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of the hydrophilic poly(BOL) membrane.

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# Step Polymerization with Unequal Reactivities of Functional Groups

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ABSTRACT: The effect of the nonequivalent reactivity of the two functional groups in a difunctional monomer on the kinetics of step polymerization with a symmetric monomer and the molecular weight distribution of the product was calculated by using a combination of kinetic and probabilistic arguments. The model involves four rate constants. It was shown that the usually assumed maximum value of 2 for the polydispersity index is wrong if the monomer possessing unequal reactivity reacts slower than the oligomers and if it is present in excess of or in exact stoichiometric proportion with the symmetric monomer. When such conditions are obtained, $\bar{M}_n$ is unaffected while $\bar{M}_w$ is increased (causing the polydispersity index to be greater than 2) considerably.

Recently we[1] considered the step polymerization of two kinds of difunctional monomers—one in which the reactive functional groups have unequal reactivities and the other for which the monomeric functional groups react at a rate that is different from those that are present as chain ends. These may be referred to as asymmetry and induced asymmetry, respectively. Symmetric diisocyanates are known[2] to exhibit induced asymmetry. The polymerization of cyclic monomers such as anhydrides turned out to be[1] mathematically equivalent to the monomers with induced asymmetry. For these cases we[1] obtained the molecular weight distribution (MWD) as a function of the extent of reaction or time. It has also been shown that the polydispersity index (PDI) shows discontinuities and can be much greater than the usual maximum value of 2 and that this is due to the contribution of the unreacted monomer. A modified polydispersity index (MPDI) obtained by defining the number and weight average molecular weights excluding the monomer contributions showed no discontinuities and had a maximum value of 2.

Many of the monomers, however, can exhibit a more complicated behavior than simple asymmetry or induced asymmetry. Thus Peebles[3] proposed that asymmetric monomers, such as 2,4-tolylene diisocyanate, can exhibit asymmetry and induced asymmetry simultaneously. Here we wish to obtain the kinetics of and MWD in step polymerization of such monomers and examine the necessity and usefulness of MPDI. We will consider an ideal batch or plug flow reactor.

## Model and Kinetics of Polymerization

Let $A_1A_2$ be a difunctional monomer showing asymmetry and induced asymmetry simultaneously. Let it react with a monomer BB which has neither asymmetry nor induced asymmetry. The reactions can be represented as

$$A_2A_1 + BB\sim \xrightarrow{k_1} A_2A_1BB\sim \tag{1}$$

$$A_1A_2 + BB\sim \xrightarrow{k_2} A_1A_2BB\sim \tag{2}$$

$$\sim A_2A_1 + BB\sim \xrightarrow{k_1^*} \sim A_2A_1BB\sim \tag{3}$$

$$\sim A_1A_2 + BB\sim \xrightarrow{k_2^*} \sim A_1A_2BB\sim \tag{4}$$

where $\sim$ represents a chain. Reactions 1 and 2 or 3 and 4 characterize asymmetry while reactions 1 and 3 or 2 and 4 characterize induced asymmetry.

From reactions 1–4 it is clear that the $A_1$ and $A_2$ groups belonging to the monomer have to be distinguished from the $A_1$ and $A_2$ groups which are present as chain ends. To make this distinction clear and to facilitate understanding,

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the $A_1$ and $A_2$ type of groups present as chain ends will be denoted as $A_1{}^*$ and $A_2{}^*$. The various types of species present at any time during the polymerization are $A_1A_2$, $(A_1{}^*A_2BB)_n$, $(A_2{}^*A_1BB)_n$, $(A_1{}^*A_2BB)_nA_2A_1{}^*$, $(A_1{}^*A_2BB)_nA_1A_2{}^*$, $(A_2{}^*A_1BB)_nA_1A_2{}^*$, and $(BBA_1A_2)_{n-1}BB$: $n \geq 1$. Let us denote their concentrations by $A$, $r_n{}^1$, $r_n{}^2$, $p_n{}^{11}$, $p_n{}^{12}$, $p_n{}^{22}$, and $q_n$, respectively. The balance equation for $(BBA_1A_2)_{n-1}BB$ is:

$$-\frac{\mathrm{d}q_n}{\mathrm{d}t} = 2q_n\Big[(k_1 + k_2)A + \sum_{m=1}^{\infty}\{k_1{}^*(r_m{}^1 + p_m{}^{12} + 2p_m{}^{11}) + k_2{}^*(r_m{}^2 + p_m{}^{12} + 2p_m{}^{22})\}\Big] - 2\sum_{m=1}^{n-1}\{k_1{}^*r_{n-m}{}^1q_m + k_2{}^*r_{n-m}{}^2q_m\} \quad (5)$$

In this equation the first term on the right-hand side represents the rate at which the species are consumed due to reaction while the second term represents the rate of their formation. Similar equations for all the other species can be written. As will be shown later, the MWD is determined by the total group concentration and thus it is sufficient if these are calculated. Let [B], $[A_1{}^*]$, and $[A_2{}^*]$ represent the concentrations of the total number of B, $A_1{}^*$, and $A_2{}^*$ groups, i.e.,

$$[B] = \sum_{n=1}^{\infty}[r_n{}^1 + r_n{}^2 + 2q_n] \quad (6)$$

$$[A_1{}^*] = \sum_{n=1}^{\infty}[r_n{}^1 + p_n{}^{12} + 2p_n{}^{11}] \quad (7)$$

$$[A_2{}^*] = \sum_{n=1}^{\infty}[r_n{}^2 + p_n{}^{12} + 2p_n{}^{22}] \quad (8)$$

By summing the appropriate balance equations the following will be obtained:

$$-\frac{\mathrm{d}[A_1{}^*]}{\mathrm{d}t} = k_1{}^*[A_1{}^*][B] - k_2A[B] \quad (9)$$

$$-\frac{\mathrm{d}[A_2{}^*]}{\mathrm{d}t} = k_2{}^*[A_2{}^*][B] - k_1A[B] \quad (10)$$

$$-\frac{\mathrm{d}[B]}{\mathrm{d}t} = (k_1 + k_2)A[B] + \{k_1{}^*[A_1{}^*] + k_2{}^*[A_2{}^*]\}[B] \quad (11)$$

These can also be written directly by recognizing that $A_1{}^*$ or $A_2{}^*$ type groups disappear by reaction with B groups while they are formed when an $A_2$ or $A_1$ group contained in the monomer reacts with a B group. Both of the concentrations of $A_1$ and $A_2$ groups are equal to the molar concentration of the $A_1A_2$ monomer and the balance equation for the monomer is

$$-\frac{\mathrm{d}A}{\mathrm{d}t} = (k_1 + k_2)A\sum_{n=1}^{\infty}(r_n{}^1 + r_n{}^2 + 2q_n) = (k_1 + k_2)A[B] \quad (12)$$

Let us consider the case where the reaction is started with monomers only. Then the initial conditions for integrating eq 11 and 12 are that $A = A_0$ and $[B] = 2B_0$ where $A_0$ and $B_0$ are the initial molar concentrations of $A_1A_2$ and BB monomers, respectively. By definition $A_1{}^*$ and $A_2{}^*$ ends are present as chain ends and since no chains are formed at $t = 0$, the appropriate initial conditions for integrating eq 9 and 10 are that $[A_1{}^*] = [A_2{}^*] = 0$.

Dividing eq 9 by 12 and integrating gives

$$\frac{[A_1{}^*]}{A_0} = \frac{K}{(K_1 - 1) - K}\left[\frac{A}{A_0} - \left(\frac{A}{A_0}\right)^{K_1/(1+K)}\right]; \qquad K_1 \neq K + 1 \quad (13a)$$

$$\frac{[A_1{}^*]}{A_0} = -\frac{K}{K + 1}\frac{A}{A_0}\ln\frac{A}{A_0}; \qquad K_1 = K + 1 \quad (13b)$$

where $K = k_2/k_1$ and $K_1 = k_1{}^*/k_1$. It is to be noted that $[A_1{}^*] = 0$ when $A = A_0$ which is consistent with the initial conditions described above. Similarly, dividing eq 10 by 12 and integrating gives

$$\frac{[A_2{}^*]}{A_0} = \frac{1}{KK_2 - K - 1}\left[\frac{A}{A_0} - \left(\frac{A}{A_0}\right)^{KK_2/(K+1)}\right]; \qquad KK_2 \neq K + 1 \quad (14a)$$

$$\frac{[A_2{}^*]}{A_0} = -\frac{1}{K + 1}\frac{A}{A_0}\ln\frac{A}{A_0}; \qquad KK_2 = K + 1 \quad (14b)$$

where $K_2$ is equal to $k_2{}^*/k_2$. Since each of the $A_1$, $A_1{}^*$, $A_2$, and $A_2{}^*$ groups can react with one B group

$$2A_0 - 2A - [A_1{}^*] - [A_2{}^*] = 2B_0 - [B] \quad (15)$$

where $B_0$ is the initial molar concentration of the BB monomer. Hence if $A$ is known, all the other group concentrations can be computed. Further, using eq 13, 14, and 15, we can integrate eq 12 to obtain $A$ and therefore any of the group concentrations as a function of time.

## Definitions of Probabilities of Reaction

When considering the simpler model in which either asymmetry or induced asymmetry is present, the instantaneous probability of reaction of a particular group was defined as the fraction of the groups that have reacted by that time. The MWD obtained following this assumption was shown to satisfy the individual species balance equations thereby providing a posteriori justification for this definition. In the following we adopt similar definitions for the more general model under consideration here and again show that the resulting MWD satisfies the species balance equations.

**Probability of Reaction of B Groups.** The probability of reaction of B groups, $\beta$, can be equated to the fraction of the initial B groups that have reacted:

$$\beta = 1 - \{[B]/2B_0\} \quad (16)$$

**Probability of Reaction of Monomeric A Groups.** First let us consider $A_1$ groups belonging to the $A_1A_2$ monomer. The concentration of $A_1$ groups of the monomer can decrease in two ways: (i) by direct reaction, i.e.,

$$A_2A_1 + BB\sim\sim \rightarrow A_2{}^*A_1BB\sim\sim \quad (1)$$

and (ii) due to the fact that when an $A_2$ group of the monomer reacts, the $A_1$ group then becomes a chain end or an $A_1{}^*$ group, i.e.,

$$A_1A_2 + BB\sim\sim \rightarrow A_1{}^*A_2BB\sim\sim \quad (2)$$

Thus loss of one monomeric $A_1$ group is the result in both instances when an $A_1$ or an $A_2$ group of a monomer reacts. Hence to follow the usual procedure of equating the probability of *reaction* of monomeric $A_1$ groups with the fractional decrease of the initial concentration of monomeric $A_1$ group would be incorrect. Instead, the probability of reaction of $A_1$ groups of monomer should be related only to the events taking place according to reaction 1. Let $A_1{}^r$ denote the total monomeric $A_1$ groups that have been consumed since the beginning of the reaction by direct reaction with B groups or according to reaction 1. The probability of reaction of monomeric $A_1$ groups, $\alpha_1$, may be defined as

$$\alpha_1 = A_1{}^r/(A + A_1{}^r) \tag{17}$$

In so defining $\alpha_1$, we are using the idea that $(A + A_1{}^r)$ number of monomeric $A_1$ groups could have reacted till that time while only $A_1{}^r$ of them have reacted. As stated earlier, this definition will be justified a posteriori by proving that the MWD obtained based on this definition is correct. Similarly, the probability of reaction of monomeric $A_2$ groups, $\alpha_2$, may be defined as

$$\alpha_2 = A_2{}^r/(A_2{}^r + A) \tag{18}$$

where $A_2{}^r$ are the monomeric $A_2$ groups consumed in direct reaction with B groups or according to reaction 2. Since $A_1{}^r$ and $A_2{}^r$ cannot be directly measured it is necessary for $\alpha_1$ and $\alpha_2$ to be related to the amount of monomer that has been consumed. This can be done as follows. From the kinetics of reactions 1 and 2, it can be seen that

$$dA_2{}^r/dt = k_2A[\mathrm{B}] \text{ and } dA_1{}^r/dt = k_1A[\mathrm{B}]$$

and hence $A_2{}^r/A_1{}^r = K$ since initially both $A_1{}^r$ and $A_2{}^r$ are zero. Also $A_1{}^r + A_2{}^r$ must equal the moles of monomer that have reacted. Hence

$$A = A_0 - A_1{}^r - A_2{}^r \tag{19}$$

Therefore from eq 17 and 18 it follows that

$$A/A_0 = (1 - \alpha_1)/(K\alpha_1 + 1) = K(1 - \alpha_2)/(\alpha_2 + K) \tag{20}$$

**Probability of Reaction of Polymeric A Groups.** First consider $A_1$ groups. The probability of reaction, $\alpha_1{}^*$, of polymeric $A_1$, i.e., $A_1{}^*$ groups, will be defined as the fraction of the available $A_1{}^*$ groups that have reacted with B groups. Since initially $[A_1{}^*] = 0$, the total number of $A_1{}^*$ groups that have been available for reaction is equal to the total number of $A_1{}^*$ groups that have been created. An $A_1{}^*$ group is created only when a monomeric $A_2$ group reacts and therefore $A_2{}^r$ are the total number of $A_1{}^*$ groups that have been created. Hence $(A_2{}^r - [A_1{}^*])$ is equal to the number of polymeric $A_1$ groups that have reacted with B groups. Thus

$$\alpha_1{}^* = (A_2{}^r - [A_1{}^*])/A_2{}^r \tag{21}$$

Similarly the probability of reaction $\alpha_2{}^*$ of polymeric $A_2$, i.e., $A_2{}^*$ groups, will be defined as

$$\alpha_2{}^* = (A_1{}^r - [A_2{}^*])/A_1{}^r \tag{22}$$

The various group concentrations can then be calculated in terms of $\beta$, $\alpha_1$, $\alpha_1{}^*$, and $\alpha_2{}^*$, and on substitution of these into eq 13, 14, and 15 we have

$$1 - \alpha_1{}^* = \frac{K\alpha_1 + 1}{\alpha_1(K_1 - 1 - K)}\left\{\frac{1 - \alpha_1}{K\alpha_1 + 1} - \left(\frac{1 - \alpha_1}{K\alpha_1 + 1}\right)^{K_1/(K+1)}\right\}; \qquad K_1 \neq K + 1 \tag{23}$$

$$1 - \alpha_2{}^* = \frac{K\alpha_1 + 1}{\alpha_1(KK_2 - K - 1)}\left\{\frac{1 - \alpha_1}{K\alpha_1 + 1} - \left(\frac{1 - \alpha_1}{K\alpha_1 + 1}\right)^{KK_2/(K+1)}\right\}; \qquad KK_2 \neq K + 1 \tag{24}$$

and

$$\frac{\alpha_1}{K\alpha_1 + 1}(1 + \alpha_2{}^*) + \frac{K\alpha_1}{K\alpha_1 + 1}(1 + \alpha_1{}^*) = \frac{2\beta}{R} \tag{25}$$

where $R = A_0/B_0$. Thus if $\alpha_1$ is known all the other probabilities can be calculated. Further by combining eq 20 with eq 12

$$\frac{d\alpha_1}{dt} = (2B_0k_1)(1 - \alpha_1)(K\alpha_1 + 1)(1 - \beta) \tag{26}$$

This can be integrated after substituting eq 23, 24, and 25 to obtain $\alpha_1$ as a function of time. Thus all the probabilities can be calculated.

## Molecular Weight Distribution

The various polymeric species will have repeat units of the type $-BA_1A_2B-$. Considering the internal arrangements of $A_1A_2$, such a unit could have formed in the following four ways: $-BA_1A_2{}^*B-$, $-BA_2A_1{}^*B-$, $-BA_1{}^*A_2B-$, and $-BA_2{}^*A_1B-$. The first of these is formed when a B end reacts with a monomeric $A_1$ group leading to the formation of an $A_2{}^*$ end which subsequently reacts with a B group. The probability of finding the first type of unit is therefore given by the product of the probabilities of occurrence of the two events required for the formation of the unit. The numbers of monomeric $A_1$ and $A_2$ groups that have reacted are $A_1{}^r$ and $A_2{}^r$ and the numbers of polymeric $A_1$ and $A_2$ (i.e., $A_1{}^*$ and $A_2{}^*$) groups that have reacted are $\alpha_1{}^*A_2{}^r$ and $\alpha_2{}^*A_1{}^r$, and hence the probability that a B reacts with a monomeric $A_1$ group is given by

$$\beta\frac{A_1{}^r}{A_1{}^r(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)}$$

Therefore the probability of formation of the first unit is given by

$$\beta\frac{A_1{}^r}{A_1{}^r(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)}\alpha_2{}^*$$

The probability of formation of the second of the above units can be similarly obtained and is given by

$$\beta\frac{A_2{}^r}{A_1{}^r(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)}\alpha_1{}^*$$

An $A_1{}^*$ group can be formed only after a monomeric $A_2$ group reacts with a B group, and hence the third of the above units can be thought of simply as the result of the reaction between a B group and a polymeric $A_1$ or $A_1{}^*$ group. Therefore, the probability of finding the third unit is given by

$$\beta\frac{\alpha_1{}^*A_2{}^r}{A_1{}^*(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)}$$

The probability of finding the fourth unit is obtained in a similar manner and is equal to

$$\beta\frac{\alpha_2{}^*A_1{}^r}{A_1{}^r(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)}$$

The probability of finding a $-BA_1A_2B-$ unit then is the sum of the above probabilities and is calculated to be equal to

$$2\beta\frac{A_2{}^r\alpha_1{}^* + A_1{}^r\alpha_2{}^*}{A_1{}^r(1 + \alpha_2{}^*) + A_2{}^r(1 + \alpha_1{}^*)} = R\alpha_1\frac{\alpha_2{}^* + K\alpha_1{}^*}{K\alpha_1 + 1} \equiv R\delta \tag{27}$$

after using eq 25 and the fact that $A_2{}^r/A_1{}^r = K$.

The total number of molecules present at any time is equal to half the number of monomeric and polymeric end groups and is given by

$$\tfrac{1}{2}(2A + [A_1{}^*] + [A_2{}^*] + [\mathrm{B}])$$

and with the use of eq 15 and 16 it can be shown to be equal to

$$(R + 1 - 2\beta)B_0$$

The concentration of any species is then given by multiplying $(R + 1 - 2\beta)B_0$ with the probability of finding the particular species.

The probability of finding a species will be derived for $p_n^{12}$ as an example. The structure of $p_n^{12}$ is

$$A_1{*}A_2B(BA_1A_2B)_{n-1}BA_1{*}A_2{*}$$

Such a molecule can be located at random in two ways. In the first way an $A_1$* end (which must have a structure $A_1$*$A_2$B– since an $A_1$* end cannot form unless a monomeric $A_2$ group reacts) which is followed by ($n$–1) number of –$BA_1A_2B$– units and one –$BA_1A_2$* unit is located. The probability of locating a $p_n^{12}$ molecule in this way is therefore given by

(probability of finding an $A_1$*end) ×
(probability of finding a sequence of ($n$ – 1) number of –$BA_1A_2B$– units) ×
(probability that the B end reacted with a monomeric $A_1$ group) ×
(probability that the $A_2$* end has not reacted)

or

$$\frac{[A_1{*}]}{2(R + 1 - 2\beta)B_0}(R\delta)^{n-1}\beta\frac{A_1^{r}}{A_1^{r}(1 + \alpha_2{*}) + A_2^{r}(1 + \alpha_1{*})}(1 - \alpha_2{*})$$

With the use of the fact that $A_2^r/A_1^r = K$ and eq 17, 20, 21, and 25, this can be shown to be equal to

$$\frac{1}{(R + 1 - 2\beta)B_0}\,\frac{B_0R^2K\alpha_1^{\,2}(1 - \alpha_1{*})(1 - \alpha_2{*})(R\delta)^{n-1}}{4(K_1 + 1)^2} \qquad (28)$$

The second way of finding a $p_n^{12}$ molecule is to locate an $A_2$* end (which must have a structure $A_2$*$A_1$B– since $A_2$* cannot form till a monomeric $A_1$ group reacts) which is followed by ($n$ – 1) number of –$BA_1A_2B$– units and one –$BA_2A_1$* unit. The probability of finding $p_n^{12}$ can be calculated in a manner similar to the above, and it is found to be equal to the probability of finding a $p_n^{12}$ type of molecule by the first method. Thus the probability of finding a $p_n^{12}$ molecule is equal to twice the probability given above in eq 28. Following this procedure, we can show that the molar concentrations are given by:

$$A = B_0R(1 - \alpha_1)/(K\alpha_1 + 1)$$
$$r_n^{\,1} = B_0RK\alpha_1(1 - \beta)(1 - \alpha_1{*})(R\delta)^{n-1}/(K\alpha_1 + 1)$$
$$r_n^{\,2} = B_0R\alpha_1(1 - \beta)(1 - \alpha_2{*})(R\delta)^{n-1}/(K\alpha_1 + 1)$$
$$p_n^{\,11} = B_0R^2K^2\alpha_1^{\,2}(1 - \alpha_1{*})^2(R\delta)^{n-1}/\{2(K\alpha_1 + 1)\}^2 \qquad (29)$$
$$p_n^{\,22} = B_0R^2\alpha_1^{\,2}(1 - \alpha_2{*})^2(R\delta)^{n-1}/\{2(K\alpha_1 + 1)\}^2$$
$$p_n^{\,12} = B_0R^2K\alpha_1^{\,2}(1 - \alpha_1{*})(1 - \alpha_2{*})\,(R\delta)^{n-1}/\{2(K\alpha_1 + 1)^2\}$$
$$q_n = B_0(1 - \beta)^2(R\delta)^{n-1}$$

It is interesting to note that the exponential nature of the MWD which occurs in the case of equal reactivities still persists with the major difference, however, that the extent of conversion of the monomer that characterizes that distribution is now replaced by $R\delta$—a complicated function of the conversion. A similar result had been obtained by Case[4] for the condensation of an anhydride with a symmetric diol. It will be interesting to speculate whether such a result is indeed more generally valid. That eq 29 are solutions of the species balance equations will be demonstrated in the Appendix. This also validates the definitions for the probabilities adopted earlier. Since the total number of $A_1A_2$ and BB units contained in all the molecules must equal $A_0$ and $B_0$, respectively, eq 29 must satisfy the following conditions:

$$A + \sum_{n=1}^{\infty}\{n(r_n^{\,1} + r_n^{\,2}) + (n + 1) \times (p_n^{\,12} + p_n^{\,11} + p_n^{\,22}) + (n - 1)q_n\} = A_0$$

and

$$\sum_{n=1}^{\infty} n(r_n^{\,1} + r_n^{\,2} + p_n^{\,12} + p_n^{\,11} + p_n^{\,22} + q_n) = B_0$$

It can be easily shown that eq 29 do satisfy the above conservation conditions.

From the distribution given in eq 29 it is possible to calculate the number average ($\bar{M}_n$) and the weight average ($\bar{M}_w$) molecular weights. The resulting polydispersity index (PDI) which is the ratio $\bar{M}_w/\bar{M}_n$ is given below.

$$\bar{M}_n = (RM_A + M_B)/(R + 1 - 2\beta) \qquad (30)$$

$$\text{PDI} = \frac{M_A^{\,2}(2\beta^2 + R - R^2\beta) + 4\beta M_AM_B + (1 + R\delta)M_B^{\,2}}{(1 - R\delta)(RM_A + M_B)^2}(R + 1 - 2\beta) \qquad (31)$$

It may be noted that the formula for $\bar{M}_n$ is unchanged by the simultaneous presence of asymmetry and induced asymmetry.

## Discussion and Results

When $K_1 = K_2 = 1$, the limit of only asymmetry must be recovered. Let us define that $\alpha_1^{a}$ and $\alpha_2^{a}$ are the fractions of $A_1$ and $A_2$ groups reacted or probabilities of reaction in this limit. Thus

$$\alpha_1^{a} = \lim_{K_1=K_2=1}\left\{\frac{A_1^{r}}{A_0} + \frac{A_2^{r}\alpha_1{*}}{A_0}\right\} = 1 - \left(\frac{A}{A_0}\right)^{1/(K+1)}$$

Similarly

$$\alpha_2^{a} = \lim_{K_1=K_2=1}\left\{\frac{A_2^{r}}{A_0} + \frac{A_1^{r}\alpha_2{*}}{A_0}\right\} = 1 - \left(\frac{A}{A_0}\right)^{K/(K+1)}$$

Hence $(1 - \alpha_1^{a})^K = (1 - \alpha_2^{a})$ which is the relation obtained for asymmetry. Moreover in this limit it can be shown that $\delta = \alpha_1^{a}\alpha_2^{a}$. With this substitution the number distribution given by eq 29 as well as the PDI given in eq 31 coincide with the results for only asymmetry.[1]

Similarly $K_1 = K_2$ and $K = 1$ corresponds to only induced asymmetry. In this limit $\alpha_1{*} = \alpha_2{*}$ and $\alpha_1 = \alpha_2$, and it can be shown that $\delta = \alpha_2{*}$. Then as in the case of only asymmetry, it is straightforward to show that the MWD given by eq 29 and PDI given by eq 31 coincide with the results for only induced asymmetry.[1]

**Polydispersity Index at the End of the Reaction.** As the fraction of monomers reacted increases $\beta$ and hence $\bar{M}_n$ increase. PDI also increases and reaches a limiting value at the end of the reaction. We will focus our attention on such a limiting value reached by the PDI. For simplicity we will assume $M_A = M_B$.

**Effect of *R*. *R* < 1.** The BB monomer is in excess. Thus at the end of the reaction only B groups will be present as chain ends and hence $\alpha_1 = \alpha_1{*} = \alpha_2 = \alpha_2{*} = \delta = 1$ and $\beta = R$, and

$$\text{PDI} = (R^2 + 6R + 1)/(R + 1)^2$$

These results are independent of the values of $K_1$, $K_2$, and $K$. Note that the maximum value PDI can take is 2.

***R* = 1.** Now $\alpha_1$, $\alpha_1^*$, $\alpha_2$, $\alpha_2^*$, $\delta$, and $\beta \to 1$ as the reaction approaches completion. Thus from eq 31

$$\lim_{\substack{\beta\to 1\\ \delta\to 1}} \mathrm{PDI} = 4 \lim_{\substack{\beta\to 1\\ \delta\to 1}} \frac{1-\beta}{1-\delta}$$

This limit can be evaluated by letting $1 - \alpha_1 = \epsilon$ and evaluating $1 - \beta$ and $1 - \delta$ as a function of $\epsilon$. This can be done by using eq 23, 24, 25, and 27. The results are

$$\lim_{\beta\to 1} \mathrm{PDI} = 2$$

$$\text{if } KK_2 \le K + 1 \text{ or } K_1 \le K + 1$$

$$\lim_{\beta\to 1} \mathrm{PDI} = 2\left\{1 + \frac{1}{1 + \dfrac{1}{KK_2 - K - 1} + \dfrac{K}{K_1 - K - 1}}\right\}$$

$$\text{if both } K_1 \text{ and } KK_2 \text{ are} > K + 1$$

This latter limit is different from that attained by the PDI as $R \to 1$ from below, showing a discontinuity. Note that the maximum value for PDI at $R = 1$ is 4 and is reached as both $K_1 - K - 1$ and $KK_2 - K - 1$ approach infinity.

***R* > 1.** Now at the end of the reaction no B groups are left since $A_1A_2$ is in excess. Hence $\beta = 1$, but the terminal values of $\alpha_1$, $\alpha_2$, $\alpha_1^*$, $\alpha_2^*$, and $\delta$ will depend on the reaction rate constants. Hence the limiting PDI will have to be established numerically. However the limiting value of PDI as $R \to 1$ from above can be discussed simply. Then letting $R = 1 + y$, where $y$ is a small quantity, it can be shown that

$$\mathrm{PDI} = 2(K\alpha_1 + 1)/\left\{(K + 1)\alpha_1 - \frac{1 - \alpha_1}{y}\right\}$$

Now $y \to 0$, the limiting value of $(1 - \alpha_1)/y$ can be obtained by using eq 23, 24, 25, and 27, and it is possible to show that

$$\lim_{y\to 0} \mathrm{PDI} = 2$$

$$\text{if } KK_2 \text{ or } K_1 < K + 1$$

$$\lim_{y\to 0} \mathrm{PDI} = 2\left\{\frac{1}{1 - \dfrac{2}{2 + \dfrac{1}{KK_2 - K - 1} + \dfrac{K}{K_1 - K - 1}}}\right\}$$

$$\text{if both } KK_2 \text{ and } K_1 > K + 1$$

This latter limit can be very large as $KK_2$ and $K_1$ increase beyond $K + 1$. Thus it is clear that the values of the PDI at the end of the reaction for $R \to 1$ from above and $R = 1$ and $R \to 1$ from below will all be different from each other if both $KK_2$ and $K_1 > K + 1$. Further the usually assumed limiting value of 2 is attained only if $R < 1$ or if either $KK_2$ or $K_1 < K + 1$ when $R > 1$. This is similar to the behavior that was encountered in the case of induced asymmetry[1] when $K_1 = K_2 > 2$ except that now even when $K_1$ or $K_2$ is greater than 2 it is still possible to have a limiting value of 2 depending on the value of $K$. Thus in the combined model, asymmetry is diminishing the effect of induced asymmetry on the limiting behavior of PDI. The presence of discontinuities and the interaction between asymmetry and induced asymmetry will be discussed under the effect of rate constants.

The above discussed behavior of PDI is illustrated in Figure 1 for $K = 1.25$, $K_1 = 3.0$, and $K_2 = 4.0$. The PDI approaches a value of 2 as $R$ is increased to unity while it approaches a value of 4 as $R$ is decreased to unity. Both these values are different from 2.67, which is the value PDI attains at the end of the reaction when $R = 1$. The PDI also displays a maximum at a value of $R$ greater than 1. The results for other values of $K$, $K_1$, and $K_2$ are similar except when either $K_1$ or $KK_2$ is less than $K + 1$. When the latter condition is satisfied the PDI is continuous with $R$ and reaches a maximum value of 2 at $R = 1$.

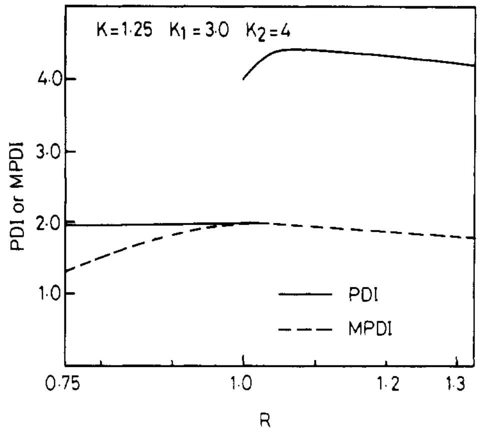

**Figure 1.** Dependence of PDI and MPDI at the end of the reaction on $R$. The point in the middle is the value of PDI at $R = 1$. The other two points are the limiting values of PDI as $R$ approaches 1 from above and below.

Earlier[1] we found that quantities defined by ignoring the presence of unreacted monomer were useful. If $\bar{M}_n'$ and $\bar{M}_w'$ are defined excluding the contributions of *both* monomers, a modified PDI (MPDI), the ratio $\bar{M}_w'/\bar{M}_n'$, had no such discontinuity, reaching a limiting value of 2 as $R \to 1$ and decreasing monotonically as $R$ is changed from 1 irrespective of the values of the rate constants. For the present general model the $\bar{M}_n'$ and MPDI are given by

$$\bar{M}_n' = \frac{(2\beta - R\delta)M_A + (2\beta - \beta^2)M_B}{2\beta - \beta^2 - R\delta}$$

$$\mathrm{MPDI} = (2\beta - \beta^2 - R\delta)[2\beta^2 + (2\beta - R\delta) \times (1 - R\delta){M_A}^2 + 4\beta M_A M_B + {M_B}^2 2R\delta + (2\beta - \beta^2)(1 - R\delta)]/\{(1 - R\delta)[(2\beta - R\delta)M_A + (2\beta - \beta^2)M_B]^2\}$$

The MPDI obtained at the end of the reaction for different values of $R$ are also shown in Figure 1 for $K = 1.25$, $K_1 = 3.0$, and $K_2 = 4.0$. The absence of discontinuities and the fact that MPDI has a maximum value of 2 at $R = 1$ are evident.

**Effect of Reaction Rate Constants.** The rate at which the $A_1A_2$ monomer is consumed is proportional to $(k_1 + k_2)$. The rate at which $A_1^*$ or polymeric $A_1$ groups react is proportional to $k_1^*$ and the rate of reaction of $A_2^*$ or polymeric $A_2$ groups is proportional to $k_2^*$. Hence if $k_1^*/(k_1 + k_2) = K_1/(K + 1)$ is greater than 1, the polymeric $A_1$ groups add to B groups faster than the monomeric $A_1$ groups. Similarly, if $k_2^*/(k_1 + k_2) = KK_2/(k_1 + k_2)$ is greater than 1, the polymeric $A_2$ groups add to B groups faster than monomeric $A_2$ groups. While the length of a polymer molecule increases by only one unit when its B end reacts with the $A_1A_2$ monomer, its length will be increased considerably if the B end were to react with a polymeric $A_1$ or $A_2$ group. Thus when both $K_1$ and $KK_2$ are greater than $(K + 1)$, longer polymer molecules are formed and a greater fraction of the $A_1A_2$ monomer remains unreacted in comparison with the case of equal reactivities. Since increasing the value of $K$ essentially speeds up the addition of monomer in preference to the building up of polymers, it follows that increasing $K$

**Table I**
**Molecular Weights at Complete Conversion for $K = 1.25$, $K_1 = 3.0$, and $K_2 = 4$**

| | | | | | | fraction of $A_1A_2$ monomer left | |
|---|---|---|---|---|---|---|---|
| $R$ | $\bar{M}_n/M_A$ | $\bar{M}_n'/M_A$ | $\bar{M}_w/M_A$ | $\bar{M}_w'/M_A$ | total no. of molecules present when $B_0 = 1$ | for the case being considered | if $K = K_1 = K_2 = 1$ |
| 1.0077 | $2.6 \times 10^2$ | $5.55 \times 10^2$ | $1.1 \times 10^3$ | $1.1 \times 10^3$ | $7.7 \times 10^{-3}$ | $4.1 \times 10^{-3}$ | $6 \times 10^{-5}$ |
| 1.042 | 49.1 | 110.1 | 215 | 216 | $4.2 \times 10^{-2}$ | $2.2 \times 10^{-2}$ | $1.6 \times 10^{-3}$ |
| 1.204 | 10.8 | 26.9 | 47 | 49.9 | 0.204 | 0.105 | $2.9 \times 10^{-2}$ |

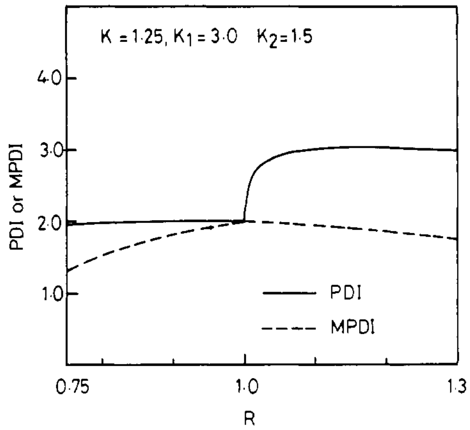

**Figure 2.** Dependence of PDI and MPDI at the end of the reaction on $R$.

counteracts the effect of large $K_1$ and $K_2$ or as stated earlier asymmetry diminishes the effects of induced asymmetry in the combined model. Now we will consider two separate cases.

**Both $K_1$ and $KK_2$ Are Greater Than ($K + 1$).** A consequence of the fact that longer polymer molecules are formed when both $K_1$ and $KK_2$ are greater than $(K + 1)$ is that $\bar{M}_w$, which gives higher weightage to longer molecules, is greater. However, since $\bar{M}_n$ is determined only by conversion, the PDI in this case is greater than that for the equal reactivity case. These conclusions are supported by the figures presented in Table I. As can be seen, when unequal reactivity exists, in comparison with the case of equal reactivity, a larger fraction of the $A_1A_2$ monomer remains unreacted and the unreacted $A_1A_2$ monomer constitutes the major part of the total number of molecules present. Since the contribution of the unreacted monomer to the total weight of the mixture is small, the above implies that the polymers are very long when unequal reactivity is present. This is also demonstrated by the fact that $\bar{M}_n'$ is nearly twice as large as $\bar{M}_n$ while $\bar{M}_w \simeq \bar{M}_w'$. That $\bar{M}_w$ is larger when unequal reactivity is present is clear since for example when $R = 1.0077$ $\bar{M}_w$ would only be $5.2 \times 10^2$ for the case of equal reactivities (PDI = 2).

By removing the contribution of the unreacted monomer, we are in essence removing the effects of unequal reactivity. Hence the MPDI which is based only on the "polymeric" portion of the reaction mixture exhibits a behavior similar to that of PDI for the case of equal reactivity.

**Either $K_1$ or $KK_2$ Is Greater Than ($K + 1$).** This implies that only one of the polymeric groups reacts faster than the $A_1A_2$ monomer. As an example let only $K_1$ be greater than $(K + 1)$. Then the polymeric $A_1$ or $A_1^*$ groups react faster than the monomer which reacts faster than the polymeric $A_2$ or $A_2^*$ groups. Thus as the reaction proceeds, when compared to the equal reactivity situation, initially longer molecules are formed due to the faster reaction rate of $A_1^*$. However, if $R \leq 1$, toward the end of the reaction there will be an accumulation of $A_2^*$ groups since both $A_1^*$ groups and the monomer are consumed by B and the reaction mixture will be composed of molecules of the type $A_2{\sim\sim}A_2^*$, $A_2^*{\sim\sim}B$, and $B{\sim\sim}B$ only. Unequal reactivity is irrelevant to such a composition and hence the PDI will finally reach a value predicted by the equal reactivity model. If $R > 1$, since B groups are exhausted before all the A groups are consumed, the above picture is not applicable and the PDI may still be greater than that predicted by the equal reactivity theory. This is shown in Figure 2.

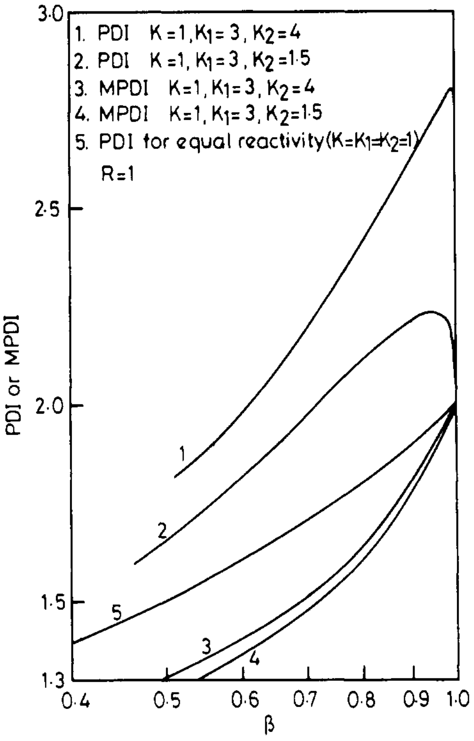

**Figure 3.** Dependence of PDI and MPDI on $\beta$ at $R = 1$.

Before concluding this section it should be pointed out that the labeling of groups as 1 and 2 is arbitrary. We have arbitrarily assumed that 1 is the slower reacting of the monomeric A groups, hence $K$ is always greater than or equal to 1. However, $K_1$ and $K_2$ can have any values.

**Polydispersity Index As a Function of Conversion.** Both PDI and MPDI are shown as a function of conversion of B groups in Figures 3 and 4. The presence of a maximum in PDI before complete conversion is achieved is due to the effects discussed just previously. The facts that PDI increases as $K_1$ and $K_2$ are increased and that increasing $K$ diminishes the effect of $K_1$ and $K_2$ are again apparent from these figures. It is again interesting to note that MPDI behaves in an expected manner, confirming that the effects observed are due to the imbalances produced in polymer formation and monomer consumption.

**Determination of the Rate Constants.** The theory contains four rate constants. Since making an experimental distinction between the 1 and 2 types of groups

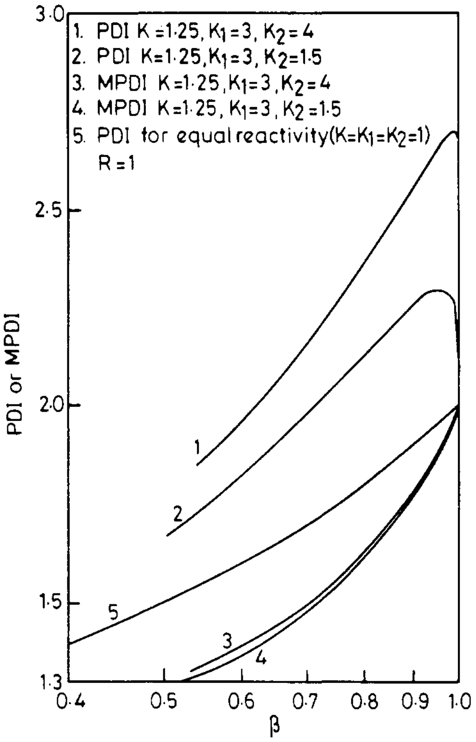

**Figure 4.** Dependence of PDI and MPDI on $\beta$ at $R = 1$.

would be difficult, these rate constants will have to be determined by an overall fit of data to the theory. Our results suggest a way of doing this. From the initial rate of reaction of monomers, $(k_1 + k_2)$ can be determined by using eq 12. The best experiment that can be used to determine $k_1^*$ and $k_2^*$ is to measure the total A group concentration and the unreacted monomer at the end of a reaction for different values of $R$. These data would provide $[A_1^*] + [A_2^*]$ and with the use of eq 13 and 14 $k_1^*$ and $k_2^*$ can be determined (since $(k_1 + k_2)$ is known) by fitting the data to the theory. At this stage if [B] is known by using eq 13, 14, and 15 it is possible to calculate $A$, $[A_1^*]$, and $[A_2^*]$ separately. Thus from measurements of [B] vs. time $k_1$ and $k_2$ can be determined by using eq 9 or 10. Alternately if the concentration of the unreacted $A_1A_2$ monomer could be measured as a function of time, the rate constants can also be obtained by fitting the theory to the data. A similar procedure was used by Wright and Cumming[5] for the tolylene diisocyanate reaction with alcohols to determine the rate constants of a complex mechanism.

## Appendix

The molar concentrations given by eq 29 can be proved to be the correct solutions by showing that they satisfy the individual species balance equations. First we shall demonstrate that eq 29 does satisfy eq 5, thereby proving that $q_n$ is a correct solution. From eq 29

$$-\frac{\mathrm{d}q_n}{\mathrm{d}t} = 2\frac{q_n}{(1-\beta)}\frac{\mathrm{d}\beta}{\mathrm{d}t} - \frac{(n-1)q_n}{\delta}\frac{\mathrm{d}\delta}{\mathrm{d}t} \qquad \text{(A1)}$$

Now it is to be shown that the right-hand side of (A1) and the right-hand side of eq 5 are equal. Substituting eq 29 into the right-hand side of eq 5 gives

$$\text{right-hand side of eq 5} = 2q_n\{(k_1 + k_2)A + k_1^*[A_1^*] + k_2^*[A_2^*]\} - 2(n-1)\frac{q_n}{\delta}\frac{(1-\beta)}{R}\left\{k_1^*\frac{RKB_0\alpha_1}{K\alpha_1 + 1}(1-\alpha_1^*) + k_2^*\frac{R\alpha_1B_0}{K\alpha_1 + 1}(1-\alpha_2^*)\right\} \qquad \text{(A2)}$$

Since $[B] = 2B_0(1 - \beta)$ from eq 11 we get

$$\frac{1}{1-\beta}\frac{\mathrm{d}\beta}{\mathrm{d}t} = (k_1 + k_2)A + k_1^*[A_1^*] + k_2^*[A_2^*] \qquad \text{(A3)}$$

Hence it is clear that the first terms of the right-hand side of eq A1 and A2 are the same. Using the definition of $\delta$, i.e., eq 27 and the fact that $A_2^r/A_1^r = K$, and eq 21, 22, 17, and 20, we can show that

$$\delta = \frac{\alpha_1}{K\alpha_1 + 1}(\alpha_2^* + K\alpha_1^*) = 1 - \frac{A}{A_0} - \frac{[A_1^*] + [A_2^*]}{A_0}$$

Hence

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = -\frac{1}{A_0}\left\{\frac{\mathrm{d}A}{\mathrm{d}t} + \frac{\mathrm{d}[A_1^*]}{\mathrm{d}t} + \frac{\mathrm{d}[A_2^*]}{\mathrm{d}t}\right\} = \frac{2}{R}(1-\beta)(k_1^*[A_1^*] + k_2^*[A_2^*])$$

with the use of eq 9, 10, and 12. Now substituting eq 21 and 22 gives

$$\frac{\mathrm{d}\delta}{\mathrm{d}t} = \frac{2(1-\beta)}{R}k_1^*\{A_2^r(1-\alpha_1^*)\} + k_2^*A_1^r(1-\alpha_2^*)$$

Using eq 17, 18, and 20 gives

$$2\frac{(1-\beta)}{R}\left\{k_1^*\frac{KRB_0\alpha_1}{K\alpha_1 + 1}(1-\alpha_1^*) + k_2^*\frac{RB_0\alpha_1}{K\alpha_1 + 1}(1-\alpha_2^*)\right\}$$

Now it is clear that the second terms of the right-hand sides of eq A1 and A2 are also identical. Hence the number distribution given by eq 29, *along with the definitions of the probabilities*, is a valid distribution. The proof is similar for the other species.

## Nomenclature

| | |
|---|---|
| $A$, $A_0$ | molar concentration of $A_1A_2$ monomer; subscript zero refers to initial condition |
| $[A_1^*]$, $[A_2^*]$ | concentration of polymeric $A_1$ and $A_2$ groups |
| $A_1^r$, $A_2^r$ | number of monomeric $A_1$ and $A_2$ groups that have reacted |
| $B_0$ | initial concentration of the BB monomer |
| [B] | concentration of B groups |
| $k_1$, $k_1^*$, $k_2$, $k_2^*$ | reaction rate constants; superscript asterisk refers to polymeric groups; subscript refers to the type of A group |
| $K$ | $k_2/k_1$ |
| $K_1$ | $k_1^*/k_1$ |
| $K_2$ | $k_2^*/k_2$ |
| $M_A$, $M_B$ | molecular weights of $A_1A_2$ and BB |
| $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_n'$, $\bar{M}_w'$ | number and weight average molecular weight; superscript prime refers to the quantities excluding the contribution of both the monomers |
| PDI | polydispersity index = $\bar{M}_w/\bar{M}_n$ |
| MPDI | $\bar{M}_w'/\bar{M}_n'$ |
| $p_n^{11}$, $p_n^{12}$, $p_n^{22}$ | molar concentration of $(AABB)_nAA$ type molecules; superscripts refer to the types of A groups present at the ends |
| $q_n$ | molar concentration of $(BBAA)_{n-1}BB$ type molecules |
| $r_n^1$, $r_n^2$ | molar concentration of $(AABB)_n$ type molecules; superscript refers to the type of A group present at the end |
| $R$ | $A_0/B_0$ |
| $\alpha_1$, $\alpha_1^*$, $\alpha_2$, $\alpha_2^*$ | probability of reaction of A groups; superscript asterisk refers to polymeric groups; subscript refers to the type of A group |
| $\beta$ | probability of reaction of B groups |
| $\delta$ | defined by eq 27 |