Control of molecular weight distribution in step-growth polymerization by an intermediate monomer feed method: effect of interchange reactions

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In a kinetically-controlled step-growth polymerization, the molecular weight distribution (MWD) of the polymers produced can be controlled via its reaction path. In this paper, the effect of intermediate monomer feed on the MWD in a batch reactor or a continuous plug flow reactor (PFR) is investigated, and a kinetic model is proposed for MWD development. The present model considers the interchange reactions during polymerization. The variance of the MWD can be increased by the intermediate monomer feed method while the interchange reactions counteract this effect. The present model has given satisfactory predictions for the polycondensation of adipic acid and 1,6-hexanediol.

(Keywords: kinetics of step-growth polymerization; method of moments; polycondensation; molecular weight distribution; mathematical model; interchange reaction; adipic acid; 1,6-hexanediol)

INTRODUCTION

Recently, step-growth polymerization has experienced revived interest as an attractive research area. This is partly due to the development of new materials such as aramides, polyphenylene sulphide (PPS), polyether ether ketone (PEEK) and polyether sulphone (PES). In order to produce higher quality polymers, precise control of the molecular weight distribution (MWD) is indispensable. In a kinetically-controlled step-growth polymerization, the MWD can be made broader by application of various reactor types, such as a continuous stirred tank reactor (CSTR) and a tubular reactor with a recycle loop[1–4]. Recently, a new method has been proposed in which additional monomers are fed to batch reactors or plug flow reactors (PFR)[5,6]. The concept of this method is shown schematically in *Figure 1*. Monomers are divided into two portions and one of them is fed intermediately at the end of stage 1. In this case the MWD would be controlled by the fraction of additional feed monomer, ϕ, the extent of reaction at the end of stage 1, p_1, and the final (or overall) extent of reaction, p_f. A kinetic model for this intermediate monomer feed method has been developed recently by assuming the following simplifying conditions[7].

1. The rate constant, k, is independent of the size of the polymer molecule.
2. The density change of the reaction system during polymerization is negligible.

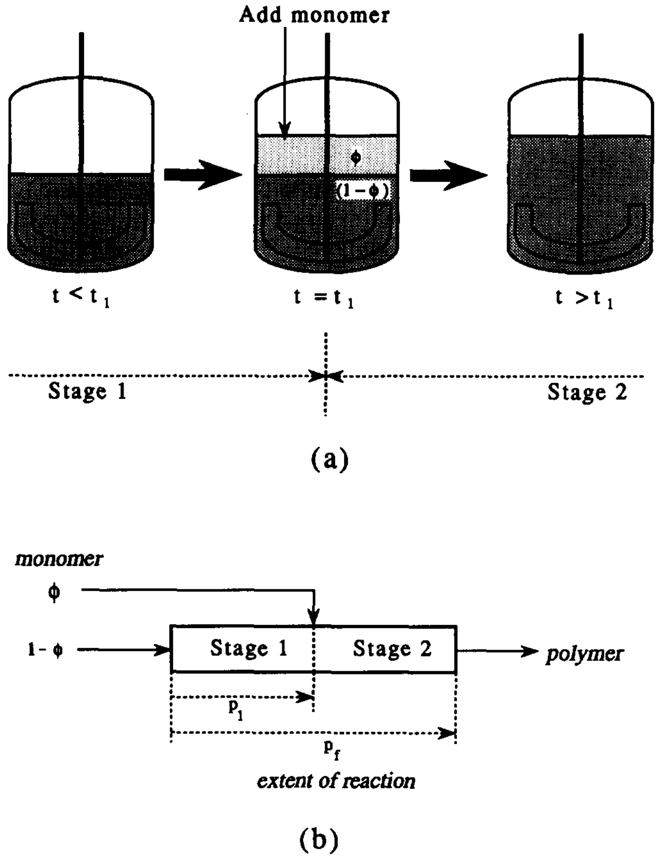

Figure 1 Schematic drawing of the intermediate monomer feed method by application of: (a) batch reactor; (b) a plug flow reactor (PFR). A fraction of monomers, ϕ is fed intermediately in the reactor

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3. Reactions are irreversible.
4. There are no side reactions such as cyclization reactions and redistribution reactions.

Assumptions (1) to (3) may be applicable for many polymerization systems by selecting an appropriate reaction condition. However, if the MWD deviates much from the most probable distribution, the redistribution reactions would change the MWD significantly even when their occurrence is relatively scarce. In the synthesis of polyesters, the effect of interchange reactions can not be neglected[8].

In this paper, after discussion of some qualitative effects of the intermediate monomer feed method on the MWD assuming no interchange reactions to occur, a new kinetic model which considers interchange reactions during polymerization is proposed. This model is applied to the polycondensation of adipic acid and 1,6-hexanediol.

THEORETICAL

Step-growth polymerization without interchange reactions

In an earlier paper[7], a kinetic model was proposed to describe an irreversible step-growth polymerization of (A-B) type monomer, (A-A) + (B-B) type monomer, and (A_f) type monomer under the simplifying assumptions described earlier. Let us first clarify the qualitative features of the effect of the intermediate monomer feed on the MWD assuming no interchange reactions to occur. For an (A-B) type monomer, the concentration of polymer molecule with chain length n, $[P_n]$ is given by[7]:

$$\frac{[P_n]}{(1-p_2)^2} = [P_n]_{20} + \sum_{j=1} [P_j]_{20}[P_{n-j}]_{20}\frac{p_2}{(Q_0)_{20}} + \sum_{\substack{j=1\\k=1}} [P_j]_{20}[P_k]_{20}[P_{n-j-k}]_{20}\left(\frac{p_2}{(Q_0)_{20}}\right)^2 + \sum_{\substack{j=1\\k=1\\l=1}} [P_j]_{20}[P_k]_{20}[P_l]_{20}[P_{n-j-k-l}]_{20} \times\left(\frac{p_2}{(Q_0)_{20}}\right)^3 + \cdots\cdots + [P_1]_{20}^n\left(\frac{p_2}{(Q_0)_{20}}\right)^{n-1} \tag{1}$$

where $(Q_0)_{20}$ is the zeroth order moment at the start of stage 2; $[P_n]_{20}$ is the concentration of polymer molecule with the degree of polymerization, n at the start of stage 2; and p_2 is the extent of reaction in the second stage of polymerization. The ith order moment of polymer molecule distribution, Q_i is defined as follows.

$$Q_i = \sum_{n=1}^{\infty} n^i [P_n] \tag{2}$$

Figure 2 shows the calculated results of the weight-chain length distribution (the weight fraction distribution) when the extent of reaction at the end of stage 1, $p_1 = 0.9$ and the weight fraction of additional monomer feed, $\phi = 0.5$. In the figure, p_2 is the extent of reaction in the second stage of polymerization based on the total number of functional groups at the start of stage 2 while p_f is the overall extent of reaction based on the total number of functional groups including the first stage of polymerization, and n is the degree of polymerization (chain length). First, the height of the peak at $n = 1$

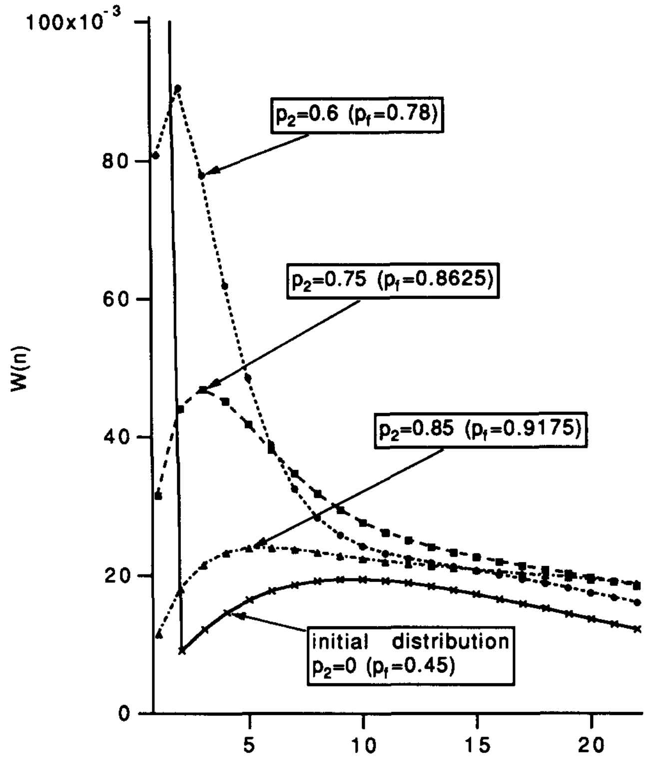

Figure 2 Weight fraction distribution development during the second stage of polymerization: (A-B) type; $p_1 = 0.9$; $\phi = 0.5$

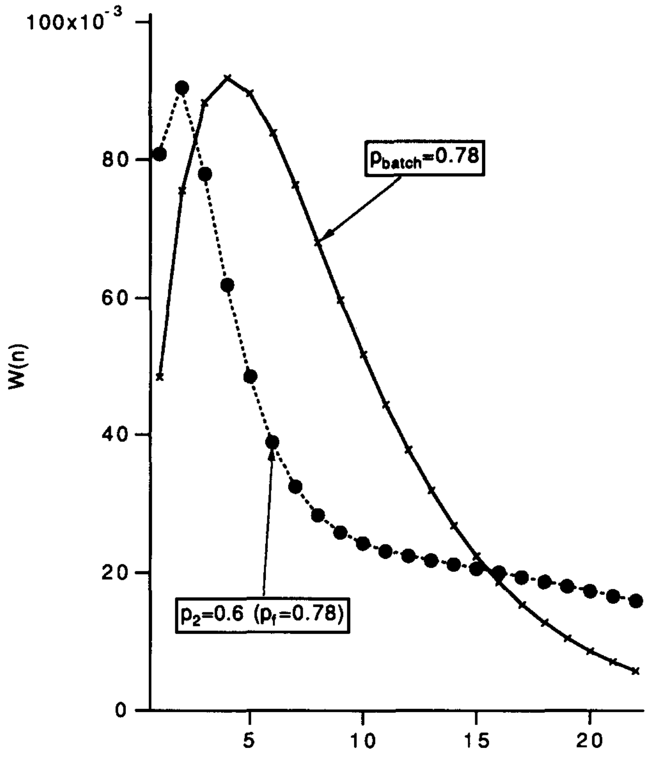

Figure 3 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.5$; $p_f = 0.78$

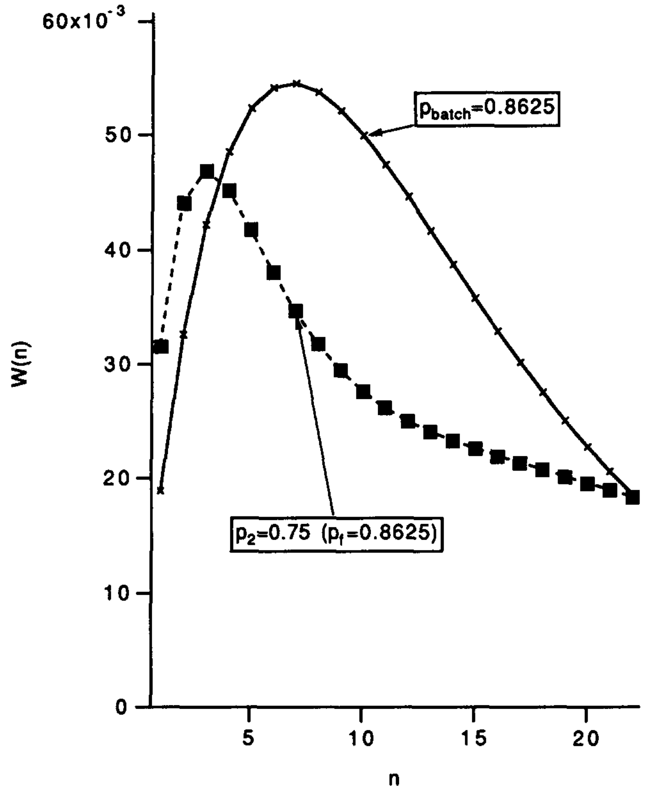

Figure 4 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.5$; $p_f = 0.8625$

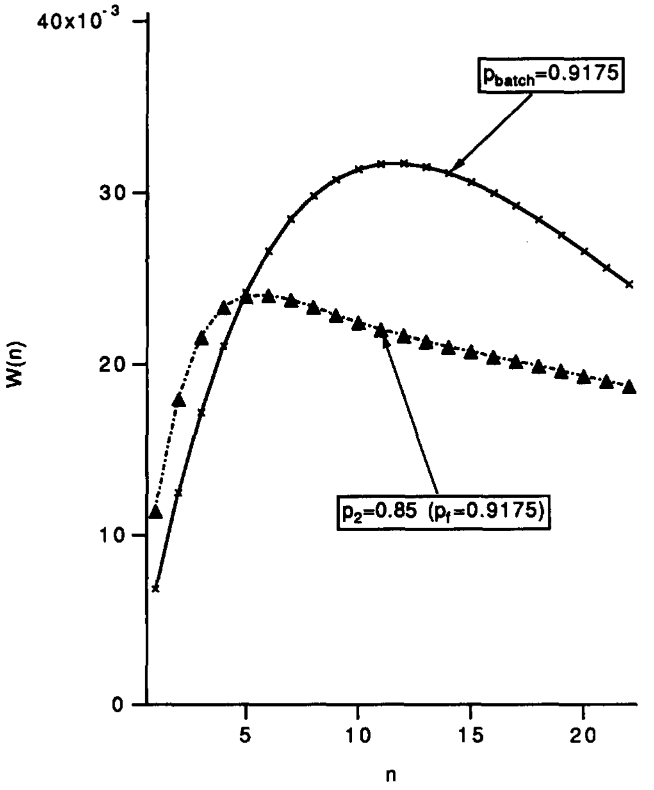

Figure 5 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.5$; $p_f = 0.9175$

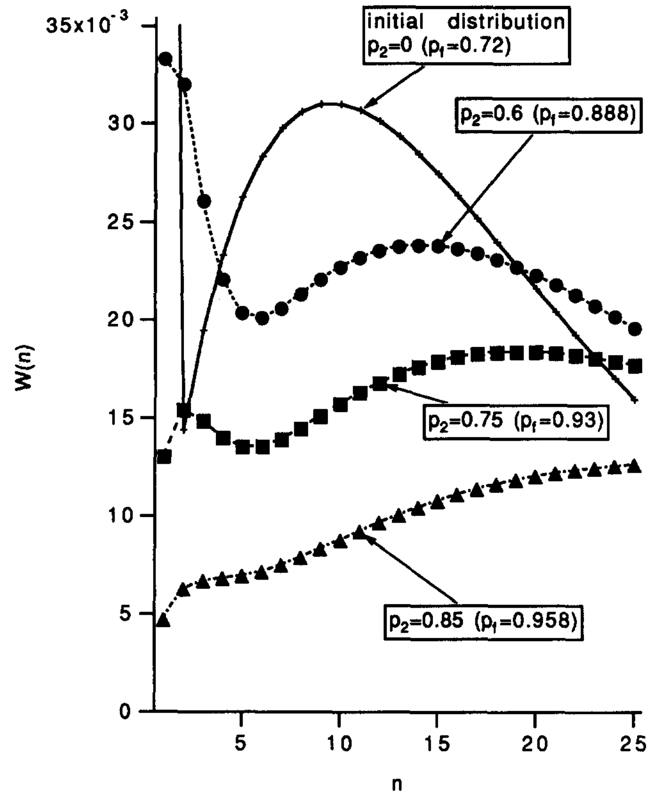

Figure 6 Weight fraction distribution development during the second stage of polymerization. (A-B) type; $p_1 = 0.9$; $\phi = 0.2$

decreases, then the peak moves to larger n as shown in *Figure 2*. In this calculation condition, the weight-chain length distribution is unimodal. However, the distribution of polymers produced is quite different from that produced in a batch reactor, i.e., the most probable distribution, as shown in *Figures 3–5*. The effect of the intermediate monomer feed on the MWD is to increase the weight fractions of both low and high molecular weight polymers, and therefore, the variance of the weight-chain length distribution is increased.

As shown in Figure 5 of ref. 7, the condition $p_1 = 0.9$ and $\phi = 0.5$ does not have a significant effect on the polydispersity index. Consider next the case $p_1 = 0.9$ and $\phi = 0.2$ in which the polydispersity index can be increased significantly. *Figure 6* shows the change of weight-chain length distribution during the second stage of polymerization for this condition. In this case the weight-chain length distribution is bimodal. Although the modality of MWD itself does not have significant meaning[9], the shape of the weight-chain length distribution is completely different from the most probable distribution, as shown in *Figures 7–9*. The effect of the intermediate monomer feed is emphasized for this case, i.e., the weight fractions of both low and high molecular weight polymers are increased significantly.

Step-growth polymerization with interchange reactions

In general, polyesters that are terminated with hydroxyl and carboxyl groups can undergo three kinds of redistribution reactions[8], as shown in *Figure 10*. For polyesters, the intermolecular alcholysis is the most important interchange reaction[8]. Qualitatively, since larger molecules have a better chance of being attacked by a greater number of smaller molecules, larger molecules will tend to become smaller while smaller

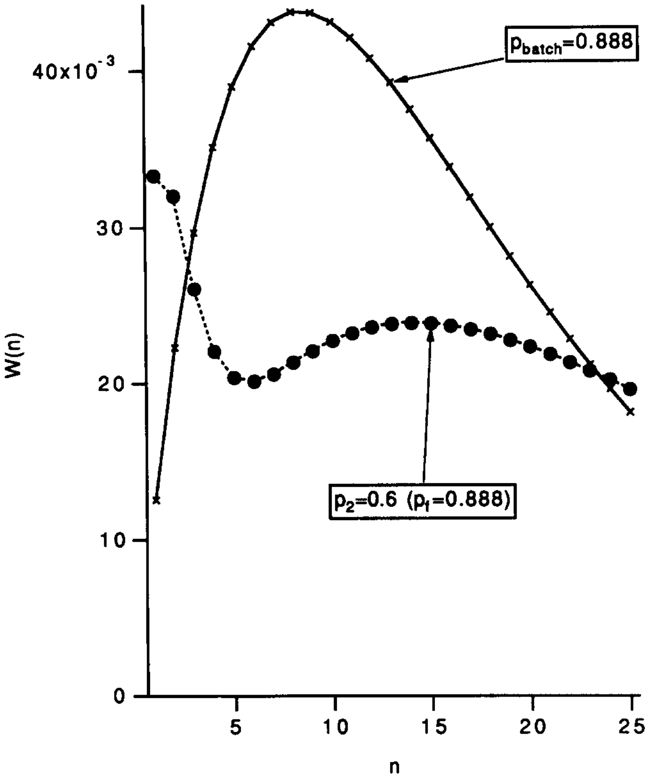

Figure 7 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.2$; $p_f = 0.888$

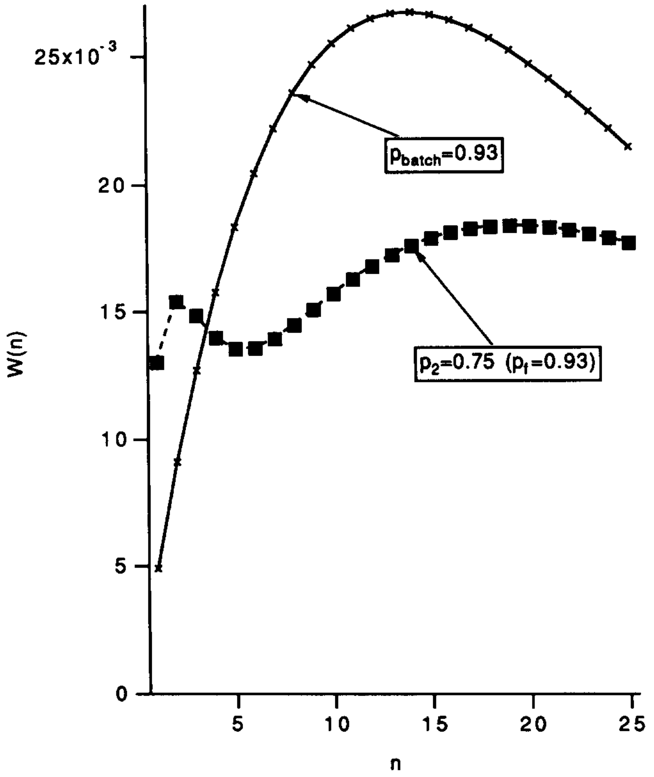

Figure 8 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.2$; $p_f = 0.93$

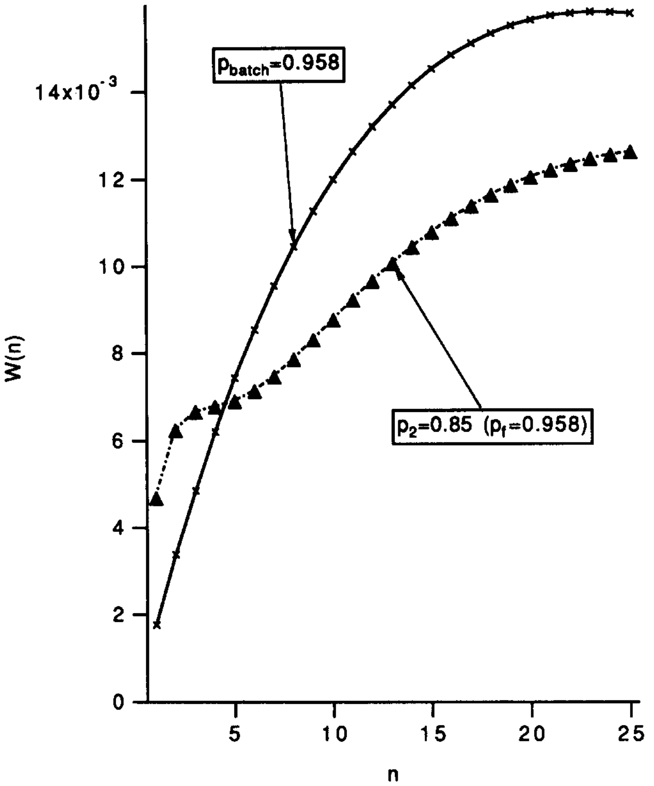

Figure 9 Comparison of the weight fraction distribution of the polymers produced by batch polymerization and the intermediate monomer feed method at the same overall extent of reaction, p_f. (A-B) type; $p_1 = 0.9$; $\phi = 0.2$; $p_f = 0.958$

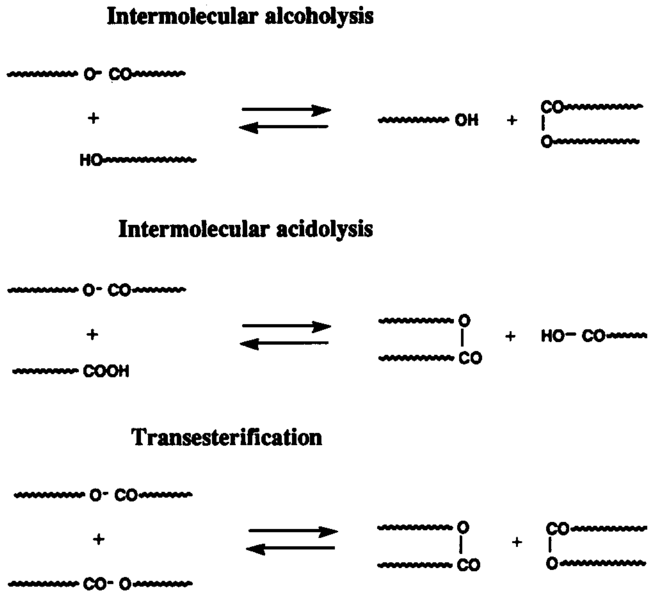

Figure 10 Schematic drawing of the redistribution reactions for polyesters

molecules will tend to increase in size through interchange reactions. This tendency clearly counteracts the effect of the intermediate monomer feed. This argument is supported by the fact that when two polymers with different most probable distributions are blended, the whole distribution tends to approach a single most probable distribution during interchange reactions[8,10]. When one considers interchange reactions, random degradations, or crosslinking reactions, information on the whole distribution is usually required to study the weight fraction of a particular degree of polymerization. Hence, the exact calculation tends to become fairly complicated except when the whole distribution can be expressed by simple distribution functions such as the Schulz–Zimm distribution and the Wesslau distribution[11,12].

We will now consider the polymerization of (A-B) type monomer assuming that only the B-group can cause interchange reactions. The reactions considered here are given by:

$$\text{propagation:}\quad P_n + P_m \xrightarrow{k} P_{m+n} \tag{3}$$

$$\text{interchange reaction:}\quad P_n + P_m \xrightarrow{k_r} P_r + P_{m+n-r} \tag{4}$$

The balance equation for P_n is given by:

$$\frac{\mathrm{d}[P_1]}{\mathrm{d}t} = -2k[P_1]Q_0 + k_r Q_0 \sum_{j=2}^{\infty} [P_j] - k_r[P_1] \sum_{j=2}^{\infty} (j-1)[P_j] \tag{5}$$

$$\frac{\mathrm{d}[P_n]}{\mathrm{d}t} = k \sum_{j=1}^{n-1} [P_j][P_{n-j}] - 2k[P_n]Q_0 + k_r Q_0 \sum_{j=n+1}^{\infty} [P_j] + k_r \sum_{j=1}^{n-1} \sum_{m=n-j+1}^{\infty} [P_j][P_m] - k_r(n-1)[P_n]Q_0 - k_r[P_n] \sum_{j=2}^{\infty} (j-1)[P_j] \qquad (n \geqslant 2) \tag{6}$$

From equations (5) and (6), the zeroth, first, and second order moment of the polymer molecule distribution, which was defined by equation (2), are given by:

$$\frac{\mathrm{d}Q_0}{\mathrm{d}t} = -kQ_0^2 \tag{7}$$

$$\frac{\mathrm{d}Q_1}{\mathrm{d}t} = 0 \tag{8}$$

$$\frac{\mathrm{d}Q_2}{\mathrm{d}t} = 2kQ_1^2 + \frac{k_r}{3}(-Q_3Q_0 + 3Q_2Q_1 - 3Q_1^2 + Q_1Q_0) \tag{9}$$

As shown in the above equations, Q_0 and Q_1 are determined solely by propagation reactions, which shows that the number-average degree of polymerization is not affected by interchange reactions. The interchange reactions change the second order moment, Q_2 through the second term of the right-hand side of equation (9). It is straightforward to show that this term is zero for the most probable distribution, and therefore, the interchange reactions do not affect the MWD in a batch reactor. This result was also proved by statistical argument[13–16]. From the physical viewpoint, equation (9) shows that the effect of interchange reactions becomes significant when the MWD deviates from the most probable distribution.

Equation (9) includes a higher order moment (Q_3). In order to solve the moment equation, a closure method is needed. One of the most frequently used closure methods is that of Hulbert and Katz[17,18].

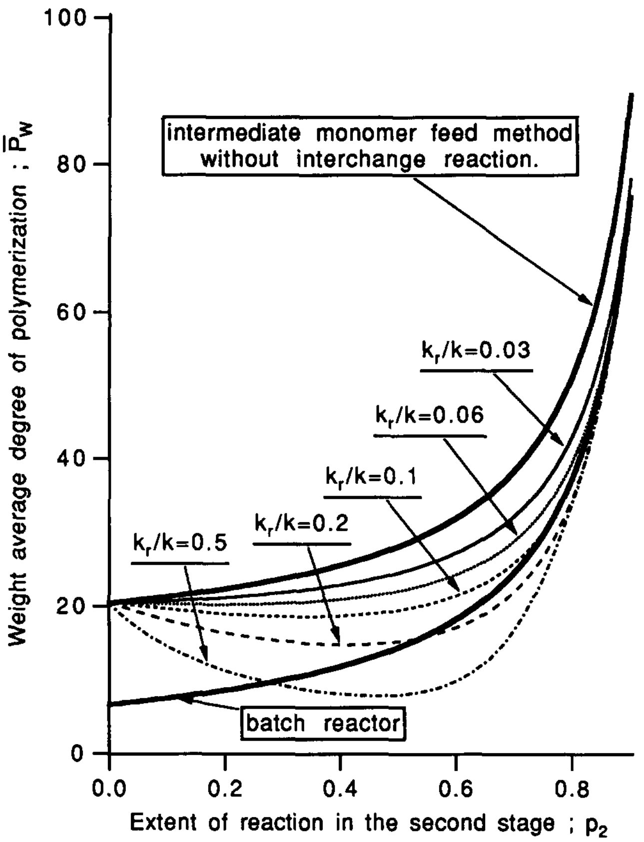

Figure 11 Calculated weight-average degree of polymerization development during the second stage of polymerization. $p_1 = 0.924$; $\phi = 0.2$

$$Q_3 = \frac{2Q_2}{Q_1Q_0}(2Q_2Q_0 - Q_1^2) \tag{10}$$

Equation (10) may be a good approximation for most polymers produced in a batch reactor. However, as shown in *Figures 2* and *6*, our initial distribution is an unusual distribution, and it is clear that equation (10) does not hold.

If no interchange reactions occur, the distribution of the degree of polymerization in the second stage of polymerization follows:

$$Q_2 - (Q_2)_{20} = \frac{2Q_1^2}{(Q_0)_{20}}\left(\frac{p_2}{1-p_2}\right) \tag{11}$$

$$Q_3 - (Q_3)_{20} = \frac{6Q_1^3}{(Q_0)_{20}^2}\left(\frac{p_2}{1-p_2}\right)^2 + \frac{6Q_1(Q_2)_{20}}{(Q_0)_{20}}\left(\frac{p_2}{1-p_2}\right) \tag{12}$$

where $(Q_0)_{20}$, $(Q_2)_{20}$, and $(Q_3)_{20}$ are the zeroth, second, and third order moments of polymer molecule distribution at the start of the second stage of polymerization. It should be noted that the first order moment, Q_1 is constant throughout the second stage of polymerization.

From equations (11) and (12), one obtains the following relationship.

$$Q_3 = (Q_3)_{20} + \frac{3\{Q_2 - (Q_2)_{20}\}\{Q_2 + (Q_2)_{20}\}}{2Q_1} \tag{13}$$

Under conditions in which the effect of interchange reactions is not very significant, equation (13) may be

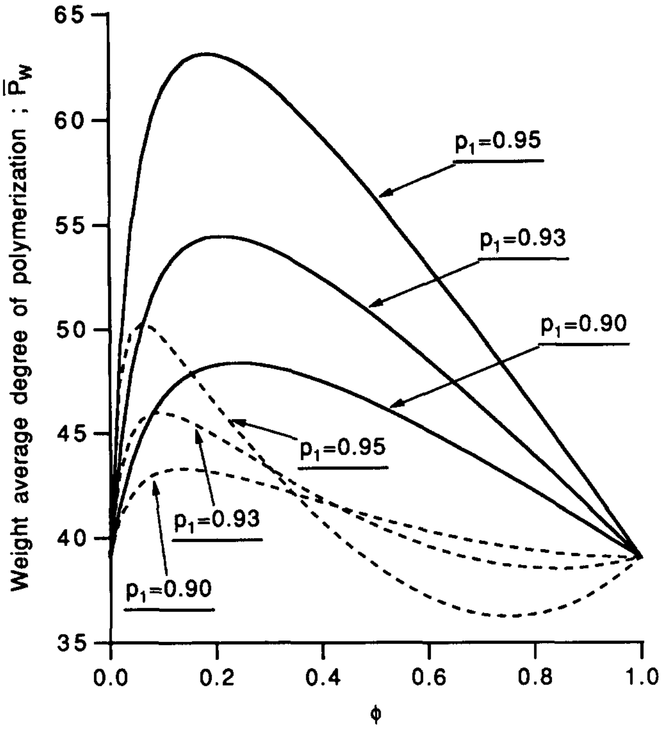

Figure 12 Effect of p_1 and ϕ on the weight-average degree of polymerization, $\bar{P}_W$ when $p_f = 0.95$: ——, without interchange reactions; ------, with interchange reactions; $k_r/k = 0.03$

used as a closure rule to solve equation (9) as a first approximation.

Figure 11 shows the results calculated when $p_1 = 0.924$ and $\phi = 0.2$. As the parameter k_r/k increases, the weight-average degree of polymerization in the second stage of polymerization approaches that of polymers produced in a batch reactor. As shown in the figure, the effect of an interchange reaction is very important even when the ratio of kinetic rate constants, k_r/k is fairly small. Since the weight average degree of polymerization should never become smaller than that in a batch reactor, the results calculated for $k_r/k = 0.2$ and 0.5 are incorrect. This is reasonable since we have assumed that the effect of interchange reactions is small in order to apply the closure rule, equation (13). However, in order for the intermediate monomer feed method to increase the polydispersity of the MWD effectively, the effect of any interchange reaction must be small, i.e., the distribution would soon approach the most probable distribution if the interchange reactions are significant. Therefore, although the applicability of equation (13) is somewhat limited, in practice, equation (13) may be a useful closure rule to solve equation (9) for the intermediate monomer feed method.

As shown in an earlier paper[7], in order to make the polydispersity of MWD larger in the intermediate monomer feed method, the extent of reaction, p_1 must be sufficiently high and there exists an optimum amount of additional monomer feed, ϕ (see *Figures 5*, *10* and *13* in ref. 7). A general feature may not change a great deal even when the interaction reactions occur. However, as shown in *Figure 12*, the weight-average degree of polymerization is made significantly smaller by interchange reactions when p_1 is large. It is also shown in *Figure 12* that the optimum ϕ for increasing the polydispersity shifts to smaller ϕ when the interaction reaction occurs. (Since the number-average degree of polymerization, $\bar{P}_N$ can not be changed by the intermediate monomer feed method[7], the weight-average degree of polymerization and the polydispersity index are, essentially, equivalent.) Again, equation (13) will not be applicable at high ϕ with high p_1, where the MWD approaches the most probable distribution rapidly.

It is clear that the present model can be used not only for step-growth polymerization of (A-B) type monomer but also for that of equivalents of (A-A) + (B-B) type monomers.

EXPERIMENTAL

High purity adipic acid and 1,6-hexanediol were used with dibutyltin oxide as catalyst. All reagents were used without further purification.

Equimolar amount of adipic acid and 1,6-hexanediol with 0.2 wt% of dibutyltin oxide were charged into a 1 l glass flask, and the temperature was raised to 160°C. The temperature was maintained at 160°C, and N_2 bubbling was continued throughout the polymerization. The byproduct, water, started to evaporate when the temperature reached about 155°C. In order to promote the forward reaction, a weak vacuum ($\sim$300 mm Hg) was applied. After about 6 h of polymerization, an additional equimolar mixture of adipic acid and 1,6-hexanediol was added, and the second stage of polymerization proceeded for about 4 h. An example of a time–conversion curve is shown in *Figure 13*.

The extent of the reaction was determined by the titration of carboxyl and hydroxyl groups. The number-average molecular weight, $\bar{M}_N$ was determined by vapour phase osmometry (v.p.o.), and the weight-average molecular weight, $\bar{M}_W$ and the MWD were determined by gel permeation chromatography (g.p.c.) (Showa Denko column KF-804, 803 and 802, with tetrahydrofuran as a mobile phase).

RESULTS AND DISCUSSION

Figures 14–16 show the experimental and calculated results for the average molecular weight in the second stage of polymerization. Since the calculated number-

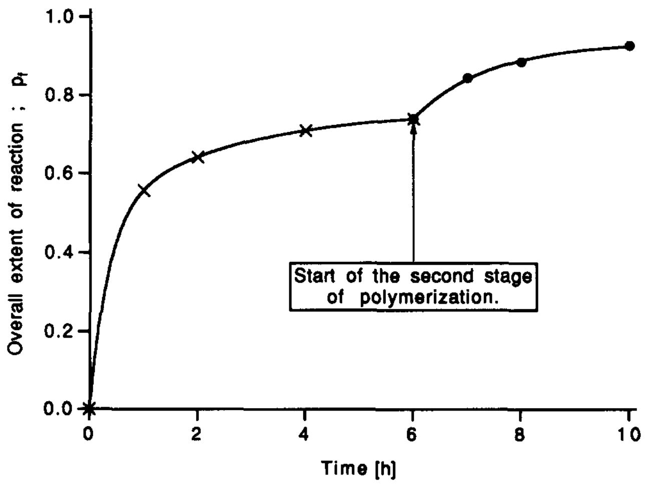

Figure 13 Example of the time–conversion curve. $p_1 = 0.924$; $\phi = 0.2$ at 160°C

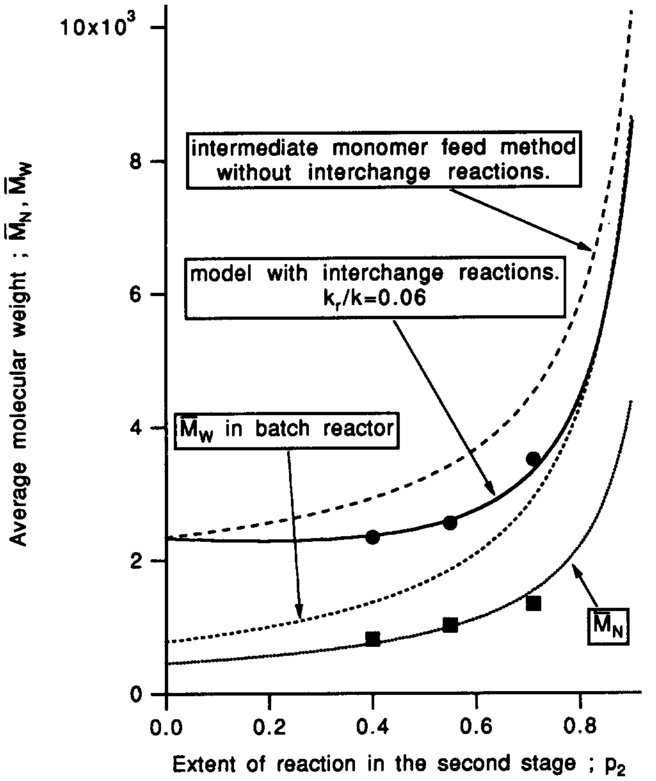

Figure 14 Comparison of the experimental results and model calculations for the weight-average molecular weight during the second stage of polymerization. $p_1 = 0.924$ and $\phi = 0.2$. The model calculations with $k_r/k = 0.06$ compare well with the experimental results

average molecular weight, $\overline{M_N}$ is the same for a batch reactor and intermediate monomer feed method, only one curve for $\overline{M_N}$ is shown. In the calculation, the average molecular weight of the monomeric unit, 114, was used to convert the degree of polymerization to the molecular weight. As shown in the figures, the measured weight-average molecular weight, $\overline{M_W}$ comes between the calculated curves for a batch reactor and the intermediate monomer feed method without considering the interchange reactions, which indicates the occurrence of interchange reactions. (Since the byproduct, water, is removed continuously at 160°C under vacuum, the reversibility of the reaction may be neglected.) The model (equation (9) with the closure rule, equation (13)) agrees well with the parameter, $k_r/k = 0.06$. Under these experimental conditions, the closure rule, equation (13) seems to be applicable.

For the synthesis of polyethylene terephthalate, it has been reported that the polycondensation and interchange reaction rates are of the same order of magnitude around 254°C, but the Arrhenius activation energy for the latter is larger[8]. In our experiment, lower reaction temperature may play a role in decreasing the interchange reaction rate.

At present, our model can not predict the whole MWD curve when the interchange reactions are not negligible. However, one may attempt qualitative discussions to compare the experimental data with the calculated results assuming no interchange reactions. *Figure 17* shows one of the comparisons of the MWD. (Please note that *Figure 17* is the distribution of molecular weights, not their logarithms, which are usually used for g.p.c. data.) Due

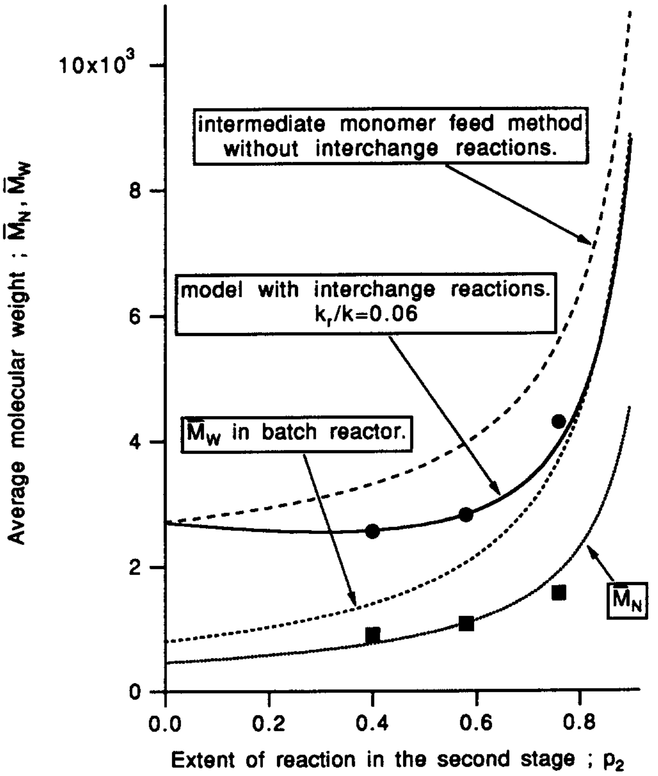

Figure 15 Comparison of the experimental results and model calculations for the weight-average molecular weight during the second stage of polymerization. $p_1 = 0.934$ and $\phi = 0.2$. The model calculations with $k_r/k = 0.06$ compare well with the experimental results

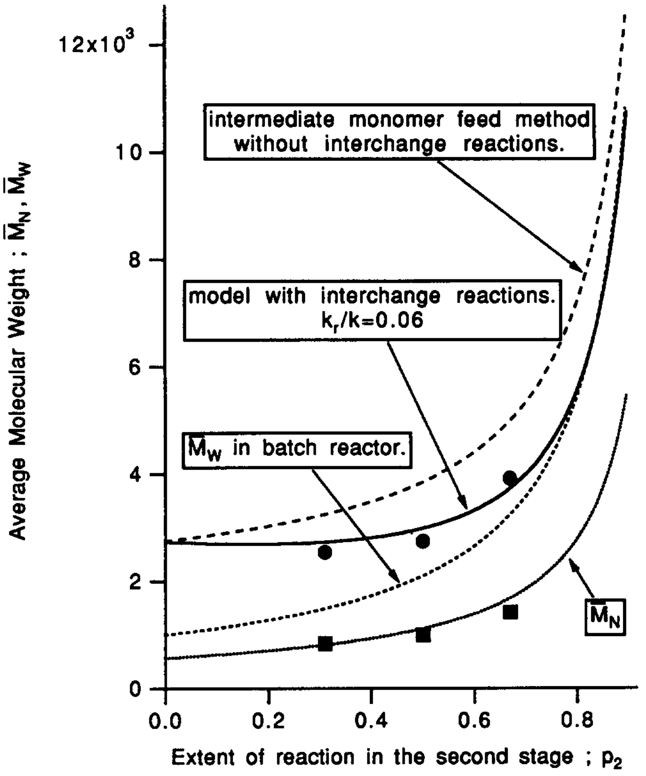

Figure 16 Comparison of the experimental results and model calculations for the weight-average molecular weight during the second stage of polymerization. $p_1 = 0.931$ and $\phi = 0.15$. The model calculations with $k_r/k = 0.06$ compare well with the experimental results

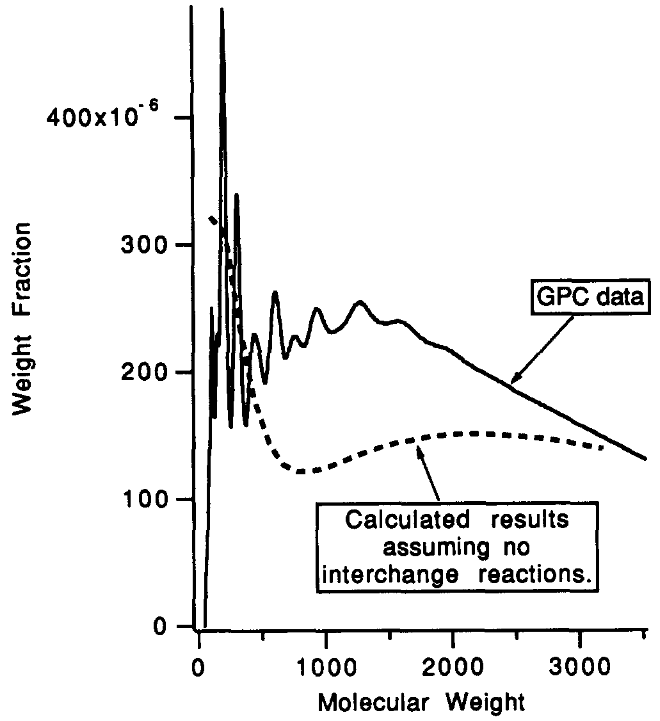

Figure 17 Comparison of the MWD between g.p.c. data and the model without interchange reactions. $p_1 = 0.934$; $\phi = 0.2$; $p_f = 0.893$

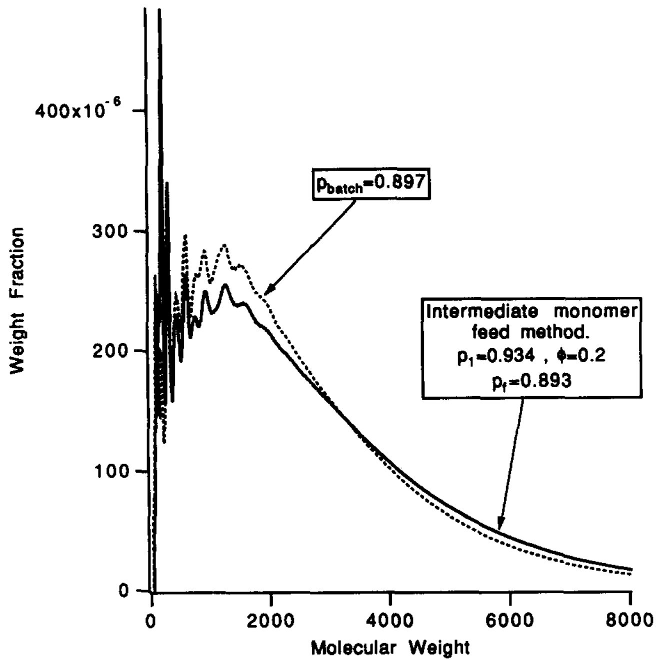

Figure 18 Comparison of the measured MWD of the polymers formed by batch polymerization and the intermediate monomer feed method: batch polymerization, $p_{\mathrm{batch}} = 0.897$; intermediate monomer feed method, $p_1 = 0.934$, $\phi = 0.2$, $p_f = 0.893$

to the interchange reactions, the variance of the MWD is much smaller for the experimental data. However, an important feature of the intermediate monomer feed method can still be found, namely, the weight fractions of both low and high molecular weight polymers are increased. This effect can also be confirmed by the comparison of the MWD of polymers synthesized by a batch reactor, and by the intermediate monomer feed method at the same overall conversion, p_f, as shown in *Figure 18*. Due to the interchange reactions, the difference of the MWD is small. However, clear difference can be seen.

When the interchange reactions occur, the MWD approaches the most probable distribution quickly, especially at high extents of reaction in the second stage of the polymerization. This is clear from the following argument. The ratio of the rate of interchange reaction, R_r and the polymerization rate, R_p is given by:

$$\frac{R_r}{R_p} = \left(\frac{k_r}{k}\right)\left(\frac{Q_1 - Q_0}{Q_0}\right)$$

$$= \left(\frac{k_r}{k}\right)\left(\frac{(\bar{P}_N)_{20}}{1 - p_2} - 1\right) \qquad (14a)$$

$$= \left(\frac{k_r}{k}\right)\left(\frac{1}{1 - p_f} - 1\right) \qquad (14b)$$

where p_2 is the extent of reaction in the second stage of polymerization, while p_f is the overall extent of reaction which is based on the total number of functional groups of the monomeric units. $(\bar{P}_N)_{20}$ is the number-average degree of polymerization at the start of the second stage of polymerization. As shown in the above equation, R_r/R_p increases rapidly as p_2 (or p_f) approaches unity, even though k_r/k is small.

It may be worth noting here that the application of equations (7) to (9) is not limited to the intermediate monomer feed method. Equations (7) to (9) are applicable to a step-growth polymerization whose ingredients are polymers with a distribution, although it is necessary to develop an appropriate closure method in order to solve equation (9).

The intermediate monomer feed method may be useful not only to produce polymers with larger variance in MWD, but to produce novel block copolymers.

CONCLUSIONS

The intermediate monomer feed method is a convenient way to control the MWD in step-growth polymerization if the reaction system is not in equilibrium. A kinetic model to predict MWD development has been proposed. The present model considers the interchange reactions during polymerization. The change in weight-average degree of polymerization can be calculated by application of a closure method. The closure method we have proposed can be used when the effect of interchange reaction is relatively small, and the model has given satisfactory predictions for the polycondensation of adipic acid and 1,6-hexanediol at 160°C. The development of the closure method may improve the accuracy of the present model.

There remain many problems to be solved to produce step-growth polymers with a desirable MWD. However, we do believe the present approach will give greater insight into improving the control method of the MWD.

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