

## 분자쇄 길이에 따라 다른 반응속도를 갖는 축합중합 반응이 CSTR에서 행해질 경우

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(1988년 3월 28일 접수)

### Condensation Polymerization in Ideal Continuous Flow-Stirred Tank Reactor with Variant Reaction Rate Constant Depending on Chain Length

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(Received March 28, 1988)

요약 : 분자쇄 길이에 따라 다른 반응속도를 갖는 비가역 축합중합 반응이 CSTR에서 행하여 질 경우에 있어서 평균 분자량, 모멘트 및 분자량 분포지수 등이 예측되었다. 첫번째로 단량체만 여타 분자량의 다량체 보다 반응성이 다른 경우에 대하여 해석해가 구해졌으며,  $k(1+q^2mn)$  형태로 반응성이 변화할 때를 새로이 고려하였는 바, 해석해가 존재할 수 있는 체류시간의 제약이 있어 그 시간 내에서는 항상 유한한 중량 평균분자량과 따라서 유한한 분자량 분포지수를 갖는 것으로 나타났다. 이것은 회분식 반응기의 경우 유한시간에서 무한의 분자량을 가질 수 있는 것과 대비될 수 있었다.

**Abstract :** Average molecular weights, moments, and polydispersity indices were calculated for irreversible linear condensation polymerization in an ideal continuous-flow-stirred-tank reactor with variant reaction rate depending on its chain length. Exact solutions were obtained for the case when only monomer has a different reactivity from its homologues. A new model for chain length dependence in form of  $k(1+q^2mn)$  was considered to give limited molecular weights within a finite residence time, and limited polydispersity index. The reason is that there is a limitation of residence time for CSTR to give us the proper analytic solution. For comparison it is worthwhile to remember that a batch reactor gives us infinite molecular weight within a finite time instead.

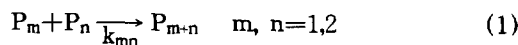
## INTRODUCTION

The theory of molecular weight distribution of linear condensation polymers is well established on the principle of equal reactivity of Flory.<sup>1</sup> Even though experimental evidences seem to be generally in favor of this principle, it seems to be still interesting to investigate the systematic deviations from the most probable distribution of Flory. The reactivity of the functional groups is known to depend on the structures of monomers or polymers. There are monomers, especially those containing aromatic rings, for which the reactivity is different from those of higher homologues. Goel et al.<sup>2</sup> have considered such case numerically in a batch reactor. Gupta et al.<sup>3</sup> have studied such case numerically in a continuous-flow-stirred-tank reactor (hereafter called CSTR). Here their case is reconsidered for the analytic results which might be very useful for further applications. In fact it gave the similar results worked out by Kumar recently.<sup>4</sup> In the latter paper, he considered reversible polycondensation generally and pointed out that it is possible to have analytic expression for the irreversible limit. Second possibility on the inequality in the reactivity could be the chain length dependence as pointed out previously.<sup>5</sup> It is still unclear why the reactivities of longer chains are greater or less than those of shorter ones. External flow or other type of forces could alter the orientational distribution of the long chain molecules, which eventually affects the reactivities of such chains. Highly oriented aromatic polyamide short fiber obtained by Yoon and al.<sup>6</sup> could be one of such cases. Nanda and Jain<sup>7</sup> was among the first to consider the chain length dependence of the reactivities of polymer chains, but their results were only useful for the early stage of polymerization because their model is physically bounded due to the zero reaction rate constant for some reactions between large chains. New model for chain length dependence was proposed to predict that the molecular weight can reach infinity for a finite time of reaction in a batch reactor by author.<sup>5</sup> It might be called

as the externally induced gelation phenomenon during linear condensation polymerization. Here the same kinetic model is applied for condensation polymerization in a CSTR.

## GENERAL KINETIC EQUATIONS

Irreversible polycondensation reactions are represented as an infinite set of elementary reactions



Where  $P_m$  is molecules having  $m$  repeating units and  $k_{mn}$  is reaction rate constant of  $P_m$  and  $P_n$ . The following set of algebraic equations generally characterizes the polymerization process in a CSTR.

$$\frac{(P_1 - P_{10})}{t} = -P_1 \sum_{n=1}^{\infty} k_{1n} P_n - k_{11} P_1^2 \quad (2)$$

$$\begin{aligned} \frac{(P_m - P_{m0})}{t} = & -P_m \sum_{n=1}^{\infty} k_{mn} P_n - k_{mm} P_m^2 \\ & + \sum_{n=1}^{m-1} k_{n,m-n} P_n P_{m-n} \end{aligned} \quad (3)$$

Where  $m^*$  is the integer part of  $m/2$ . Second subscript 0 in  $P$  means the feed concentration for polymers, and  $t$  is residence time in a CSTR. For the illustrative purpose, let us consider the Gupta's case first.

### Gupta's Model

In this kinetic scheme, polymerization process is modelled by two parameter  $k_1$  and  $k$  only :

$$\begin{aligned} k_{11} &= k_1 / 2 \\ k_{mn} &= k \quad m \neq n \\ k_{nn} &= k / 2 \quad n \geq 2 \end{aligned} \quad (4)$$

If  $k_1$  is equal to  $k$ , it is the case of equal reactivity. It is easy to construct a set of nondimensionalized equations for a given initial condition. Here the simplest initial condition is used, that is the only monomer exists at the beginning with the concentration  $M_0$ .

$$\frac{(P_1-1)}{\tau} = -2P_1Q_0 - 2(g-1)P_1^2 \quad (5)$$

$$\frac{P_2}{\tau} = -2P_2Q_0 + gP_1^2 \quad (6)$$

$$\frac{P_m}{\tau} = -2P_mQ_0 + \sum_{n=1}^{m-1} P_nP_{m-n} \quad (m \geq 2) \quad (7)$$

where  $g=k_1/k$  and  $\tau=kM_0t/2$ .

Moments  $Q_i$ 's are defined by equation (8) and every  $Q_i$  and  $P_m$  are nondimensionalized by  $M_0$ .

$$Q_i = \sum_{n=1}^{\infty} n^i P_n \quad (8)$$

In order to calculate the number-averaged and weight-averaged molecular weight,  $Q_0$ ,  $Q_1$  and  $Q_2$  are only necessary. It is easy to construct a  $Q_i$  equation in general by summing equations (5)~(7).

$$\frac{(Q_0-1)}{\tau} = -Q_0^2 - (g-1)P_1^2 \quad (9)$$

$$\frac{(Q_1-1)}{\tau} = 0 \quad (10)$$

$$\frac{(Q_i-1)}{\tau} = \sum_{j=1}^{i-1} {}_iC_j Q_j Q_{i-j} + (g-1)(2^i-2)P_1 \quad (11)$$

where  ${}_iC_j$  is the permutation symbol. These sets of equations permit the exact analytic solutions which were not noticed by the inventor of the model. The results are :

$$Q_0 = \frac{1}{2\tau} \left\{ \left( 1 + 2\tau + \frac{f-1}{2g} \right)^{1/2} - 1 \right\} \quad (12)$$

$$Q_1 = 1 \quad (13)$$

$$Q_2 = 1 + 2\tau + \frac{(1+4g\tau-f)^{1/2}}{4g\tau} \quad (14)$$

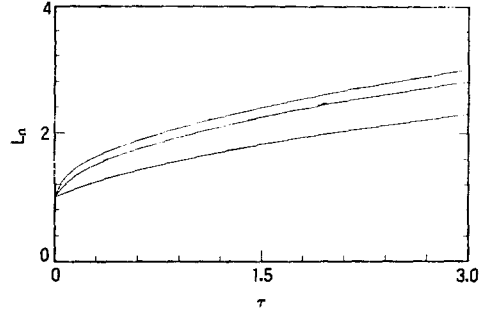


Fig. 1. Normalized number averaged molecular weight ( $L_n$ ) of Gupta's model vs. dimensionless time ( $\tau$ ) (from the top  $g=10, 5, 1$ ).

and

$$P_1 = \frac{(1+4g\tau-f)^{1/2}}{(8g(g-1)\tau^2)^{1/2}} \quad (15)$$

where  $f = (1+8g\tau+16g\tau^2)^{1/2}$ .

It is possible to calculate  $Q_n$  and  $P_m$  successively in principle.

According to the definition of number-averaged and weight-averaged chain lengths  $L_n$  and  $L_w$  it is easy to have the following relationships.

$$L_n = Q_1 / Q_0 \quad (16)$$

$$L_w = Q_2 / Q_1 \quad (17)$$

The normalized number average molecular weight ( $L_n$ ) and weight averaged molecular weight ( $L_w$ ) are plotted against the dimensionless time  $\tau$  in Fig. 1 and 2.  $g$  was chosen to be 1, 5, 10 since as shown in previous paper,<sup>5</sup> the reactivity between monomers is quite larger than those of polymers for the reaction between diethylene glycol and adipic acid.

PDI from such kinetics is plotted in Fig. 3.

**New Model**

Here a new model with the variant reaction rate which strongly depends on the chain length was applied in a CSTR. It is not claimed that such a dependence corresponds to any real situation,

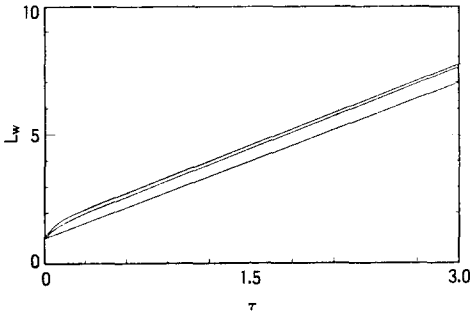


Fig. 2. Normalized weight averaged molecular weight ( $L_w$ ) of Gupta's model vs. dimensionless time ( $\tau$ ) (from the top  $g=10, 5, 1$ ).

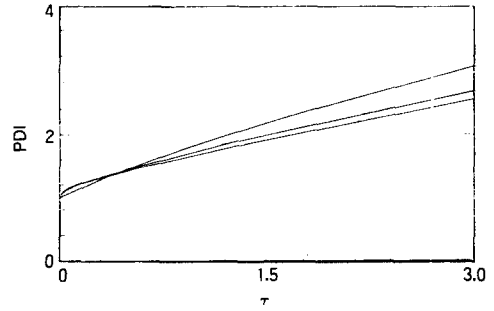


Fig. 3. Polydispersity index ( $L_w/L_n$ ) of Gupta's model vs. dimensionless time ( $\tau$ ) (from the bottom in the region of large  $\tau$   $g=10, 5, 1$ ).

but there is a strong possibility that polymerization could be accelerated by the external field such as shear flow. If the reaction rate varies as given in equation (18) then it is easy to construct not only the mass balance equations but also corresponding moments equations for the same feed conditions mentioned previously.

$$k_{mn} = k(1+q^2mn) \quad m \neq n$$

$$k_{nn} = \frac{k(1+q^2n^2)}{2} \quad m, n=1, 2, \dots \quad (18)$$

$$\frac{(P_1-1)}{\tau} = -2P_1Q_0 - 2q^2P_1Q_1 \quad (19)$$

$$\frac{P_2}{\tau} = -2P_2Q_0 - 4q^2P_2Q_1 + (1+q^2)P_1^2 \quad (20)$$

$$\frac{P_m}{\tau} = -2P_mQ_0 - 2mq^2P_mQ_1 + \sum_{n=1}^{m-1} (1+q^2n(m-n))P_nP_{m-n} \quad (21)$$

and

$$\frac{(Q_0-1)}{\tau} = -Q_0^2 - q^2Q_1^2 \quad (22)$$

$$\frac{(Q_1-1)}{\tau} = 0 \quad (23)$$

$$\frac{(Q_i-1)}{\tau} = \sum_{j=1}^{i-1} iC_j \{Q_jQ_{i-j} + q^2Q_{j+1}Q_{i-j+1}\} \quad (24)$$

$Q_i$  can be obtained successively.

$$Q_0 = \frac{[(1+4\tau - 4q^2\tau^2)^{1/2} - 1]}{2\tau} \quad (25)$$

$$Q_1 = 1 \quad (26)$$

$$Q_2 = \frac{[1 - (1 - 8q^2\tau - 16q^2\tau^2)^{1/2}]}{4q^2\tau} \quad (27)$$

$L_n$  and  $L_w$  are obtained from  $Q_0, Q_1$  and  $Q_2$ .

$$L_n = \frac{1 + (1 + 4\tau - 4q^2\tau^2)^{1/2}}{(1 - q^2\tau)} \quad (28)$$

$$L_w = \frac{2(1 + 2\tau)}{1 + (1 - 8q^2\tau - 16q^2\tau^2)^{1/2}} \quad (29)$$

$L_n, L_w$  and PDI are plotted in Fig. 4, 5 and 6 respectively. It is clear that dimensionless time  $\tau$  should be less than a certain finite time  $\tau_{max}$ . It is obtained from eq (27).

$$\tau_{max} = \frac{1}{4} [(1 + \frac{1}{q^2})^{1/2} - 1] \quad (30)$$

At that time, the weight-averaged molecular weight does not reach infinity so that gelation does not occur if we introduce whatever small value of  $q$ . It is still unclear what kind of phenomenon could occur after that maximum residence time given by eq.(30). It is worthwhile to notice that if  $q$  approaches zero, then the number averaged

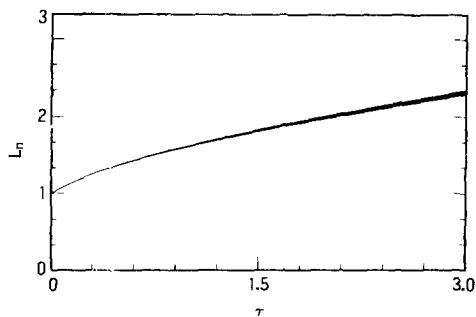


Fig. 4. Normalized number averaged molecular weight ( $L_n$ ) of the new model vs. dimensionless time ( $\tau$ ) (from the top  $q=0.075, 0.05, 0, 0.05i, 0.075i$ ).

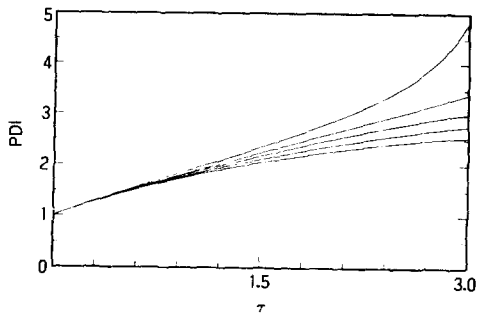


Fig. 6. Polydispersity index ( $L_w/L_n$ ) of the new model vs. dimensionless time ( $\tau$ ) (from the top  $q=0.075, 0.05, 0, 0.05i, 0.075i$ ).

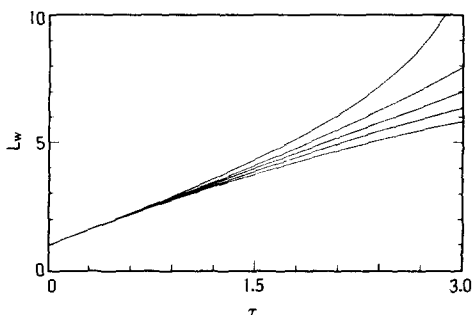


Fig. 5. Normalized weight averaged molecular weight ( $L_w$ ) of the new model vs. dimensionless time ( $\tau$ ) (from the top  $q=0.075, 0.05, 0, 0.05i, 0.075i$ ).

and weight averaged molecular weights at that time are order of  $1/q^{1/2}$  and  $1/q$ , respectively, so that PDI (polydispersity index  $L_w/L_n$ ) is order of  $1/q^{1/2}$  not infinity.

These results are applicable for the case of  $q=iq^*$ , that is, the case when the rate constant is decreased with increasing chain length. Here  $i$  is the base of the imaginary number ( $i^2=-1$ ) and by using  $q=iq^*$ , every results can be rewritten. As mentioned in the introduction, it is only valid for the early stage of polymerization, due to the limitation of the molecular size. By definition of the reactivity constant,  $L_n$  should be less than the order of  $1/q^*$ . If  $\tau$  is less than the order of  $1/q^*$ , obtained  $L_n$  would be in the order of  $1/q^{*1/2}$  which is in an acceptable range. But

if  $\tau$  exceeds the order of  $1/q^*$ , for example, reaches the order of  $1/q^{*2}$ , then  $L_n$  would reach the order of  $1/q^*$ , which implies an unphysical negative reactivity constant. Therefore  $\tau$  must be less than order of  $q^{*\alpha}$  where  $\alpha$  should be less than 2. Then  $L_n$  would be order of  $1/q^{*\alpha/2}$ , and  $L_w$  would be order of  $2/q^{*\alpha}$ . Consequently PDI would be  $2/q^{*\alpha/2}$ .

## DISCUSSIONS

Now it is clear that there are some limitations on the number-averaged chain length and weight-averaged chain length both for the reactivity increasing or decreasing with chain length. As far as the polydispersity index is concerned, it could reach extremely high value compared with that obtained in a batch reactor, but there is still a limitation like  $1/q^{1/2}$  so that by applying external field during polymerization it could be reduced to low level. Any experimental evidence for the proposed theory is not available right now, it would be real challenge to find out whether it is possible to have such a phenomenon during linear condensation polymerization and if possible whether the theoretical predictions are good quantitatively. In order to mimic the real situation more precisely, attempts should be carried out for the more accurate rate dependence model of the small molecules. One of them could be the combination of the two models given in this

paper. The other unsolved problem is the rheo-kinetic origin of the variant kinetic constant like the expression given by equation(18). Finally this kind of reaction kinetics can be applied for the real situation like reversible polycondensation reaction. In fact it is going on in my laboratory to simulate the reaction kinetics of polycondensation of polyester in a finisher including this concept.

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