Kiho Ekiteki Kogaku, The Society of Chemical Engineering of Japan, ed., Nikkan Kogyo Shinbunsya, Tokyo, Japan (1969).

Schlichting, H., *Boundary Layer Theory*, 4 ed., p. 507 (1960).

Shyu, C. N., and T. Miyauchi, "Axial Dispersion in Gas-Bubble Columns," *Kagaku Kogaku*, 35, 663 (1971).

Tadaki, T., and S. Maeda, "On the Shape and Velocity of Single Bubble Rising in Various Liquids," *ibid.*, 25, 254 (1961).

Takahashi, R., and K. Washimi, "Steam Crack Vacuum Residue," *Hydrocarbon Process.*, No. 93 (1976).

Towell, G. D., C. P. Strand, and G. H. Ackerman, "Mixing and Mass Transfer in Large Diameter Bubble Columns," Preprint of A.I.Ch.E. Int. Chem. Eng. Joint Meeting, London, p. 1272 (1965).

Towell, G. D., and G. H. Ackerman, "Axial Mixing of Liquid and Gas in Larger Bubble Reactors," Chemical Reaction Engineering, Proceedings of the fifth European/second International Symposium on Chemical Reaction Engineering, Amsterdam, B3-1 (1972).

Ueyama, K., and T. Miyauchi, "Slip Velocity between Bubbles and Liquid in a Bubble Column," Preprint of 7th Fall Meeting, Soc. Chem. Eng., Japan (1973).

————, "Time-Averaged Navier-Stokes Equations as Basic Equations for the Flow of the Mixed Phase," *Kagaku Kogaku Ronbunshu*, 2, 595 (1976).

————, "Behavior of Bubbles and Liquid in a Bubble Column," *ibid.*, 3, 19 (1977*a*).

————, "Effects of Viscosity of Liquid and Diameter of Column on Internal Circulating Flow in a Bubble Column," *ibid.*, 115 (1977*b*).

van Krevelen, D. W., and P. J. Hoftijzer, "Studies of Gas-Bubble Formation," *Chem. Eng. Progr.*, 46, 29 (1950).

Yamagoshi, T., B.S. thesis, *Dept. of Chem. Eng.*, Univ. Tokyo, Japan (1969).

Yoshida, A., B.S. thesis, *Dept. of Chem. Eng.*, Univ. Tokyo, Japan (1971).

Yoshitome, H., "Average Ascending Velocity of Air Bubble in Water from Perforated Plate," *Kagaku Kogaku*, 27, 27 (1963).

———, Dr. Eng. dissertation, Tokyo Inst. Technol., Japan (1967).

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Kinetics of Step Polymerization with Unequal Reactivities

K. S. GANDHI
and
S. V. BABU
Department of Chemical Engineering
Indian Institute of Technology
Kanpur 208016 India

The kinetics of step polymerization involving a monomer with unequal reactivities has been obtained. The polydisperity index (PDI) has also been calculated both as a function of conversion and the initial stoichiometric ratio. It has been shown that the usually assumed maximum value of 2 for PDI can lead to erroneous molecular weight.

SCOPE

Step polymers such as polyesters, polyurethanes, etc., can be considered as products of reaction between two difunctional monomers. While it is usually assumed that the two groups of the monomer are equally reactive, many exceptions exist. Thus, a glycol containing a primary and a secondary hydroxyl group is an asymmetric monomer since the two groups may be expected to react at different rates. Similarly, the two functionalities of a cyclic monomer, such as an anhydride, can be expected to react at different rates. Moreover, possibly owing to resonance and conformational effects, reaction of one of the groups of the monomer may induce asymmetry and alter the reactivity of the other group. Such induced asymmetry is found in diisocyanates. In this paper, the effect of the unequal reactivities on the kinetics of polymerization and the evolution of the polymeric product as characterized by the polydisperity index (PDI) will be studied.

CONCLUSIONS AND SIGNIFICANCE

It is shown that the results for monomers with induced asymmetry can be obtained from the results for cyclic monomers necessitating discussion of only one of them. If K, the ratio of the reaction rate constants of the two groups, is increased beyond unity, the rate of consumption of the groups, as may be expected, is found to increase. This is true for both asymmetry and induced asymmetry.

In the asymmetric case, both the number average molecular weight ($\overline{M}_n$) and the PDI increased with conversion or time. The PDI at the end of the reaction is independent of K for $R < 1$. However, the PDI at the end of the reaction goes through a minimum followed by a broad maximum as R is increased beyond 1. This is shown to be due to the presence of unreacted monomer. A modified PDI defined by excluding the contribution of the monomers does not exhibit these extrema and decreases monotonically as R is changed from 1.

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With induced asymmetry also, $\overline{M_n}$ increases with conversion and time. The PDI also increases for all values of K and $R > 1$ and goes through a maximum for $R = 1$ if K is around 2. The limiting values of PDI at the end of the reaction as $R \rightarrow 1$ from below and above are different from each other and from its value at $R = 1$. This discontinuity causes the PDI to increase sharply towards the end of the reaction. These effects are also due to unreacted monomer and are shown to vanish when a modified PDI is defined as in the case of asymmetric monomers. It was shown that the usually assumed maximum value of 2 for PDI leads to erroneous weight average molecular weight.

Step polymerization can generally be considered as a reaction between functional groups. Such polymerizations have been analyzed assuming that all the functional groups in a monomer are equally reactive. However, examples of monomers for which the equal reactivity assumption is invalid are plenty. Three types of such monomers are commonly encountered.

1. Asymmetric monomers in which the groups are not chemically equivalent, for example, a glycol with a primary and a secondary hydroxyl group, since the two hydroxyl groups need not be equally reactive.
2. Cyclic monomers, for example, anhydrides. The anhydride group generates a carboxyl group on reaction with a hydroxyl group, but the reactivities of the anhydride and carboxyl groups are known to be different.
3. Monomers with induced asymmetry. In such monomers, the functional groups are equally reactive till one of them reacts. However, upon reaction of one group, the reactivity of the other group is altered. For example, in diisocyanates, the reactivity of an isocyanate group depends on whether the other group has reacted or not (Lenz, 1967).

The effect of unequal reactivities on molecular weight distribution (MWD) has been investigated by Case (1958). However, he presented the MWD as a function of the probabilities of reaction of the functional groups and did not provide either the relationships between the probabilities or their relationship to the time of polymerization or conversion. Hence, neither the MWD nor the evolution of the polymeric product could be studied. It is the objective of this work to provide such a relationship and to study the effects of unequal reactivity on the polymerization kinetics. In the following we will first consider the asymmetric monomer, then show that the cyclic monomers and monomers with induced asymmetry are mathematically equivalent, and finally consider monomers with induced asymmetry.

ASYMMETRIC MONOMER

Let A_1A_2 be a difunctional asymmetric monomer which polymerizes with a symmetric difunctional monomer BB. The two groups A_1 and A_2 react at different rates with B and are identical otherwise. The reactions that can occur are

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

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

where $\sim$ represents a chain. Let α, β, and γ, respectively, represent the fraction of the initial B, A_1, and A_2 groups that have reacted at any time. Then, for a batch reactor

$$\frac{d\beta}{dt} = \frac{2k_1A_0}{R}(1-\beta)(1-\alpha) \tag{1}$$

$$\frac{d\gamma}{dt} = \frac{2k_2A_0}{R}(1-\gamma)(1-\alpha) \tag{2}$$

$$\frac{d\alpha}{dt} = A_0(1-\alpha)[k_1(1-\beta) + k_2(1-\gamma)] \tag{3}$$

where A_0 is the initial molar concentration of the asymmetric monomer, $R = A_0/B_0$, and B_0 is the initial molar concentration of BB. Note that the initial group concentration of both A_1 and A_2 is equal to A_0.

Dividing (1) by (2), we get

$$\frac{d\beta}{d\gamma} = \frac{1}{K}\frac{(1-\beta)}{(1-\gamma)} \quad \text{or} \quad \beta = 1 - (1-\gamma)^{1/K} \tag{4}$$

where $K = k_2/k_1$. Asymmetry vanishes if $K = 1$, and then $\beta = \gamma$. From stoichiometry

$$\alpha = R(\beta + \gamma)/2 \tag{5}$$

Using (4) and (5), we can compute any two conversions in terms of the third, provided R and K are specified. Further, any of the conversions can be obtained as a function of time by integration of (1), (2), or (3). Thus, γ can be obtained by a numerical integration of (2), after we substitute (4) and (5) into (2). γ so obtained is plotted against k_1A_0t in Figure 1 for $R = 1.0$ and several values of K. When K is increased, it is equivalent to increasing k_2, and hence γ is larger for a given value of k_1A_0t. The behavior is similar for values of R and K other than those shown in Figure 1.

The various types of molecules present at any time are A_1A_2, $(BBA_1A_2)_{n-1}BB$, $(A_1A_2BB)_nA_1A_2$, $(A_1A_2BB)_nA_2A_1$,

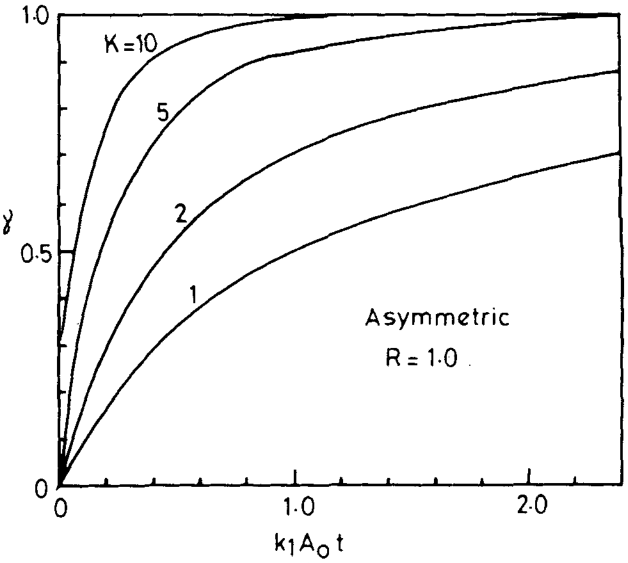

Fig. 1. Fraction of A_2 groups reacted γ as a function of time for asymmetric monomer for several values of K.

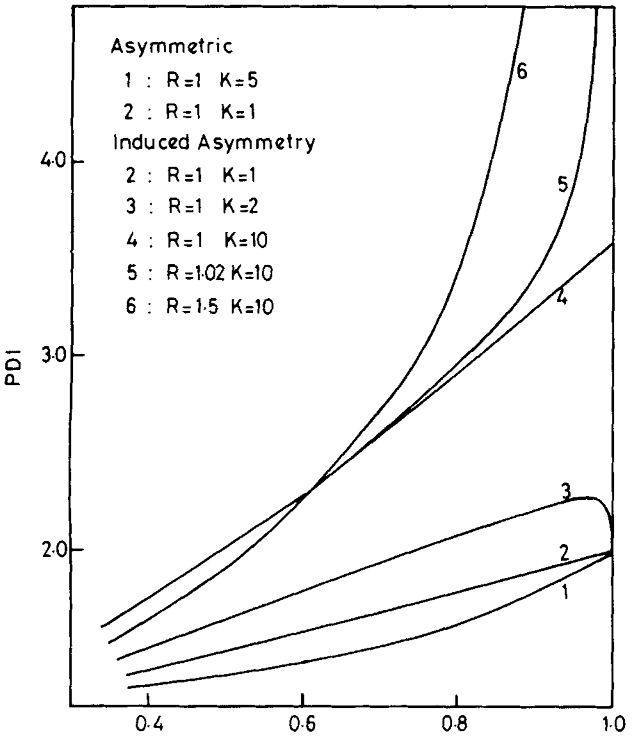

Fig. 2. The polydispersity index ($\overline{M}_w/\overline{M}_n$) as a function of fraction of B groups reacted α for asymmetry and induced asymmetry for several values of K and R. The terminal value of PDI is 18 for $R = 1.02$ and is 12.1 for $R = 1.5$. Both are off scale in the figure.

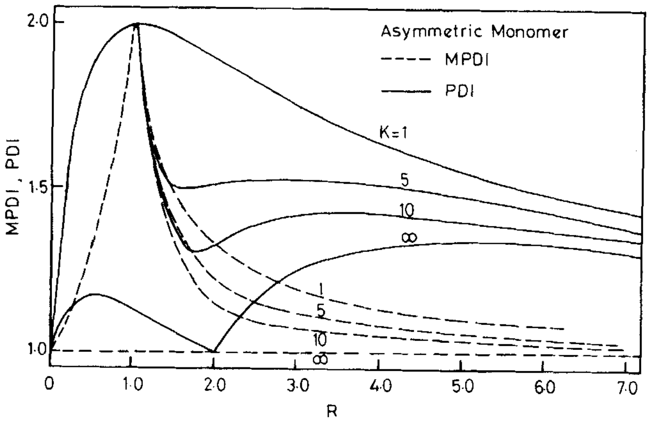

Fig. 3. The polydispersity index (—)and the modified polydispersity index (- - -) at the end of the reaction as a function of initial stoichiometric ratio R of reactants for asymmetry for several values of K.

$(A_2A_1BB)_nA_1A_2$, $(A_1A_2BB)_n$, and $(A_2A_1BB)_n$; $n \geq 1$. Let the molar concentrations of these species be denoted, respectively, by A, q_n, p_n^{12}, p_n^{11}, p_n^{22}, r_n^1, r_n^2. It may be noted that $\sum_{n=1}^{\infty} (r_n^1 + r_n^2 + 2q_n)/2B_0 = 1 - \alpha$ and β and γ are similarly related to these quantities. Now it will be assumed that α, β, and γ, respectively, are equal to the probabilities of reaction of B, A_1, and A_2 groups. Then, Case's (1958) results on MWD for the unsymmetric monomer can be rearranged to obtain

$$\frac{q_n}{(1-\alpha)^2} = \frac{r_n^1}{R(1-\beta)(1-\alpha)\gamma} = \frac{r_n^2}{R(1-\gamma)(1-\alpha)\beta}$$

$$= \frac{4p_n^{11}}{R^2(1-\beta)^2\gamma^2} = \frac{4p_n^{22}}{R^2(1-\gamma)^2\beta^2}$$

$$= \frac{2p_n^{12}}{R^2(1-\beta)(1-\gamma)\beta\gamma} = B_0(R\beta\gamma)^{n-1}; \quad n \geq 1 \qquad (6)$$

and

$$A = RB_0(1-\gamma)(1-\beta)$$

The above assumption is valid and mathematically consistent with the kinetic model contained in (1), (2), and (3) since it can be shown that Equations (6) are solutions of the respective balance equations which can be written in a manner similar to that of Kilkson (1964), keeping in mind the asymmetry of one monomer. This is straightforward but tedious and is not done here. From (6), the number average ($\overline{M}_n$) as well as weight average ($\overline{M}_w$) molecular weight can be evaluated. It is customary to use the polydisperity index (PDI), which is equal to $\overline{M}_w/\overline{M}_n$, to characterize MWD. The $\overline{M}_n$ and PDI are given by (Case, 1958)

$$\overline{M}_n = (RM_A + M_B)/(R + 1 - 2\alpha) \qquad (7)$$

$$\text{PDI} = (R + 1 - 2\alpha)$$

$$\frac{M_B^2(1 + R\beta\gamma) + 4\alpha M_A M_B + M_A^2[R + R^2(\beta^2 + \gamma^2)/2]}{(1 - R\beta\gamma)(RM_A + M_B)^2} \qquad (8)$$

It should be pointed out that even though (7) and (8) were obtained by Case (1958) earlier, it has not been possible to compute the evolution of PDI as a function of time since α, β, and γ were not known as a function of time. In fact, the PDI could not be evaluated even as a function of conversion since Case (1958) did not derive the relationship between β and γ. The only case for which PDI could be computed based on his results was for $R \leq 1$ and for complete conversion of the asymmetric monomer when $\beta = \gamma = 1$ and $\alpha = R$. However, these are identical with the results obtained for a symmetric monomer ($K = 1$) and hence do not throw any light on the effects of unequal reactivity.

Since the conversions can be obtained as a function of time, the evolution of PDI will be discussed in terms of conversion, instead of time, as it is more convenient to do so. For simplicity, we will assume $M_A = M_B$.

Since α increases with time, it is clear from (7) that $\overline{M}_n$ also increases with time. Figure 2 shows PDI as a function of α for $R = 1$ and $K = 1$ (corresponding to a symmetric monomer) and $K = 5$. From the results, it is clear that $\overline{M}_w$ increases faster than $\overline{M}_n$ with time, and the PDI reaches a limit of 2 at the end of the reaction. This behavior is, again, typical for other values of R and K except that the limiting value of PDI at the end of the reaction is a function of R and K.

If $R < 1$, BB is in excess, and hence at the end of the reaction, $\beta = \gamma = 1$ and $\alpha = R$. Thus

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

which is independent of K. However, if $R > 1$, then A_1A_2 is in excess, and at the end of the reaction, $\alpha = 1$. The individual values of β and γ in this case depend upon K and have to be obtained by solving (4) and (5) simultaneously. Figure 3 shows the PDI at the end of the reaction as a function of R for several values of K. The monotonic decrease of PDI as R is increased from unity for $K = 1$ is the usual result. However, for larger values of K, as R is increased beyond one, the PDI goes through a minimum followed by a broad maximum. An extreme case of such behavior is provided by the mathematical limit of $K \rightarrow \infty$. In this limit, $\beta = 0$ and A_1A_2

acts like a monofunctional monomer, permitting formation of only trimers of the type $A_1A_2BBA_2A_1$. Increasing R beyond unity corresponds to starting with A_1A_2 in excess of BB, and when $K \to \infty$, all the excess A_1A_2 monomer goes into the trimer as long as $R \leqq 2$. When $R = 2$, the reaction mixture is monodispersed since it contains only trimers. Any further increase in R, that is, $R > 2$, corresponds to adding additional A_1A_2 which can not react and which only dilute the monodispersed mixture, thus increasing the PDI. If R is increased further, the mixture will tend towards pure monomer, decreasing the PDI. The maximum and minimum in PDI obtained for finite values of K are also due to similar effects. As R is increased from unity, a significant amount of the excess A_1A_2 monomer goes into the polymer, and this amount decreases with increasing R. Thus, as R is increased further, a sizeable amount of the excess A_1A_2 monomer remains unreacted and merely dilutes the reaction mixture, resulting in increased PDI. A further increase in R will make the system approach the pure monomer again, thus decreasing the PDI. Hence, one may expect that at the point where the PDI goes through a minimum, half the amount of the excess monomer that is added to increase R remains unreacted. The unreacted monomer concentration is given by $RB_0(1 - \beta)(1 - \gamma)$. Thus, if R is increased by ϵ, the excess amount of monomer added is ϵB_0, and the fraction of this which remains unreacted is given by $\{[R(1 - \beta)(1 - \gamma)]_{R+\epsilon} - [R(1 - \beta)(1 - \gamma)]_R\}/(R + \epsilon - R)$. Hence, at the minimum

$$\frac{d}{dR}[R(1-\beta)(1-\gamma)] = \tfrac{1}{2}$$

This, indeed, has been confirmed by numerical calculation.

This explanation of the maximum and minimum is further confirmed by recalculating $\overline{M}_w$, $\overline{M}_n$, and PDI, excluding the contribution of both the monomers. Such a modified PDI (MPDI) and number average molecular weight ($\overline{M}_n'$) are given, for $M_A = M_B$, by

$$\overline{M}_n' = \frac{4\alpha - R\beta\gamma - \alpha^2}{2\alpha - R\beta\gamma - \alpha^2} M_A$$

$$\text{MPDI} = \frac{(\alpha - R\beta\gamma)^2 + R\beta\gamma(1-\alpha)^2 + 8\alpha}{(1 - R\beta\gamma)(4\alpha - R\beta\gamma - \alpha^2)^2}(2\alpha - R\beta\gamma - \alpha^2)$$

The variation of MPDI with R for several values of K is also shown in Figure 3. The maximum and minimum are absent, confirming that these were caused by the unreacted monomer.

When K is increased beyond 1, the A_2 groups are less in number, and the polymers are more likely to have A_1 ends. But $K > 1$ implies lower reactivity of A_1 ends, and hence the number of polymer molecules is likely to be less. This, in turn, leads to smaller weight fraction of larger molecules and hence narrower MWD. Figure 2 also shows that, for a given value of R, the PDI (as well as MPDI) decreases with increasing K, resulting in a narrower MWD.

CYCLIC MONOMERS

Denote a cyclic monomer by AC and the symmetric monomer with which it polymerizes by BB. C is generated only after the A group reacts with B. Thus, the C group in an AC monomer can react with B only after A has reacted. Taking an anhydride as an example of a cyclic monomer, A will be the anhydride group and C the carboxyl group. The reactions for such systems are

$$\sim\!\sim\!\sim BB + AC \xrightarrow{k_1} \sim\!\sim\!\sim BBAC$$

$$\sim\!\sim\!\sim BB + CA\sim\!\sim\!\sim \xrightarrow{k_2} \sim\!\sim\!\sim BBCA\sim\!\sim\!\sim$$

It is to be noted that the A group can not be present as an end of a chain and must always be present as a monomer only. Let α and β, respectively, be the fractions of initial B groups and cyclic monomers that have reacted. Let γ be the ratio of the number of C groups that have reacted to the initial number of AC molecules. Since each A group that reacts generates a C group, the concentration of the C groups at any time is given by $A_0(\beta - \gamma)$, where A_0 is the initial molar concentration of the cyclic monomer. The kinetic equations for the system are

$$\frac{d\beta}{dt} = \frac{2k_1A_0}{R}(1-\beta)(1-\alpha) \quad (9)$$

$$\frac{d\gamma}{dt} = \frac{2k_2A_0}{R}(\beta-\gamma)(1-\alpha) \quad (10)$$

$$\frac{d\alpha}{dt} = A_0(1-\alpha)[k_1(1-\beta) + k_2(\beta-\gamma)] \quad (11)$$

where $R = A_0/B_0$, and B_0 is the initial molar concentration of BB. Dividing (10) by (9), we get

$$\frac{d\gamma}{d\beta} = K\frac{(\beta-\gamma)}{(1-\beta)}$$

and solving this

$$\begin{aligned}\gamma &= \beta - \frac{(1-\beta)}{K-1}[1 - (1-\beta)^{K-1}] \quad K \neq 1 \\ &= \beta + (1-\beta)\ln(1-\beta) \quad K = 1\end{aligned} \quad (12)$$

Again, by stoichiometry

$$\alpha = R(\beta + \gamma)/2 \quad (13)$$

The various types of molecules present at any time are AC, $(CABB)_nAC$, $(CABB)_n$, and $(BBAC)_{n-1}BB$; $n \geqq 1$. Let their molar concentrations be respectively represented by A, p_n, r_n, and q_n. Now, if we again assume that α and β are, respectively, equal to the probabilities of reaction of a B group and of the cyclic monomer, Case's (1958) results on MWD can be rearranged to obtain

$$\frac{p_n}{(\alpha - R\gamma)^2} = \frac{r_n}{2(1-\alpha)(\alpha - R\gamma)} = \frac{q_n}{(1-\alpha)^2} = B_0(R\gamma)^{n-1}; \quad n \geqq 1 \quad (14)$$

and

$$A = A_0(1-\beta)$$

The consistency and validity of the above assumption can be shown, as for the asymmetric monomer, by proving that Equations (14) are solutions of the appropriate balance equations. The $\overline{M}_n$ is still given by (7), but for this case the PDI is given by (Case, 1958)

$$\text{PDI} = \frac{M_B^2(1+R\gamma) + 4\alpha M_AM_B + M_A^2[2\alpha^2 + R(1-R\gamma)]}{(1-R\gamma)(RM_A + M_B)^2}(R + 1 - 2\alpha) \quad (15)$$

It may be pointed out again that as in the case of the

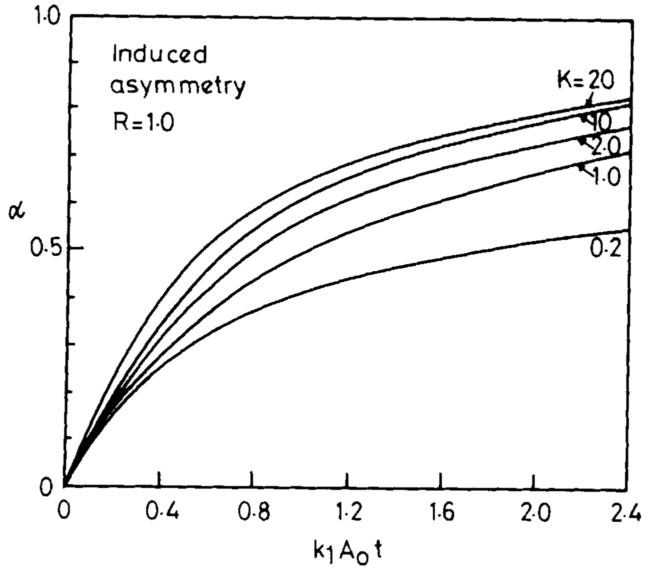

Fig. 4. Fraction of *B* groups reacted α as a function of time for induced asymmetry for several values of *K*.

asymmetric monomer, even though (14) and (15) were derived earlier by Case (1958), they could not be used for computing PDI either as a function of conversion or time. It will be shown below that the results for cyclic monomers are equivalent to the results for monomers with induced asymmetry. Hence, only monomers with induced asymmetry will be discussed in detail.

MONOMERS WITH INDUCED ASYMMETRY

Consider the polymerization of *AA* and *BB*, but let induced asymmetry be present in *AA*. Thus, once one of the *A* groups of the monomer reacts, the other *A* group reacts at a rate different from the first group. But if one of the *A* groups of *AA* monomer reacts, the other *A* group is present at the end of a chain. Hence, the consequence of induced asymmetry is that any *A* group attached to a polymer reacts at a rate different from the *A* groups of the monomer. The reactions for this system, then, are

$$AA + BB \xrightarrow{k_1} AABB$$

$$BB + AA \xrightarrow{k_2} BBAA$$

Let α and β, respectively, be the fraction of initial *B* groups and moles of *AA* that have reacted. Let γ be the ratio of number of *A* groups attached to a chain that have reacted to the initial number of *AA* molecules. Since each *AA* monomer that reacts generates an *A* group at the end of a chain, the concentration of *A* groups present at the end of a chain at any time is given by $A_0(\beta - \gamma)$, where A_0 is the initial molar concentration of *AA*. The rate equations are

$$\frac{d\beta}{dt} = \frac{4k_1A_0}{R}(1-\beta)(1-\alpha) \tag{16}$$

$$\frac{d\gamma}{dt} = \frac{2k_2A_0}{R}(1-\alpha)(\beta-\gamma) \tag{17}$$

$$\frac{d\alpha}{dt} = A_0(1-\alpha)[2k_1(1-\beta) + k_2(\beta-\gamma)] \tag{18}$$

where $R = A_0/B_0$, and B_0 is the initial molar concentration of *BB*. Equations (16) to (18) are identical with (9) to (11) if $2k_1$ in (16) to (18) is replaced by k_1.

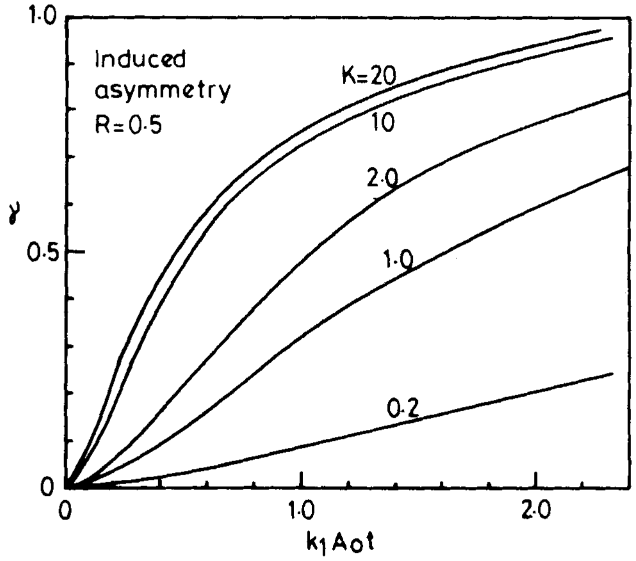

Fig. 5. The fraction of polymeric *A* groups (based on the monomer molecules) which have reacted as a function of time for several values of *K*.

Thus, the fractional conversions in the case of induced asymmetry and for cyclic monomers are mathematically equivalent under the transformation $2k_1 \rightarrow k_1$. Thus, (12) is altered to

$$\gamma = \beta - \frac{2(1-\beta)}{K-2}\left[1-(1-\beta)^{\frac{K-2}{2}}\right] \quad K \neq 2$$
$$= \beta + (1-\beta)\ln(1-\beta) \quad K = 2 \tag{19}$$

where $K = k_2/k_1$, while (13) still holds. The various types of molecules present are AA, $(AABB)_nAA$, $(AABB)_n$, and $(BBAA)_{n-1}BB$; $n \geq 1$. If we denote the molar concentration of these species, respectively, by A, p_n, r_n, and q_n, it can be shown that Equations (14) are solutions of the balance equations of the various species, with α, β, and γ given by (16) to (18). Hence, the $\overline{M}_n$ and PDI are given, respectively, by (7) and (15), where M_A now represents the molecular weight of *AA*. Thus, the results on MWD for induced asymmetry are also equivalent to those obtained for a cyclic monomer as long as k_1 in the results for the latter is replaced by $2k_1$.

RESULTS FOR INDUCED ASYMMETRY

Equation (18) was integrated after substitution of (13) and (19) to obtain α as a function of k_1A_0t. A typical plot of α against k_1A_0t is shown in Figure 4 for $R = 1.0$ and several values of K. As expected, when K is increased, which is equivalent to increasing k_2, α increases more rapidly with time. By using (13) and (19) along with results of the above integration, γ versus time is plotted in Figure 5, displaying the sigmoidal type of behavior observed.

The PDI and $\overline{M}_n$ are again chosen to characterize the evolution of the polymeric product. Again, for simplicity, it was assumed that $M_A = M_B$. As α increases with time, it is clear that $\overline{M}_n$ increases with time. A plot of PDI against α for several values of R and K is shown in Figure 2. For most values of R and K, it is clear that $\overline{M}_w$ increases faster than $\overline{M}_n$ as is usually expected. However, for $R = 1$ and for values of K around 2, the PDI goes through an unusual maximum. For example, the PDI for $R = 1$ and $K = 2$ has a maximum near $\alpha = 0.97$ and then decreases, reaching the limiting value of

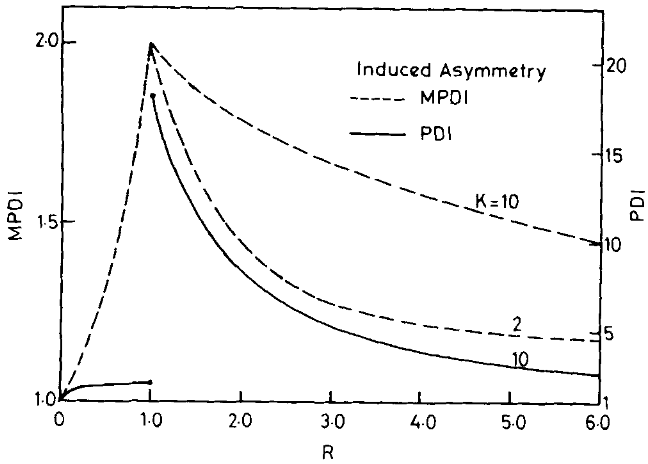

Fig. 6. The polydispersity index (—) and the modified polydispersity index (----) at the end of the reaction as a function of initial stoichiometric ratio for several values of K. Note the discontinuity in PDI at $R = 1$.

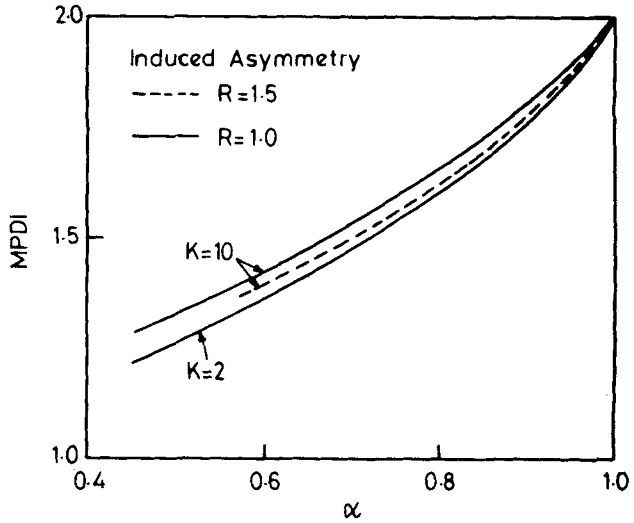

Fig. 7. The modified polydispersity index as a function of α (extent of reaction of B groups).

2 at the end of the reaction. Moreover, the limiting values of PDI at the end of the reaction also show very peculiar behavior.

For $R < 1$ at the end of the reaction, the PDI is given by $(R^2 + 6R + 1)/(1 + R)^2$ and is independent of K. However, for $R = 1$ at the end of the reaction, PDI is 2 if $K \leq 2$ and is $4(K - 1)/K$ if $K \geq 2$. Thus, the limit of PDI as $R \to 1$ from below and the value of PDI at $R = 1$ are different if $K > 2$, showing a discontinuity. The terminal value of PDI for $R > 1$ has to be computed numerically. However, the limit reached by PDI as $R \to 1$ from above can be obtained by an analysis of PDI around $\alpha = 1$ and $R = 1$. Let $\alpha = 1 - \delta$ and $R = 1 + \epsilon$, where δ and ϵ are small quantities. Then, keeping only terms of first order in δ and ϵ, it can be shown that

$$\begin{aligned} \mathrm{PDI} &= 2\,\frac{\epsilon + 2\delta}{\dfrac{\epsilon}{K-1} + \delta\left(\dfrac{K}{K-1}\right)} && K > 2 \\ &= 2 && K \leq 2 \end{aligned}$$

The limit obtained by first letting $\epsilon \to 0$ and then $\delta \to 0$ corresponds to approaching the end of the reaction at $R = 1$, and the limit is $4(K - 1)/K$ as mentioned earlier. The limit obtained by first letting $\delta \to 0$ and then $\epsilon \to 0$ corresponds to the value of PDI at the end of the reaction as $R \to 1$ from above, and it is given by $2(K - 1)$. Thus, we have another discontinuity, between the PDI at $R = 1$ and the limit of PDI as $R \to 1$ from above, if $K > 2$.

This behavior is shown in Figures 2 and 6. For illustration, we confine ourselves to $K = 10$. For $R = 1$, as shown in Figure 2, PDI rises gradually and reaches a limiting value of 3.6. But when R is changed to 1.02, the PDI is almost unchanged till α reaches a value of about 0.9, then starts increasing dramatically to reach a value of 18 (off scale in Figure 2) at $\alpha = 1$. The behavior is similar for $R = 1.5$ except that limiting value of PDI is 12.1 (off scale in Figure 2). A qualitative explanation of this steep increase may be as follows. A value of K larger than 1 implies that when α is close to 1, any decrease in the monomer concentration leads to the formation of very high polymers. When $R > 1$, as $\alpha \to 1$, the reaction products are therefore a mixture of monomer and increasing amounts of high polymers. This leads to a sharp increase in the PDI.

Even though a similar qualitative explanation of either the discontinuity in PDI at the end of the reaction at $R = 1$ or the maximum observed in PDI as a function of conversion cannot be given, we feel that these effects are also due to the unreacted monomer.

That these effects are again due to unreacted monomer is confirmed by looking at the modified PDI and $\overline{M}_n'$ defined, as in the case of the asymmetric monomer, by excluding the contribution of both the monomers.

$$\overline{M}_n' = M_A(R\beta + 2\alpha - \alpha^2)/(R\beta - \alpha^2)$$

$$\mathrm{MPDI} = \frac{(1 - R\gamma)(R\beta + 2\alpha - \alpha^2) + 4\alpha + 2\alpha^2 + 2R\gamma}{(R\beta + 2\alpha - \alpha^2)^2(1 - R\gamma)}$$

$$(R\beta - \alpha^2)$$

The MPDI at the end of the reaction is shown as a function of R in Figure 6, and the MPDI is shown as a function of conversion α in Figure 7. The absence of maximum as well as discontinuities is evident.

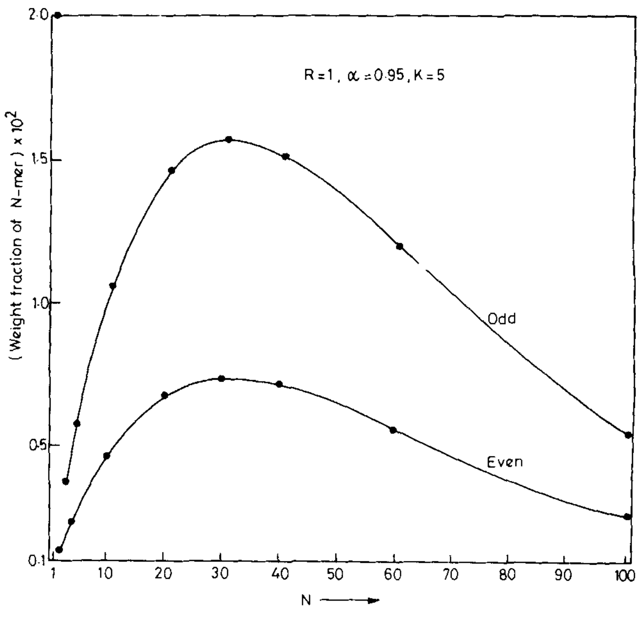

Fig. 8. Weight fraction of molecules containing N monomer units. N is sum of the numbers of AA and BB units present in the molecule.

Our results point to the weakness in assuming, as is usually done, that the maximum value of PDI for condensation reactions in a well-mixed batch reactor is 2. Thus, if a polymerization reaction is controlled by monitoring the number average molecular weight, the resulting $\overline{M}_w$ can be widely different, depending on whether R was slightly below or above 1. Thus, for $K = 10$, if R is 0.99, $\overline{M}_n$ is 100 M_A, and $\overline{M}_w$ is 200 M_A, but if R is changed to 1.01, $\overline{M}_n$ remains the same, but $\overline{M}_w$ becomes 1 800 M_A. In this connection, it is to be noted that the maximum value attained by MPDI (and not the PDI) for all R is 2, but a modified definition of number average has to be employed to get the value of $\overline{M}_w$. Since the unreacted monomer contributes only negligibly to $\overline{M}_w$, this is almost the same as $\overline{M}_w'$. Thus, though $\overline{M}_n$ and $\overline{M}_n'$ will be widely different, the $\overline{M}_w$ and $\overline{M}_w'$ are almost equal.

When $K > 2$, another unusual feature is observed in the MWD itself. At sufficiently large but incomplete conversion, the probability $\alpha - \gamma$ of finding an unreacted A group attached to a polymer is so low that it is less than the product of the probability γ of reaction of an A group attached to a polymer and the probability $(1 - \alpha)$ of finding an unreacted B group. Hence, the weight fraction of the species of the type $(BBAA)_n$ is lower than the weight fraction of the species of the type $(BBAA)_nBB$. Thus, the weight fraction of any species containing an even number of units is less than the weight fraction of the next larger species containing one more unit, even when n is large. This disparity in the weight fractions is so large that two separate curves, one each for molecules containing even and odd number of units, may be drawn as done in Figure 8 for $K = 5$. This disparity is present, though in a decreased form, even when $\alpha \rightarrow 1$.

NOTATION

A = molar concentration of A_1A_2 or AC or AA
A_0 = initial molar concentration of A_1A_2 or AA or AC
B_0 = initial molar concentration of BB
K = k_2/k_1
k_1, k_2 = reaction rate constants of the monomer
M_A = molecular weight of A_1A_2 or AA or AC
M_B = molecular weight of BB
$\overline{M}_n$ = number average molecular weight
$\overline{M}_n'$ = number average molecular weight, excluding the monomeric contribution
$\overline{M}_w$ = weight average molecular weight
$\overline{M}_w'$ = weight average molecular weight, excluding the monomeric contribution
p_n = molar concentration of polymer having $(n + 1)$ units of A_1A_2 or AC or AA and n units of BB, the superscripts indicate the end group in case of A_1A_2
q_n = molar concentration of polymer having $(n - 1)$ units of A_1A_2 or AC or AA and n units of BB
r_n = molar concentration of polymer having n units of A_1A_2 or AC or AA and n units of BB, superscript indicates the end group in case of A_1A_2
R = A_0/B_0
t = time
α = fraction of initial B groups that reacted
β = fraction of initial A_1 groups or cyclic monomer or monomer with induced asymmetry that reacted
γ = ratio of initial A_2 groups or C groups or polymeric A groups that reacted to the initial number of the corresponding monomer molecules

LITERATURE CITED

Case, L. C., "Molecular Distributions in Polycondensations Involving Unlike Reactants. II. Linear Distributions," *J. Polymer Sci.*, 29, 455 (1958).

Kilkson, H., "Effect of Reaction Path and Initial Distribution on Molecular Weight Distribution of Irreversible Condensation Polymers," *Ind. Eng. Chem. Fundamentals*, 3, 281 (1964).

Lenz, R. W., *Organic Chemistry of Synthetic High Polymers*, Interscience, New York (1967).

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Effectiveness Factors and Mass Transfer in Trickle-Bed Reactors

Rates of hydrogenation of α-methyl styrene were measured at 40.6°C and 1 atm in a recycle, trickle-bed reactor using a palladium/aluminum oxide catalyst. Data for different hydrogen concentrations in the gas and liquid feed streams suggested that except, at high liquid flow rates, on part of the outer surface of the catalyst the mass transfer limitation was very small, indicating a gas covered type of surface. A procedure was developed for evaluating effectiveness factors for the nonuniform boundary conditions existing when part of the particle surface is covered by gas.

MORDECHAY HERSKOWITZ
R. G. CARBONELL
and
J. M. SMITH
University of California
Davis, California 95616

SCOPE

In downflow of liquid and gas over a bed of catalyst particles, in the gas continuous regime (Charpentier, 1976), the outer surface of the particles may not be completely covered with liquid. Fractional coverages f, or wetting efficiencies, have been measured indirectly (for example, Colombo et al., 1976; Satterfield, 1975; Satterfield and Ozel, 1973; Schwartz et al., 1976; Morita and Smith, 1978) and found to be between about 0.6 and 1.0. If at least one limiting reactant is in the gas phase, as in hydrodesulfurization, incomplete coverage may affect the global rate and reactor design. The rate is expected to

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