Analysis of heterogeneous step polymerization with unequal reactivities*

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A mathematical model has been developed for the heterogeneous step polymerization of AA with BB when the solubility of either AA or BB is limited. The model incorporates the feature of unequal reactivity of a monomer with induced asymmetry. The polydispersity index (*PDI*) has been calculated as a function of conversion, reactivity ratio, stoichiometric ratio and monomer solubility. Unusually high *PDI*s (as high as 80) are observed in heterogeneous step polymerizations. The *PDI* is found to be greater than 2 even when the equal-reactivity hypothesis holds good. Using the mathematical model developed here, the experimental observation of the formation of high-molecular-weight products in poly(phenylene sulphide) syntheses at low conversions can be explained quantitatively for the first time.

(Keywords: mathematical modelling; polymerization; reactivity ratios)

INTRODUCTION

The kinetics and molecular-weight distribution (*MWD*) of homogeneous step polymerization have received the attention of many investigators starting from Flory in 1961[1]. Recently the influence of unequal reactivity on *MWD* was also considered in great detail[2–4]. In all the previous studies, it was generally assumed that monomers are completely miscible with each other. There are many industrially important examples where the solubility of one of the monomers is small. For example, the solubility of terephthalic acid in ethylene glycol in poly(ethylene terephthalate) synthesis and the solubility of sodium sulphide in 1,4-dichlorobenzene in poly(phenylene sulphide) synthesis are very small. It is surprising to note that there have been no prior attempts at modelling a heterogeneous step polymerization reactor. Our main objective here is to develop such a mathematical model and examine the influence of various operating parameters on the molecular weight and *MWD*.

Another objective of this work is to examine the influence of unequal reactivity on the *MWD* in a heterogeneous step polymerization reactor. Even though many step polymers follow the equal-reactivity hypothesis, there are many examples where the equal-reactivity hypothesis fails[5–7]. Examples are glycols having primary and secondary hydroxyl groups[2], epichlorohydrin[5], dichlorobenzene[6] and diisocyanates[2]. Unequal reactivities of monomers can be classified into two types (asymmetry and induced asymmetry). In asymmetry, functional groups on the monomer are not chemically equivalent and react at different rates. In induced asymmetry, functional groups on the monomer are equally reactive till one of them reacts. The reaction of one functional group then alters the reactivity of the second functional group.

Gandhi and Babu[3] investigated the effect of unequal reactivities on *MWD* and showed that, under certain conditions, the usually assumed limit of 2 for the polydispersity index (*PDI*) is not valid. Ozizmir and Odian[2] investigated the effect of unequal reactivities from the polymerization point of view and obtained conditions for the synthesis of high-molecular-weight product. In general the *PDI* is found to be greater than 2 only with induced asymmetry. Hence monomers with induced asymmetry are considered in detail in this work. Polymer manufacturers are generally concerned with preparing high-molecular-weight polymers having narrow *MWD*s. Hence our objective is to examine the influence of various operating conditions for homogeneous and heterogeneous step polymerizations for preparing high-molecular-weight products having narrow *MWD*s.

Recently, the kinetics of poly(phenylene sulphide) formation has received the attention of many investigators[6,8,9], owing to its high thermal stability and good chemical resistance to solvents, acids and bases. It is observed[8] that high-molecular-weight compounds are formed even at 20% conversion, compared with normal polycondensation reactions where high-molecular-weight products are formed only at conversions above 99%. This is generally attributed to the formation of intermediates with higher reactivities compared with the reactivity of the starting monomer. However, no attempts have been made in the past for a quantitative analysis. We present such an analysis by using the model developed for a heterogeneous step polymerization reactor. Later we intend to show that the formation of highly reactive intermediates is alone not sufficient to account for the formation of high-molecular-weight products at low conversions. In addition, the conditions that will lead to the formation of high-molecular-weight products at low conversion are examined within the framework of the model.

FORMULATION OF THE PROBLEM

Consider the polymerization of AA and BB, and let induced asymmetry be present in AA. The reaction scheme for induced asymmetry can be written as:

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$$\mathrm{AA} + \mathrm{BB}\sim\sim \xrightarrow{k_1} \mathrm{AABB}\sim \tag{1}$$

$$\sim\sim\mathrm{AA} + \mathrm{BB}\sim\sim \xrightarrow{k_2} \sim\sim\mathrm{AABB}\sim \tag{2}$$

where the wavy lines represent polymer chains, and k_1 and k_2 are second-order reaction rate constants. Here an A group at the end of a polymer molecule will react at a rate different from that for an A group of a monomer. The various types of molecules present in the reaction mixture are AA, BB, $(\mathrm{AABB})_n\mathrm{AA}$, $(\mathrm{BBAA})_n\mathrm{BB}$ and $(\mathrm{AABB})_n$, with $n \geqslant 1$. The concentration of these species is given by a, b, p_n, q_n and r_n. Previous workers[3] considered $(\mathrm{BBAA})_{n-1}\mathrm{BB}$ type species. When $n=1$, they have only BB type species. In this work, BB and $(\mathrm{BBAA})_n\mathrm{BB}$ are considered separately and not combined. This modification has been done mainly to consider the solubility of BB while developing a mathematical model for a heterogeneous step polymerization reactor.

Whenever the solubility of a monomer is small, it first dissolves and then reacts, and the process continues until the monomer is completely dissolved and reacted. At any time, the reaction mixture contains undissolved monomer in the solid phase and the reaction mixture in the liquid phase. For simplicity, it is assumed that the process is controlled by reaction kinetics and mass-transfer limitations do not play any role. With this assumption, the mass-balance equations for a heterogeneous batch reactor are:

$$\frac{\mathrm{d}a^*}{\mathrm{d}\theta} = -2ac_1V^* \tag{3}$$

$$\frac{\mathrm{d}b^*}{\mathrm{d}\theta} = -2bc_2V^* \tag{4}$$

$$\frac{\mathrm{d}q_n}{\mathrm{d}\theta} = 2\left(-q_nc_2 + Kbr_n + K\sum_{m=1}^{n-1} r_mq_{n-m}\right)V^* \qquad n \geqslant 1 \tag{5}$$

$$\frac{\mathrm{d}p_n}{\mathrm{d}\theta} = 2\left(-Kp_nc_1 + ar_n + K\sum_{m=1}^{n-1} r_mp_{n-m}\right)V^* \qquad n \geqslant 1 \tag{6}$$

$$\frac{\mathrm{d}r_1}{\mathrm{d}\theta} = [-r_1(c_2 + Kc_1) + 4ab]V^* \tag{7}$$

$$\frac{\mathrm{d}r_n}{\mathrm{d}\theta} = \left(-r_n(c_2 + Kc_1) + 4aq_{n-1} + 4Kbp_{n-1} + 4K\sum_{m=1}^{n-2} p_{n-m-1}q_m + K\sum_{m=1}^{n-1} r_mr_{n-m}\right)V^* \qquad n \geqslant 2 \tag{8}$$

where

$$c_1 = 2\left(b + \sum_{m=1}^{\infty} q_m\right) + \sum_{m=1}^{\infty} r_m \tag{9}$$

$$c_2 = 2\left(a + K\sum_{m=1}^{\infty} p_m\right) + K\sum_{m=1}^{\infty} r_m \tag{10}$$

$$K = k_2/k_1 \tag{11}$$

$$\theta = k_1b_0t/V_0 \tag{12}$$

$$V^* = V_0/V \tag{13}$$

All the concentrations in equations (3)–(8) are normalized with respect to the initial number of moles of BB at $t=0$ (b_0). Here a^* and b^* are the (dimensionless) total concentrations (mol/b_0) of AA and BB present in the liquid and solid phases; a and b are the (dimensionless) concentrations of AA and BB in the liquid phase; q_n, p_n and r_n represent the concentrations (mol/b_0) of the respective species, as above; and V, V_0 and t represent, respectively, the volume of the reaction mixture in the liquid phase (cm^3/b_0), the total reactor volume (cm^3/b_0) and the reaction time (s).

Numerical integration of equations (3)–(8) for $n=1$ to ∞ is cumbersome and needs large computational time. Since polymer properties are characterized by the first few moments (viz. zeroth, first and second moments), these are calculated in this work:

$$\hat{p} = \sum_{n=1}^{\infty} p_n \qquad p' = \sum_{n=1}^{\infty} np_n \qquad p'' = \sum_{n=1}^{\infty} n^2p_n \tag{14}$$

Similarly $\hat{q}$, $\hat{r}$, q', r' and q'', r'' can be defined. Using equation (14), moment-balance equations are obtained from equations (3)–(8) and these are given in *Table 1*.

The number-average molecular weight (M_n) is, by definition:

$$M_\mathrm{n} = \frac{aM_\mathrm{A} + bM_\mathrm{B} + \sum_{n=1}^{\infty}[(nM + M_\mathrm{A})p_n + (nM + M_\mathrm{B})q_n + nMr_n]}{a + b + \sum_{n=1}^{\infty}(p_n + q_n + r_n)} \tag{15}$$

Here M_A and M_B are, respectively, the molecular weights of AA and BB and $M = M_\mathrm{A} + M_\mathrm{B}$. Using equation (14), equation (15) can be rewritten as:

$$M_\mathrm{n} = \frac{aM_\mathrm{A} + M_\mathrm{B} + M(p' + q' + r') + M_\mathrm{B}\hat{q} + M_\mathrm{A}\hat{p}}{a + b + \hat{p} + \hat{q} + \hat{r}} \tag{16}$$

Table 1 Mass-balance and moment-balance equations

	$\mathrm{d}a^*/\mathrm{d}\theta = 2a[2(b+\hat{q}) + \hat{r}]V^*$	(1.1)
	$\mathrm{d}b^*/\mathrm{d}\theta = -2b[2(a+K\hat{p}) + K\hat{r}]V^*$	(1.2)
Zeroth moments		
	$\mathrm{d}\hat{q}/\mathrm{d}\theta = [-4\hat{q}(a+K\hat{p}) + 2Kb\hat{r}]V^*$	(1.3)
	$\mathrm{d}\hat{p}/\mathrm{d}\theta = [-4K\hat{p}(b+\hat{q}) + 2a\hat{r}]V^*$	(1.4)
	$\mathrm{d}\hat{r}/\mathrm{d}\theta = [-2\hat{r}(a+K\hat{p}) + 2K(b+\hat{q}) + K\hat{r} + 4(b+\hat{q})(a+K\hat{p})]V^*$	(1.5)
First moments		
	$\mathrm{d}q'/\mathrm{d}\theta = [-4q'(a+K\hat{p}) + 2Kr'(b+\hat{q})]V^*$	(1.6)
	$\mathrm{d}p'/\mathrm{d}\theta = [-4Kp'(b+\hat{q}) + 2r'(a+K\hat{p})]V^*$	(1.7)
	$\mathrm{d}r'/\mathrm{d}\theta = \{-2r'[(a+K\hat{p}) + K(b+\hat{q})] + 2(a+K\hat{p})(2q'+\hat{q}+b) + 2(\hat{q}+b)(2Kp'+K\hat{p}+a)\}V^*$	(1.8)
Second moments		
	$\mathrm{d}q''/\mathrm{d}\theta = \{-2q''(a+K\hat{p}) + 2K[r''(\hat{q}+b) + 2r'q']\}V^*$	(1.9)
	$\mathrm{d}p''/\mathrm{d}\theta = \{-4Kp''(b+\hat{q}) + 2[r''(a+K\hat{p}) + 2Kr'p']\}V^*$	(1.10)
	$\mathrm{d}r''/\mathrm{d}\theta = \{-2r''[(a+K\hat{p}) + K(b+\hat{q})] + 4(a+K\hat{p})(q''+2q'+\hat{q}+b) + 4K(b+\hat{q})(p''+2p') + 2K(r'^2+4p'q')\}V^*$	(1.11)

Similarly, the weight-average molecular weight (M_w) can be written as:

$$M_w = \frac{aM_A^2 + bM_B^2 + M^2(p'' + q'' + r'') + M_B^2\hat{q} + M_A^2\hat{p} + 2M(M_B q' + M_A p')}{aM_A + bM_B + M(p' + q' + r') + M_B\hat{q} + M_A\hat{p}} \tag{17}$$

and

$$PDI = M_w/M_n \tag{18}$$

Excluding the contribution of both the monomers, expressions for the modified number-average molecular weight (M'_n) and weight-average molecular weight (M'_w) can be obtained from equations (16) and (17):

$$M'_n = \frac{M(p' + q' + r') + M_B\hat{q} + M_A\hat{p}}{\hat{p} + \hat{q} + \hat{r}} \tag{19}$$

$$M'_w = \frac{M^2(p'' + q'' + r'') + M_B^2\hat{q} + M_A^2\hat{p} + 2M(M_B q' + M_A p')}{M(p' + q' + r') + M^B\hat{q} + M_A\hat{p})} \tag{20}$$

Similarly, the modified *PDI* (*MPDI*) is given by

$$MPDI = M'_w/M'_n \tag{21}$$

Conversions of A and B groups are calculated from:

$$\text{conv. of A} = 1 - (2a^* + 2\hat{p} + \hat{r})/2R \tag{22}$$

$$\text{conv. of B} = 1 - (2b^* + 2\hat{q} + \hat{r})/2 \tag{23}$$

Numerical integration of equations (1.1)–(1.11) in *Table 1* requires information about V^*, a and b. They are related to the solubility of AA and BB, as shown below.

Homogeneous system

In this case, reactants AA and BB are completely miscible. Hence $V^* = 1$, $a = a^*$ and $b = b^*$. Equations (1.1)–(1.11) can be numerically integrated for any set of conditions.

Heterogeneous system

Solubility of BB. Here, only undissolved BB is present in the solid phase. Monomer AA and reaction products are assumed to be completely in the liquid phase. Hence $a = a^*$. The volume of the reaction mixture is given by:

$$V = RV_A + V_B\left(b + \sum_{n=1}^{\infty} (n+1)q_n + nr_n + np_n\right) \tag{24}$$

Here $R = a_0/b_0$ is the stoichiometric ratio, a_0 is the initial number of moles of AA at $t = 0$, and V_A and V_B are molar volumes (cm^3/mol) of AA and BB. The second term on the right-hand side of equation (24) represents dissolved BB (b) and BB incorporated in the polymer molecules. While writing down equation (24), it is assumed that there is no change in density (ρ) of the reaction mixture, and for simplicity it is taken as 1 g cm^{-3}. When BB is completely dissolved, the reactor volume is given by:

$$V_0 = RV_A + V_B \tag{25}$$

Assuming that the solubility of BB is β (g/g of reaction mixture), b can be calculated from:

$$b = \beta V\rho/M_B \tag{26}$$

Substituting equation (24) into (26) and using $\rho = 1$ g cm^{-3}, we get:

$$b = \frac{\beta[RV_A + V_B(p' + q' + r' + \hat{q})]}{M_B(1 - \beta)} \tag{27}$$

and

$$V^* = \frac{V_0}{V} = \frac{RV_A + V_B}{RV_A + V_B(p' + q' + r' + \hat{q})}(1 - \beta) \tag{28}$$

Equations (27) and (28) are valid until BB is completely dissolved. Otherwise $b = b^*$ and $V^* = 1$. Equations (27), (28) and (1.1)–(1.11) are the balance equations for a heterogeneous step polymerization reactor when the solubility of BB is limited. Note that the reaction mixture is homogeneous when BB is completely dissolved.

Solubility of AA. In this case, undissolved AA is present in the solid phase and all other species are in the liquid phase. Hence $b = b^*$. Equations similar to equations (27) and (28) can easily be written for the present case:

$$a = \frac{\alpha[V_A(p' + q' + r' + \hat{p}) + V_B]}{M_A(1 - \alpha)} \tag{29}$$

$$V^* = \frac{RV_A + V_B}{V_A(p' + q' + r' + \hat{p}) + V_B}(1 - \alpha) \tag{30}$$

where α is the solubility of AA (g/g of reaction mixture). Again, equations (29) and (30) are valid only when undissolved AA is present. Otherwise $a = a^*$ and $V^* = 1$. Equations (29), (30) and (1.1)–(1.11) represent the balance equations when the solubility of AA is limited.

RESULTS AND DISCUSSION

The preceding equations were solved numerically using the modified fourth-order Runge–Kutta and Gill method. For simplicity, results are presented for $M_A = M_B$ and $V_A = V_B$.

Homogeneous system

Numerical results are tabulated in *Tables 2* and *3* for several values of R and K. *Table 2* shows *PDI* and concentrations of AA and BB at 99.99% conversion of the minority reactant. As intuitively expected when K is increased, the concentration of AA increases. Therefore, *PDI* increases. However, b remains constant and it is independent of K. The increase in *PDI* is more significant for $R \geq 1$. The modified *PDI* (without considering unreacted monomers) is around 2 for all the cases considered. (The values in parentheses in *Table 2* indicate *MPDI*.) To reduce the *PDI*, monomers have to be removed from the polymer. This may not be feasible nor economic in most industrial step polymerization processes. Another alternative for reducing *PDI* is by decreasing R (see *Table 2*). The *PDI* is around 2 for $R = 0.99$. However, the number-average molecular weight varies in each case considered in *Table 2*. Hence, it is important to consider the number-average molecular weight together with the *PDI* for finding the best operating conditions.

Table 3 shows the conditions for obtaining a number-average molecular weight of $100M_A$, which is generally sufficient to obtain good mechanical strength in step polymers. In all the cases, the reaction time to obtain $M_n = 100M_A$ is a minimum for $R = 1$. Increasing R above 1 causes an increase in both reaction time and *PDI*. However, decreasing R below the stoichiometric

Table 2 Influence of R and K on PDI and on the concentration of unreacted monomers for a homogeneous system

	$R=0.99$			$R=1.00$			$R=1.01$		
K	$a\times10^5$	$b\times10^4$	PDI^a	$a\times10^5$	$b\times10^8$	PDI	$a\times10^3$	$b\times10^8$	PDI
1	1×10^{-3}	1.02	2.00 (1.98)	1.0×10^{-3}	1.0	2.00 (2.00)	0.101	1.0	2.00 (1.98)
10	8.49	1.02	2.02 (1.98)	8.89	1.0	3.60 (2.00)	8.981	1.0	16.55 (2.00)
50	9.36	1.02	2.02 (1.98)	9.80	1.0	3.92 (2.00)	9.89	1.0	66.33 (2.00)

[a] Values in parentheses indicate modified PDI

Table 3 Influence of R and K on PDI and θ ($M_n=100M_A$) for a homogeneous system

	$R=0.9802$		$R=0.99$		$R=1.00$		$R=1.01$		$R=1.02$	
K	θ	PDI	θ	PDI	θ	PDI	θ	PDI	θ	PDI
1	189.1	2.0	54.7	1.99	49.5	1.99	54.0	1.99	129.7	2.00
10	94.5	2.0	27.4	2.56	24.8	3.56	27.0	5.89	64.9	16.91
50	94.5	2.0	27.4	2.63	24.8	3.88	27.0	7.39	64.9	76.16

ratio of 1 has the favourable effect of decreasing PDI even though the reaction time increases. For $R=0.9802$ and $K=50$, we obtain a PDI of 2. This is expected for a normal step polymerization. When one of the monomers shows induced asymmetric behaviour, the best strategy is to use slightly less than the stoichiometric ratio of 1, so that the PDI of the polymer will be ~2.

Heterogeneous system

Solubility of BB (β). The influence of β on PDI as a function of unreacted groups is shown in *Figure 1*. In all the cases, computational results are shown up to 99.5% conversion of A groups. When $\beta<1$, the reaction mixture is heterogeneous in the beginning, and, as the reaction proceeds, BB dissolves and reacts. After a particular conversion, the reaction mixture becomes homogeneous. When $\beta<1$, the PDI goes through a maximum and approaches the value for the homogeneous case at high conversions, as shown in *Figure 1*. However, no maximum is observed for the homogeneous case. At any time, for $\beta<1$, the PDI is high compared with the homogeneous case. The increase in PDI can be due to the presence of unreacted monomers[3]. When the reaction is heterogeneous, β is constant until monomer BB is completely dissolved and the total moles of BB (b) in the reaction mixture increases due to the continuous dissolution of BB (see equation (26)). To verify this, the modified PDI ($MPDI$) (equation (21)) without considering the contribution of unreacted monomers is calculated (see *Figure 2*). It is important to note that $MPDI$ also goes through a maximum. At a given conversion, the $MPDI$ is small compared with the PDI. This indicates that the distribution of the polymer formed in a heterogeneous system is broader even when the contribution of unreacted monomers is not taken into account and the $MPDI$ can be greater than 2. This can be explained as follows. Whenever the solubility of BB is limited, the concentration of A groups is more than the concentration of B groups in the reaction mixture. Then, the instantaneous stoichiometric ratio (R) is greater than 1, even though the overall stoichiometric ratio is 1. Thus, A groups on

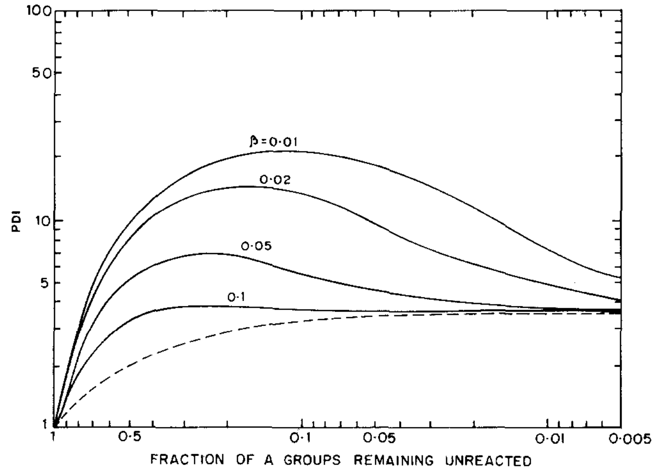

Figure 1 Effect of β on PDI for heterogeneous (——) and homogeneous (– – –) systems; $R=1$, $K=10$

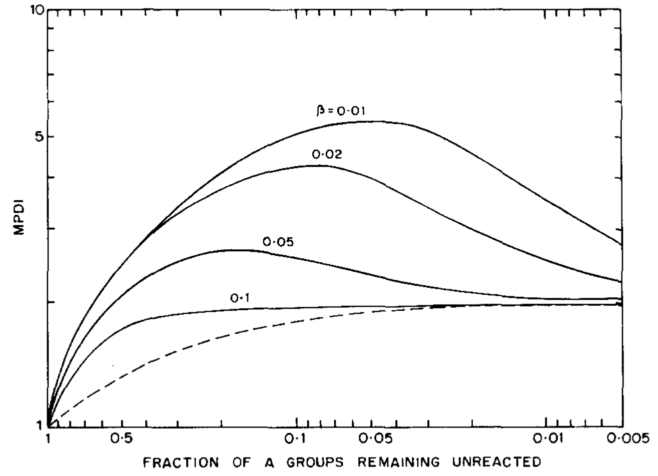

Figure 2 Effect of β on $MPDI$ for heterogeneous (——) and homogeneous (– – –) systems; $R=1$, $K=10$

AA and on polymer molecules compete with each other to react with B groups. When $K>1$ (i.e. polymer molecules are more reactive), reaction products are therefore a mixture of monomer and increasing amounts of high polymer. This leads to an increase in *PDI* and *MPDI*.

Figure 3 shows the influence of reactivity ratio K on *PDI* for $\beta=0.01$. For comparison, results are also shown for the homogeneous case. As expected, *PDI* increases with K in both cases. The influence of K on *PDI* increases with decreasing β (*Figure 3*). However, the influence of K on *PDI* is small in the homogeneous case. The effect of stoichiometric ratio (R) on *PDI* is observed only at high conversions (see *Figure 4* and also *Table 4*). The influence of R is different for $K>1$ and $K=1$. The two main opposing factors influencing *PDI* are solubility and K. As solubility increases, *PDI* decreases (see *Figure 1*), whereas *PDI* increases with an increase in K. When $K>1$, the concentration of unreacted AA in the reaction mixture increases with K (see *Table 2* for homogeneous case). This leads to an increase in *PDI*. When $K=1$, both the monomers are equally reactive. As R increases, the concentration of BB (equation (27)) increases in the reaction mixture, and this leads to a decrease in *PDI*. *Figure 5* shows the influence of β on the reaction time. Obviously reaction time increases as β decreases. For 99% conversion, the dimensionless reaction time θ is 39.93 for $\beta=0.01$ compared with 24.8 for the homogeneous case. *Figures 2–4* clearly show that increasing β (either by increasing temperature or by using a suitable solvent) has the advantage of decreasing *PDI* and reaction time.

In poly(phenylene sulphide) (PPS) synthesis, 1,4-dichlorobenzene (AA) is reacted with sodium sulphide (BB) in *N*-methylpyrrolidone at 200–250°C. Koschinski and Reichert[8] and Koch and Heitz[9] observed the formation of high-molecular-weight products ($DP=20$) even at low conversions ($\simeq 20\%$) (see *Figure 6*), compared with a normal polycondensation process where high-molecular-weight products are formed only at high conversions ($\simeq 99\%$). This unusual observation is thought to be due to the high reactivity of an A group at the end of a polymer molecule compared with the reactivity

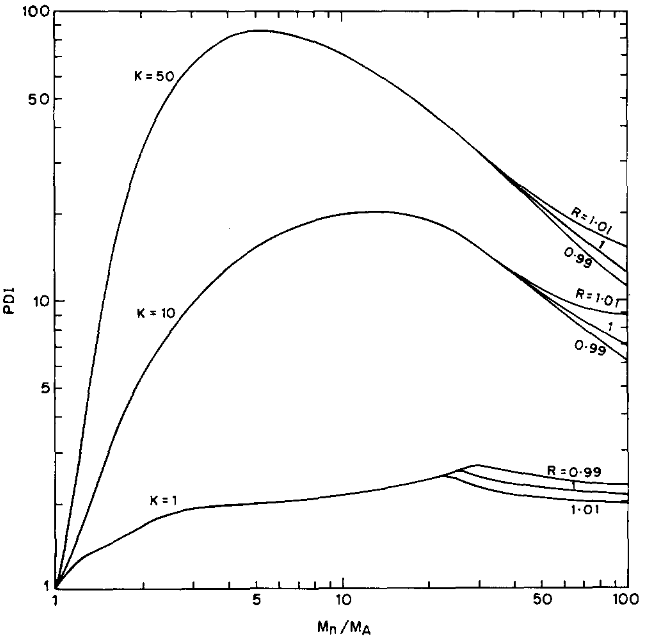

Figure 4 Effect of stoichiometric ratio (R) on *PDI* as a function of M_n/M_A; $\beta=0.01$

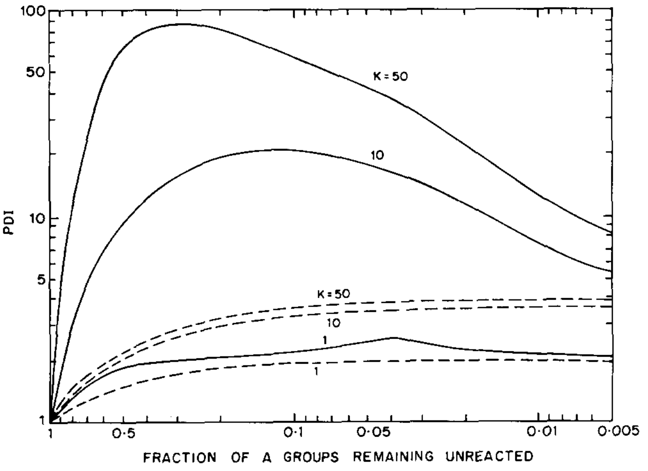

Figure 3 Effect of reactivity ratio (K) on *PDI* for heterogeneous (——) and homogeneous (– – –) systems; $R=1$, $\beta=0.01$

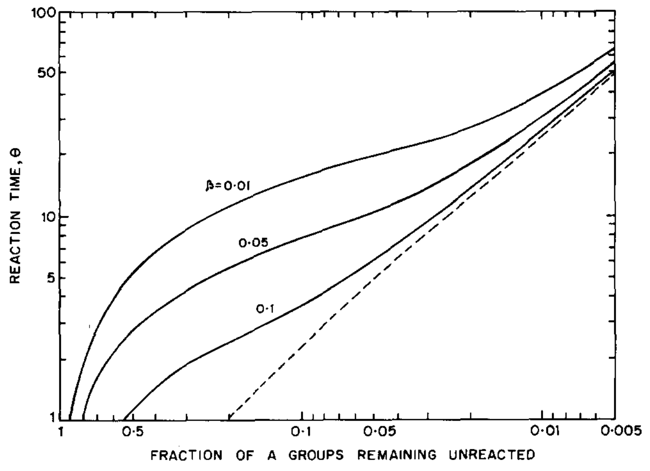

Figure 5 Effect of β on reaction time (θ) for heterogeneous (——) and homogeneous (– – –) systems; $R=1$, $K=10$

Table 4 Influence of β on *PDI* ($M_n=100M_A$) for a heterogeneous system

	PDI								
	$K=1$			$K=10$			$K=50$		
β	$R=0.99$	1.00	1.01	$R=0.99$	1.00	1.01	$R=0.99$	1.00	1.01
0.01	2.3	2.11	2.02	6.21	7.02	9.15	11.38	12.44	15.76
0.05	2.03	2.01	2.00	2.78	3.78	6.10	2.92	4.16	7.67
1.00	1.99	1.99	1.99	2.56	3.56	5.89	2.63	3.88	7.39

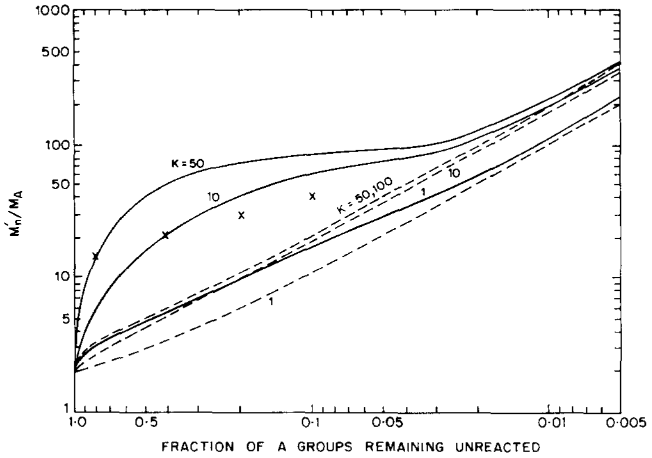

Figure 6 Effect of reactivity ratio (K) on M'_n/M_A for heterogeneous (——) and homogeneous (---) systems; $R=1$, $\beta=0.01$. (The crosses indicate experimental points[8])

of an A group monomer. It is important to examine this problem more quantitatively. The number-average molecular weight M'_n/M_A increases with K as shown in *Figure 6*. However, M'_n/M_A is small at low conversions for a homogeneous syste. For example, even when $K=100$, M'_n/M_A is only 3.42 at 21.24% conversion. Hence the formation of highly reactive intermediates alone cannot explain the above unusual observation. However, it can be explained when we take into account the limited solubility of Na_2S in the reaction mixture. The solubility[10] of Na_2S in *N*-methylpyrrolidone is only 1–3% even at 230°C, and 1,4-dichlorobenzene is completely miscible with the solvent. This shows that the reaction mixture is heterogeneous in the beginning and the solubility of Na_2S has to be taken into account in calculating the number-average molecular weight and *PDI*. The full curves in *Figure 6* show the effects of K for the heterogeneous system. When $\beta=0.01$, M'_n/M_A is 15.2 at 20% conversion for $K=50$. For comparison, experiment data of Koschinski *et al.*[8] are shown in *Figure 6*. It shows that high molecular weights are formed at low conversions only when the solubility of Na_2S is small and K is significantly greater than 1. This is true in the case of PPS synthesis. *Figure 7* shows the influence of β on M'_n/M_A. Decreasing β causes an increase in the formation of high-molecular-weight products at low conversion. It is important to mention here that modelling of a PPS reactor is more complex since PPS precipitates out of solution after reaching a certain molecular weight. Then reaction occurs in both the homogeneous phase and the precipitated polymer phase. Any model developed for the formation of PPS should take these steps into account. However, the model developed here is useful for analysing the initial stages of PPS synthesis, i.e. before the process of precipitation of PPS starts.

Solubility of AA (α). It is desirable to examine this case and see whether the results are similar to the previous case. *Figure 8* shows the influence of α on *PDI* as a function of unreacted groups. Clearly the following points emerge. The *PDI* increases continuously and reaches a plateau. The *PDI* curve does not go through a maximum as in the previous case where the solubility of BB is limited (see *Figure 1*). Again *PDI* is always found to be less than that of the homogeneous case. However, *PDI* at high conversions is the same and it is independent of α (see *Figure 8*). These observations can be explained qualitatively as follows.

Whenever the solubility of AA is limited ($\alpha<1$), the reaction mixture contains fewer A groups compared with B groups. Therefore, most of the polymer molecules in the reaction mixture will contain B end-groups. The freshly dissolved monomer AA will react with monomer BB or with B end-groups of the polymer molecule at the same rate. Since monomer A is not completely dissolved, the instantaneous stoichiometric ratio (R) in the reaction mixture is less than 1. Therefore, *PDI* is less than that of the homogeneous case. The intersection points of various curves in *Figure 8* (for different α values) with the homogeneous case correspond to the points where AA is completely dissolved. The effect of K on *PDI* is shown in *Figure 9*. For $K=1$, the influences of α and β on *PDI* are the same (see *Figure 3*).

CONCLUSIONS

A mathematical model has been developed for a heterogeneous step polymerization reactor. The model takes into account the influence of induced asymmetry of the monomer (AA). When β is small, the *PDI* goes through a maximum and the *MWD* is broader than that of the homogeneous case. Increasing β is found to be useful for decreasing the *PDI*. When α is small, the *PDI* is less than

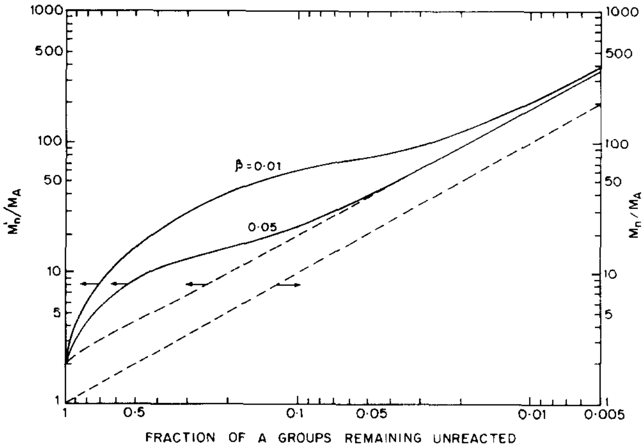

Figure 7 Effect of β on M'_n/M_A and M_n/M_A for heterogeneous (——) and homogeneous (---) systems; $R=1$, $K=10$

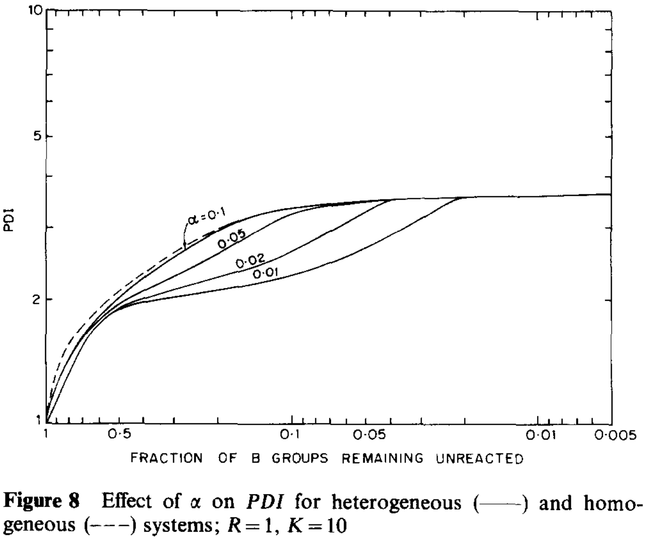

Figure 8 Effect of α on *PDI* for heterogeneous (——) and homogeneous (---) systems; $R=1$, $K=10$

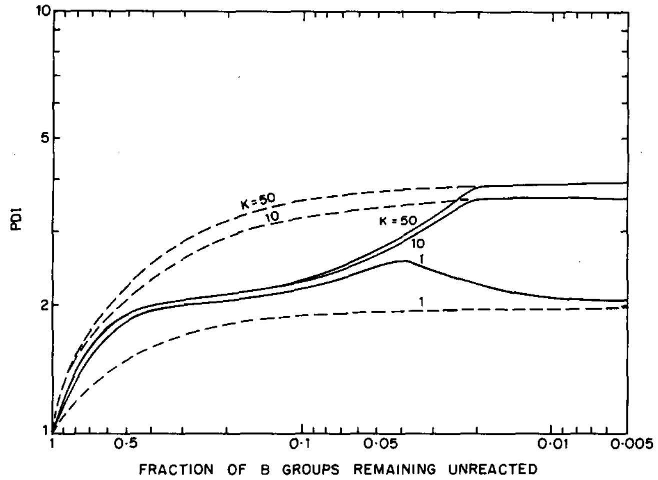

Figure 9 Effect of reactivity ratio (K) on *PDI* for heterogeneous (——) and homogeneous (– – –) systems; $R=1$, $\alpha=0.01$

or equal to that of the homogeneous system. A strategy is developed for obtaining a narrow *MWD* for a homogeneous system. Using the mathematical model developed here, the formation of high-molecular-weight products at low conversions in PPS synthesis is explained for the first time.

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