Control of molecular-weight distribution in step-growth polymerization: the intermediate monomer feed method

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In irreversible step-growth polymerization, the molecular-weight distribution (MWD) of the polymers produced can be controlled via the reaction path. In this paper, the effect of intermediate monomer feed on MWD in batch reactors or continuous plug flow reactors is investigated using a kinetic approach. It is found that the polydispersity index ($\overline{P_W}/\overline{P_N}$) of the MWD can be made larger than 2 and that its magnitude can be controlled by the extent of reaction in the first stage (before additional monomers are fed), p_1, the final extent of reaction, p_f, and the amount of monomer fed additionally, ϕ. For non-linear polymerization, the effect of intermediate monomer feed is more significant than that for linear polymers, and the extent of reaction at the gel point, p_c, can be lowered significantly.

(**Keywords: kinetics; step-growth polymerization; method of moments; polycondensation; molecular-weight distribution; modelling**)

INTRODUCTION

Historically, a significant effort has been made to produce synthetic polymers with smaller variance of the molecular-weight distribution (MWD), i.e. mono-disperse polymers. However, in commercial polymeric materials, polymers with narrower distributions are not always superior to those with broader distributions, since various properties are required at the same time. For example, in the toner binders for copying machines, polymers with braoder distribution may be preferable because polymers with low molecular weights are necessary for the binder to adhere to the paper satisfactorily, while those with high molecular weights are needed to prevent them from sticking to the heat roller, which is called the fusing station[1].

In step-growth polymerization, the MWD can be made broader by application of various reactor types such as the continuous stirred tank reactors (CSTR) and tubular reactors with a recycle loop[2-5]. However, these methods may possess shortcomings in that they need a long start-up period and have problems in the stability of the system.

In this paper, a new method in which additional monomers are fed to batch reactors or plug flow reactors (PFR) is considered[6,7]. This policy is schematically shown 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. Note that the final extent of reaction, p_f, is the only variable to control the MWD

of polymers produced in batch reactors, plug flow reactors (PFR) and homogeneous continuous stirred tank reactors (HCSTR).

Various statistical derivations for the MWD in step-growth polymerization have been developed[8-16] since the pioneering work of Flory[17,18] and Stock-mayer[19]. However, in order to investigate the effect of reaction path, i.e. to apply to various reactor types other than batch reactors, kinetic approaches based on the use of material balances may have greater generality, although several attempts at statistical methods to account for the kinetic features of the reaction systems have been made[20,21]. As for the kinetic approaches, in order to solve an infinite set of differential equations describing the chemical kinetics, various techniques have been applied such as generating functions, Z-transforms, the continuous variable technique, etc.[2-5,22-35]. In this research, the method of moments was applied to the step-growth polymerization of several types, i.e. polymerizations of (A-B) type monomer, of (A-A) type plus (B-B) type monomers, and of (A_f) type monomers that have f functional groups. When f is larger than or equal to 3, non-linear polymers are produced and gelation may be observed during polymerization. In this research, the following simplifying conditions are assumed: namely, (1) the rate constant k is independent of the size of the polymer molecule, (2) reactions are irreversible, (3) there are no side reactions such as cyclization reactions, and (4) the density change of the reaction system during polymerization is negligible.

THEORETICAL

Step-growth polymerization of (A-B) type monomer

Let us first consider the step-growth polymerization of (A-B) type monomer, in which the reacting functional

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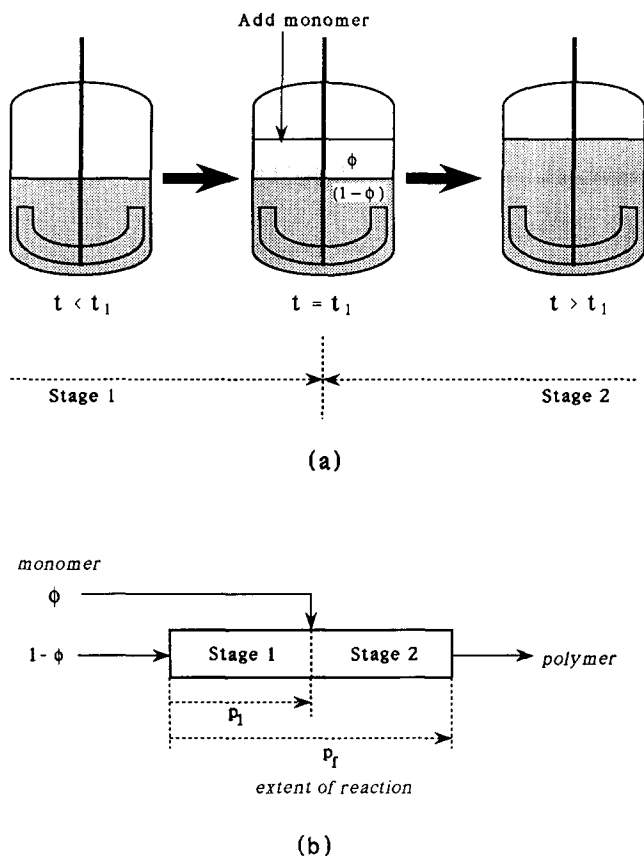
(a)

(b)

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

groups A and B exist in the same molecule. Some examples of this kind of monomer are hexamethylene adipamide [COOH-(CH$_2$)$_4$-CONH-(CH$_2$)$_6$-NH$_2$] and aminocaproic acid [COOH-(CH$_2$)$_5$-NH$_2$]. Let the reaction between A and B groups occur irreversibly, according to second-order kinetics, with a rate constant independent of chain length, so that the overall decrease in concentration of end-groups is given by:

$$\frac{d[A]}{dt} = \frac{d[B]}{dt} = -k[A][B] = -k[A]^2 \quad (1)$$

where t is the reaction time and k is the rate constant.

Let us define the ith-order moment of the polymer molecule distribution, Q_i:

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

where n is the degree of polymerization and $[P_n]$ is the concentration of polymer molecule with degree of polymerization n.

The monomer (P$_1$) is consumed whenever it reacts with any molecular species, and its mole balance equation is given by:

$$d[P_1]/dt = -2k[P_1]Q_0 \quad (3)$$

where Q_0 is the zeroth-order moment of the polymer molecule distribution.

The balance equation for P$_n$ ($n \geqslant 2$) is given by:

$$\frac{d[P_n]}{dt} = k \sum_{j=1}^{n-1} [P_j][P_{n-j}] - 2k[P_n]Q_0 \quad (n \geqslant 2)$$
$$(4)$$

From equations (3) and (4), the ith-order moment Q_i is given by:

$$\frac{dQ_i}{dt} = k \sum_{j=0}^{i} \binom{i}{j} Q_{i-j}Q_j - 2kQ_iQ_0 \quad (5)$$

Equation (5) can be used to calculate the *MWD* starting from any initial distribution.

Now we are to consider the number- and weight-average degrees of polymerization as functions of the extent of reaction. Useful lower-order moment equations are as follows:

$$dQ_0/dt = -kQ_0^2 \quad (6)$$

$$dQ_1/dt = 0 \quad (7)$$

$$dQ_2/dt = 2kQ_1^2 \quad (8)$$

Equation (6) is equivalent to equation (1). From equation (7), one obtains:

$$Q_1 = Q_{10} = \text{constant} \quad (9)$$

where Q_{10} is the initial value of Q_1. Q_0 can be related with the extent of reaction based on a stoichiometric consideration, namely:

$$Q_0 = \sum_{n=1}^{\infty} [P_n] = [A]_0(1-p) = Q_{00}(1-p) \quad (10)$$

where $[A]_0$ is the initial concentration of A groups, p is the extent of reaction and Q_{00} is the initial value of Q_0.

Therefore, from equations (9) and (10), the number-average degree of polymerization, $\overline{P}_N$, is given by:

$$\overline{P}_N = \frac{Q_1}{Q_0} = \frac{Q_{10}}{Q_{00}(1-p)} = \frac{\overline{P}_{NO}}{1-p} \quad (11)$$

where $\overline{P}_{NO}$ is the initial number-average degree of polymerization. By dividing equation (8) by $dp/dt = kQ_{00}(1-p)^2$, and by using equation (9), one obtains:

$$\frac{d\overline{P}_W}{dp} = \frac{d(Q_2/Q_1)}{dp} = \frac{2\overline{P}_{NO}}{(1-p)^2} \quad (12)$$

Equation (12) can be solved analytically. The weight-average degree of polymerization, $\overline{P}_W$, is given by:

$$\overline{P}_W = \overline{P}_{WO} + \frac{2\overline{P}_{NO}p}{1-p} \quad (13)$$

where $\overline{P}_{WO}$ is the initial weight-average degree of polymerization.

Note that when the effect of density change during polymerization is considered, equation (11) is still valid while equation (13) may need a modification. One should make it clear that equations (11) and (13) can be used for any initial polymer distribution.

Now let us consider the case when some portion of monomer is added intermediately, namely, the intermediate monomer feed method. The notations used are shown in *Figure 2*. The number- and weight-average degrees of polymerization at the end of stage 1, $\overline{P}_{N1}$ and $\overline{P}_{W1}$, and those at the start of stage 2, $\overline{P}_{N20}$ and $\overline{P}_{W20}$, are given by:

$$\overline{P}_{N1} = 1/(1-p_1) \quad (14)$$

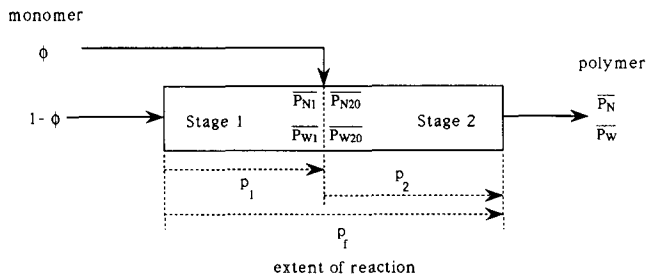$$\overline{P}_{W1} = (1+p_1)/(1-p_1) \quad (15)$$

Figure 2 Schematic drawing of the present method, showing the notation used in the text
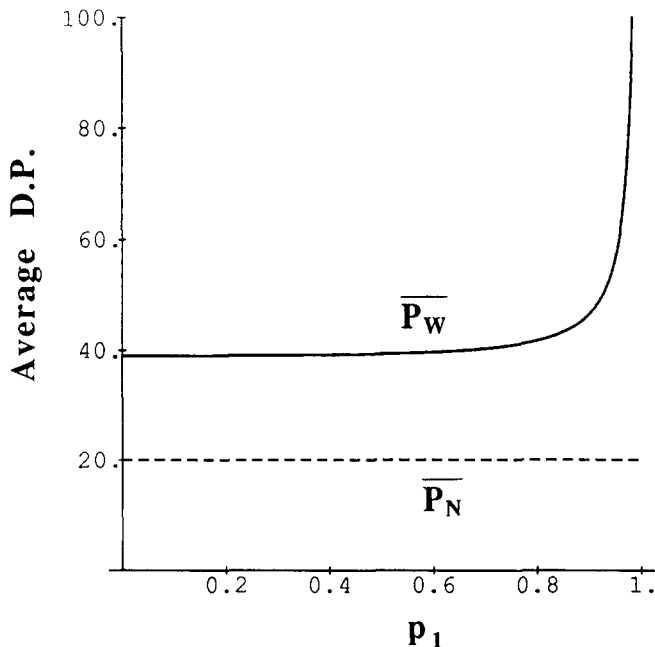

Figure 3 Effect of the extent of reaction in stage 1, p_1, on the final average degree of polymerization, $\overline{P_N}$ and $\overline{P_W}$ ((A-B) type). The final extent of reaction is $p_f = 0.95$ and the fraction of monomer fed at the start of stage 2 is $\phi = 0.5$

$$\overline{P_{N20}} = \frac{\overline{P_{N1}}}{1 + (\overline{P_{N1}} - 1)\phi} \tag{16}$$

$$\overline{P_{W20}} = (1 - \phi)\overline{P_{W1}} + \phi \tag{17}$$

The extent of reaction inside stage 2, p_2, is given by:

$$p_2 = \frac{p_f - (1 - \phi)p_1}{1 - (1 - \phi)p_1} \tag{18}$$

By substituting $\overline{P_{N20}}$, $\overline{P_{W20}}$ and p_2, which are given by equations (14)–(18), into $\overline{P_{N0}}$, $\overline{P_{W0}}$ and p in equations (11) and (13), respectively, one obtains the following equations:

$$\overline{P_N} = 1/(1 - p_f) \tag{19}$$

$$\overline{P_W} = \frac{1 + (1 - 2\phi)p_1}{1 - p_1} + \frac{2[p_f - (1 - \phi)p_1]}{[1 - (1 - \phi)p_1](1 - p_f)} \tag{20}$$

Note that the number-average degree of polymerization, $\overline{P_N}$, is determined only by the final extent of reaction, p_f, and cannot be controlled either by the extent of reaction in stage 1, p_1, or by the fraction of monomer fed at the start of stage 2, ϕ. *Figure 3* shows the effect

of p_1 on the average degree of polymerization when the final extent of reaction $p_f = 0.95$ and the fraction of additional monomer feed $\phi = 0.5$. It is found that, in order to make the variance of *MWD* larger, the degree of polymerization at the end of stage 1 must be sufficiently large. *Figure 4* shows the effect of ϕ on the average degree of polymerization when $p_f = 0.95$ and $p_1 = 0.9$. If the final extent of reaction, p_f, and the extent of reaction in stage 1, p_1, are fixed, there exists a ϕ value which makes the polydispersity index, $\overline{P_W}/\overline{P_N}$, maximum. *Figure 5* shows a three-dimensional plot that shows the effect of both p_1 and ϕ on the weight-average degree of polymerization, when $p_f = 0.95$. (Note that, since the
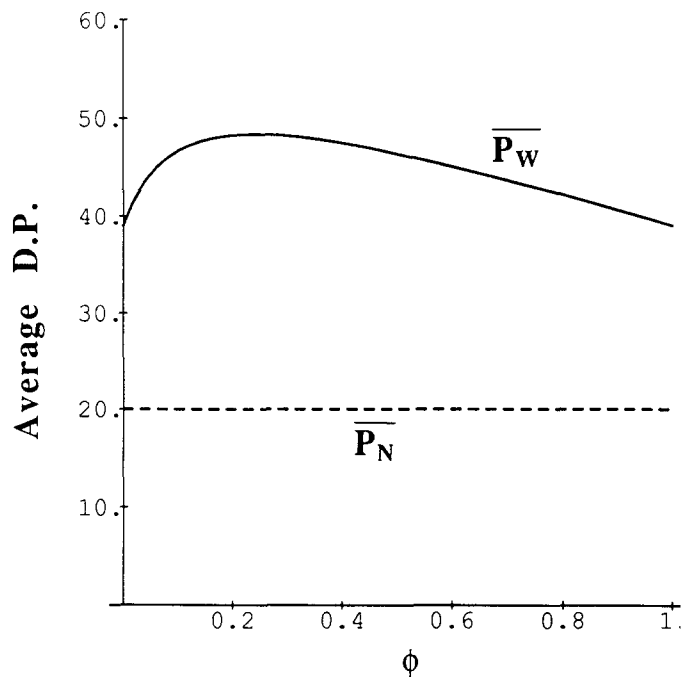

Figure 4 Effect of the fraction of monomer fed at the start of stage 2, ϕ, on the final degree of polymerization, $\overline{P_N}$ and $\overline{P_W}$ ((A-B) type), for $p_f = 0.95$ and $p_1 = 0.9$
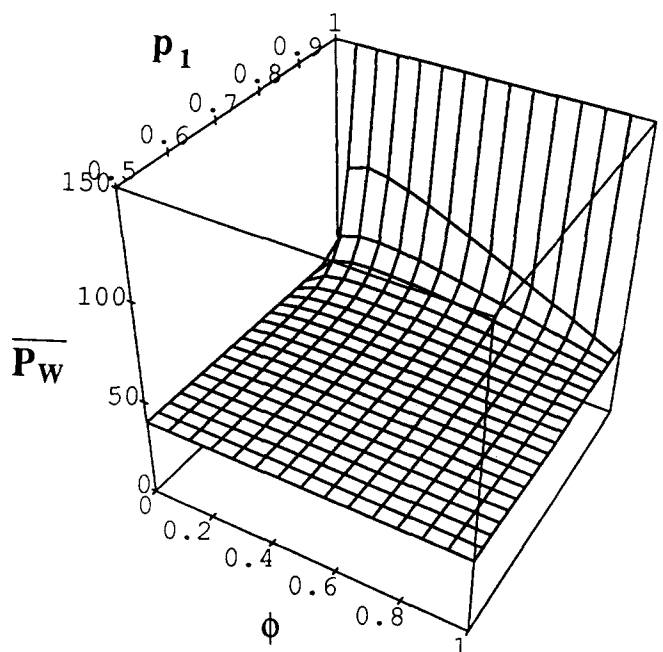

Figure 5 Effect of p_1 and ϕ on $\overline{P_W}$ when $p_f = 0.95$ ((A-B) type)

Table 1 Kinetic scheme and individual mer concentrations

Zeroth moment, Q_0:

$$dQ_0/dt = -kQ_0^2$$

$$Q_0 = \frac{Q_{00}}{1 + kQ_{00}t} = Q_{00}(1 - p)$$

$[P_1]$:

$$d[P_1]/dt + 2kQ_0[P_1] = 0$$

$$[P_1] = [P_1]_0\left(\frac{1}{1 + kQ_{00}t}\right)^2 = [P_1]_0(1 - p)^2$$

$[P_2]$:

$$d[P_2]/dt + 2kQ_0[P_2] = k[P_1]^2$$

$$[P_2] = \left(\frac{1}{1 + kQ_{00}t}\right)^2\left[[P_2]_0 + \frac{[P_1]_0^2}{Q_{00}} + \frac{[P_1]_0^2}{Q_{00}}\left(\frac{1}{1 + kQ_{00}t}\right)\right] = (1 - p)^2\left[[P_2]_0 + \left(\frac{p}{Q_{00}}\right)[P_1]_0^2\right]$$

$[P_3]$:

$$d[P_3]/dt + 2kQ_0[P_3] = 2k[P_1][P_2]$$

$$[P_3] = \left(\frac{1}{1 + kQ_{00}t}\right)^2\left[[P_3]_0 + \frac{2[P_1]_0[P_2]_0}{Q_{00}} + \frac{[P_1]_0^3}{Q_{00}^2} - \left(\frac{2[P_1]_0[P_2]_0}{Q_{00}} + \frac{2[P_1]_0^3}{Q_{00}^2}\right)\left(\frac{1}{1 + kQ_{00}t}\right) + \frac{[P_1]_0^3}{Q_{00}^2}\left(\frac{1}{1 + kQ_{00}t}\right)^2\right]$$

$$= (1 - p)^2\left[[P_3]_0 + 2[P_1]_0[P_2]_0\left(\frac{p}{Q_{00}}\right) + [P_1]_0^3\left(\frac{p}{Q_{00}}\right)^2\right]$$

$[P_4]$:

$$d[P_4]/dt + 2kQ_0[P_4] = k(2[P_1][P_3] + [P_2]^2)$$

$$[P_4] = \left(\frac{1}{1 + kQ_{00}t}\right)^2\left[[P_4]_0 + \frac{2[P_1]_0[P_3]_0 + [P_2]_0^2}{Q_{00}} + \frac{3[P_1]_0^2[P_2]_0}{Q_{00}^2} + \frac{[P_1]_0^4}{Q_{00}^3}\right.$$

$$- \left(\frac{2[P_1]_0[P_3]_0 + [P_2]_0^2}{Q_{00}} + \frac{6[P_1]_0^2[P_2]_0}{Q_{00}^2} + \frac{3[P_1]_0^4}{Q_{00}^3}\right)\left(\frac{1}{1 + kQ_{00}t}\right)$$

$$\left. + \left(\frac{3[P_1]_0^2[P_2]_0}{Q_{00}^2} + \frac{3[P_1]_0^4}{Q_{00}^3}\right)\left(\frac{1}{1 + kQ_{00}t}\right)^2 - \frac{[P_1]_0^4}{Q_{00}^3}\left(\frac{1}{1 + kQ_{00}t}\right)^3\right]$$

$$= (1 - p)^2\left[[P_4]_0 + (2[P_1]_0[P_3]_0 + [P_2]_0^2)\left(\frac{p}{Q_{00}}\right) + 3[P_1]_0^2[P_2]_0\left(\frac{p}{Q_{00}}\right)^2 + [P_1]_0^4\left(\frac{p}{Q_{00}}\right)^3\right]$$

relationship $(1 - \phi)p_1 \leqslant p_f$ must hold (see equation (18)), the values of P_W at $(p_1, \phi) = (1, 0)$ and $(0.975, 0)$ are not shown in *Figure 5*.)

Since the ith-order moment equation is given, in principle, it would be possible to calculate the *MWD*. The Laguerre polynomials are usually used to calculate the *MWD* from moment equations[34,36-40]. However, this method is restricted, practically, to cases where the polydispersity index is not large, say less than 3, since the series does not converge rapidly. Here, we are to use a direct calculation method which was used by Stafford[32,33]. The individual mer concentrations up to $n = 4$ are shown in *Table 1*. Therefore, $[P_n]$ in stage 2 is given by:

$$\frac{[P_n]}{(1 - p_2)^2} = [P_n]_{20} + \sum_{j=1} [P_j]_{20}[P_{n-j}]_{20}\frac{p_2}{(Q_0)_{20}}$$

$$+ \sum_{\substack{j=1, \\ k=1}} [P_j]_{20}[P_k]_{20}[P_{n-j-k}]_{20}\left(\frac{p_2}{(Q_0)_{20}}\right)^2$$

$$+ \sum_{\substack{j=1, \\ k=1, \\ l=1}} [P_j]_{20}[P_k]_{20}[P_l]_{20}[P_{n-j-k-l}]_{20}$$

$$\times \left(\frac{p_2}{(Q_0)_{20}}\right)^3 + \cdots + [P_1]_{20}^n\left(\frac{p_2}{(Q_0)_{20}}\right)^{n-1} \tag{21}$$

where $(Q_0)_{20}$ is the zeroth-order moment at the start of stage 2, and $[P_n]_{20}$ is the concentration of polymer molecule with degree of polymerization n at the start of stage 2. The above equation can also be derived based on a statistical argument. *Figure 6* shows one of the calculated results when $p_1 = 0.9$ and $\phi = 0.5$. First, the height of the peak at $n = 1$ decreases, then the peak moves to larger n as shown in *Figure 6*.

If polymer chains are severed randomly, any distribution approaches the distribution whose polydispersity index $P_W/P_N = 2$ (refs 41, 42). Therefore, when the effect of reverse reactions cannot be neglected, the breadths of *MWD* should be smaller than those calculated from the present investigation, so that these calculated results should be understood as the maximum breadth of the *MWD* for the intermediate monomer feed method. (This is a clear difference from a batch polymerization starting solely from monomers where reverse reactions do not change the 'most probable distribution'[18,28,32,43].)

Step-growth polymerization of (A-A) and (B-B) type monomers

In general, the calculation of *MWD* for the polymerization of (A-A) and (B-B) type monomers is more complicated than that for (A-B) type. If the stoichiometric
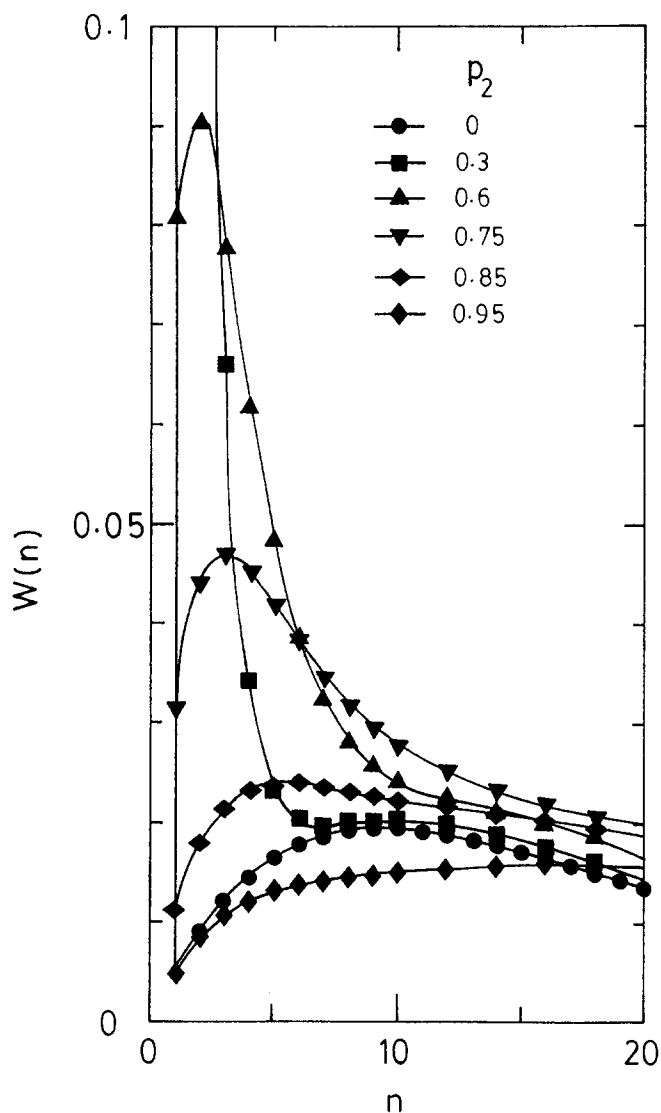
Figure 6 Weight fraction distribution development during polymerization in stage 2 ((A-B) type), for $p_1 = 0.9$ and $\phi = 0.5$

imbalance, $r = [A]_0/[B]_0$ ($[A]_0 \leqslant [B]_0$), is not equal to unity, one needs to treat polymer chains with even-numbered n-mers and those with odd-numbered n-mers separately[17,18,23,33,34,44]. In batch reactors starting only from a monomer mixture, the weight fraction (or segment fraction) distribution:

$$W(n) = \frac{n[P_n]}{\sum_{n=1}^{\infty} n[P_n]} \qquad (22)$$

is shown in *Figure 7*. As shown in the figure, each distribution of the even-numbered and odd-numbered polymer chains follows a 'most probable distribution'.

We are to classify the polymer chains into three groups as shown in *Table 2*. The mole balance equations can be written for batch reactors as follows:

$$\frac{d[A_n]}{d\tau} = \sum_{j=1}^{n-1} [A_j][C_{n-j}]$$

$$- [A_n]\left(2 \sum_{j=1}^{\infty} [B_j] + \sum_{j=1}^{\infty} [C_j]\right) \qquad (23)$$

$$\frac{d[B_n]}{d\tau} = \sum_{j=1}^{n-1} [B_j][C_{n-j}]$$

$$- [B_n]\left(2 \sum_{j=1}^{\infty} [A_j] + \sum_{j=1}^{\infty} [C_j]\right) \qquad (24)$$

$$\frac{d[C_n]}{d\tau} = 2 \sum_{j=1}^{n} [A_j][B_{n-j+1}] + \frac{1}{2} \sum_{j=1}^{n-1} [C_j][C_{n-j}]$$

$$- [C_n]\left(\sum_{j=1}^{\infty} [A_j] + \sum_{j=1}^{\infty} [B_j] + \sum_{j=1}^{\infty} [C_j]\right) \qquad (25)$$

where $\tau = 2kt$, and k is the rate constant which is defined with respect to the number of functional groups.

The ith-order moment of each type of polymer chain distribution can be defined as follows:

$$Q_{A,i} = \sum_{n=1}^{\infty} (2n - 1)^i [A_n] \qquad (26)$$

$$Q_{B,i} = \sum_{n=1}^{\infty} (2n - 1)^i [B_n] \qquad (27)$$

$$Q_{C,i} = \sum_{n=1}^{\infty} (2n)^i [C_n] \qquad (28)$$

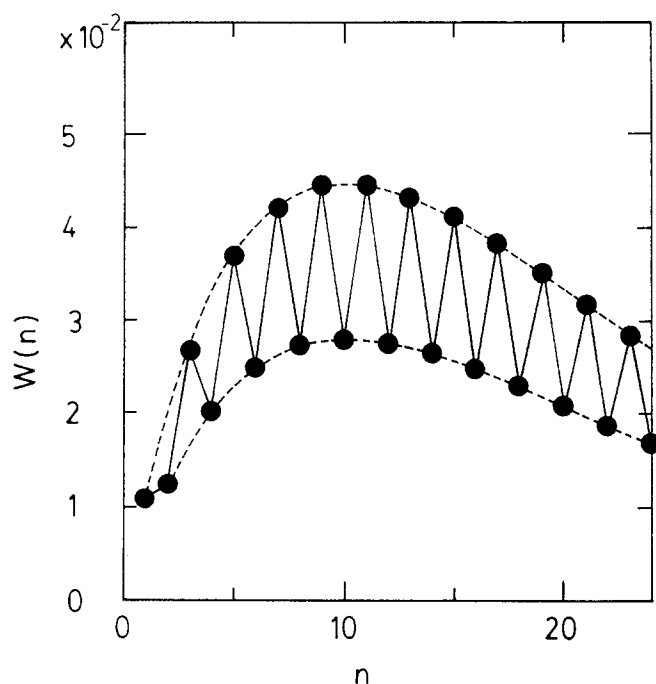From equations (23)–(28), it is straightforward to derive

Figure 7 Weight fraction distribution of the polymer chains formed from (A-A) and (B-B) type monomers in batch polymerization. The extent of reaction $p = ([A]_0 - [A])/[A]_0 = 0.95$ and $[A]_0/[B]_0 = 1/1.1$

Table 2 Notations used for the polymerization of (A–A) and (B–B) type monomers

Notation	Structure	Number of monomeric units
A_n	$(AA-BB)_{n-1}AA$	$2n - 1$
B_n	$(BB-AA)_{n-1}BB$	$2n - 1$
C_n	$(AA-BB)_n$	$2n$

the ith-order moment equations:

$$\frac{dQ_{A,i}}{d\tau} = \sum_{j=1}^{i} \binom{i}{j} Q_{C,j} Q_{A,(i-j)} - 2Q_{B,0} Q_{A,i} \qquad (29)$$

$$\frac{dQ_{B,i}}{d\tau} = \sum_{j=1}^{i} \binom{i}{j} Q_{C,j} Q_{B,(i-j)} - 2Q_{A,0} Q_{B,i} \qquad (30)$$

$$\frac{dQ_{C,i}}{d\tau} = 2 \sum_{j=0}^{i} \binom{i}{j} Q_{A,j} Q_{B,(i-j)} + \frac{1}{2} \sum_{j=0}^{i} \binom{i}{j} Q_{C,j} Q_{C,(i-j)}$$

$$- Q_{C,i}(Q_{A,0} + Q_{B,0} + Q_{C,0}) \qquad (31)$$

Equations (29)–(31) enable one to calculate the MWD starting from any initial distribution. We now consider the derivation of the number- and weight-average degrees of polymerization, $\overline{P_N}$ and $\overline{P_W}$. $\overline{P_N}$ can be derived from a simple stoichiometric consideration. The mole fractions of functional groups of type A at time 0 and t are given by:

$$\frac{[A]_0}{[A]_0 + [B]_0} = \frac{r}{1 + r} \qquad (32)$$

$$\frac{[A]}{[A] + [B]} = \frac{(1 - p)r}{(1 - p)r + (1 - rp)} \qquad (33)$$

where r is the stoichiometric imbalance, $r = [A]_0/[B]_0$ ($[A]_0 \leqslant [B]_0$), and p is the extent of reaction which is defined with respect to the number of A groups, namely $p = 1 - [A]/[A]_0$. Therefore:

$$p = 1 - \frac{2Q_0[A]/([A] + [B])}{2Q_{00}[A]_0/([A]_0 + [B]_0)}$$

$$= 1 - \left(\frac{Q_0}{Q_{00}}\right)\left(\frac{(1 + r)(1 - p)}{1 + r - 2rp}\right) \qquad (34)$$

Solving for Q_0/Q_{00}:

$$\frac{Q_0}{Q_{00}} = \frac{1 + r - 2rp}{1 + r} \qquad (35)$$

Since the total number of monomeric units does not change during batch polymerization, $Q_1 = Q_{10}$ ($= Q_{A,1} + Q_{B,1} + Q_{C,1}$) is constant. (Equations (29)–(31) also give this result.) Therefore:

$$\overline{P_N} = \frac{Q_1}{Q_0} = \left(\frac{1 + r}{1 + r - 2rp}\right)\overline{P_{N0}} \qquad (36)$$

By solving the zeroth-, first- and second-order moment equations, one obtains the following equation for $\overline{P_W}$ (see Appendix):

$$\overline{P_W} = \overline{P_{W0}} + \overline{P_{N0}} \times$$

$$\left(\frac{p(1+r)\{(X^2+4ab)[2-p(1+r)]+4X[(a+b)-(a+rb)p]\}}{2(b-a)[p^2(a-r^2b)-2p(a-rb)-(b-a)]}\right) \qquad (37)$$

where $a = (Q_{A,0})_0/Q_1$ and $(Q_{A,0})_0$ is the initial value of $Q_{A,0}$, $b = (Q_{B,0})_0/Q_1$, and X is given by:

$$X = \frac{1}{\overline{P_{N0}}}\left(\frac{(Q_{B,1})_0 - (Q_{A,1})_0}{Q_1}\left(\frac{1-r}{1+r}\right)\right.$$

$$\left. - \frac{(Q_{A,0})_0 + (Q_{B,0})_0}{Q_{00}}\right) \qquad (38)$$

When $\overline{P_{W0}} = \overline{P_{N0}} = 1$, namely, starting from a monomer mixture, equation (37) reduces to:

$$\overline{P_W} = \frac{(1 + rp^2)(1 + r) + 4rp}{(1 - rp^2)(1 + r)} \qquad (\overline{P_{W0}} = \overline{P_{N0}} = 1) \quad (39)$$

which agrees with the result of other authors[8,33].

Table 3 Equations for the calculation of the number- and weight-average degrees of polymerization for the intermediate monomer feed method ((A-A) + (B-B) type monomers)

Number-average degree of polymerization, $\overline{P_N}$:

$$\overline{P_N} = \frac{1 + r}{1 + r - 2rp_f}$$

Weight-average degree of polymerization, $\overline{P_W}$:

$$\overline{P_W} = \overline{P_{W20}} + \overline{P_{N20}} \frac{p_2(1 + r_2)\{(Y^2 + 4a_{20}b_{20})[2 - p_2(1 + r_2)] + 4Y[(a_{20} + b_{20}) - (a_{20} + r_2b_{20})p_2]\}}{2(b_{20} - a_{20})[p_2^2(a_{20} - r_2^2b_{20}) - 2p_2(a_{20} - r_2b_{20}) - (b_{20} - a_{20})]}$$

with

$$Y = \left(\frac{\eta}{\overline{P_{N20}}}\right)\left(\frac{1 - r_2}{1 + r_2}\right) - (a_{20} + b_{20})$$

$$\eta = \frac{(Q_{B,1})_{20} - (Q_{A,1})_{20}}{(Q_1)_{20}} = \phi\frac{1 - r}{1 + r} + (1 - \phi)\left(\frac{1 - r}{1 + r}\right)\left(\frac{1 + rp_1^2}{1 - rp_1^2}\right)$$

$$a_{20} = \frac{(Q_{A,0})_{20}}{(Q_1)_{20}} = (1 - \phi)\left(\frac{1 - r}{1 + r}\right)\left(\frac{r(1 - p_1)^2}{(1 - rp_1)^2 - r(1 - p_1)^2}\right) + \phi\left(\frac{r}{1 + r}\right)$$

$$b_{20} = \frac{(Q_{B,0})_{20}}{(Q_1)_{20}} = (1 - \phi)\left(\frac{1 - r}{1 + r}\right)\left(\frac{(1 - rp_1)^2}{(1 - rp_1)^2 - r(1 - p_1)^2}\right) + \left(\frac{\phi}{1 + r}\right)$$

$$\overline{P_{N20}} = \frac{\overline{P_{N1}}}{1 + (\overline{P_{N1}} - 1)\phi} \qquad \overline{P_{N1}} = \frac{1 + r}{1 + r - 2rp_1}$$

$$\overline{P_{W20}} = (1 - \phi)\overline{P_{W1}} + \phi \qquad \overline{P_{W1}} = \frac{(1 + rp_1^2)(1 + r) + 4rp_1}{(1 - rp_1^2)(1 + r)}$$

$$p_2 = \frac{p_f - (1 - \phi)p_1}{1 - (1 - \phi)p_1} \qquad r_2 = \frac{r[(1 - \phi)(1 - p_1) + \phi]}{(1 - \phi)(1 - rp_1) + \phi}$$
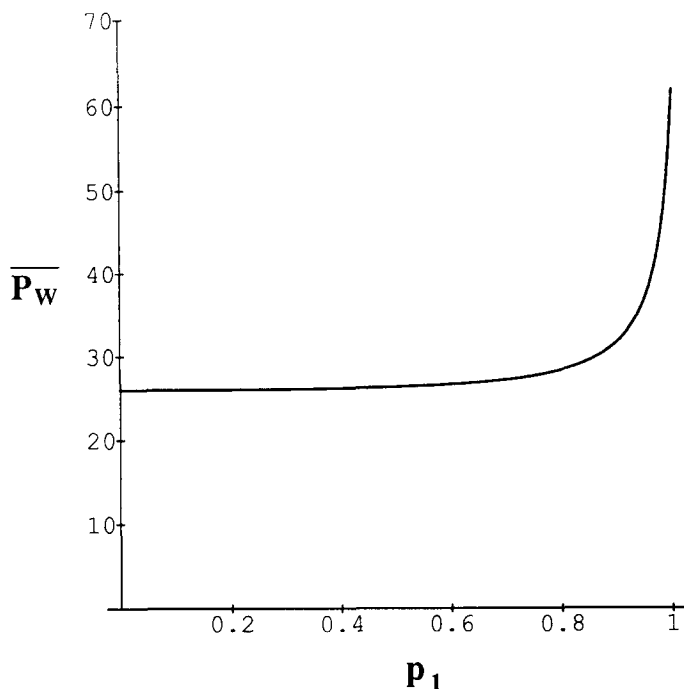
Figure 8 Effect of p_1 on $\overline{P_W}$ ((A-A) + (B-B) type), for $p_f = 0.95$, $\phi = 0.5$ and $r = 0.95$
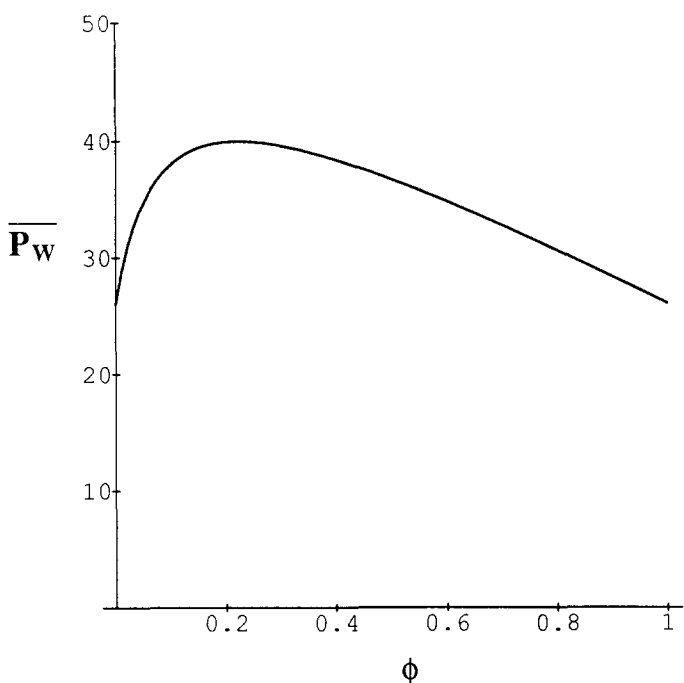

Figure 9 Effect of ϕ on $\overline{P_W}$ ((A-A) + (B-B) type), for $p_f = 0.95$, $p_1 = 0.95$ and $r = 0.95$

When some portion of the monomer mixture is added intermediately, the equations shown in *Table 3* can be used to calculate the number- and weight-average degrees of polymerization. (The notations used are shown in *Figure 2*.) Note that $\overline{P_N}$ is the same as that for batch polymerization, so that it cannot be controlled by either p_1 or ϕ.

Figure 8 shows the effect of p_1 on the weight-average degree of polymerization, $\overline{P_W}$, when p_f and ϕ are fixed. *Figure 9* shows the effect of ϕ on $\overline{P_W}$ when p_f and p_1 are fixed, and *Figure 10* shows a three-dimensional plot for

$\overline{P_W}$ when the final extent of reaction $p_f = 1$. For batch reactors, the maximum attainable value for $\overline{P_W}$ is 78 when $r = 0.95$; however, if the intermediate monomer feed method is applied, the maximum value for $\overline{P_W}$ increases to 127.

Step-growth polymerization of A_f type monomer

Next, let us consider the cases where monomers with f functional groups ($f \geqslant 2$) polymerize. For $f = 4$, the etherification of pentaerythritol $[(C(CH_2OH)_4]$ may fall into this category. If the functionality, f, is larger than or equal to 3, non-linear polymers are formed, and a polymer with infinite molecular weight, i.e. a gel molecule, may be formed in the course of network formation. For example, if the functionality $f = 3$, gelation is predicted to occur at the extent of reaction $p = 0.5$ for batch reactors[18]. On the other hand, in a homogeneous continuous stirred tank reactor (HCSTR), the system becomes unstable when the extent of reaction $p > (3 - 2\sqrt{2}) \simeq 0.17$, and therefore the maximum polydispersity index is limited to $(\overline{P_W}/\overline{P_N})_{max} = 4/1.35 \simeq 3$ (ref. 35). As will be shown in this section, the breadth of MWD can be controlled easily by application of the intermediate monomer feed method.

The number of functional groups for a polymer chain with degree of polymerization n is $(f - 2)n + 2$, and therefore the mole balance equations are given by:

$$\frac{d[P_1]}{dt} = -fk[P_1] \sum_{j=1}^{\infty} \{(f - 2)j + 2\}[P_j] \tag{40}$$

$$\frac{d[P_n]}{dt} = \frac{k}{2} \sum_{j=1}^{n-1} \{(f - 2)(n - j) + 2\}$$

$$\times \{(f - 2)j + 2\}[P_{n-j}][P_j]$$

$$- \{(f - 2)n + 2\}k[P_n]$$

$$\times \sum_{j=1}^{\infty} \{(f - 2)j + 2\}[P_j] \qquad (n \geqslant 2) \tag{41}$$
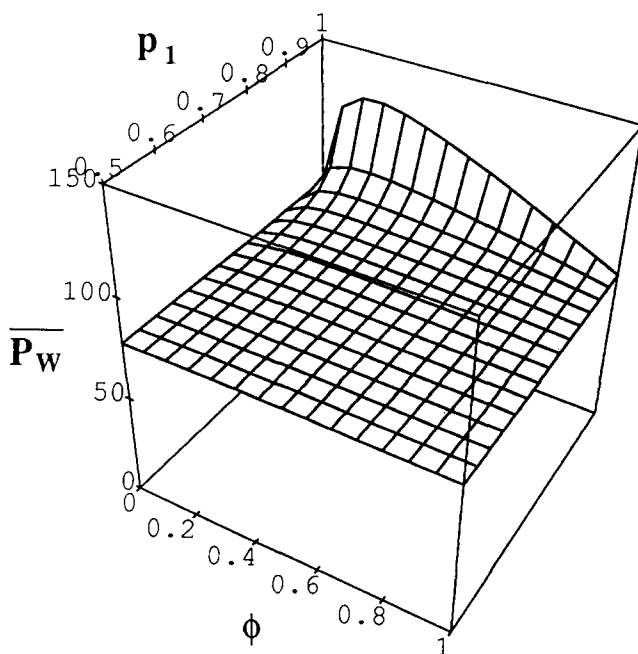

Figure 10 Effect of p_1 and ϕ on $\overline{P_W}$ ((A-A) + (B-B) type), for $p_f = 1.0$ and $r = 0.95$

where the rate constant k is again defined with respect to the number of functional groups, so that:

$$d[A]/dt = -k[A]^2 \qquad (42)$$

From equations (40) and (41), one obtains:

$$\frac{dQ_i}{dt} = \sum_{n=1}^{\infty} n^i \frac{d[P_n]}{dt}$$

$$= \frac{k}{2} \sum_{j=0}^{i} \left[\binom{i}{j} \{(f-2)Q_{j+1} + 2Q_j\} \right.$$

$$\times \left. \{(f-2)Q_{i+1-j} + 2Q_{i-j}\} \right]$$

$$- k\{(f-2)Q_{i+1} + 2Q_i\}\{(f-2)Q_1 + 2Q_0\} \qquad (43)$$

Since the ith-order moment equation is given, in principle, it is possible to know the MWD starting from any distribution.

We now consider the derivation of the number- and weight-average degrees of polymerization. The number-average degree of polymerization, $\overline{P_N}$, can again be derived from a stoichiometric consideration. The concentration of functional group [A] is given by:

$$[A] = \sum_{n=1}^{\infty} \{(f-2)n + 2\}[P_n] = (f-2)Q_1 + 2Q_0 \qquad (44)$$

On the other hand, since $[A] = [A]_0(1-p)$:

$$(f-2)Q_1 + 2Q_0 = [(f-2)Q_{10} + 2Q_{00}](1-p) \qquad (45)$$

Since Q_1 does not change during batch polymerization:

$$\overline{P_N} = \frac{Q_1}{Q_0} = \frac{2\overline{P_{N0}}}{[(f-2)\overline{P_{N0}} + 2](1-p) - (f-2)\overline{P_{N0}}} \qquad (46)$$

The weight-average degree of polymerization can be derived as follows. From equation (43):

$$dQ_2/dt = k[(f-2)Q_2 + 2Q_1]^2 \qquad (47)$$

By application of the extent of reaction, p, equation (42) can be written as:

$$dp/dt = k[A]_0(1-p)^2$$

$$= k[(f-2)Q_{10} + 2Q_{00}](1-p)^2 \qquad (48)$$

From equations (47) and (48):

$$\frac{dQ_2}{dp} = \frac{[(f-2)Q_2 + 2Q_1]^2}{[(f-2)Q_{10} + 2Q_{00}]}\left(\frac{1}{(1-p)^2}\right) \qquad (49)$$

or

$$\frac{d\overline{P_W}}{dp} = \frac{[(f-2)\overline{P_W} + 2]^2}{[(f-2)\overline{P_{N0}} + 2]}\left(\frac{\overline{P_{N0}}}{(1-p)^2}\right) \qquad (50)$$

(Note that $Q_1 = Q_{10}$.) Equation (50) can be solved to give:

$$\overline{P_W} = \frac{[(f-2)\overline{P_{w0}}+2][(f-2)\overline{P_{N0}}+2](1-p)}{(f-2)\{[(f-2)\overline{P_{N0}}+2](1-p)-(f-2)\overline{P_{N0}}[(f-2)\overline{P_{w0}}+2]p\}}$$

$$- \left(\frac{2}{f-2}\right) \qquad (51)$$

Equations (46) and (51) can be used to calculate the number- and weight-average degrees of polymerization for irreversible step-growth polymerization starting from any initial distribution.

When the intermediate monomer feed method is used, the equations shown in *Table 4* can be used to calculate $\overline{P_N}$ and $\overline{P_W}$. We now consider some of the calculated results for functionality $f = 3$. *Figure 11* shows the effect of p_1 on the average degree of polymerization when $p_f = 0.4$ and $\phi = 0.5$. When p_1 is larger than 0.5, gelation
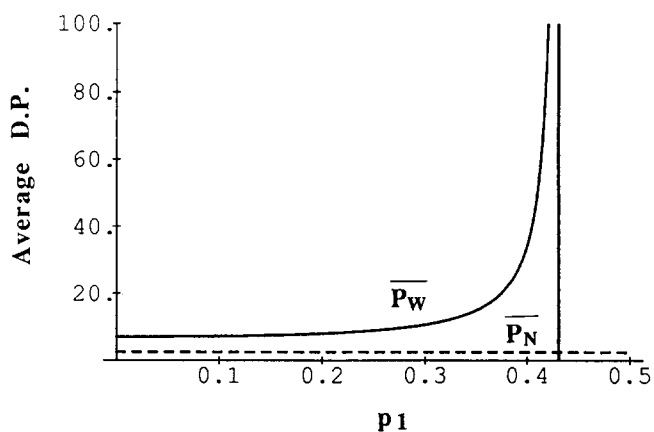
Figure 11 Effect of p_1 on the average degree of polymerization (A_3 type), for $p_f = 0.4$ and $\phi = 0.5$

Table 4 Equations for the calculation of the number- and weight-average degrees of polymerization for the intermediate monomer feed method (A_f type monomer)

Number-average degree of polymerization, $\overline{P_N}$:

$$\overline{P_N} = 2/(2 - fp_f)$$

Weight-average degree of polymerization, $\overline{P_W}$:

$$\overline{P_W} = \frac{[(f-2)\overline{P_{w20}} + 2][(f-2)\overline{P_{N20}} + 2](1-p_2)}{(f-2)\{[(f-2)\overline{P_{N20}} + 2](1-p_2) - (f-2)\overline{P_{N20}}[(f-2)\overline{P_{w20}} + 2]p_2\}} - \frac{2}{f-2}$$

with

$$\overline{P_{N20}} = \frac{\overline{P_{N1}}}{1 + (\overline{P_{N1}} - 1)\phi} \qquad \overline{P_{N1}} = \frac{2}{2 - fp_1}$$

$$\overline{P_{w20}} = (1 - \phi)\overline{P_{w1}} + \phi \qquad \overline{P_{w1}} = \frac{1 + p_1}{1 - (f-1)p_1}$$

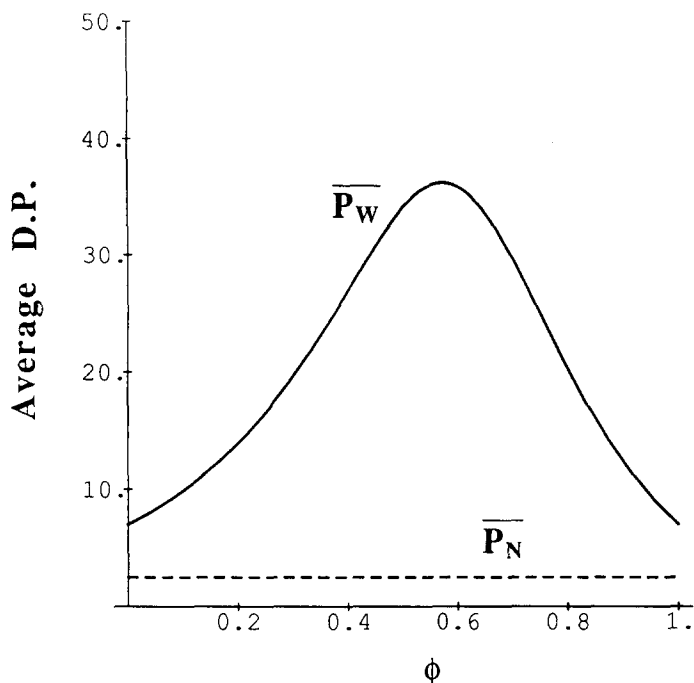$$p_2 = \frac{p_f - (1 - \phi)p_1}{1 - (1 - \phi)p_1}$$

Figure 12 Effect of ϕ on the average degree of polymerization (A_3 type), for $p_f = 0.4$ and $p_1 = 0.4$
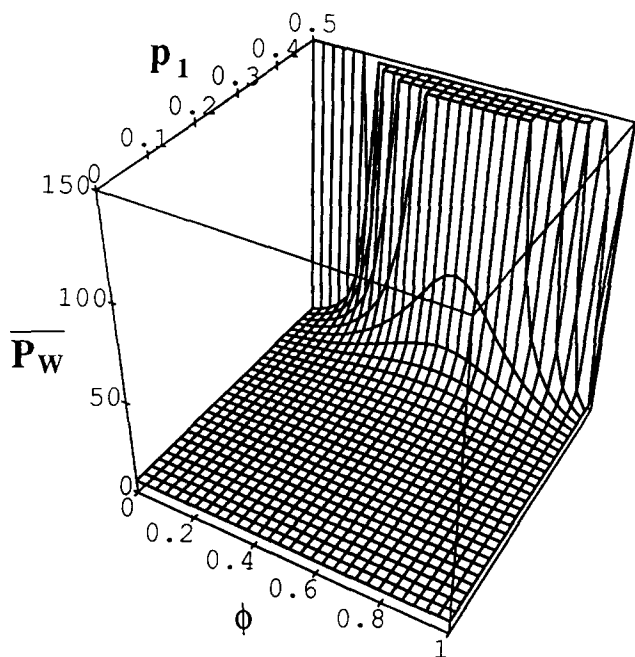

Figure 13 Effect of p_1 and ϕ on $\overline{P_W}$ (A_3 type), for $p_f = 0.4$

should be observed in stage 1. When $0.43 < p_1 < 0.5$, gelation is predicted to occur before the final extent of reaction p_f reaches 0.4. *Figure 12* shows the effect of ϕ on the average degree of polymerization, and *Figure 13* shows the effect of both p_1 and ϕ. As shown in these figures, the intermediate monomer feed method changes the *MWD* more significantly than that for linear polymers.

It is well known that gelation occurs earlier for polymers with broader distribution. By application of the intermediate monomer feed method, the extent of

reaction at the gel point, p_c, can be made lower. Gelation is predicted to occur when the denominator of equation (51) goes to zero, and therefore the extent of reaction in stage 2 at the gel point, $(p_2)_c$, must satisfy the following equation:

$$[(f-2)\overline{P_{N20}} + 2][1 - (p_2)_c]$$
$$- (f-2)\overline{P_{N20}}[(f-2)\overline{P_{W20}} + 2](p_2)_c = 0 \quad (52)$$

By application of the equations shown in *Table 4*, the final (overall) extent of polymerization at the gel point, $(p_f)_c$, is therefore given by:

$$(p_f)_c = \frac{\phi p_1[(f-3) + p_1(f^2 - 4f + 5) - \phi p_1(f-2)^2] - (1-p_1)^2}{(f-1)[\phi p_1(p_1 + f - 3) - (1-p_1)^2]} \quad (53)$$

Figures 14–16 show the calculated results for $f = 3$. If the added monomers are mixed completely at once, the onset of gelation would be controlled in the range $0 < (p_f)_c \leqslant 0.5$.
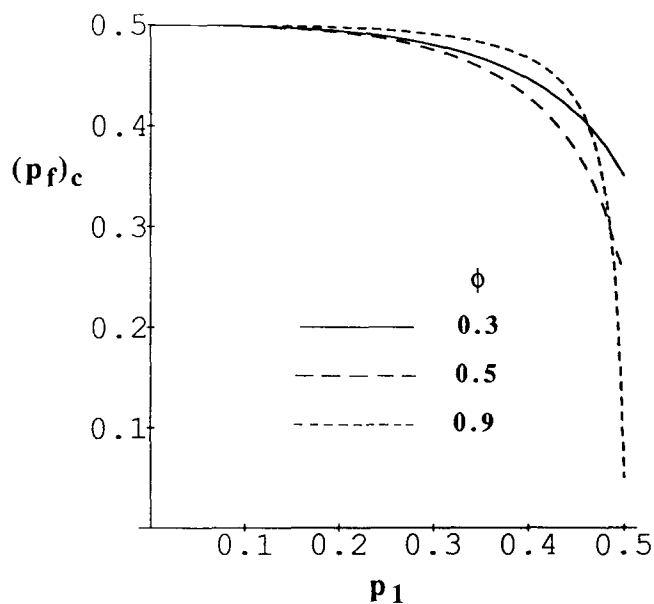

Figure 14 Effect of p_1 on the final (overall) extent of reaction at the gel point, $(p_f)_c$ (A_3 type)
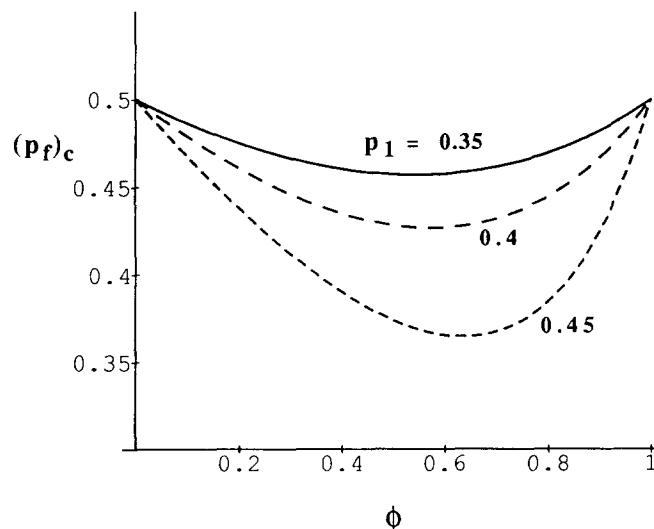

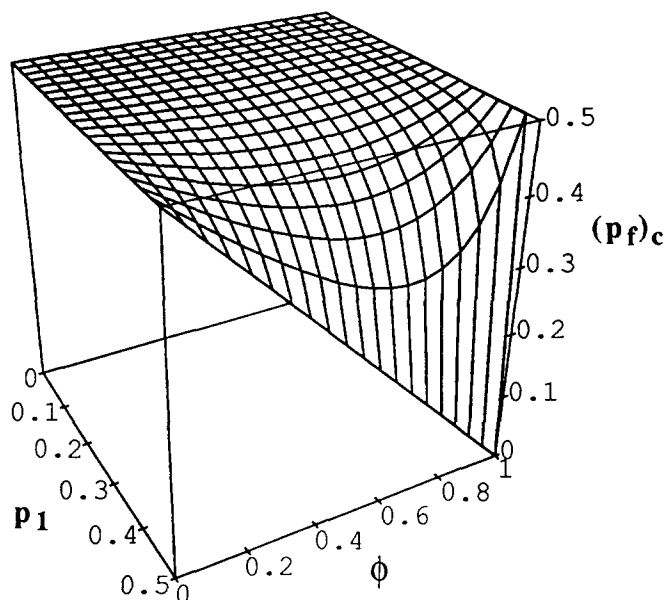**Figure 15** Effect of ϕ on $(p_f)_c$ (A_3 type)

Figure 16 Effect of p_1 and ϕ on $(p_f)_c$ (A$_3$ type)

CONCLUSIONS

The intermediate monomer feed method is a convenient way to control the MWD in step-growth polymerization. The variance of MWD can be controlled by three variables, namely, the extent of reaction at the end of stage 1, p_1, the final (or overall) extent of reaction, p_f, and the fraction of monomer fed at the start of stage 2, ϕ. In order to broaden the MWD effectively, the extent of reaction in stage 1 should be sufficiently high. There is an optimum ϕ to maximize the variance of MWD for a given set of p_1 and p_f. In non-linear polymerizations, the effect of intermediate monomer feed is more significant than that for linear polymerizations. The onset of gelation, p_c, can be controlled in a wide range by application of the intermediate monomer feed method.

Many simplifying assumptions are used in this research, namely:

(1) The rate constant, k, is independent of the size of the polymer molecule.
(2) Reactions are irreversible.
(3) There are no side reactions such as cyclization reactions.
(4) The density change of the reaction system during polymerization is negligible.

Therefore, in a real system there would be a deviation from the present results quantitatively. However, we do believe that the present investigation will give great insight into the development of a method of control of MWD in step-growth polymerization.

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APPENDIX

Derivation of the weight-average degree of polymerization, $\overline{P_w}$, for the polymerization of $(A\text{-}A)$ and $(B\text{-}B)$ type monomers

In order to derive the functional form of $\overline{P_w}$, let us consider the zeroth-, first- and second-order moment

equations. From equations (29)–(31) in the text:

$$dQ_{A,0}/d\tau = -2Q_{A,0}Q_{B,0} \tag{A1}$$

$$dQ_{B,0}/d\tau = -2Q_{B,0}Q_{A,0} \tag{A2}$$

$$dQ_{C,0}/d\tau = 2Q_{B,0}Q_{A,0} - \tfrac{1}{2}Q_{C,0}^2 - Q_{C,0}(Q_{A,0} + Q_{B,0}) \tag{A3}$$

$$dQ_{A,1}/d\tau = Q_{C,1}Q_{A,0} - 2Q_{A,1}Q_{B,0} \tag{A4}$$

$$dQ_{B,1}/d\tau = Q_{C,1}Q_{B,0} - 2Q_{B,1}Q_{A,0} \tag{A5}$$

$$dQ_{C,1}/d\tau = 2(Q_{A,1}Q_{B,0} + Q_{B,1}Q_{A,0}) - Q_{C,1}(Q_{A,0} + Q_{B,0}) \tag{A6}$$

$$dQ_{A,2}/d\tau = Q_{C,2}Q_{A,0} + 2Q_{A,1}Q_{C,1} - 2Q_{A,2}Q_{B,0} \tag{A7}$$

$$dQ_{B,2}/d\tau = Q_{C,2}Q_{B,0} + 2Q_{B,1}Q_{C,1} - 2Q_{B,2}Q_{A,0} \tag{A8}$$

$$dQ_{C,2}/d\tau = 2(Q_{A,2}Q_{B,0} + 2Q_{A,1}Q_{B,1} + Q_{B,2}Q_{A,0}) + Q_{C,1}^2 - Q_{C,2}(Q_{A,0} + Q_{B,0}) \tag{A9}$$

From equations (A7)–(A9), the second-order moment, Q_2 ($= Q_{A,2} + Q_{B,2} + Q_{C,2}$), is given by:

$$dQ_2/d\tau = Q_1^2 - (Q_{B,1} - Q_{A,1})^2 \tag{A10}$$

From equation (A1) and (A2), $(Q_{B,0} - Q_{A,0})$ is kept constant during batch polymerization. A stoichiometric consideration gives:

$$Q_{B,0} - Q_{A,0} = Q_{00}(1 - r)/(1 + r) = L = \text{constant} \tag{A11}$$

By substituting equation (A11) into equation (A1), one obtains:

$$Q_{A,0} = \frac{L(Q_{A,0})_0\xi}{L + (Q_{A,0})_0(1 - \xi)} \tag{A12}$$

where $L = Q_{B,0} - Q_{A,0}$ and $\xi = \exp(-2L\tau)$. From

equations (A4), (A5) and (A11), $(Q_{B,1} - Q_{A,1})$ is given by:

$$d(Q_{B,1} - Q_{A,1})/d\tau = LQ_1 - (Q_{B,1} - Q_{A,1}) \times (Q_{A,0} + Q_{B,0}) \tag{A13}$$

Equations (A11)–(A13) give the following equation:

$$Q_{B,1} - Q_{A,1} = Q_1\frac{b' + a'\xi}{b' - a'\xi} + \frac{\sqrt{\xi}}{b' - a'\xi} \times \{[(Q_{B,1})_0 - (Q_{A,1})_0]L - Q_1(a' + b')\} \tag{A14}$$

where $a' = (Q_{A,0})_0$ and $b' = (Q_{B,0})_0$.

From the relationship between the extent of reaction, p, and the time, τ ($= 2kt$), namely:

$$\frac{dp}{d\tau} = \frac{Q_{00}}{1 + r}(1 - p)(1 - rp) \tag{A15}$$

ξ can be expressed by using p as follows:

$$\xi = \left(\frac{1 - p}{1 - rp}\right)^2 \tag{A16}$$

From equations (A10) and (A15), one obtains:

$$\frac{dQ_2}{dp} = \frac{(1 + r)[Q_1^2 - (Q_{B,1} - Q_{A,1})^2]}{Q_{00}(1 - p)(1 - rp)} \tag{A17}$$

Since Q_1 is constant during batch polymerization, the above equation can be rewritten as follows:

$$\frac{d\overline{P_W}}{dp} = \overline{P_{N0}}\left(\frac{(1 + r)[1 - (Q_{B,1} - Q_{A,1})^2/Q_1^2]}{(1 - p)(1 - rp)}\right) \tag{A18}$$

By application of equations (A14) and (A16), equation (A18) can be solved analytically to give equation (37) in the text.