Caprolactam Polymerization.   Polymerization in Backmix Flow Systems

K. NAGASUBRAMANIAN and H. K. REIMSCHUESSEL,
Corporate Chemical Research Laboratory, Allied Chemicals Corporation, Morristown, New Jersey 07960

Synopsis

A reactor system consisting of a cascade of N perfectly mixed stirred tanks followed by a plug flow reactor was analyzed.   Compared with a single-stage closed system, a substantial reduction in the total reaction time was indicated for systems using cascades of three or more stirred tanks.   Calculations for both the micromixed and the segregated systems showed no significant difference between the respective total residence times.

INTRODUCTION

Optimization studies on the water-initiated polymerization of caprolactam have been reported previously[1,2] for processes utilizing tubular plug flow reactors.   The processes considered in these studies consisted of two stages and were characterized by the nonexistence of operating limitations with respect to achieving both true plug flow and instantaneous removal of the free water present in the system after a certain conversion X had been reached.   Although realization of these conditions is not easily achieved, there are processes that operate according to the basic principles upon which these studies were based.   On the other hand, processes have been proposed[3] and are being practiced that utilize a cascade of stirred-tank reactors.   In these cases, advantage is obviously taken of the good heat and mass transfer attainable in this reactor system.   The efficiency of this process type, however, decreases considerably when high conversions are required as it is in case of the polymerization of caprolactam.   The present study is concerned again with a basically two- stage process.   Its first stage consists of a cascade of stirred-tank reactors and the second, of a tubular flow reactor.   This reactor configuration constitutes a combination of the two forenamed types of processes, and a corresponding analysis and optimization entails, in addition to the kinetics of the polymerization the consideration of the dynamics of the system (such as mixing in the reactors).   In this paper we shall present results for some limiting cases.

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PROCESS DESCRIPTION

The process of polymerization has been outlined in Figure 1. It consists of a set of N stirred tank reactors followed by a tubular reactor. To obtain the highest possible rates of conversion, the reactor segment consisting of the stirred tanks 1 to $(N - 1)$ is an essentially closed system.[4] Removal of the free water is carried out only in the Nth tank. Whereas in the previous treatment[2] this removal was assumed to occur instantaneously, a finite rate of water removal will be considered in the present case.
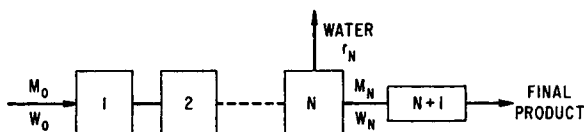

Fig. 1. General process outline.

To define the dynamics of the system, the contents of the stirred tanks are assumed to be perfectly mixed. Thus, the residence time density (RTD) function (1) may be used[5]:

$$f(t) = \theta^{-1} \exp(-t/\theta) \tag{1}$$

where θ is the residence time in the stirred tank and is equal to V/F where V is reactor volume and F is feed rate.

For a given number of stirred tanks, we are interested in achieving high conversions $(X > 90\%)$ and minimizing the total residence time in the system. Since no water is removed in the tubular reactor section, the amount of water to be removed in reactor N is determined by the feed concentration (W_0) and the desired final polymer molecular weight.

In this study, all calculations were made on the basis of one mole of feed lactam. The water concentration in the feed was taken to be 0.1. The desired final degree of polymerization was 262.0. At a polymerization temperature of 265°C, this corresponds to

$$W_N + S_N = 0.01 \tag{2}$$

where the subscript refers to the number of the tank, W = water concentration, and S = chain concentration. Table I summarizes the data used in these calculations.

Under the conditions of perfect mixing, the performance of a stirred tank would lie between the extremes of micro- and macromixing.[3] Calculations for the two ideal cases can be made from the knowledge of basic kinetics.

MICROMIXED REACTORS

If the contents of the tanks are assumed to be perfectly mixed on a molecular level, the process equations can be written directly from batch kinetics

TABLE I
Chemical Reactions, Equilibrium, and Rate Constants

i	Reaction	$k_i^0 \left[\dfrac{kg}{hr\ mole}\right]$	$k_i'^0 \left[\dfrac{kg^2}{hr\ mole^2}\right]$	K_i
1	$HN(CH_2)_5CO + H_2O \rightleftharpoons H_2N(CH_2)_5COOH$	0.0048	0.988	$0.002633\ \dfrac{kg}{mole}$
2	$H[NH(CH_2)_5CO]_nOH + H[NH(CH_2)_5CO]_mOH \rightleftharpoons H[NH(CH_2)_5CO]_{n+m}OH + H_2O$	5.999	93.263	498.72
3	$H[NH(CH_2)_5CO]_nOH + HN{-}(CH_2)_5{-}CO \rightleftharpoons H[NH{-}(CH_2)_5CO]_{n+1}OH$	5.999	122.3	$1.31\ \dfrac{kg}{mole}$

TABLE II
Rate Equations[a]

$$\frac{dM_i}{dt} = \frac{M_{(i-1)} - M_i}{\theta_i} - (k_1^0 + k_1'^0 s_i m_0)\left[M_i w_i m_0 - \frac{s_{1,i}}{K_1}\right] - (k_3^0 + k_3'^0 s_i m_0)\left[s_i M_i m_0 - \frac{(s_i - s_{1,i})}{K_3}\right] \quad (3)$$

$$\frac{ds_i}{dt} = \frac{s_{(i-1)} - s_i}{\theta_1} - m_0(k_2^0 + k_2'^0 s_i m_0)\left[s_i - \frac{w_i(1 - s_i - M_i)}{K_2}\right] + (k_1^0 + k_1'^0 s_i m_0)\left[M_i w_i m_0 - \frac{s_{1,i}}{K_1}\right] \quad (4)$$

$$\frac{ds_{1,i}}{dt} = \frac{s_{1,(i-1)} - s_{1,i}}{\theta_i} + (k_1^0 + k_1'^0 s_i m_0)\left[M_i w_i m_0 - \frac{s_{1,i}}{K_1}\right] - 2m_0(k_2^0 + k_2'^0 s_i m_0)\left[s_i s_{1,i} - \frac{w_i(s_i - s_{1,i})}{K_2}\right] - s_{1,i}(k_3^0 + k_3'^0 s_i m_0)\left[M_i m_0 - \frac{1}{K_3}\right] \quad (5)$$

$$w_i = w_0 - s_i \text{ for } i \neq N \quad (6)$$

$$w_i = w_0 - s_i - r_N \text{ for } i = N \quad (7)$$

[a] Subscripts $i - 1$, i, N refer to the tanks, under consideration; θ = residence time, hr; M = monomer concentration = $1 - X$; S = chain concentration; S_1 = amino-caproic acid concentration; W = water concentration; W_0 = water concentration in the feed; r = water removal rate, hr^{-1}; $m_0 = 1/g$ = units conversion factor = $[0.11316 + 0.18016 (W + S)]^{-1}$ moles/kg.[s] All concentration are moles/kg of initial caprolactam.
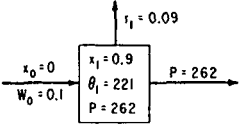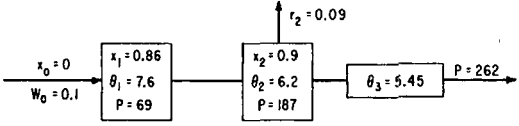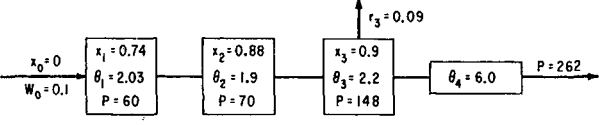
Fig. 2. Computation results; micromixed system. t_0 = total reaction time in a single stage plug flow or batch reactor = 18 hr.

by incorporating the input-output terms.   Thus, for tank i, the process is defined by the rate equations listed in Table II.   At steady state, the time derivatives vanish and the resulting algebraic equations can be solved sequentially to give the interdependence of M, S, S_1, W and θ, for a given inlet conversion and polymerization temperature.

To minimize the total reaction time $\sum_{i=1}^{N+1} \theta_i$, a search in the operating region has to be carried out over the variables M, S, and S_1.   Approximate location of the optimum can be found by carrying out a single variable search in M (assuming others to remain constant) by the dynamic programming technique.[6]   The exact calculations are then carried out by trial and error, around the approximate optimum.   Calculations were carried out in an IBM 360/50 computer, using known batch kinetics.   The results are summarized in Figure 2 (for up to three tanks).

For each additional tank in the system, the percent improvement in $\sum \theta$ becomes smaller and smaller.   It can be seen, however, that even with three tanks a significant improvement over the single-step process is achieved. The required water removal rate in tank N (r_N) could be achieved through suitable process design.

SEGREGATED REACTORS

As opposed to molecular mixing, the reactor contents may be perfectly mixed only on a macroscopic scale.   The individual segments react in-
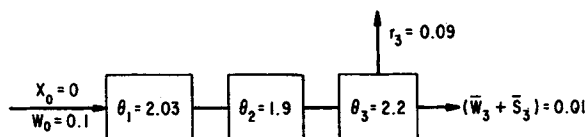
Fig. 3. Computation results; three-tank, micromixed system.

dependently of one another and are mixed at the exit. As before, the over-all RTD function is given by eq. (1).

The performance of such a reactor can be determined directly from batch kinetics by integrating the parameters over all the reactor elements. For example, conversion in the segregated reactor would be given as

$$\bar{X} = \int_0^\infty X(t)f(t)dt \qquad (9)$$

where $f(t)$ is the RTD function and $X(t)$ is the batch conversion. (Quantities pertaining to the segregated case are identified with a bar.) Similar expressions apply for $\bar{M}$, $\bar{S}$, $\bar{S}_1$, and $\bar{W}$.

An optimization of sets of segregated reactors can be carried out in a manner analogous to the micromixed case. However, because of the numerical integrations needed, the procedure is much more tedious and time consuming.

For comparison purposes, calculations were carried out for the three tank system obtained earlier (Fig. 3). For the given residence times θ_1, θ_2, and θ_3, the product characteristics at the exit of reactor 3 were calculated as follows:

Since no water is removed in the first two tanks, the calculations for these two can be carried out in a single step by using the combined RTD function

$$f(t) = [\theta_1 - \theta_2]^{-1}[\exp(-t/\theta_1) - \exp(-t/\theta_2)]. \qquad (10)$$

Calculations for the third tank would involve some trial and error. At the exit, the condition $\bar{W} + \bar{S} = 0.01$ would have to be satisfied. Assum-
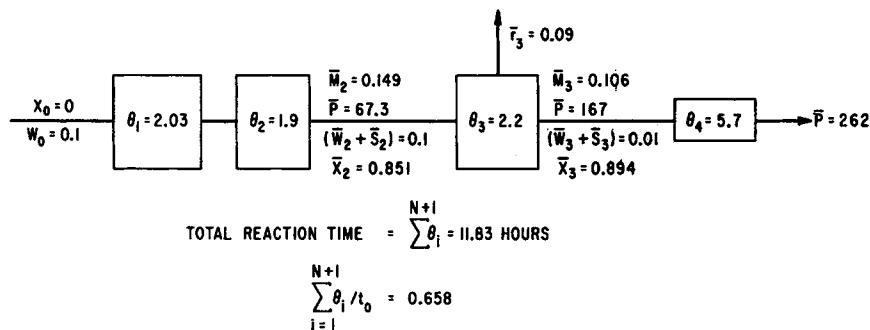

Fig. 4. Computation results; three-tank, segregated system.

ing the water removal rate from each reactor segment to be proportional to its water content, we can write the differential equation for water concentration in the segments as

$$dw/dt = (-ds/dt) - \alpha W \tag{11}$$

where α is a proportionality constant determined from the condition

$$\bar{W} + \bar{S} = 0.01. \tag{2}$$

On integrating eq. (11) from $t = 0$ to $t = \infty$ and using the relation (2), we get

$$\alpha = 0.09/(\theta_3 \bar{W}). \tag{12}$$

Substituting in eq. (11) we get

$$dw/dt = -ds/dt - (0.09W)/\theta_3 \bar{W}). \tag{13}$$

A proper value for $\bar{W}$ is now found by trial and error, to satisfy eq. (2). The results are summarized in Figure 4. It is seen that if all the reactors are totally segregated, the performance is not significantly different from the micromixed case, as long as the perfect mixing condition is satisfied. In fact, the tendency of the reactor contents to remain segregated at high conversions, coupled with the possibly micromixed state of the low viscosity polymer in the first tank, would further improve the product quality in terms of molecular weight and conversion. The situation could however be different if only one or two stirred tanks were used.

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