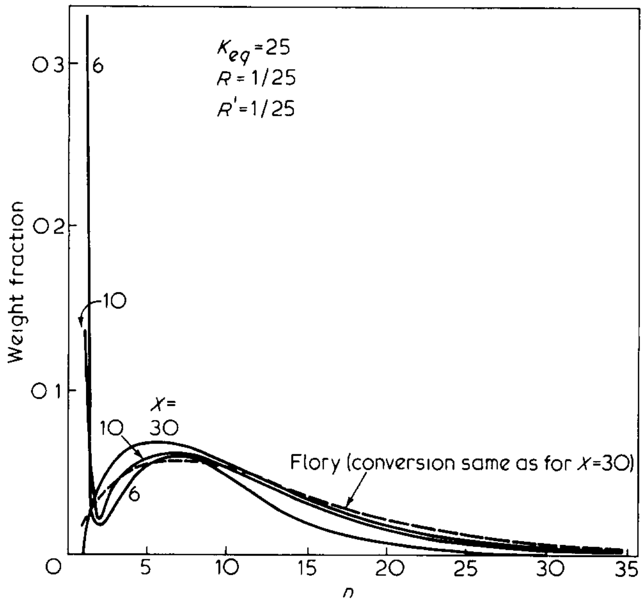

Figure 10 *MWD* for $K_{eq}=25$, $R=1/25$, $R'=1/25$. Flory's distribution corresponding to same conversion as that for $X=30$ also shown

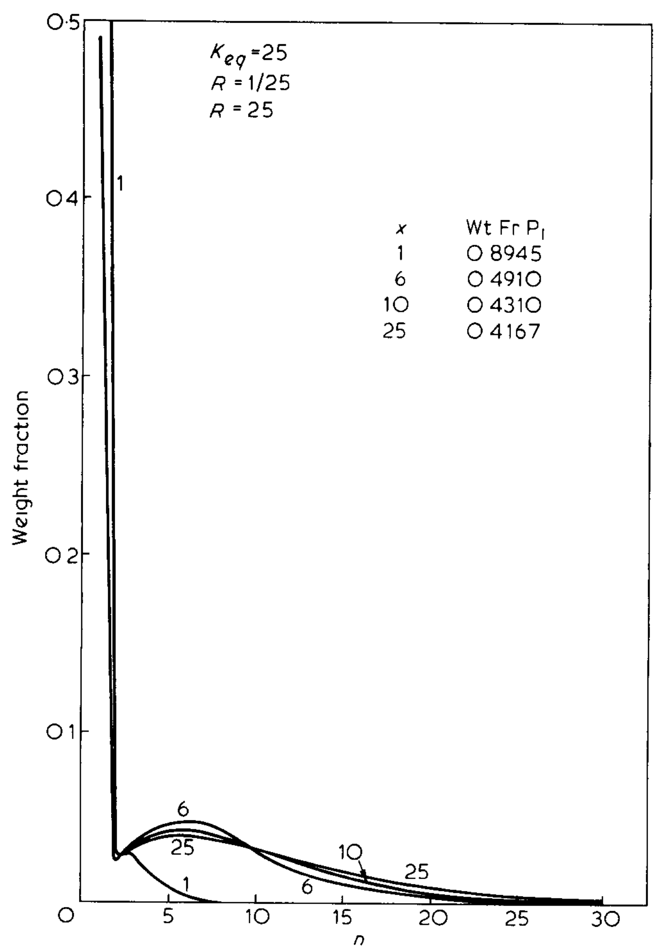

Figure 9 *MWD* for $K_{eq}=25$, $R=1/25$, $R'=25$. Value of $[P_1]$ indicated where it falls outside the graph

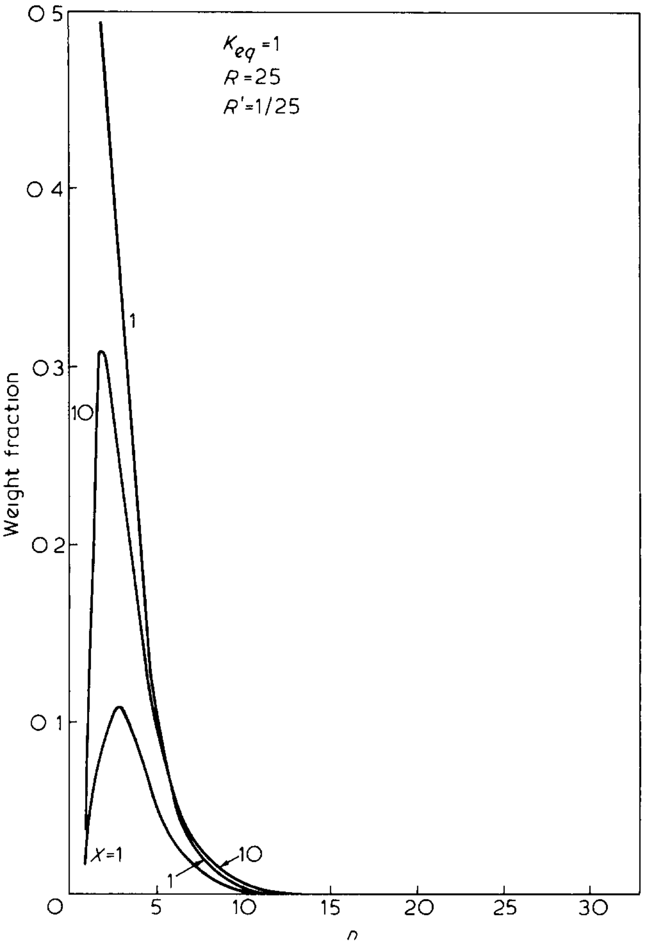

Figure 11 *MWD* for $K_{eq}=1$, $R=25$, $R'=1/25$. Curve for $X=1$ is split into two. Lower curves at any X are for odd-n, upper curves for even-n

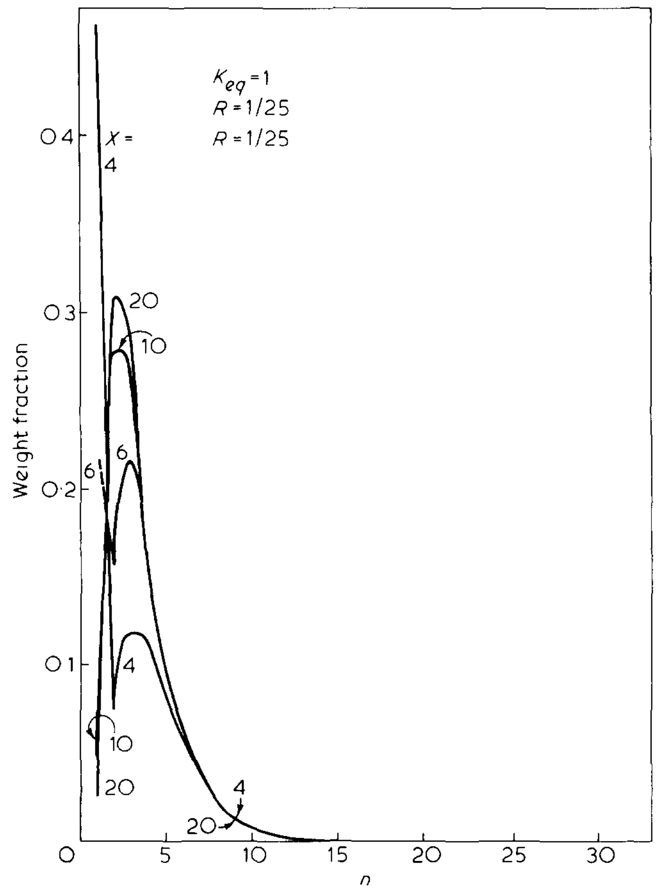

Figure 12 *MWD* for $K_{eq}=1$; $R=R'=1/25$

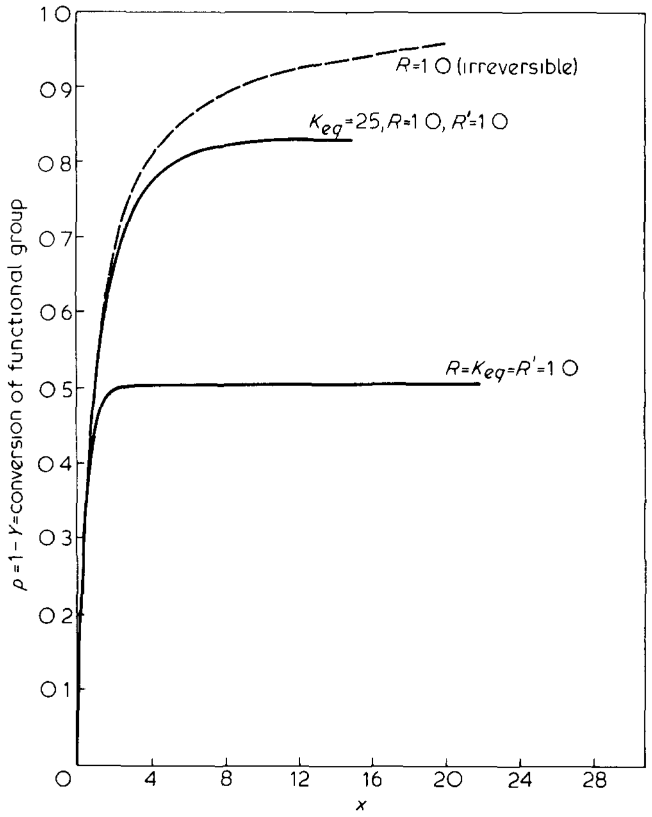

Figure 13 Conversion vs. X for the equal reactivity cases ($R=R'=1$) for three values of K_{eq}

values of n and one for even values. No such split is observed at high values of X. A similar split in the *MWD*s was observed for the irreversible polymerization for model I[28] for values of $R>1$. However, in the latter case, the split persists until very high values of X whereas for reversible polymerizations, it is not exhibited for X as low as ~ 20. The separation between the curves is larger for the irreversible case.

For values of R below unity, it is observed that there is a preponderance of monomer in the reaction mass till fairly high values of X and the *MWD*s behave qualitatively in a similar manner to what was observed for the irreversible case with $R<1$. A comparison of *Figures 10* and *12* reveals that as the reverse reactions are speeded up (i.e. K_{eq} reduces), this effect is reduced. Thus, in general, the presence of the reverse reactions is seen to tone-down the effects observed earlier for the irreversible polycondensation of monomers exhibiting unequal reactivity of functional groups.

In *Figure 10* is also shown the most probable Flory distribution for $X=30$ corresponding to the same conversion of functional groups ($=0.8558$) as obtained for the reversible polymerization. It is observed that the *MWD*s are different. A similar study on reversible polycondensations with equal reactivities ($R=R'=1$) yielded Flory's most probable distributions and the corresponding conversions are shown as a function of X in *Figure 13*. Thus it is observed that even though Flory's most probable function can represent the *MWD*s for both reversible and irreversible polycondensations when the equal reactivity hypothesis is valid, it is not so when the functional groups exhibit unequal reactivities.

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