Molecular weight distribution and moments for condensation polymerization of monomers having reactivity different from their homologues

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Molecular weight distributions and moments for condensation polymerization of monomer with unequal reactivities have been studied. When the monomer is more reactive than other species, the *MWD* curves are found to be different for even and odd mers. When the monomer is less reactive than other species, substantial amounts of unreacted monomer are left and a polydispersity index found by excluding the monomer is found to be a more appropriate representation of the dispersion of the curves. Values of this index at constant conversion are found to be larger or smaller depending on whether the monomer is more or less reactive compared with other homologues in the system, respectively.

INTRODUCTION

In condensation polymerization, the reactivity of functional groups depends greatly on the structure of monomers or polymers. There are monomers, especially those containing aromatic rings, for which the reactivity is different from those of higher homologues. For example, Lenz *et al.*[1] studied the kinetics of phenylene sulphide polymerization and found that the monomer reacts at a much slower rate than the dimer, trimer, etc., but the latter react at equal rates. A similar phenomenon has also been observed in the formation of poly(ethylene terephthalate) by the ester interchange reaction[2–4], polyimides[5], polyurethanes[6,7] and recently in the condensation of divinylbenzene and *p*-cresol[8].

Theoretical modelling of the rates of polymerization for such systems, as well as the molecular weight distributions and averages, have received relatively little attention in the literature. Gordon *et al.*[9] have computed the average molecular weight and the chain length distribution for *f*-functional polycondensations wherein the free energy of activation of forming a bond between units with m and n links is proportional to $m + n$. Several workers[10–13] have studied the reactions carried out on polymer chains wherein the rate of reaction at a given site depends on whether or not the adjacent site has reacted. Nanda *et al.*[14] assumed a linear dependence of the rate constant with degree of polymerization and derived analytical expressions for the molecular weight distribution and its first two moments for condensation polymerization. They found that the polydispersity index deviates appreciably from the most probable value of 2 (ref 15 and 16); it is less than 2 when the reactivity decreases with chain length and larger than two when it increases. More recently Gandhi *et al.*[17] have studied the molecular weight distribution and the polydispersity index using kinetic schemes for asymmetric monomers in which one functional group has a reactivity different from that of the other group. Since, in their study, they neglected the change in reactivity with chain length, their model is inapplicable to the systems discussed above. Their model can be regarded only as a limiting case of polymerizations with unequal rate constants.

The kinetic model of Kumar *et al.*[18] which accounts for monomers having different reactivities, has been used in this paper to calculate the molecular weight distribution and its moments.

FORMULATION

Polycondensation reactions are represented as an infinite set of elementary reactions:

$$\mathrm{P}_m + \mathrm{P}_n \xrightarrow{k_{p,mn}} \mathrm{P}_{m+n} + \text{Condensation product}; \qquad m, n = 1,2\ldots \tag{1}$$

where P_m and P_n are molecules having m and n repeat units respectively and $k_{p,mn}$ is the corresponding rate constant. The kinetic scheme proposed in this work[18] models this complex situation in terms of two parameters, k_{11} and k_p only:

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

This assumption is rigorously valid for some systems[1,5] and for others, it would be a good first-order approximation. The rate of reaction between monomer, P_1, and a higher homologue, P_n $(n > 1)$, will be guided by the nature of substituent groups of both P_1 and P_n. In the most general case, $k_{p,1n}$ would be a function of both P_1 and P_n. The present model thus amounts to assuming that the reaction between P_1 and P_n is controlled primarily by P_n rather than by P_1. Alternatively, this model can be considered as one limiting case

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analysis of real polymerizations and can give valuable insight into the actual phenomena.

Mass balance equations for P_1, P_2, etc. for batch reactors are:

$$\frac{d[P_1]}{dt} = -(k_{11} - k_p)[P_1]^2 - k_p[P_1]\,[P] \tag{3a}$$

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

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

where the square brackets represent various molar concentrations. [P], the sum of the concentrations of individual mers, $P_1, P_2, P_3, \ldots$, can be obtained by summing the equations for $[P_i]$ to give:

$$\frac{d[P]}{dt} = -\frac{1}{2}(k_{11} - k_p)[P_1]^2 - \frac{1}{2}k_p[P]^2 \tag{4}$$

We find the molecular weight distribution (*MWD*) by solving these equations.

The kth moment of the *MWD* is defined as

$$\lambda_k = \sum_{n=1}^{\infty} n^k[P_n]; k = 0, 1, 2, \ldots \tag{5}$$

The mean of the number chain length distribution[19] is defined by:

$$\mu_n = \frac{\sum_{n=1}^{\infty} n[P_n]}{\sum_{n=1}^{\infty}[P_n]} = \frac{\lambda_1}{\lambda_0} \tag{6}$$

Similarly, the mean of the weight chain length distribution is given by:

$$\mu_w = \frac{\sum_{n=1}^{\infty} n^2[P_n]}{\sum_{n=1}^{\infty} n[P_n]} = \frac{\lambda_2}{\lambda_1} \tag{7}$$

with the polydispersity index, ρ, as:

$$\rho = \frac{\mu_w}{\mu_n} \tag{8}$$

Expressions for λ_0, λ_1 and λ_2 are obtained by using the generating function technique. The generating function, $G(s,t)$, is

$$G(s,t) = \sum_{n=1}^{\infty} s^n[P_n] \tag{9}$$

The various moments are then given by[19]:

$$\lambda_k = \sum_{i=0}^{\infty} a_{ki}\left[\frac{\partial^i G(s,t)}{\partial s^i}\right]_{s=1}; k = 0, 1, 2, \ldots \tag{10}$$

where the coefficients a_{ki} are given by the matrix

$$a_{ki} \Rightarrow \begin{bmatrix} 1 & 0 & 0 & 0 & 0\ldots \\ 0 & 1 & 0 & 0 & 0\ldots \\ 0 & 1 & 1 & 0 & 0\ldots \\ 0 & 1 & 3 & 1 & 0\ldots \\ 0 & 1 & 7 & 6 & 1 \\ \vdots & & & & \end{bmatrix} \tag{11}$$

Individual equations for $d[P_n]/dt$ are multiplied by s^n and added to obtain $G(s,t)$ as:

$$\frac{\partial G(s,t)}{\partial t} = -k_p[P]\,G(s,t) - (k_{11} - k_p)[P_1]^2\left(s - \frac{s^2}{2}\right) + \frac{k_p}{2}G^2(s,t) \tag{12}$$

In the literature, two types of moments have been suggested[19] – one in which the monomer, P_1, is considered as a part of the polymer (Case I) for which equations (6) and (7) apply, and the other in which the monomer is excluded (Case II). For the first case, using initial conditions:

$$[P_1] = [P] = [P_1]_0, \qquad [P_2] = [P_3] = \ldots = 0; \text{at } t = 0 \tag{13}$$

we obtain:

$$\frac{d\lambda_{0,\mathrm{I}}}{dt} = \frac{\partial G(1,t)}{\partial t} = \frac{d[P]}{dt} \tag{14a}$$

$$\frac{d\lambda_{1,\mathrm{I}}}{dt} = 0; \lambda_{1,\mathrm{I}} = \lambda_{1,\mathrm{I}}(t = 0) = [P_1]_0 \tag{14b}$$

$$\frac{d\lambda_{2,\mathrm{I}}}{dt} = k_p\lambda_{1,\mathrm{I}}^2 + (k_{11} - k_p)[P_1]^2 = k_p[P_1]_0^2 + (k_{11} - k_p)[P_1]^2 \tag{14c}$$

where the subscript I on the λ's indicates case I. For case II, i.e., when the monomer is excluded from the computation of the moments, one obtains

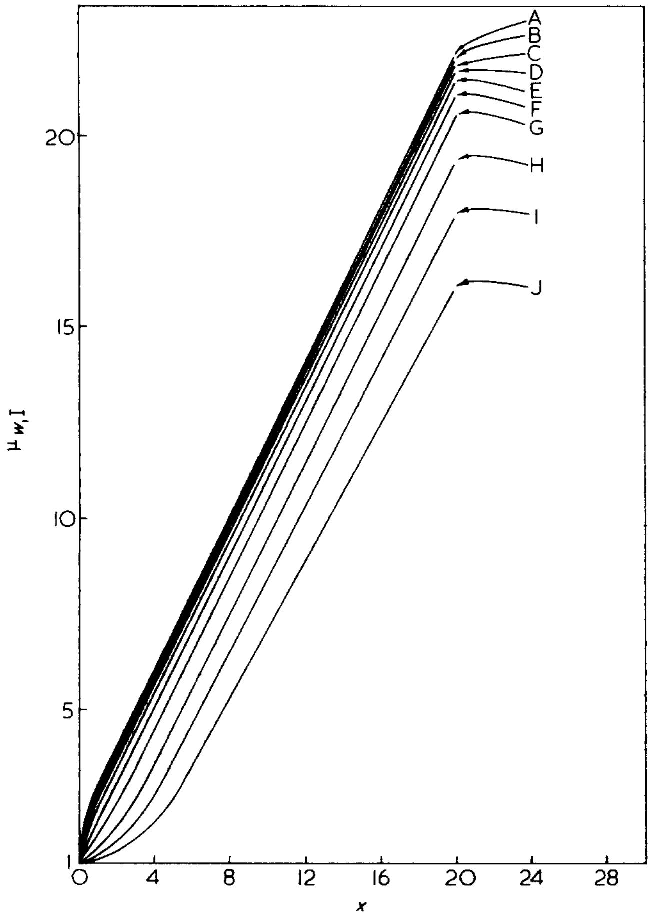

Figure 1 $\mu_{w,I}$ vs. X for different values of R: A, 100; B, 25; C, 10; D, 4; E, 2; F, 1; G, 0.5; H, 0.2; I, 0.1; J, 0.05

$$\lambda_{0,\mathrm{II}} = [\mathrm{P}] - [\mathrm{P}_1] \tag{15a}$$

$$\frac{d\lambda_{1,\mathrm{II}}}{dt} = -\frac{d[\mathrm{P}_1]}{dt} \tag{15b}$$

$$\frac{d\lambda_{2,\mathrm{II}}}{dt} = 2(k_{11} - k_p)[\mathrm{P}_1]^2 + k_p[\mathrm{P}][\mathrm{P}_1] + k_p[\mathrm{P}_1]_0 \tag{15c}$$

The initial conditions for the moments, corresponding to equation (13), are given by

$$\lambda_{0,\mathrm{I}} = \lambda_{1,\mathrm{I}} = \lambda_{2,\mathrm{I}} = [\mathrm{P}_1]_0 \tag{16a}$$

$$\lambda_{0,\mathrm{II}} = \lambda_{1,\mathrm{II}} = \lambda_{2,\mathrm{II}} = 0; \text{at } t = 0 \tag{16b}$$

The above equations are written in terms of the following dimensionless variables[18]:

$$X = k_p[\mathrm{P}_1]_0 t \tag{17a}$$

$$Y = [\mathrm{P}]/[\mathrm{P}_1]_0 \tag{17b}$$

$$Z_n = [\mathrm{P}_n]/[\mathrm{P}_1]_0; n = 1, 2 \ldots \tag{17c}$$

$$R = k_{11}/k_p \tag{17d}$$

$$M_{k,\mathrm{I}} = \lambda_{k,\mathrm{I}}/[\mathrm{P}_1]_0 \qquad \mathrm{k} = 0, 1, 2 \tag{17e}$$

$$M_{k,\mathrm{II}} = \lambda_{k,\mathrm{II}}/[\mathrm{P}_1]_0 \qquad k = 0, 1, 2 \tag{17f}$$

to give the final equations as:

$$dY/dX = \frac{1}{2}(R - 1)Z_1^2 - \frac{1}{2}Y^2 \tag{18a}$$

$$dZ_1/dX = -(R - 1)Z_1^2 - YZ_1 \tag{18b}$$

$$dZ_2/dX = \frac{R}{2}Z_1^2 - YZ_2 \tag{18c}$$

$$\frac{dZ_n}{dX} = \frac{1}{2}\sum_{m=1}^{n-1} Z_m Z_{n-m} - YZ_n; \; n = 3,4 \ldots \tag{18d}$$

$$\frac{dM_{0,\mathrm{I}}}{dX} = -\frac{1}{2}(R - 1)Z_1^2 - \frac{1}{2}M_{0,\mathrm{I}}^2 \tag{18e}$$

$$M_{1,\mathrm{I}} = 1 \tag{18f}$$

$$\frac{dM_{2,\mathrm{I}}}{dX} = (R - 1)Z_1^2 + 1 = \frac{d\mu_w}{dX} \tag{18g}$$

$$M_{0.\mathrm{II}} = M_{0,\mathrm{I}} - Z_1 \tag{18h}$$

$$M_{1,\mathrm{II}} = 1 - Z_1 \tag{18i}$$

$$\frac{dM_{2,\mathrm{II}}}{dX} = 2(R - 1)Z_1^2 + Z_1 M_{0,\mathrm{I}} + 1 \tag{18j}$$

with appropriate initial conditions which may be easily deduced from equations (13), (16) and (17).

Equations (18a) and (18b) are solved using the fourth order Runge–Kutta method for simultaneous equations[20] to give Y and Z. Thereafter, Z_2, Z_3, etc., are calculated successively. The fourth order Runge–Kutta method does not work for the latter, however, because the initial values of $Z_2, Z_3, \ldots$ are all zero. To overcome this difficulty, the second order Runge–Kutta method is used to obtain the values of $Z_2, Z_3, \ldots$ at the first increment of X and in subsequent increments, the fourth-order technique is used. Equation (18e) is identical in form to equation (18a) and there is no need to recompute $M_{0,\mathrm{I}}$. Simpson's 1/3 and 3/8 rules are used to obtain $M_{2,\mathrm{I}}$ and $M_{2,\mathrm{II}}$.

RESULTS AND DISCUSSION

Results for μ_n, μ_w and ρ (for Cases I and II) are shown in *Figures 1–5* for several values of R. Results for $\mu_{n,\mathrm{I}}$ vs. X were identical to those obtained earlier[18]. In *Figure 2*, ρ_I is given as a function of X and an inflection is found to occur for $R < 1$. This is absent in ρ_II as shown in *Figure 5*. The inflection in ρ_I is because of large amounts of unreacted monomer in the reaction mass. ρ_I is found to be larger for $R < 1$ than for $R = 1$ for the same reason. Moreover, the asymptotic value of ρ_II for $R = 1$ is also found to be 2 and is attained at values of X far beyond 20 shown in *Figure 5*. It is observed that ρ_II will be larger or smaller than 2 depending upon whether R is greater or less than unity. With monomer included in the computations, ρ_I goes beyond 2 even for

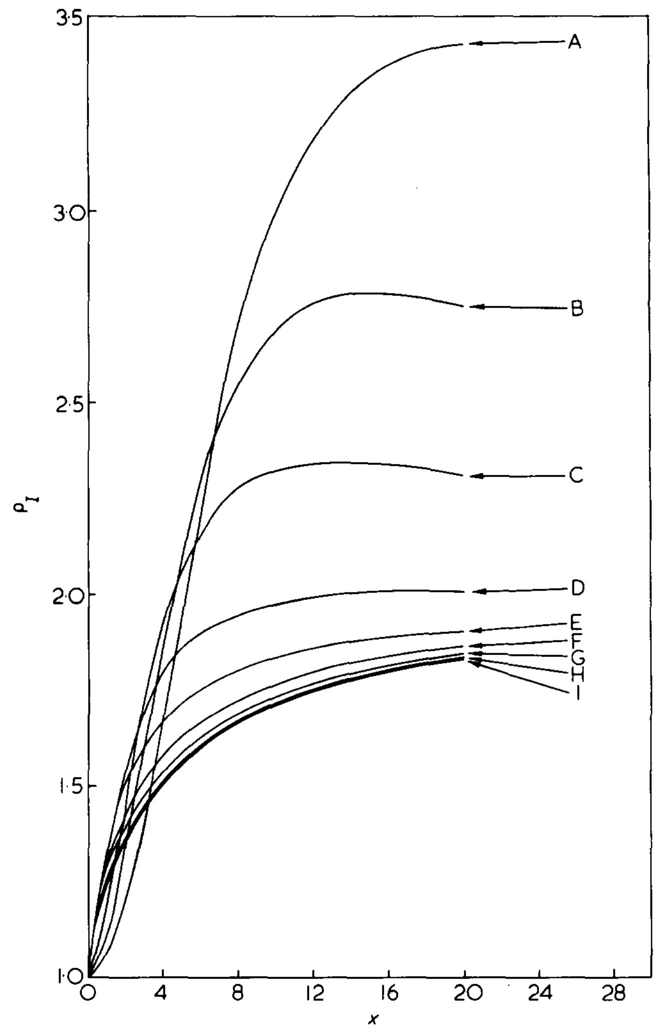

Figure 2 ρ_I vs. X for different values of R: A, 0.05; B, 0.1; C, 0.2; D, 0.5; E, 1.0; F, 2.0; G, 4; H, 10; I, 25, 100

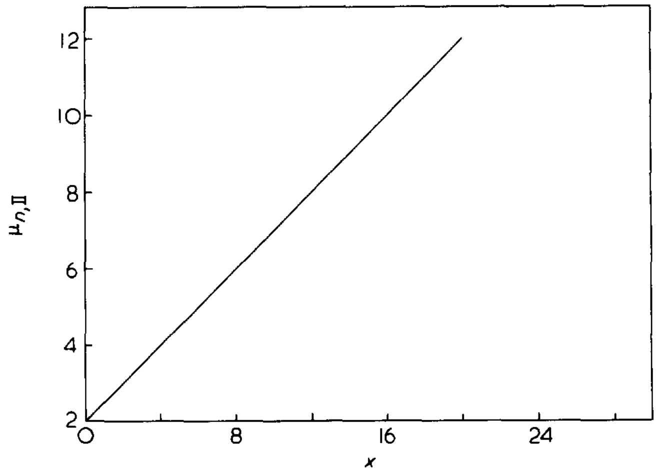

Figure 3 $\mu_{n,II}$ vs. X. Same graph is obtained for all R

values of X as low as 5, for R below unity. A close study of *Figures 2* and *5* thus establishes the superiority of the second definition of the moments over the first one. It may be added that our results for ρ_I are in the same direction as those of Nanda *et al.*[14] using a different kinetic scheme.

Figure 6 shows the weight fraction vs. degree of polymerization, n, for $R = 0.1$. In all these curves, there is a sharp fall in the ordinate in going from $n = 1$ or 2 before the regular pattern of the *MWD* plots emerges. The values indicated in this Figure show that substantial amounts of monomer are still present in the system. This is because of the lower reaction rate of the monomer and the higher reaction rate of the dimer, trimer, etc. Flory's most probable *MWD* plots for corresponding values of X are also shown in *Figure 6*. A comparison of the curves for equal values of X reveals that the *MWD* is much sharper for $R = 0.1$. This confirms the earlier conclusion that the excess of monomer is responsible for the higher value of ρ_I for $R < 1$ and shows again that ρ_{II} is a better measure of the dispersion of the *MWD* curves.

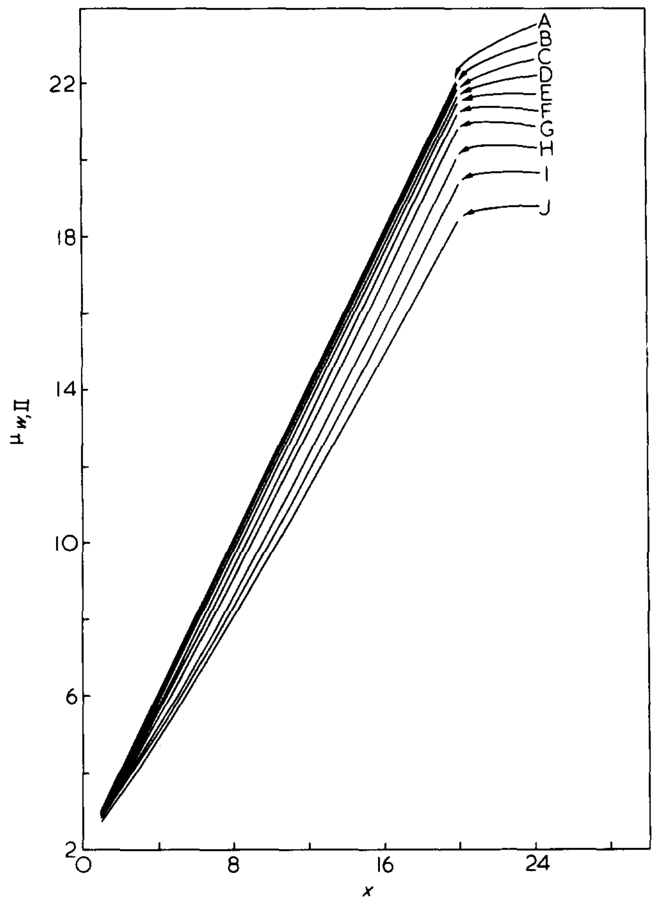

Figure 4 $\mu_{w,II}$ vs. X for different R: A, 100; B, 25; C, 10; D, 4; E, 2; F, 1; G, 0.5; H, 0.2; I, 0.1; J, 0.05

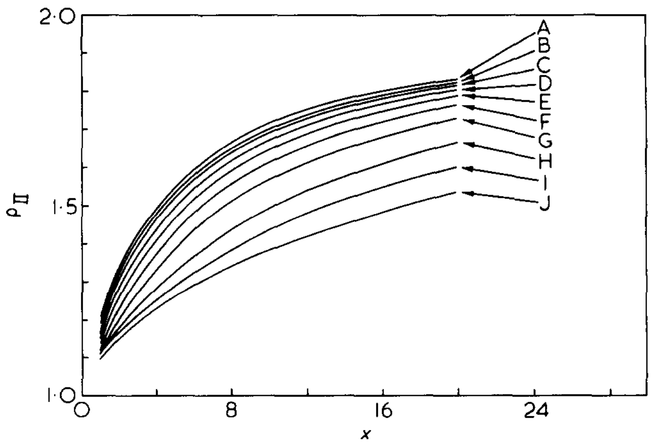

Figure 5 ρ_{II} vs. X for different R: A, 100; B, 25; C, 10; D, 4; E, 2; F, 1; G, 0.5; H, 0.2; I, 0.1; J, 0.05

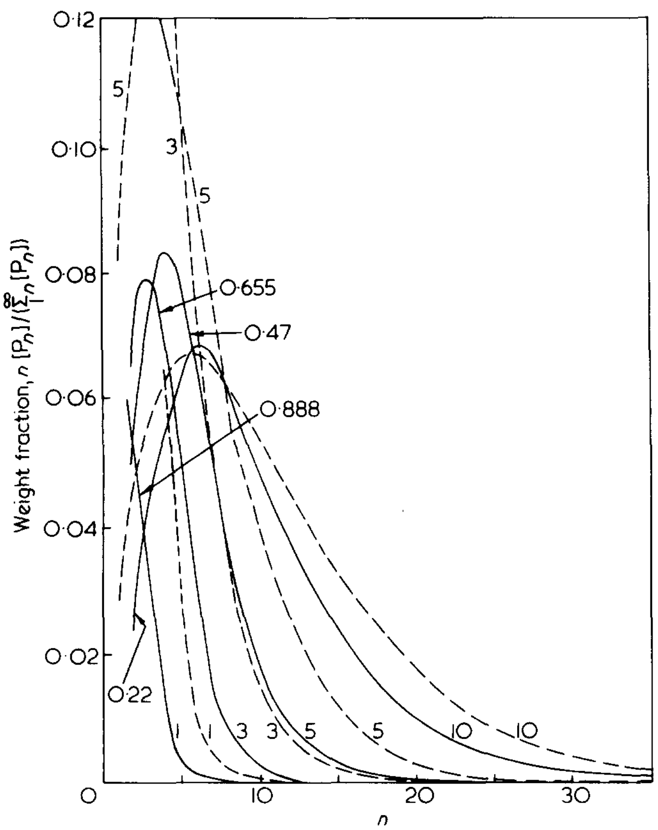

Figure 6 Weight fraction vs. n for $R = 0.1$ at different values of X. Flory's distribution for corresponding X shown by broken lines. Numbers against arrows show weight fraction of monomer for R=0.1

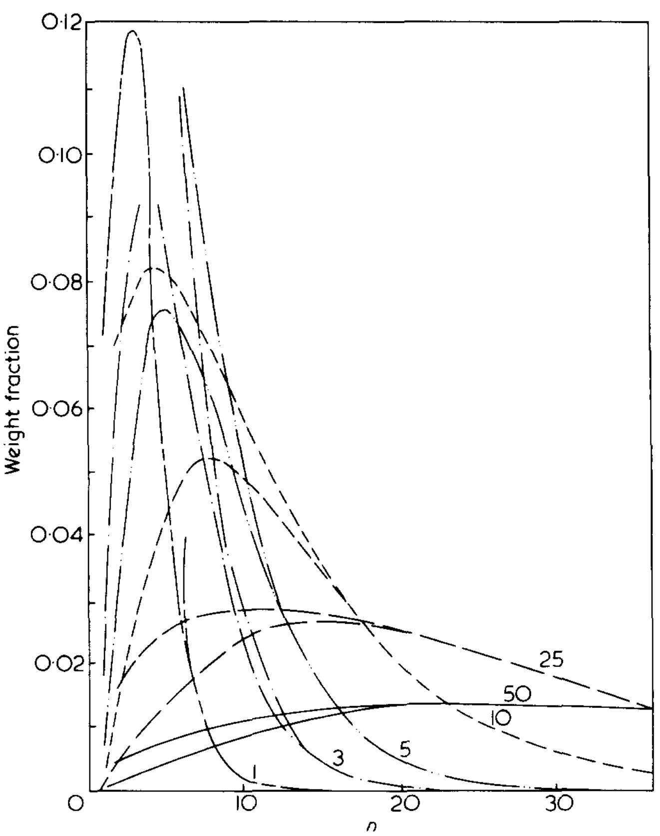

Figure 7 Weight fraction vs. n for $R = 10$ at different values of X. Upper curve for any X corresponds to even-ordered and lower curve to odd-ordered homologues

Results[21] for $R = 0.5$, 0.2 and 0.05 lead to similar qualitative conclusions (results can be supplied on request).

For values of R above unity, the general features of the curves remain the same, except that one does not find any dip in the curves from $n = 1$ or 2. This is reasonable because the monomer is depleted very rapidly due to its higher reactivity. However, a new phenomenon manifests itself; for a given value of X, the *MWD* curve splits into two, one for odd values of n and another for even values of n, as shown in *Figure 7* for $R = 10$. The two curves merge at high values of n, the merger occurring at higher and higher values of n as X increases at least until $X = 25$. This effect also dies down as X increases. Results[21] for $R = 2, 4, 10, 25$ and 100 show that for the same X, the separation between the even and odd n graphs increases as R increases. This phenomenon can be explained physically as follows. At large R, the monomer is depleted rapidly, initially, giving the dimer. The P_2 former can then react with P_1 or P_2 to give P_3 and P_4, respectively, but since there is little of P_1 left, formation of P_4 is predominant. Similarly, there is much less formation of P_5 because of the lower amounts of P_1 and P_3 (P_5 can be formed by $P_1 + P_4$ or $P_2 + P_3$), and so on. Thus it is expected that there will be a relative preponderance of even-ordered homologues compared with odd ordered ones. The difference would decrease at large n or X.

On comparing the distributions for $R = 10$ and 1, it is seen that the *MWD* is broader for values of R above unity. This is consistent with the observation in *Figure 5* that ρ_{II} is larger for $R > 1$ than for $R = 1$ at equal values of X. It is further noted that ρ_I is very sensitive to the amount of monomer present and even though, for $R > 1$, only small amounts of P_1 are present in the reaction mass, ρ_I is smaller compared with that for $R = 1$ at any value of X, whereas ρ_{II} shows the reverse behaviour.

CONCLUSIONS

Molecular weight distribution and their moments have been analysed for the kinetic scheme of condensation polymerization with P_1 reacting with P_1 at a rate higher than that of other reactions. The inadequacy of the polydispersity index, ρ_I, is pointed out and it is observed that polydispersity indices beyond 2 are expected for $R > 1$. The molecular weight distributions for $R > 1$ are found to split into two smooth curves for even and odd ordered homologues, this effect decreasing with decreasing values of R or increasing values of X.

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