The Effect of the Removal of One Product on the Optimum Yield in an Equilibrium Process

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SUMMARY

Except for a first-order dissociation, complete conversion is not possible in an equilibrium process no matter how efficient the removal of a by-product may be. In a first-order dissociation process, complete reaction is only possible when the ratio of the rate constants of the forward to the backward reaction is greater than unity.

INTRODUCTION

In an equilibrium process it seems to be commonly assumed that complete conversion can be obtained by continuous or stepwise removal of one of the reactants involved in the back reaction, provided that a sufficiently efficient technique is employed. In this paper we present a theoretical investigation into the truth of this assumption. An equilibrium polycondensation process is chosen as the model to be investigated.

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THEORETICAL DEVELOPMENT

The equilibrium polycondensation model we choose is the condensation of a bifunctional monomer, e.g., an ω-hydroxycarboxylic acid.

$$HO-R_i-COOH + HO-R_j-COOH \underset{k_1}{\overset{k}{\rightleftharpoons}} HO-R_{i+j}-COOH + H_2O \qquad (1)$$
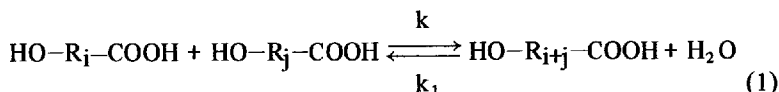
Hydrolysis of the $(i + j)$ mer leads not only to i- and j- mers, but to all other mers up to $(i + j - 1)$.

Satisfactory yields of polyesters are normally only obtained in practice when one of the by-products, e.g., water, is removed from the system.

At equilibrium, the over-all reaction equation can be written as [1]

$$k[M]^2 = k_1[H_2O]([M_1]_0 - [M]) \qquad (2)$$

where $[H_2O]$, $[M]$, and $[M_1]_0$ are the molar concentrations of water and polymer at equilibrium, and the initial monomer molar concentration, respectively.

Flory [2] defines a parameter, p, as the fraction of functional groups, i.e., $-OH$ and $-COOH$, which have reacted at any given stage of the reaction.

If [1]

$$r = k[M]/k_1[H_2O]; \quad p = r/(1 + r) \qquad (3)$$

When $p = 1$, all the monomer is joined into one large cyclic molecule, and complete conversion of monomer to polymer has been achieved. For the equilibrium process of Eq. (1), $p = 1$ requires $r \to \infty$, i.e., $H_2O \to O$ for nonzero values of k_1.

The weight-average and number-average degrees of polymerization, $\overline{X}_w$ and $\overline{X}_n$, can be written as [1, 2]

$$\overline{X}_w = (1 + p)/(1 - p) = 1 + 2r$$

$$\overline{X}_n = 1/(1 - p) = 1 + r \qquad (4)$$

Polycondensation is considered to lead to a Schulz-Flory, or most probable, distribution of mer sizes [2]. A common test of a most probable distribution is to see if $\overline{X}_w/\overline{X}_n = 2$.

$$\overline{X}_w/\overline{X}_n = (1 + p/1 - p)/(1/1 - p) = 1 + p, \tag{5}$$

i.e., it is only 2 when $p = 1$, i.e., at 100% conversion. Alternatively,

$$\overline{X}_n = 1/(1 - p); \quad p = 1 - 1/\overline{X}_n \tag{6}$$

i.e.,

$$\overline{X}_w/\overline{X}_n = 2 - 1/\overline{X}_n$$

As 100% conversion is reached, $1/\overline{X}_n$ is zero, since $\overline{X}_n$ goes to infinity, i.e., $\overline{X}_w/\overline{X}_n$ is 2 at 100% conversion. At $p = 1$, i.e., 100% conversion, all monomer units initially present have reacted to form one large cyclic molecule with no size distribution, and $\overline{X}_w/\overline{X}_n \equiv 1$.

Flory [2] did not use a kinetic approach to his analysis of the polycondensation distribution, and under his approach, values of p from 0 up to and including 1 are possible. This leads to an unavoidable paradox in the significance of p and the $\overline{X}_w/\overline{X}_n$ ratio which must indicate inconsistencies in Flory's model.

Since the distribution of mer sizes obtained in the equilibrium polycondensation process by a kinetic approach [1] is identical to that obtained by Flory [2], it is of interest to investigate if the same paradox involving p and $\overline{X}_w/\overline{X}_n$ is also shown by r and $\overline{X}_w/\overline{X}_n$. To this end, we investigate the region of high conversion of monomer to polymer in the equilibrium polycondensation process. In particular, we want to investigate if (a) the function r in the relation

$$\overline{X}_w/\overline{X}_n = (1 + 2r)/(1 + r) \tag{7}$$

approaches a limiting value of unity as conversion of monomer to polymer nears completion on removal of water, or (b) if there is an upper limit, below complete conversion, to the yield of polymer achievable on removal of water from the reaction described by Eq. (1).

If water is removed stepwise from the reaction represented by Eq. (1), after each removal, the system relaxes to a new equilibrium position of higher polymer yield. Initially, before much water is removed, polymer and water molar concentrations are of the same order, but at equilibrium positions corresponding to stages where more and more water has been removed, the water molar concentration at equilibrium approaches the square of that of polymer (see Table 1), and the value of r increases without limit.

The ratio X_w/X_n in Eq. (7) has a value of unity when $r = 0$. According

Table 1. Molar Concentrations of [M] and [H_2O], Together with Values of p, r, and $\overline{X}_n$, Calculated According to Eq. (8) for a Polycondensation Process Described by Eq. (1), Where $k/k_1 = 4$

Polymer concentration (moles)	Water concentration (moles)	Water (moles) removed	p	r	$\overline{X}_n$
0.333	0.667	0	2/3	2	3
0.1	0.0444	0.867	9/10	9	10
0.01	0.000404	0.9986	99/100	99	100
0.001	4×10^{-6}	0.99899	999/1000	999	1000
10^{-9}	4×10^{-18}	Virtually all	$(10^9 - 1)/10^9$	$(10^9 - 1)$	10^9
6.45×10^{-13}	1.66×10^{-24}	"	Almost 1	$(1.55 \times 10^{12} - 1)$	1.55×10^{12}
1×10^{-13}	4×10^{-26}	"	" "	$(1 \times 10^{13} - 1)$	10^{13}

to Eq. (3), p = 0 when r = 0. This corresponds to a system where only monomer is present and no reaction has occurred. The system is truly monodisperse when r = p = 0. Also, according to Eq. (7), $\bar{X}_w/\bar{X}_n$ approaches a value of 2 as $r \to \infty$, p = 1 (Eq. 3). So the paradox, if complete conversion is possible, involving p and $\bar{X}_w/\bar{X}_n$ also involves r and $\bar{X}_w/\bar{X}_n$.

We are therefore forced to the conclusion that a paradox in r and $\bar{X}_w/\bar{X}_n$ can only be avoided if condition (b) holds, i.e., there is an upper limit, below complete conversion, to the amount of polymer that can be produced in the reaction described by Eq. (1).

Taking $k = 4k_1$, and assuming an initial monomer concentration, $[M_1]_0$, of 1 g-mole, water concentrations are calculated for different polymer concentrations according to

$$4[M]^2 = [H_2O](1 - [M]) \tag{8}$$

It is assumed that excess water can be efficiently removed. The results are shown in Table 1.

For $[M] = 1 \times 10^{-13}$ moles, there is less than one molecule of water remaining in the system—despite the fact that the system is still capable of producing $\sim 10^{11}$ molecules of water on the formation of the $\sim 10^{11}$ bonds which still remain to be formed.

If we substitute into Eq. (8) the concentration corresponding to one water molecule, we have

$$4[M]^2 = [1/(6.023 \times 10^{23})](1 - M) \tag{9}$$

we obtain $[M] = 6.45 \times 10^{-13}$ moles.

Assume this last remaining water molecule is removed. On formation of another bond, $[M]$ is decreased below the value appropriate to one water molecule, and the equilibrium is no longer in balance. This means that when there are 6.45×10^{-13} moles of polymer present and water is removed, the system cannot relax into a new equilibrium position of higher polymer yield because there are no equilibrium positions corresponding to a higher polymer yield.

Although the figure 6.45×10^{-13} moles of polymer has little significance in that it would be extremely difficult, in practice, to measure it, it has large theoretical significance in terms of the paradox in $\bar{X}_w/\bar{X}_n$ and r.

So, for $k/k_1 = 4$, the maximum yield of polymer from 1 mole of monomer occurs at a polymer concentration of 6.45×10^{-13} moles.

There is an upper limit on the value of r (at $X_n = 1.55 \times 10^{12}$ g-mole^{-1}). There is no paradox in the ratio $\overline{X}_w/\overline{X}_n$ and the value of r at this polymer yield limit because the polymer produced at this point contains 10^{11} molecules, sufficient to give a most probable distribution of mer sizes.

Note that if a first-order reaction is considered

$$A \underset{k_1}{\overset{k}{\rightleftharpoons}} B + c \tag{10}$$

and we calculate the concentration of the species A on the basis of there being initially 1 g-mole of A, which corresponds to a concentration of 1 molecule of B, then at this concentration of B the concentration of A is $k_1/k \times 1.66 \times 10^{-24}$ moles. This is less than one molecule (i.e., complete conversion) for values of $k > k_1$.

In any bimolecular reaction which is at equilibrium, i.e.,

$$A + B \underset{k_1}{\overset{k}{\rightleftharpoons}} C + D \tag{11}$$

complete conversion cannot be achieved no matter how efficient the removal of a by-product may be.

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