

# Effect of Diacid Stabilizers on Kinetics of Hydrolytic Polymerization of $\epsilon$ -Caprolactam in Industrial Reactors

Ashwini K. Agrawal,<sup>1</sup> Deepak K. Gupta,<sup>1</sup> Kotilingam Devika,<sup>1</sup> Tomonobu Manabe<sup>2\*</sup>

<sup>1</sup>Department of Textile Technology, Indian Institute of Technology, New Delhi 110 016, India

<sup>2</sup>Modipon Fibers Company, Modinagar 201 204, Uttar Pradesh, India

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**ABSTRACT:** The rate constants in hydrolytic polymerization of  $\epsilon$ -caprolactam are dependent on the concentration of carboxylic acid groups in the reaction medium. Therefore, the use of diacid stabilizers for regulating molecular weight are likely to have favorable effect on the kinetics of polymerization compared to monoacid stabilizers, which are traditionally used in such polymerizations. To understand the kinetics of polymerization in the presence of diacid stabilizer compared to monoacid stabilizer, mathematical kinetic models were developed using the end group approach. These models were used to quantify the effect of both stabilizers on nylon-6 synthesis in a closed isothermal batch reactor at different temperatures in the range of 245–265°C. The kinetic model for the diacid-stabilized system was then extended to

an industrial VK tube reactor using the process model developed earlier for the monoacid stabilized system. Both the mathematical modeling and experimental results showed that the presence of diacid stabilizer could significantly enhance the overall kinetics of the reaction compared to the monoacid stabilized system and in turn, resulted in reduction of the polymerization time by about 20–25%. The study suggests that diacid stabilizers may be used preferably over monoacid stabilizers in synthesis of nylon-6 to reduce the cost of polymerization. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2065–2075, 2007

**Key words:** polymerization kinetics; nylon-6; VK tube; diacid stabilizer; modeling

## INTRODUCTION

Nylon-6 is losing its market share to other commodity polymers such as polypropylene and polyester because of the higher cost of its raw materials. Solution to this problem is to use efficient processes or introduce additional functionality to the polymer to realize better premium on nylon products in the market. To achieve this goal it is important to understand basic reaction kinetics and polymerization in industrial reactors. Kinetics of hydrolytic polymerization of  $\epsilon$ -caprolactam has been extensively studied<sup>1–10</sup> in batch reactors. These kinetic models were also used to investigate the polymerization process in continuous tube reactors.<sup>5,11–19</sup> Recently, we had reported modeling of an industrial VK (Vereinfacht Konitruierliches) tube reactor, using monocarboxylic acid (monoacid) stabilizer, where the effect of the complex internal structure (heat exchanger, internal gratings) of the reactor was considered.<sup>20</sup> The effect of hydrostatic pressure inside the re-

actor was taken into account to predict water profile through out the reactor. Using temperature and pressure profile, lowest water content (LWC) point was predicted, which was found to be critical in determining the properties of the end product. The model was found to be very useful in controlling and optimizing the performance of an industrial VK tube reactor.

In the aforementioned studies, although most of the reaction parameters that affect kinetics of the nylon-6 synthesis, such as temperature, water concentration, and monoacid stabilizer concentration, have been considered, the effect of the type of stabilizer on reaction kinetics has not been investigated.

It is reported<sup>3</sup> that the carboxylic functional groups act as a catalyst in the hydrolytic polymerization of  $\epsilon$ -caprolactam, and therefore, the rate constants for all reactions ( $k_i$ ) in hydrolytic polymerization of  $\epsilon$ -caprolactam can be shown to depend on the concentration of the [—COOH] groups available at any point in the reaction system. This effect has been quantified by the following empirical relation:<sup>2–6,12,16,21</sup>

$$\text{Rate constant } (k_i) = k_i^0 + k_i^c [\text{COOH}] \quad (1)$$

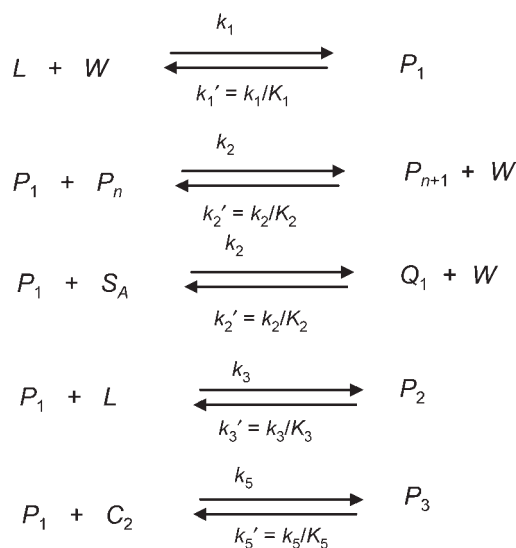
In synthesis of nylon-6, apart from monoacid stabilizers, dicarboxylic acid (diacid) stabilizers can also be used to regulate the molecular weight of the polymer. In recent years, diacid stabilizers are gaining importance in this polymerization because they can be read-

\*Present address: Manufacturing Technology Consultant, 545 White Oak Road, Blue Bell, Pennsylvania 19422.

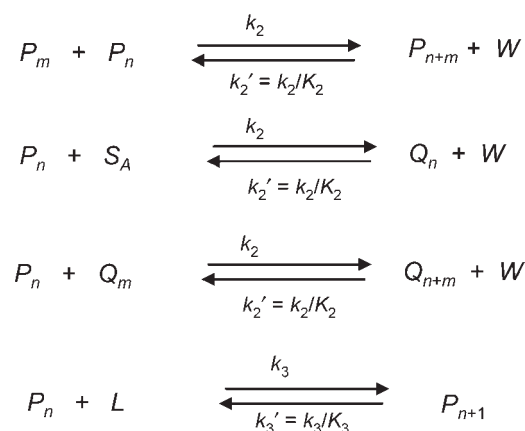
Correspondence to: A. Agrawal (ashwini\_agrawal@yahoo.com).

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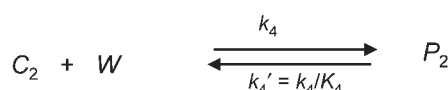
Reaction involving term  $P_1$ .



Reaction involving term  $P_n$ .



Reaction involving other terms.



Scheme 1

ily used for introducing different functionality, such as anionic dye sites using sulfonic acid salts, for producing cationic dyeable nylons.<sup>22</sup> The diacid stabilizers have an extra carboxylic acid group and therefore, may change the concentration of carboxylic acid in the reaction media compared to monoacid stabilizers. This is likely to favorably affect the reaction kinetics and reduce the cost of polymerization. However, the kinetics of diacid stabilizers has not been reported in the literature.

In this study an attempt has been made to investigate the effect of diacid stabilizer in comparison to monoacid stabilizer on the kinetics of hydrolytic polymerization of

$\epsilon$ -caprolactam. For this mathematical polymerization models were developed for the two stabilizer cases and compared with the industrial case studies.

## MODELING AND EXPERIMENTAL METHODS

### Kinetic models

There are two modeling approaches that can be applied in representing the polymerization kinetics: first the molecular species approach and second is the functional group approach. In the molecular species approach, all the molecular species present in the reactor, including oligomers of varying degree of polymerization, should be considered. In this, each polymer chain is tracked as a special entity in the kinetic scheme. However in the second approach, only different types of functional groups that take part in the reaction are treated as separate entities. Molecular species model is more comprehensive (is able to predict polydispersity) while leading to a large number of equations to be solved. On the other hand, functional group model still provides necessary information such as concentrations of important reactants and number average molecular weight of the polymer in the reaction mixture, while the numbers of equations are limited and easier to handle.

We have used the second approach, i.e., functional group approach to construct mathematical models for the two stabilizer cases. These models are given below.

For diacid stabilized system

The kinetic scheme for polymerization of  $\epsilon$ -caprolactam in the presence of diacid stabilizer is given in Scheme 1.

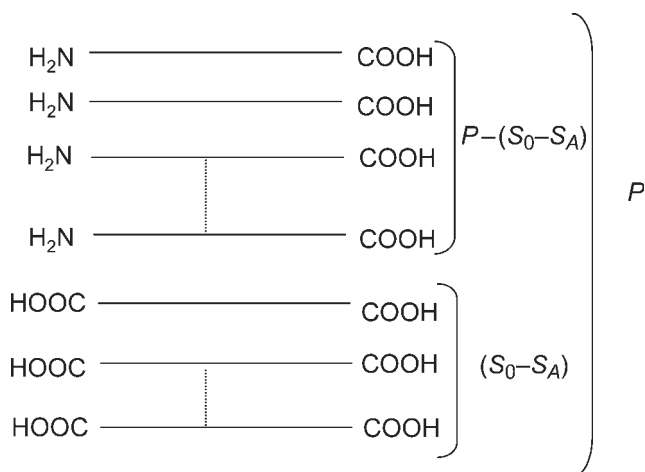
Where  $L$  = Caprolactam  $\text{OC} - (\text{CH}_2)_5 - \text{NH}$ ;  $W$  = water ( $\text{H}_2\text{O}$ );  $P$  = total polymer chains =  $P_n + Q_m$ ;  $P_n$  = polymer chain with "n" repeat units and having amino end group on one end,  $\text{HO} - [\text{OC} - (\text{CH}_2)_5 - \text{NH}]_n - \text{H}$ ;  $Q_m$  = polymer chain with "m" repeat units and a diacid molecule giving rise to chains with acid groups at both ends,  $[\text{HOOC} - \text{COOH}]$ ;  $C_2$  = cyclic dimer;  $S_0$  = diacid at the beginning of the reaction;  $S_A$  = diacid at any time "t."

If the initial concentration of the added diacid is " $S_0$ " and its concentration at time "t" is  $S_A$ , then concentration of the blocked chains would be  $(S_0 - S_A)$ . Assuming there is no loss of diacid. Therefore, the concentration of various species reactants/functional groups may be expressed as shown in Scheme 2.  $P$  is concentration of all chains—with or without diacid stabilizer molecule. From Scheme 2, the amino and carboxylic end group concentrations can be written as

$$[\text{—NH}_2] = P - (S_0 - S_A) \quad (2)$$

$$\begin{aligned}
 [\text{—COOH}] &= [P - (S_0 - S_A)] + [(S_0 - S_A)] \\
 &= [P + S_0 - S_A] \quad (3)
 \end{aligned}$$

Using the above, the mass balance equations for concentration of caprolactam ( $L$ ), aminocaproic acid ( $P_1$ ),



Scheme 2

polymer ( $P$ ), cyclic dimer ( $C_2$ ), diacid ( $S_A$ ), and aminocaproic acid reacted with diacid stabilizer ( $Q_1$ ) can be written as shown in Table I. In contrast to the monoacid system where the monoacid reacts to block the chain at one end, the mass balance equations for the diacid system must take into account the important fact that  $Q_m$  chains have reactive groups at both ends. Additionally, only one diacid reacts with one polymer chain  $P_n$ , but the diacid molecule may be present anywhere in the chain due to its bifunctional nature.

Mass balance of caprolactam involves ring-opening and polyaddition reactions. In ring-opening step of the caprolactam, water attacks only at one position in caprolactam, and so the disappearing rate for caprolactam is  $(-k_1LW)$  and it is regenerated by the backward rate ( $k'_1P_1$ ). In polyaddition reaction, caprolactam ( $L$ ) reacts only at the amino end of a growing chain, i.e., chains  $[P - (S_0 - S_A)]$ . Its disappearance is associated with the rate  $[-k_3L(P - (S_0 - S_A))]$  and is reformed only from one end of the chains containing amine end groups i.e.,  $[k'_3(P - (S_0 - S_A) - P_1)]$ .

In the mass balance of the cyclic dimer, ring-opening, and polyaddition reactions will participate. In the ring-opening of the cyclic dimer, water attacks at two positions in the dimer, and so forward rate constant should be expressed as  $2k_4$ , with the forward and backward rates being  $(-2k_4C_2W)$  and  $(k'_4P_2)$ , respectively.

Cyclic dimer also undergoes addition reaction at any of the two-amide linkages, with the unblocked polymer chains  $[P - (S_0 - S_A)]$  and is associated with the rate  $[-2k_5C_2(P - (S_0 - S_A))]$  and can be reformed by the rate  $[k'_5((P - S_0 + S_A) - P_1 - P_2)]$ .

In mass balance equation for  $P_1$ , all types of reactions will take part. Ring-opening reactions will be given as stated earlier, however, with reversed signs, polyaddition to caprolactam ( $L$ ) is given by  $[-k_3P_1L + k'_3P_2W]$  and to cyclic dimer ( $C_2$ ) is  $[-2k_5P_1C_2 + k'_5P_3]$ .

For the condensation reaction of  $P_1$  with the rest of the polymer chains, the  $[-COOH]$  of  $P_1$  reacts with  $[-NH_2]$  groups of the polymer chains and  $[-NH_2]$  groups of  $P_1$  may react with the  $[-COOH]$  groups of the other polymer chains. So disappearance rate for  $P_1$  due to polycondensation can be written as follows.

Forward rate =  $-k_2P_1[P - (S_0 - S_A)] - k_2P_1[P + S_0 - S_A] = [-2k_2P_1P]$  and backward rate is equal to  $[2k'_2W(P - Q_1 - P_1)]$ .

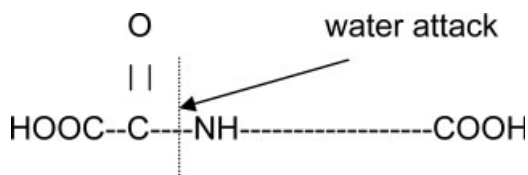
The  $P_1$  chain may also react with any of the two ends of diacid to form  $Q_1$  and regenerated by the attack of water on the amide linkage of  $Q_1$  associated with the rates of  $[-2k_2S_AP_1]$  and  $[k'_2WQ_1]$ .

In mass balance equation of diacid ( $S_A$ ), diacid react in two ways with the total amino groups  $[P + S_A - S_0]$  in the reaction mixture with the rate  $[-2k_2S_A(P + S_A - S_0)]$  and can be reformed by the attack of water on the first amide linkage only as shown in Scheme 3. Since there is a very small possibility of having polymer chains ( $Q_n$ ) with diacid at the end, the backward rate has been considered to involve only  $Q_1$  rather than  $Q_n$  (a reasonable approximation). The attack of water on the  $Q_1$  will always generate diacid only. So the backward rate would be associated with  $[k'_2WQ_1]$ .

Mass balance equation for polymer ( $P$ ), Table I, eq. (3), is unaffected by any of the two addition reactions because total number of polymer chains do not change with this reaction. However, ring-opening of  $L$  and  $C_2$ , and condensation reactions between the polymer chains will be involved in this equation. In polycondensation reaction, any  $[-COOH]$  end group may react with any  $[-NH_2]$  end group. Therefore, forward reaction is written as decrease in polymer concentration by the rate  $[k_2(P + S_0 - S_A)(P - (S_0 - S_A))]$ . Backward reaction of polycondensation involves reaction of water with all amide linkages. In chains with amine end groups,  $P_n$ ,

TABLE I  
Mass Balance Equations for Diacid Stabilized System

1.	$dL/dt = -k_1LW + k'_1P_1 - k_3L(P - S_0 + S_A) + k'_3(P - S_0 + S_A - P_1)$
2.	$dP_1/dt = k_1LW - k'_1P_1 - 2k_2P_1P + 2k'_2W(P - Q_1 - P_1) - k_3P_1L + k'_3P_2 - 2k_2P_1S_A + k'_2Q_1W - 2k_5P_1C_2 + k'_5P_3$
3.	$dP/dt = k_1LW - k'_1P_1 - k_2(P + S_0 - S_A)(P - S_0 + S_A) + k'_2W(L_0 - L - P + S_0 - S_A) + 2k_4WC_2 - k'_4P_2$
4.	$dC_2/dt = -2k_4WC_2 + k'_4P_2 - 2k_5C_2(P - S_0 + S_A) + k'_5(P - S_0 - S_A - P_1 - P_2)$
5.	$dS/dt = -2k_2S_A(P - S_0 + S_A) + k'_2WQ_1$
6.	$dQ_1/dt = 2k_2P_1S_A - k'_2WQ_1 - 2k_2Q_1(P - S_0 + S_A) + k'_2W(S_0 - S_A - Q_1)$

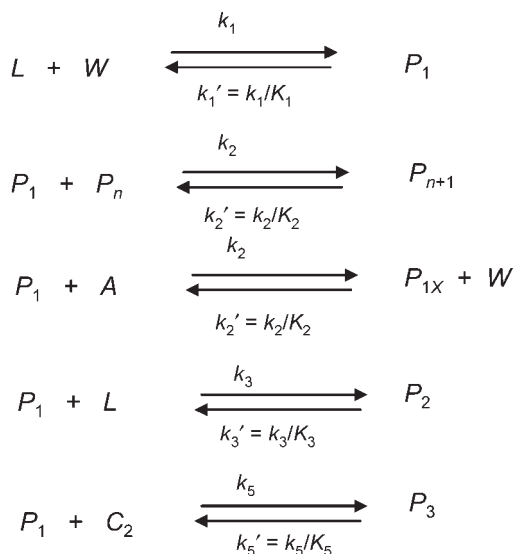


Scheme 3

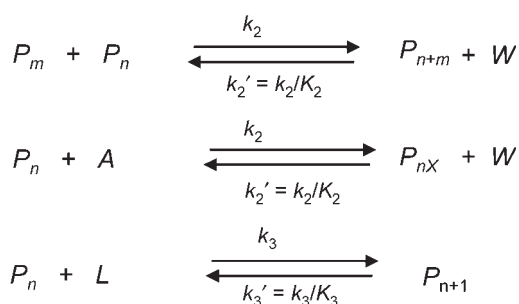
the numbers of amide linkages are equal to  $(n - 1)$ , while in chains with diacid molecule,  $Q_n$ , there are  $n$  amide linkages. These can be expressed by number of reacted caprolactam units  $(L_0 - L)$  minus one each in  $P_n$  chains, i.e.,  $[(L_0 - L) - (P - (S_0 - S_A))]$ .

In mass balance equation of  $Q_1$ , it is formed with reaction of diacid and  $P_1$  in two ways  $[2k_2P_1S_A]$ , while it

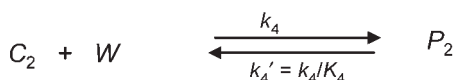
Reaction involving term  $P_1$ .



Reaction involving term  $P_n$ .



Reaction involving other terms.



Scheme 4

disappears on hydrolysis with water in only one way, i.e.,  $[-k_2'WQ_1]$ .  $Q_1$  also reacts with any other polymer with amino ( $-\text{NH}_2$ ) group at a rate of  $[-2k_2Q_1(P - S_0 + S_A)]$  and it is formed back by hydrolysis from all  $Q_n$  except  $Q_1$  at a rate of  $[k_2'W(S_0 - S_A - Q_1)]$ .

In this model as a closure condition, the concentrations of  $P_2$  and  $P_3$  are assumed to be equal to  $P_1$  for the backward rates. This is a reasonable assumption because the concentration of linear oligomers is expected to be very small compared to the higher molecular weight chain towards the end of the reaction.

For monoacid stabilized system

The kinetic scheme for polymerization of  $\epsilon$ -caprolactam in the presence of monoacid stabilizer is given in Scheme 4.

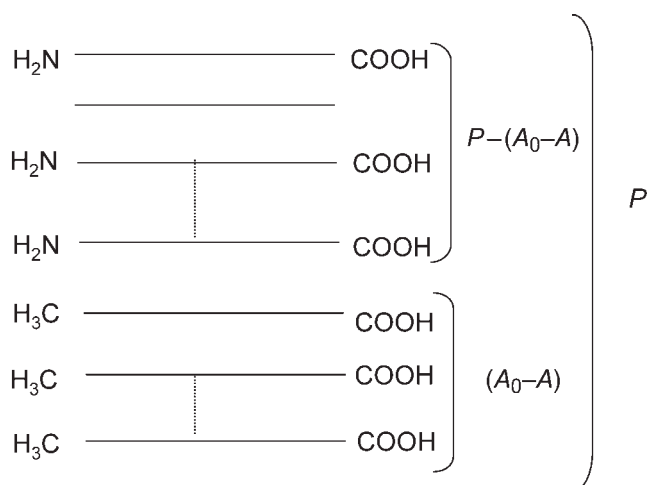
Where  $P_n = \text{HO} - [\text{OC} - (\text{CH}_2)_5 - \text{NH}]_n - \text{H}$ ;  $A = \text{acetic acid, CH}_3\text{COOH}$ ;  $P_{nx}$  = chain containing "n" repeat units and blocked on amine end by acetic acid,  $[\text{H}_3\text{C} - \text{COOH}]$ .

If the initial concentration of the added acetic acid is " $A_0$ " and its concentration at time " $t$ " is  $A$ , then concentration of the blocked chains would be  $(A_0 - A)$ . Assuming there is no loss of acetic acid, the concentration of various species reactants/functional groups may be expressed as shown in Scheme 5.

$$[-\text{NH}_2] = [P - (A_0 - A)] \quad (4)$$

$$[-\text{COOH}] = [P - (A_0 - A) + (A_0 - A)] = P \quad (5)$$

$P$  is concentration of all chains-blocked or unblocked. The mass balance equations for concentration of caprolactam ( $L$ ), aminocaproic acid ( $P_1$ ), polymer ( $P$ ), cyclic dimer ( $C_2$ ), acetic acid ( $A$ ), and blocked aminocaproic acid ( $P_{1x}$ ) can be written as shown in Table II.



Scheme 5



TABLE II  
Mass Balance Equations for Monoacid Stabilized System

1.	$dL/dt = -k_1LW + k'_1P_1 - k_3L(P - A_0 + A) + k'_3(P - A_0 + A - P_1)$
2.	$dP_1/dt = k_1LW - k'_1P_1 - k_2P_1(2P - A_0 + A) + k'_2W(2P - A_0 + A - P_1) - k_3P_1L + k'_3P_2 - k_2P_1A + k'_2P_{1x}W - 2k_5P_1C_2 + k'_5P_3$
3.	$dP/dt = k_1LW - k'_1P_1 - k_2P(P - A_0 + A) + k'_2W(L_0 - L - P + A_0 - A) + 2k_4WC_2 - k'_4P_2$
4.	$dC_2/dt = -2k_4WC_2 + k'_4P_2 - 2k_5C_2(P - A_0 + A) + k'_5(P - A_0 + A - P_1 - P_2)$
5.	$dA/dt = -k_2A(P - A_0 + A) + k'_2W(A_0 - A)$
6.	$dP_{1x}/dt = k_2AP_1 - k_2WP_{1x} - k_2P_{1x}(P - A_0 + A) + k'_2W(A_0 - A - P_{1x})$

Equations for caprolactam and cyclic dimer are similar to the diacid case.

In polycondensation reaction of monoacid stabilized system,  $-\text{COOH}$  end groups, which are present with all polymer chains  $[P]$ , will react with unblocked  $\text{NH}_2$  groups. The forward rate will be given by  $[k_2P[P - (A_0 - A)]]$  and the backward rate is determined by the concentration of hydrolysable groups given by  $[(L_0 - L) - (P - (A_0 - A))]$ .

In reaction between  $P_1$  and other polymer chains, the  $[-\text{COOH}]$  of  $P_1$  may react with available  $[-\text{NH}_2]$  groups and  $[-\text{NH}_2]$  group of  $P_1$  may react with the available  $[-\text{COOH}]$  groups of the other polymer chains. The disappearance of  $P_1$  can be expressed as  $[k_2P_1(2P - A_0 + A)]$  and backward reaction is possible only at chain ends with either  $[-\text{NH}_2]$  or  $[-\text{COOH}]$  groups and is given by  $[k'_2W(2P - A_0 + A - P_1)]$ .

The  $P_1$  chain may react with the acetic acid to form the blocked  $P_{1x}$  and reformed by the water attack on  $P_{1x}$  associated with the rates  $[-k_2P_1A]$  and  $[k'_2P_{1x}W]$ . The  $P_1$  chain may add to the cyclic dimer at two positions in its structure and form  $P_3$ . The forward and backward rates are given by  $(-2k_5P_1C_2)$  and  $k'_5P_3$  (as only one way), respectively. Acetic acid will react only with the unblocked polymer chains  $[P - (A_0 - A)]$ , associated with the rate  $[-k_2A(P - A_0 + A)]$  and is reformed by the attack of water only on first amide group from the blocked ends of  $P_{1x}$  chains  $(A_0 - A)$  as shown in Scheme 6. In the mass balance equation of  $P_{1x}$  it is formed by the rate  $[k_2AP_1]$  and disappeared by the rate  $[-k'_2WP_{1x}]$ .  $P_{1x}$  may also react with the amino groups  $[P - A_0 + A]$  associated with the rate  $[-k_2P_{1x}(P - A_0 + A)]$  and can be regenerated with the rate  $[k'_2(A_0 - A - P_{1x})W]$ .

### Simulation of isothermal closed batch reactor

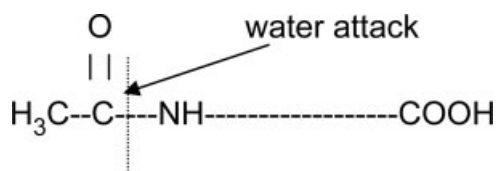
The developed mathematical kinetic models for both monoacid and diacid stabilized system were utilized to investigate the effect of diacid stabilizer on the performance of the polymerization process in comparison to the monoacid stabilizer. For this, three different temperatures were considered in the range 245–265°C with defined initial water concentration in an idealized closed batch reactor. This study was carried out to understand the changes that are brought about in the

reaction kinetics of the two systems. Simulated reactions in a closed isothermal reactor were carried out using the following initial conditions:  $[L] = 8.837$  mol/kg of charged caprolactam;  $[P_1] = 0.0$  mol/kg;  $[W] = 0.22$  mol/kg of charged caprolactam;  $[A_0] = [S_0] = 0.088$  mol/kg of charged caprolactam;  $T = 245, 255, \text{ and } 265^\circ\text{C}$ .

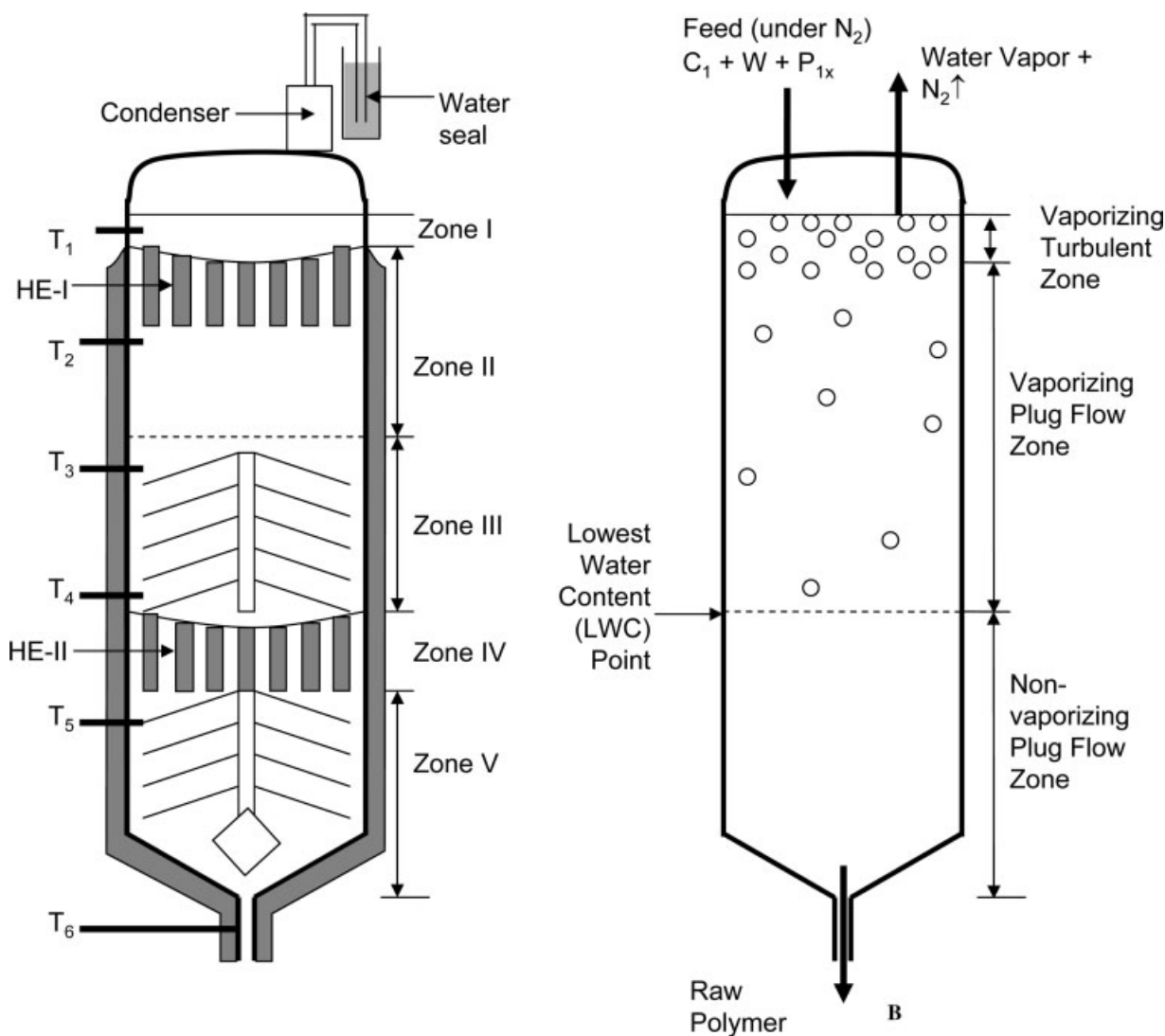
### Simulation of industrial VK tube reactor

The same VK Tube reactor, which was used in our previous study on monoacid catalyzed system,<sup>20</sup> was used for modeling the diacid system. It consisted of five different zones, in each of which the temperature is independently controlled, and thermocouple wells at six locations, where the temperature of reaction mass is measured. A schematic representation of the reactor is given in Figure 1(A). Feed consisting of molten caprolactam, water, and a bifunctional acid is fed under a nitrogen cover at the top of the column. The purged nitrogen is made to escape through a water seal located at the top of the reactor. The reaction mixture in zone I is heated when it passes through the heat exchanger I (HE-I). Thereafter (zone III upper and lower), the melt is heated by the heating jackets and the ongoing exothermic reactions. The temperature of the reaction mass gradually increases from the top surface to the middle zone until the highest temperature ( $T_h$ ) is reached. Thereafter, the temperature is reduced to the final temperature using another heat exchanger and stabilized towards the bottom of the column using a jacket. The products, polymer and unreacted monomer, are removed at the bottom of the reactor.

According to our previous study,<sup>20</sup> VK column reactor could be considered as a reactor consisting of two main zones—vaporizing and nonvaporizing as shown in Figure 1(B) with LWC point at the interface of the two zones. The water content at this point was found to



Scheme 6



**Figure 1** VK reactor: (A) schematic diagram of industrial VK tube reactor depicting the various zones (zones I–V), heat exchangers (HE-1 and HE-2), and temperature measuring points ( $T_1$ – $T_6$ ); (B) VK tube reactor model consisting of three main zones: vaporizing turbulent (top) zone, vaporizing plug-flow zone, and nonvaporising plug-flow zone.

be critical in determining the final properties of the polymer.

Concentration of different species were calculated by solving the set of different mass balance equations given in Tables I and II using the Runge-Kutta-Gills (fourth order) method with a step size of 0.01 h from the start to the end of each polymerization. Polymer properties such as the number-average molecular weight ( $M_n$ ), concentration of end groups ( $[-\text{COOH}]$ ) and ( $[-\text{NH}_2]$ ), and the amount of unreacted caprolactam were calculated.

#### Experimental case studies for diacid stabilized system in VK tube

##### Reaction parameters

The following data were taken as initial conditions (at time = 0.0 h) for all polymerizations in the four case

studies of VK tube:  $[C_1] = 8.837$  mol/kg;  $[P_1] = 0.0$  mol/kg;  $[C_2] = 0.0$  mol/kg; water added =  $[W] = 1.39$  mol/kg of mixture = 2.5 wt % of caprolactam feed; initial temperature = 200°C (assumed).

The initial concentrations of diacid acid fed at the top of the reactor for the four cases are given in Table III.

The water concentration profile from top to bottom of the reactor along with the temperature and pressure profile were determined as per the details given elsewhere.<sup>20</sup> Temperatures along the axis of the reactor were collected for the four different industrial polymerizations. Temperatures of the polymer melt in different zones were calculated as an average of 10–12 values measured at every 2-h interval. The average temperature values are presented in Table III. The pressure profile along the axis of the reactor and the time spent by the reaction mixture in each zone were calculated using the mechanical dimensions and internal design of the reactor.

TABLE III  
Experimental Data Collected from an Industrial VK Tube Reactor for Four Different Polymerization Cases

Parameters/properties <sup>a</sup>	Case 1	Case 2	Case 3	Case 4
Polymerization time (h)	12.049	10.87	12.01	11.67
Diacid charged (mol/kg)	0.0125	0.01239	0.01258	0.005899
Melt temp. (°C)				
$T_1$ (Zone I)	247.1	229.2	247.3	241.2
$T_2$ (Zone II)	247.2	243.8	247.4	241.6
$T_3$ (Zone III upper)	249.4	249.3	249.4	246.8
$T_4$ (Zone III Lower)	272.4	271.8	273.1	270.2
$T_5$ (Zone IV)	257.4	257.3	257.6	257.2
$T_6$ (Zone V)	252.6	253.7	252.7	253.0
Extractables (%)	9.948	10.58	9.948	10.17
$M_n$ (g/mol)	16236.20	15788.4	16236.20	16349.67
[–COOH] (mol/kg)	0.06592	0.06530		0.0600
[NH <sub>2</sub> ] (mol/kg)	0.04083	0.04033	0.04083	0.0471

<sup>a</sup> Polymer properties such as [NH<sub>2</sub>] and [COOH] are for the raw chips at the end of the reaction. Concentrations are per kilogram of caprolactam feed.  $M_n$  is for extracted chips. Melt temperature is the temperature of the polymerization mass at the sensor positions in the respective zones.

#### Properties of the polymer in case studies

Polymer samples at the end of the polymerization were collected in the raw form (i.e., before extraction of monomer) after every 2 h. The collected raw chips were analyzed for amino end groups, carboxylic end groups, and relative viscosity (RV) as per the methods given in the literature.<sup>23</sup> The average values obtained are listed in Table III.

$M_n$  was calculated from the measured raw chips RV by using the following empirical equation.<sup>22</sup>

Number-average Molecular weight

$$M_n = 113.16F(RV - 1) \quad (6)$$

where  $F$  is the constant (107.5) evaluated for the above VK tube for diacid stabilized systems. The  $F$  was esti-

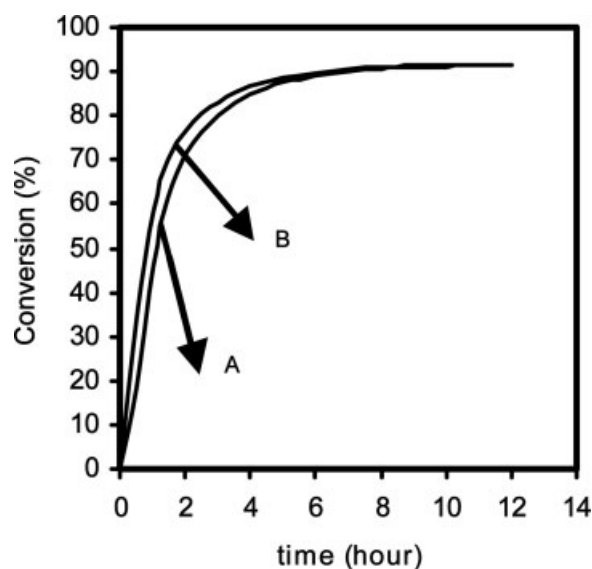


Figure 2 Comparison of conversion with time at 265°C for (A) mono- and (B) diacid stabilized systems in closed isothermal batch reactor.

mated by measuring RV and  $M_n$  for a number of different polymerization cases over a long period of time and deriving the slope as per the above equation.

The percent of extractables is determined by refluxing 15.0 g of raw chips for 8 h in 80 mL of distilled water, and the refractive index was obtained using an immersion refractometer. The percent of extractables was obtained using the standard calibration table of refractive indices for various concentrations of caprolactam.

## RESULTS AND DISCUSSION

### Isothermal closed batch reactor

Before modeling of the VK tube reactor, the effect of the diacid stabilizer in comparison to monoacid stabilizer was investigated in the closed isothermal batch reactor. As expected from the rate equation, the polymerization reactions proceeded at a much higher rate in the diacid

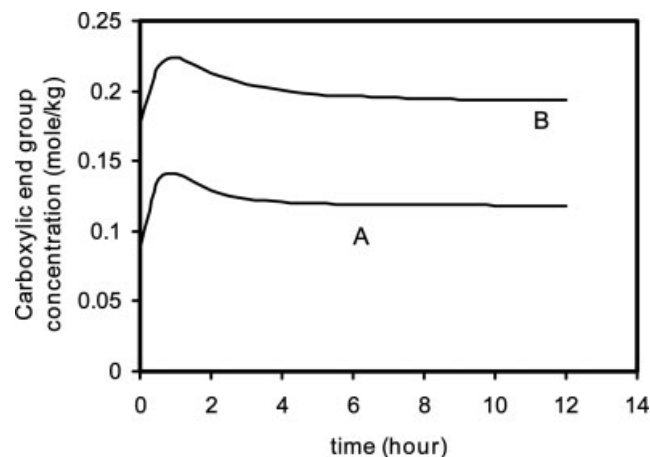
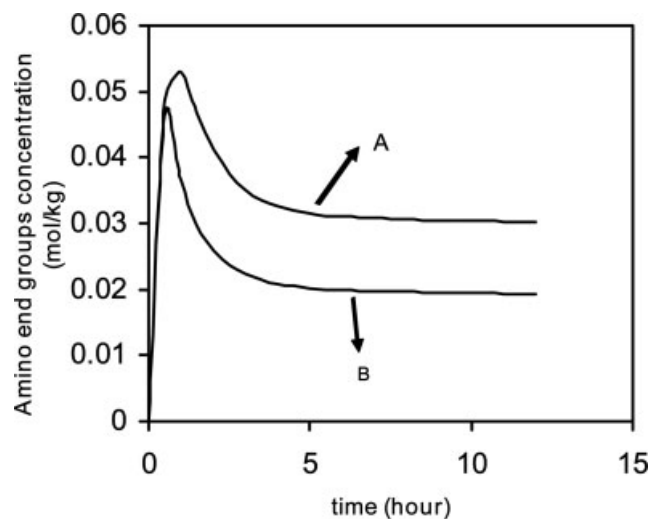


Figure 3 Comparison of total carboxylic end groups with time at 265°C for (A) mono- and (B) diacid stabilized systems in closed isothermal batch reactor.



**Figure 4** Comparison of amino end groups with time at 265°C for (A) mono- and (B) diacid stabilized systems in closed isothermal batch reactor.

catalyzed system due to the presence of the two [—COOH] group in its chemical structure. On the other hand, monoacid has only one [—COOH] group in its chemical structure and therefore, showed lower catalytic activity. It is well known that the carboxylic (—COOH) groups catalyze all the kinetics reactions involved in the polymerization of caprolactam. Though the rates of conversion and molecular weight build up were observed to be higher in the case of diacid stabilized system, both monoacid and diacid worked with equal effectiveness as stabilizers in controlling the molecular weight at the end of the polymerization.

Figures 2–4 show the comparison of the two systems polymerized at 265°C for build up of conversion, carboxylic groups, and amino groups with respect to the reaction time. It can be observed that from the beginning of the reaction, the concentration of the carboxylic end groups in case of diacid stabilized system is higher than the monoacid stabilized system. The difference remains through out the reaction and results in higher catalytic activity for all polymerization reactions

As can be observed from Table IV, in diacid and monoacid, the conversion reached the similar values, which confirmed the fact that conversion is independent of the type or concentration of stabilizer used. How-

ever, molecular weight was a bit higher in diacid-stabilized system. Also, the build up of molecular weight was faster in this system.

The concentration of amino end groups rises faster resulting in a peak occurring earlier to that in monoacid stabilized system. The concentration of amino end groups in case of monoacid stabilized system reaches maximum at about 1.0 h while in case of diacid stabilized system at about 0.5 h. Also, lesser number of amino end groups were obtained in the final polymer in case of diacid-stabilized system due to higher concentration of carboxylic end groups at the equilibrium.

### Industrial VK tube reactor

The study of kinetic models in closed isothermal batch reactor suggests considerably higher reaction rate in case of diacid system. To verify the role of diacid, the developed model was employed to study polymerization in the same industrial VK tube, which was earlier used for the case of monoacid stabilized system.<sup>20</sup> Actual case studies on diacid system were recorded and values compared with the predicted values of the model.

The predicted profile of water in the reactor for Case I using diacid system is shown in Figure 5.

The predicted concentrations of amino and total carboxylic end groups have been plotted for case I in Figures 6 and 7, respectively. The concentrations of both end groups increase rapidly with conversion as the number of chains increases in the reaction, and they reached a maximum at about 2.5–3 h. Thereafter, the concentrations of end groups decrease as the molecular weight increases. At all times, the concentration of the carboxylic end groups was higher than that of the amino end groups because of the presence of unreacted diacid and the chains containing diacid moiety. A comparison of the values at the end of polymerization in Table V shows a high degree of accuracy for the amino and carboxylic end groups.

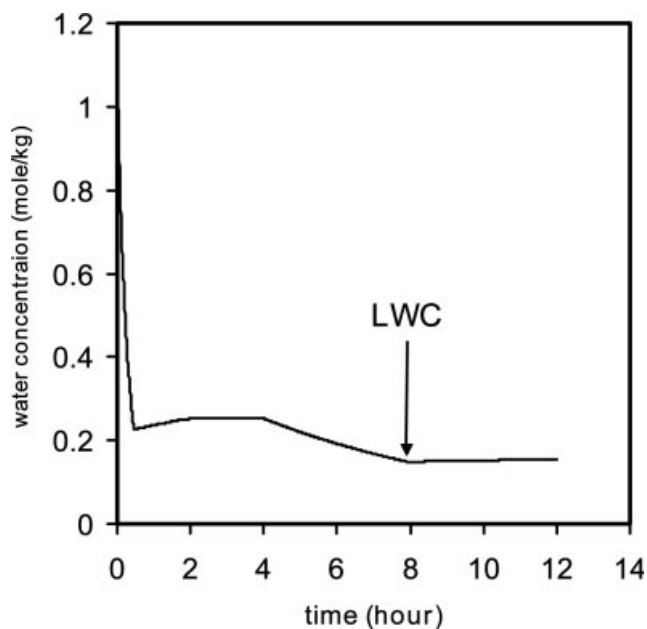
The experimental concentration of extractable is only 9.95%, which is close to the predicted value of the caprolactam concentration of about 8.8% at the end of the reaction (Table V). These values are similar to the monoacid case suggesting that the polymerization is able to

**TABLE IV**  
Comparison of Polymer Properties in a Closed Isothermal Batch Reactor at Equilibrium (More than 16 h)

Properties	245°C		255°C		265°C	
	Monoacid	Diacid	Monoacid	Diacid	Monoacid	Diacid
Conversion (%)	92.75	92.81	92.19	92.26	91.61	91.69
NAMW (Gms/mol)	8215.22	9126.18	8079.98	9011.94	7982.15	8937.68
[NH <sub>2</sub> ] (mol/kg)	0.0256	0.0157	0.0268	0.0164	0.0275	0.0166
<sup>a</sup> [COOH] (mol/kg)	0.1136	0.1917	0.1148	0.1924	0.1155	0.1926

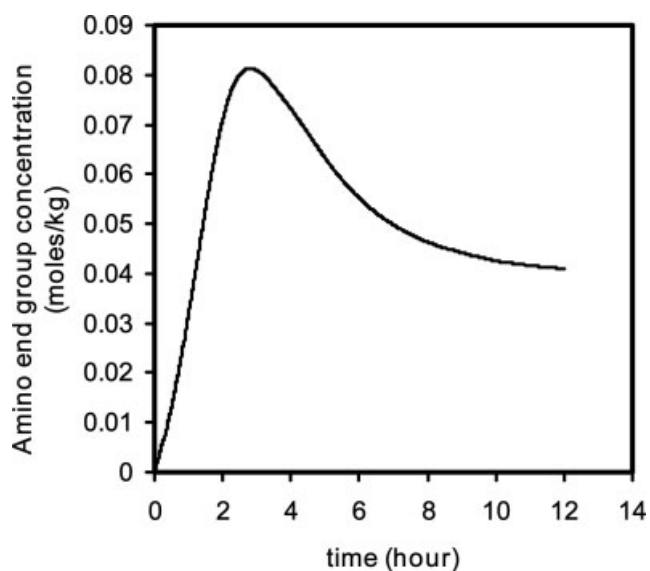
<sup>a</sup> Indicates total concentration of carboxylic end group of both polymer and free acid.





**Figure 5** Predicted profile of water concentration along the reactor axis in VK tube for Case I.

reach equilibrium in a shorter reaction time. Similar to the monoacid case,<sup>20</sup> the experimental values are higher by about 11.65%. If  $C_2$  and  $P_1$  concentrations are added to caprolactam concentration, the error reduces to 9.93%. The other three cases also show a similar trend. The underestimated values are justified by the fact that the experimental extractable contain about 15–20 wt % of cyclic and linear oligomers in addition to unreacted caprolactam, which the current model is incapable of calculating.



**Figure 6** Predicted profile for the concentration of amino end groups in VK tube reactor for Case I.

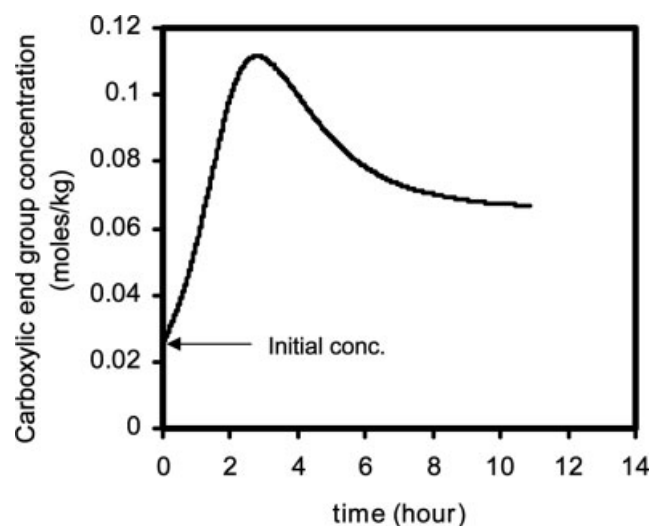
The predicted and experimental values of the number average molecular weight, conversion, and end-group concentrations at the end of reaction are compared in the Table V for the four cases. The calculated values are close to the experimental values with errors ranging from 3.0 to 6.1% for all the four cases. This comparison of the number average molecular weight further supports the accuracy of the model because the experimental values of  $M_n$  were determined by eq. (2), which is based on the measured RV of unextracted polymer chips, and were not calculated using end group concentrations. The results suggest that the kinetic model developed for diacid-stabilized system is reasonable and is capable of estimating polymer properties with high accuracy.

#### Extent of equilibrium in diacid case

The calculation for the extents of the ring-opening, polycondensation, and polyaddition reactions are important in determining whether, for a given set of parameters, the polymerization reaches the desired equilibrium or not. Although it is not necessary to reach an absolute equilibrium in synthesis of nylon-6, near equilibrium conditions are still desirable for a stable system with dependable results. The extent of a reaction can be determined by studying the  $\psi_i$  factor, which is defined for a reaction  $i$  by the expression:

$$\Psi_i = (R_{if} - R_{ib})/R_{if} \quad i = 1, 2, 3 \quad (7)$$

where  $R_{if}$  and  $R_{ib}$  are the forward and backward rates of reaction for a given reaction  $i$ . Reaction reaches equilibrium when  $\psi_i$  factor becomes zero; in other words, when the forward reaction rate becomes equal to the backward reaction rate. The  $\psi_i$  factors for all of



**Figure 7** Predicted profile of concentration of total carboxylic end groups (polymer end group and free diacid) in VK tube reactor for Case I.

TABLE V  
Comparison of Calculated Values with Experimental Values of Polymer Properties for the Four Cases

Properties	Case 1			Case 2			Case 3			Case 4		
	Actual	Model	Error (%)	Actual	Model	Error (%)	Actual	Model	Error (%)	Actual	Model	Error (%)
[NH <sub>2</sub> ] (mol/kg)	0.0408	0.041	0.66	0.0403	0.0418	3.39	0.0408	0.0406	0.56	0.0471	0.0482	2.3
Mn (g/mol)	16236	17032	4.9	15788.4	16765	6.1	16236	17151	5.6	16349	16811	3.0
Extractable (%)	9.948			10.58			9.948			10.17		
C1 (wt%)		8.79	11.65		9.09	14.06		8.80	11.57		8.94	12.08
C1 + C2 + P <sub>1</sub>		8.96	9.93		9.26	12.30		8.97	9.83		9.12	10.32
[COOH] (mol/kg)	0.0659	0.0661	0.27	0.0653	0.0666	0.199		0.0657		0.0600	0.0599	0.16

the major reactions, ring-opening, polycondensation, and polyaddition have been plotted versus reaction time in Figure 8. All the reactions tend to reach equilibrium together at about 7 h. This time is significantly shorter by about 20–25% compared to monoacid stabilized system on the same VK tube reported in our earlier paper.<sup>20</sup> This suggests that the use of diacid increases availability of carboxylic end groups to an extent that a significant difference in overall reaction kinetics is observed for hydrolytic polymerization of  $\epsilon$ -caprolactam.

## CONCLUSIONS

Mathematical kinetic models have been developed for hydrolytic polymerization of  $\epsilon$ -caprolactam for both monoacid and diacid stabilized systems. In developing the models, concentrations of all reacting species have been estimated based on concentration of various end groups (i.e., using end group approach). The models were used to investigate the difference between the kinetics of diacid and monoacid stabilized system in a closed isothermal batch reactor at three different temperatures and constant water concentration condition. Kinetics of all polymerization reactions of diacid stabilized system was found to be significantly higher than those of monoacid stabilized system. This change was attributed to higher catalytic action of diacid stabilizer in comparison to monoacid stabilizer. The developed model for diacid was used for investigating polymerization in an industrial VK tube reactor running on a

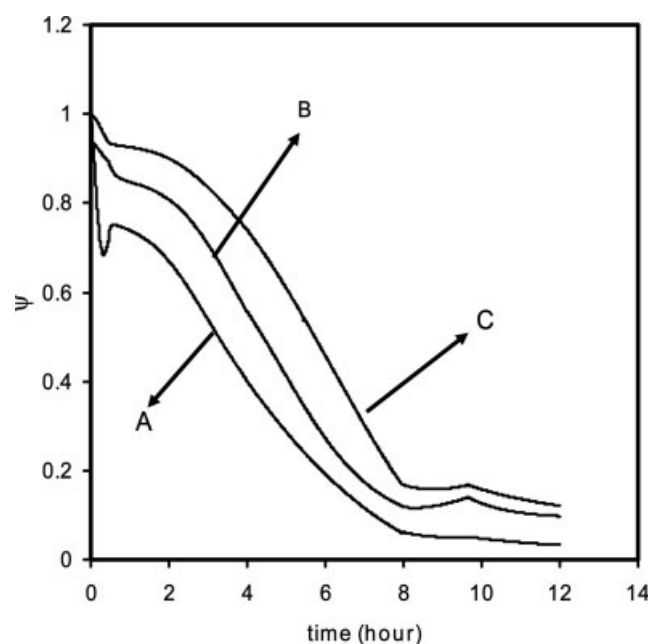


Figure 8  $\psi_i$  factor for the three major reactions versus reaction time for in VK tube reactor Case I: (A) ring-opening reaction, (B) polycondensation reaction, and (C) polyaddition reaction.

diacid stabilizer. The process model used for the VK tube reactor was similar to our earlier study on monoacid system.<sup>20</sup> Because of higher rates of reactions, diacid stabilized system achieved equilibrium faster than monoacid stabilized system and resulted in shorter polymerization time by 20–25%. This study suggests that the use of diacid stabilizers is preferable over monoacid stabilizers because they not only permit introduction of new functional groups in nylon-6 polymer, but also significantly enhance the kinetics of the polymerization reaction.

### NOMENCLATURE

$[A_0]$	Concentration of monofunctional acid at $t = 0$ , mol/kg	$R_{ib}$	rate of the $i$ th backward reaction as described above, mol/(kg h).
$[A]$	Concentration of monofunctional acid at time ' $t$ ', mol/kg	$[S_0]$	concentration of diacid at $t = 0$ , mol/kg
$[C_2]$	Concentration of cyclic dimer, mol/kg	$[S_A]$	concentration of diacid at time ' $t$ ', mol/kg
$F$	Factor for the VK tube	$t$	time of reaction, h
$k_i$	Forward rate constant for $i$ th reaction	$T$	Temperature of the melt, K
$k'_i$	Backward rate constant for $i$ th reaction	$[W]$	Concentration of water, mol/kg
$K_i$	Equilibrium constant for $i$ th reaction	$\psi_i$	ratio of net rate of reaction to the forward rate of reaction for $i$ th reaction
$[L]$	Concentration of caprolactam at time ' $t$ ', mol/kg		
LWC	Lowest water content point in the VK tube reactor		
$[P]$	$\sum_{n=1}^{\infty}$ concentration of polymer, mol/kg		
$[P_1]$	Concentration of aminocaproic acid, mol/kg		
$[P_2]$	Concentration of chain containing two repeat unit, mol/kg		
$[P_3]$	Concentration of chain containing three repeat unit, mol/kg		
$[P_{nx}]$	Concentration of polymer chains blocked by monofunctional acid, mol/kg		
$[Q_n]$	Concentration of polymer chains containing diacid moiety, mol/kg		
$[Q_1]$	Concentration of polymer chain formed when amino end group of $P_1$ react with diacid moiety, mol/kg		
RV	Relative viscosity of raw chips		
$R_{if}$	Rate of the $i$ th forward reaction, where $i = 1, 2, 3$ is for ring-opening, polycondensation and polyaddition reactions, respectively.		

### References

- Reimschuessel, H. K. J Polym Sci Part D: Macromol Rev 1977, 12, 65.
- Tai, K.; Teranishi, H.; Arai, Y.; Tagawa, T. J Appl Polym Sci 1979, 24, 211.
- Tai, K.; Teranishi, H.; Arai, Y.; Tagawa, T. J Appl Polym Sci 1980, 25, 77.
- Reimschuessel, H. K.; Nagasubramanian, K. Chem Eng Sci 1972, 27, 1119.
- Tai, K.; Arai, Y.; Tagawa, T. J Appl Polym Sci 1982, 27, 731.
- Gupta, S. K.; Naik, C. D.; Tandon, P.; Kumar, A. J Appl Polym Sci 1981, 26, 2153.
- Gupta, S. K.; Kumar, A.; Tandon, P.; Naik, C. D. Polymer 1981, 22, 481.
- Kumar, V. S.; Gupta, S. K. Ind Eng Chem Res 1997, 36, 1202.
- Sareen, R.; Gupta, S. K. J Appl Polym Sci 1995, 58, 2357.
- Wajge, R. M.; Rao, S. S.; Gupta, S. K. Polymer 1994, 35, 3722.
- Jacobs, H.; Schweigman, C. Proc 5th Eur/2nd Intl Symp Chem React Eng (Amsterdam) 1972, B7, 1.
- Pal, D.; Gupta, S. K. Polymer 1989, 30, 1918.
- Srivastava, D.; Gupta, S. K. Polym Eng Sci 1991, 31, 596.
- Gupta, S. K.; Tjahjadi, M. J Appl Polym Sci 1987, 33, 933.
- Ramesh, G. M.; Gupta, S. K. Polymer 1993, 34, 1716.
- Gupta, A. Ind J Fibre Text Res 1995, 20, 117.
- Gupta, S. K.; Kumar, A.; Agrawal, K. K. J Appl Polym Sci 1982, 27, 3089.
- Xiao, W.; Huang, N.; Tang, Z.; Filippini-Fantoni, R. Macromol Mater Eng 2003, 288, 235.
- Ahn, Y. C. Polym Eng Sci 1997, 37, 484.
- Agrawal, A. K.; Devika, K.; Manabe, T. Ind Eng Chem Res 2001, 40, 2563.
- Gupta, S. K.; Kumar, A. Reaction Engineering of Step Growth Polymerization; Plenum Press: New York, 1987.
- Manabe, T. In Manufactured Fibre Technology; Gupta, V. B.; Kothari, V. K., Eds.; Chapman & Hall: London, 1997; p 260.
- Vaidya, A. A. Production of Synthetic Fibres; Prentice Hall of India: New Delhi, 1988.