

Effects of Carboxylic Additives on the Polymerization Characteristics of Nylon-6 Reactors with Diffusional Water Removal

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ABSTRACT: The effects of carboxylic acid on the polymerization characteristics of nylon-6 were investigated in reactor models that consist of a continuous-flow stirred tank reactor (CSTR) and a tubular reactor with a diffusional water-removal system, which are connected in series. Mathematical models for the CSTR and the tubular reactor were established and solved by numerical methods. In the CSTR, with an increase of the feed acetic acid content, the monomer conversion, and the molecular weights are increased. In the tubular reactor, the acid behaves like a catalyst and a modifier at the same time in the polymerization of nylon 6. The effects of the feed acetic acid content and the diffusional water removal on the zeroth, first, and second moments and the polydispersity index of the polymer were investigated. The polydispersity index is greatly affected by the feed content of carboxylic acid in the CSTR, but it finally approaches to values of ~ 2 in the tubular reactor. The diffusional water removal is found to have little effect on the polydispersity index of the polymer. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1226–1237, 2001

Key words: nylon 6; reactor; modeling; acid; molecular weight

INTRODUCTION

Significant research in the area of the design and optimization of industrial nylon-6 reactors has been reported in the scientific literature. As a polymer of considerable commercial significance, nylon-6 is produced by water-initiated polymerization of ϵ -caprolactam. Reimschuessel and Nagasubramanian^{1,2} initially suggested the following three major reversible reactions for the mechanism of nylon-6 polymerization: (a) a ring-opening reaction, in which the ring of the monomer, ϵ -caprolactam, is opened by water molecules to form aminocaproic acid; (b) a polycon-

densation reaction in which the amine and carboxylic end-groups react to form large polymer chains via amide linkages, while water forms as a condensation product; and (c) a polyaddition reaction in which monomers add on to the growing polymer chains. Later, Tirrell et al.³ incorporated the reaction with monofunctional acids (modifiers) in their kinetic scheme. Arai and co-workers⁴ coupled the ring-opening and polyaddition reactions of cyclic dimer into the basic reactions of Reimschuessel and Nagasubramanian.^{1,2}

Models of three-stage nylon-6 reactors with intermediate mass transfer were studied by Gupta et al.⁵ by solving the mass-transfer equations numerically. In their study, only the diffusional mass transfer of water through the reaction mass was considered under an isothermal condition.

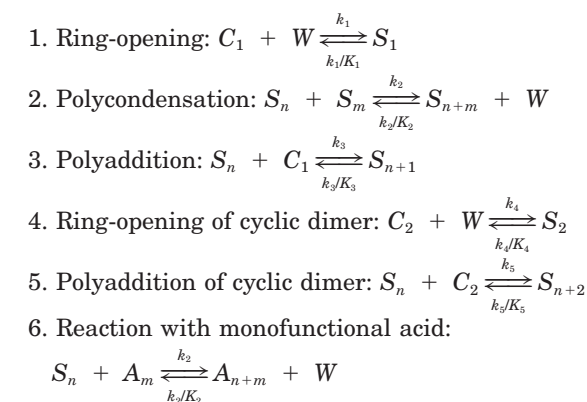
Tai et al.⁶ studied the thermal effects in a plug flow reactor using their kinetic constants. They reviewed the effects of the position of heat exchanger in a commercial VK column reactor on the temperature profile and reactor performance. Gupta and his research group⁷⁻¹¹ published many research articles concerning the polymerization of nylon-6. The research was on the optimum temperature profile of nylon-6 polymerization in a plug flow reactor,⁷ the optimization of the reactor with respect to the controlled degree of polymerization,⁸ the modeling of a countercurrent flow reactor,⁹ the optimization of a reactor with a velocity distribution of the laminar flow,¹⁰ and the modeling of a semibatch nylon-6 reactor.¹¹ Gupta and Gandhi¹² described rigorous models of the VK column using two continuous-flow stirred tank reactors (CSTRs) and one plug flow reactor with recycling and back-mixing. Recently, Ahn¹³ studied the effect of diffusional water removal and heat transfer in a nylon-6 reactor and showed that the interfacial area and temperature are the major factors affecting the degree of polymerization and polydispersity. The same author¹⁴ also modeled the top portion of a commercial atmospheric nylon-6 reactor by a CSTR. He suggested a positive way of saving energy without affecting the reaction characteristics, which is to keep the reaction temperature and the water concentration constant by reducing both the feed water content and the jacket temperature. The nonisothermal models of a CSTR and a plug flow reactor were further combined into one system and used to simulate the commercial VK column and to study its performance.¹⁵

In this study, systems of a CSTR and a tubular reactor connected in series were considered as idealized models of an atmospheric nylon-6 polymerization reactor that is designed to effectively remove the condensation water from reaction mass by diffusion after some initial location. The effects of carboxylic acid and diffusional water removal on the performance of the reactor system were studied under nonisothermal conditions with respect to the molecular weight and its distribution.

PROCESS MODELING

The basic reactions, as briefly mentioned in the Introduction, are coupled together to form a complete reaction system. The kinetic scheme used is

Table I Kinetic Scheme for Nylon-6 Polymerization



C_1 , ϵ -caprolactam; W , water; S_n , polymer of chain length n with amine end-group at one end; A_m , polymer of chain length m with acetyl end-group at one end.

summarized in Table I. The rate constants are those corresponding to the reaction between functional groups. The expressions for the rate constants, equilibrium constants, and moments can be found in the previous literature.^{15,16} Data for the related thermodynamic parameters were given by Arai et al.⁴ The ring opening of ϵ -caprolactam is endothermic since the enthalpy of the linear aminocaproic acid produced is higher than that of ϵ -caprolactam. On the other hand, the ring opening of the cyclic dimer is exothermic since the equilibrium concentration of the cyclic dimer increases with increasing temperature, as observed by Arai et al.⁴

In an atmospheric nylon-6 VK column reactor, the content of water participating in the reaction is determined as follows: An excessive amount of water is added to the reactants and is evaporated by a heat exchanger located at the top of the reactor. The water content that participates in the reaction is determined by Raoult's law according to the temperature of the mixture. The vapor is condensed and refluxed through a condenser located over the top of the reactor. This top portion of the column reactor can be modeled by a CSTR and the remaining portion of the column reactor can be treated as a tubular reactor.^{14,15}

In the tubular reactor part, an idealized two-stage model for contacting inert dry gas with the reaction mass is considered to examine the effect of mass transfer on the polymerization reaction of ϵ -caprolactam. Inert gas bubbles are injected into an intermediate position of the tubular reactor

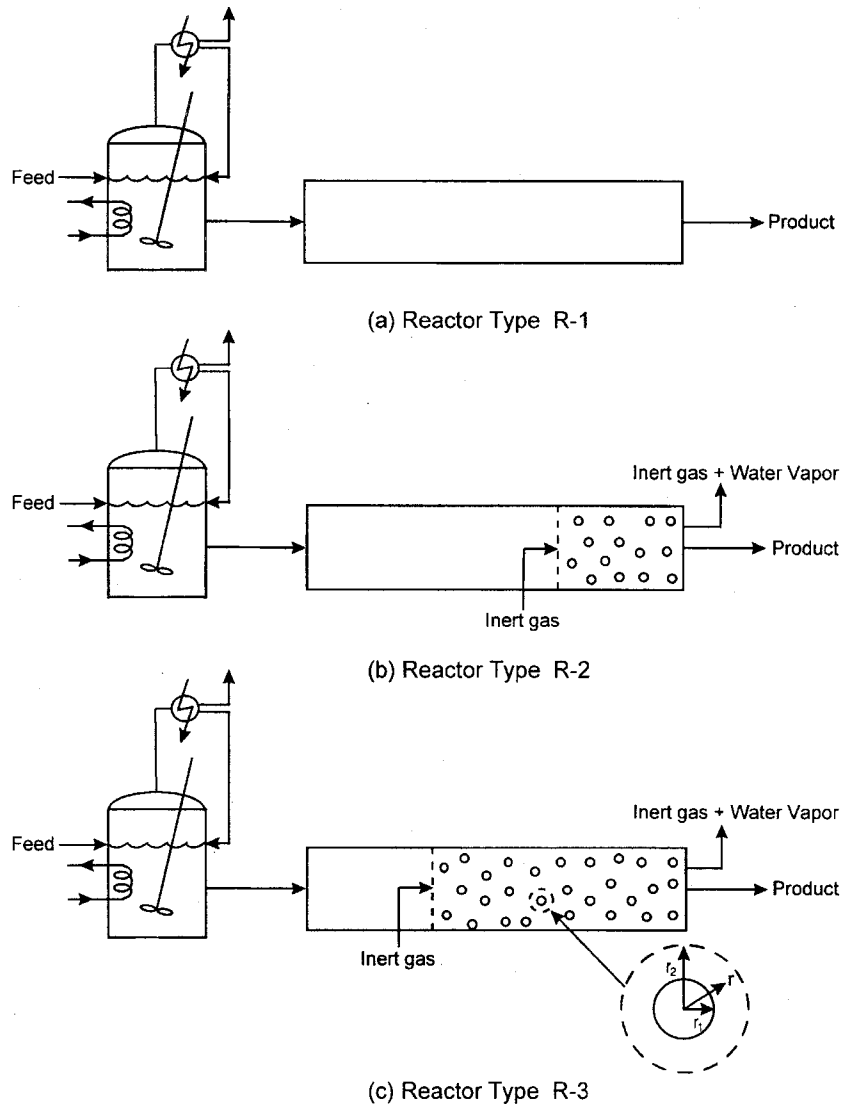


Figure 1 Schematic diagram of the nylon-6 polymerization reactor systems.

and removed at the end position. For analysis, an idealized hollow sphere model is introduced and the average diameter of gas bubbles is selected as the size of the hollow sphere. Three types of tubular reactors are chosen for the analysis: a plug flow reactor without mass transfer, a plug flow reactor with mass transfer starting at the two-third position of the reactor length, and a plug flow reactor with mass transfer starting at the one-third position of the reactor length. These idealized models of the reactor system are schematically described in Figure 1.

In a CSTR, as we briefly mentioned, the equilibrium concentration of water in the liquid phase is determined by Raoult's law. Jacobs and

Schweigman¹⁷ obtained an experimental formula for the water concentration in terms of the temperature as follows:

$$[W] = \frac{1}{1.8} [1.76 - 0.0060(T - 273.15)] \quad (1)$$

where T is the absolute temperature in units of K.

The following expressions for the calculation of density, ρ , and specific heat, c_p , of the reaction mass were reported by Jacobs and Schweigman¹⁷ and was adopted in this study:

$$\rho = 10^3 \{1.0065 + 0.0123[C_1] + (T - 495) \times (0.00035 + 0.00007[C_1])\}^{-1} \quad (2)$$

$$c_p = 1000 \left\{ 2.76 \frac{[C_1]}{[C_1]_0} + \frac{[C_1]_0 - [C_1]}{[C_1]_0} (2.035 + 0.00141T) \right\} \quad (3)$$

where $[C_1]$ denotes the concentration of ϵ -caprolactam and the subscript 0 denotes the feed. The units of ρ and c_p are in kg/m^3 and $\text{J kg}^{-1} \text{K}^{-1}$, respectively.

For the CSTR, the material and energy-balance equations are established and solved by the Newton–Raphson method.¹⁴ For the reactions in Table I, the same rate expressions as in the literature^{14–16} were used in this model. Then, the material and energy balances are set up for the CSTR as follows:

$$F_i - F - F_v = 0 \quad (4)$$

$$F_i[C_1]_i - F[C_1] + \rho VR_{C_1} = 0 \quad (5)$$

$$F_i[W]_i - F[W] - \frac{1000}{18} F_v + \rho VR_W = 0 \quad (6)$$

$$F_i[S_1]_i - F[S_1] + \rho VR_{S_1} = 0 \quad (7)$$

$$F_i[S_c]_i - F[S_c] + \rho VR_{S_c} = 0 \quad (8)$$

$$F_i[C_2]_i - F[C_2] + \rho VR_{C_2} = 0 \quad (9)$$

$$F_i[A_1]_i - F[A_1] + \rho VR_{A_1} = 0 \quad (10)$$

$$F c_p (T_i - T) + F_v c_{pW} (T_i - 373.15) - F_v \Delta H_{\text{vap}} + \rho V \{ (-\Delta H_1)R_1 + (-\Delta H_2)(R_2 + R_6) + (-\Delta H_3)R_3 + (-\Delta H_4)R_4 + (-\Delta H_5)R_5 \} + U^* A^* (T_j - T) = 0 \quad (11)$$

where F_i is the flow rate of the feed [kg/h]; F , the flow rate of the reaction mass [kg/h]; F_v , the flow rate of the vapor [kg/h]; R_j , the rate of formation of the component j or the rate of the reaction j [$\text{mol kg}^{-1} \text{h}^{-1}$]; c_{pW} , the specific heat of water [$\text{J kg}^{-1} \text{K}^{-1}$]; ΔH_{vap} , the latent heat of vaporization [J/kg]; U^* , the overall heat-transfer coefficient [$\text{J h}^{-1} \text{m}^{-2} \text{K}^{-1}$]; A^* , the heat-transfer area [m^2]; T_j , the jacket temperature [K]; and the subscript i , the feed input. S and A are the polymers with amine or acetyl end-groups, respectively. The

summation of $[S]$ and $[A]$ is equal to the carboxylic end-group concentration $[S_c]$, that is:

$$[S_c] = [S] + [A] \quad (12)$$

Equations (1)–(12) constitute simultaneous equations for 12 unknowns, since the linear components $[S_2]$ and $[S_3]$ are related to $[S_1]$ by the following closure condition²:

$$[S_1] = [S_2] = [S_3] \quad (13)$$

and $[C_1]_0$ and $[A]$ are related to F as follows:

$$[C_1]_0 = \frac{[C_1]_i F_i}{F} \quad (14)$$

$$[A] = \frac{[A_1]_i F_i}{F} \quad (15)$$

The simultaneous equations were solved by the Newton–Raphson method for the unknown solution vector

$$\underline{x} = [F, F_v, [C_1], [W], [S_1], [S], [S_c], [C_2], [A_1], T, c_p, \rho]^T \quad (16)$$

Balance equations for the first and second moments have also been established for the CSTR and solved by the Newton–Raphson method¹⁴ to give the degree of polymerization and polydispersity.

For the tubular reactor, the mass and energy balance equations are given in Table II, where D_W is the diffusivity of water molecules in the polymeric reaction mass, and $k/\rho c_p$ ($=\alpha$), the thermal diffusivity. In writing these equations, the following assumptions were made:

1. Only the condensation product, water W , can diffuse. The monomeric and polymeric species do not diffuse.
2. The interfacial water concentration $[W]_1$ at $r = r_1$ is taken to be constant and treated as a parameter.

The equations for the moments μ_ν and μ'_ν ($\nu = 0, 1, 2$) were derived following the same procedure as in the literature.^{15,16} To avoid the hierarchy of equations regarding the components

Table II Mass and Energy-Balance Equations for the Tubular Reactor

$$\begin{aligned} \frac{\partial \mu_0}{\partial t} &= R_{\mu_0}, & \frac{\partial \mu_1}{\partial t} &= R_{\mu_1}, & \frac{\partial \mu_2}{\partial t} &= R_{\mu_2} \\ \frac{\partial \mu'_0}{\partial t} &= 0, & \frac{\partial \mu'_1}{\partial t} &= R_{\mu'_1}, & \frac{\partial \mu'_2}{\partial t} &= R_{\mu'_2} \\ \frac{\partial [C_1]}{\partial t} &= R_{C_1}, & \frac{\partial [C_2]}{\partial t} &= R_{C_2}, & \frac{\partial [S_1]}{\partial t} &= R_{S_1}, & \frac{\partial [A_1]}{\partial t} &= R_{A_1} \\ \frac{\partial [W]}{\partial t} &= D_W \left(\frac{\partial^2 [W]}{\partial r^2} + \frac{2}{r} \frac{\partial [W]}{\partial r} \right) + R_W \\ \frac{\partial T}{\partial t} &= \frac{k}{\rho c_p} \left(\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} \right) + \frac{1}{c_p} [(-\Delta H_1)R_1 + (-\Delta H_2)R_2 \\ &\quad + (-\Delta H_3)R_3 + (-\Delta H_4)R_4 + (-\Delta H_5)R_5 + (-\Delta H_6)R_6] \end{aligned}$$

Boundary Conditions^a:

$$\begin{aligned} t = t_0, r_1 < r \leq r_2: y &= y_0 \\ t_0 < t \leq t_1, r = r_1: \frac{\partial y}{\partial r} &= 0 \\ t_0 < t \leq t_1, r = r_2: \frac{\partial y}{\partial r} &= 0 \\ t \geq t_1, r = r_1: [W] &= [W]_1, \\ \frac{\partial y}{\partial r} &= 0 \text{ for variables other than water} \\ t \geq t_1, r = r_2: \frac{\partial y}{\partial r} &= 0 \end{aligned}$$

^a y denotes temperature or concentration of all the chemical components including water.

$[S_2]$, $[S_3]$, μ_3 , and μ'_3 , the closure condition and the Schultz-Zimm distribution function are introduced.^{15,16,18}

The set of equations in Table II are solved along with the above relations. The boundary conditions required for the systems are shown in the table. When the residence time $t = 0$, the feed enters the feed end of the column reactor, the portion of which is modeled as a CSTR. t_0 is the time when the products from the CSTR enter the tubular reactor, which is equal to the space time of the CSTR. t_1 is the time when the reaction mass starts to contact the inert dry gas bubbles. The equations in Table II are transformed into a finite-difference form by using the forward difference for both the time-derivative and the first-order space-derivative terms and the central difference for the second-order space-derivative terms. These difference equations can be solved explicitly with a time increment Δt of 0.005 h. The spatial increment Δr should satisfy the following convergence criterion.¹⁹

$$\frac{(\Delta r)^2}{(\Delta t)D_W} \geq 4 \quad (17)$$

$$\frac{(\Delta r)^2}{(\Delta t)\alpha} \geq 4 \quad (18)$$

Thus, the radial distance from r_1 to r_2 is divided into 10 equal meshes and each mesh point is numbered from 1 to 11 in an increasing order. The concentrations and temperature are displayed as spatially averaged values in the figures. The spatial averages of the concentrations and temperature are obtained using the following equation:

$$\bar{y} = \frac{3}{r_2^3 - r_1^3} \int_{r_1}^{r_2} y r^2 dr \quad (19)$$

From the solutions of the zeroth, first, and second moments, the number- and weight-average chain lengths and the polydispersity index can be computed.

RESULTS AND DISCUSSION

For the analysis, the size of the reactor was selected in reference to a commercial VK column reactor that is frequently used for nylon-6 polymerization. The reactor is assumed to have a capacity of processing 12 tons per day (= 500 kg/h) based on ϵ -caprolactam. The top portion of the reactor, where a heat exchanger is located, is to be modeled as a CSTR. The volume of this part is assumed to be 0.6 m³ and the heat exchanger located here has the area of 46 m². The overall heat-transfer coefficient of 239.87 J h⁻¹ m⁻² K⁻¹ is assigned as before.⁷ Based on the ϵ -caprolactam consumption, the amount of water to be added is fixed at 4.0 vol % and the amount of acetic acid is varied from 0 to 0.5 vol % with an increment of 0.1 vol %. In units of mol/kg, the concentration of the feed water corresponds to ~ 2.09 mol/kg while the acid concentration ranges from 0 to 0.0821 mol/kg with an interval of ~ 0.0165 mol/kg. The feed and jacket temperatures are set at 85 and at 260°C, respectively. For the process conditions given above, the residence time t_0 of the CSTR is to be ~ 1.06 h as shown in Table III. In the downstream of the reactor, which is modeled as a tubular reactor, inert dry gas

Table III Effects of the Feed Acid Content on the Polymerization in CSTR

Parameter	Feed Acetic Acid Content					
	In [vol %]					
	0.0	0.1	0.2	0.3	0.4	0.5
	In [mol/kg]					
	0.0	0.0165	0.0329	0.0493	0.0657	0.0821
F [kg/h]	501.741	502.360	502.935	503.485	504.020	504.546
F_v [kg/h]	17.867	17.762	17.702	17.666	17.645	17.633
$[C_1]$ [mol/kg]	8.7660	8.4999	8.1846	7.8906	7.6327	7.4100
$[W]$ [mol/kg]	0.1871	0.1865	0.1859	0.1853	0.1848	0.1843
$[S_1]$ [mol/kg]	0.0008	0.0011	0.0012	0.0012	0.0012	0.0012
$[S]$ [mol/kg]	0.0057	0.0176	0.0247	0.0290	0.0316	0.0331
$[S_c]$ [mol/kg]	0.0057	0.0346	0.0588	0.0801	0.0996	0.1181
$[C_2]$ [mol/kg]	0.0000	0.0002	0.0004	0.0006	0.0008	0.0009
$[A_1]$ [mol/kg]	0.0000	0.0163	0.0315	0.0461	0.0602	0.0739
T [°C]	237.21	237.37	237.57	237.75	237.90	238.04
c_p [J kg ⁻¹ K ⁻¹]	2753.0	2752.8	2752.7	2752.5	2752.5	2752.4
ρ [kg/m ³]	885.64	888.32	891.52	894.53	897.20	899.52
μ_1	0.0421	0.2974	0.5732	0.7941	0.9517	1.0547
μ_2	0.5576	9.5420	25.8288	42.7484	56.7334	66.7394
μ'_1	0.0	0.0311	0.0967	0.1967	0.3234	0.4680
μ'_2	0.0	0.5182	3.1571	8.7364	16.9718	27.0818
Conversion [%]	0.46	3.36	6.84	10.09	12.93	15.39
λ_n	7.39	9.49	11.39	12.37	12.80	12.89
λ_w	13.24	30.62	43.27	51.96	57.81	61.62
Polydispersity	1.79	3.23	3.80	4.20	4.52	4.78
t_0 [h]	1.059	1.061	1.064	1.066	1.068	1.070

bubbles are injected into the reaction mass to absorb the moisture. The typical dimension of the inert dry gas bubbles was selected such that the inner radius (r_1) is 0.005 m and the center-to-center distance ($2r_2$) is 0.060 m.

The ring-opening reaction of ϵ -caprolactam forms amine and carboxylic end groups at each end of the molecule. The active site that is chemically attacked by a monomer is the amine end-group. Therefore, to control the degree of polymerization, a monofunctional acid is used to substitute an inactive end group for the active amine end group. In this research, acetic acid was chosen for the monofunctional acidic catalyst and its effect on the polymerization of nylon-6 was investigated.

As for the CSTR, the calculated results for the given process conditions are summarized in Table III in view of the effects of the feed acid content on the polymerization characteristics. The results shows that although the feed acid content is in-

creased from 0 to 0.5 vol % the reactor temperature does not change much from 237°C and the water concentration remains at ~ 0.18 mol/kg. However, the conversion is greatly affected by the feed acid content that is shown to increase from 0.46 to 15.39%. The number- and weight-average chain lengths also change as a function of the feed acid content. For the given range of the feed acid concentration, the number-average chain length increases from 7.39 to 12.89, and the weight-average chain length, from 13.24 to 61.62. As a result, in CSTR, the polydispersity index increases from 1.79 to 4.78 as the feed acid content is increased in the given range. Thus, in CSTR, it can be said that the conversion and the oligomer characteristics are greatly affected by the feed acid content.

The reaction mass from the CSTR continue to flow into the tubular reactor systems where the reactions will propagate further to form macromolecules. The interfacial concentration of water

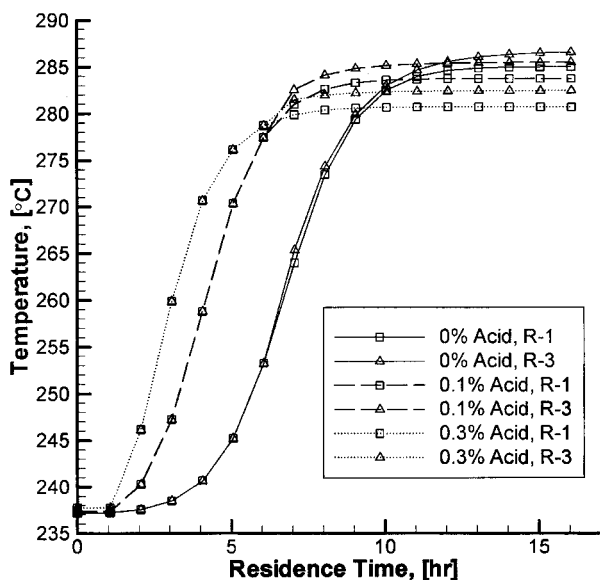


Figure 2 Temperature profiles in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

is assumed to be 0.088 mol/kg (= 0.001 mol/mol-caprolactam) based on the discussions of Gupta et al.⁵ The diffusivity of water in the reaction mass, D_w , is taken to be 0.9×10^{-4} m²/h as reported by Nagasubramanian and Reimschuessel²⁰ and the thermal conductivity of the reaction mass, k , is taken to be 691.24 J h⁻¹ m⁻¹ K⁻¹, assuming that the reaction mass consists of 90% of nylon-6 and 10% of ϵ -caprolactam at 285°C.

The temperature profiles of the reactor systems are shown in Figure 2. The residence time in the figure spans over the entire reactor model including the CSTR and the tubular reactor. Therefore, the residence time t_0 of the CSTR can be identified to be about 1 h and the time location t_1 of the inert gas injection in the tubular reactor about 6 h for the reactor type R-3. Since the acetic acid has a carboxylic end group which promotes the initiation of polymerization in an autocatalytic manner, the temperature profiles are shifted upstream with the addition of the acetic acid. On the other hand, the peak temperature is lowered as the feed acid content is increased since the acid behaves also like an inhibitor to chain growth. The removal of water by diffusion results in the temperature increase, since, by reducing the water concentration, it breaks the equilibrium and promotes the polycondensation reaction that is exothermic.

In Figure 3, we can see that the addition of

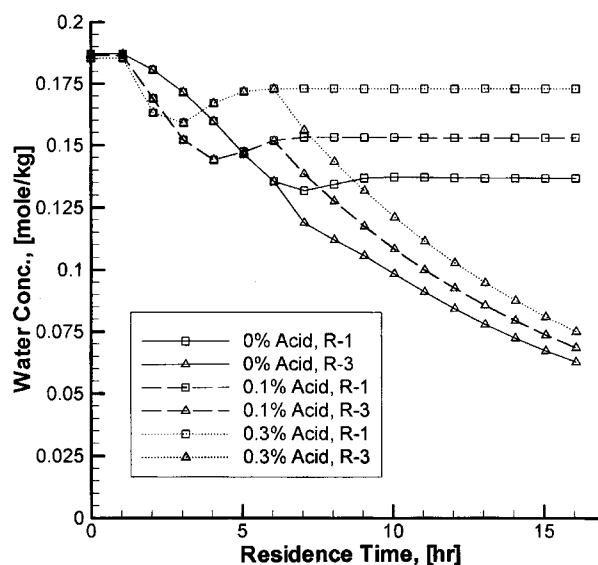


Figure 3 Profiles of the water concentration in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

acetic acid promotes consumption of water in the earlier step of polymerization, but the water concentration increases later. This is also due to the dual characteristics of the acetic acid, that is, a catalyst and a modifier. In the earlier step, the

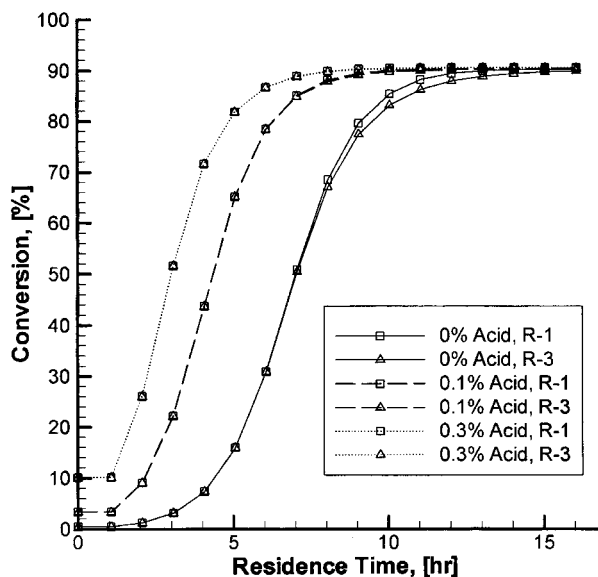


Figure 4 Profiles of the monomer conversion in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

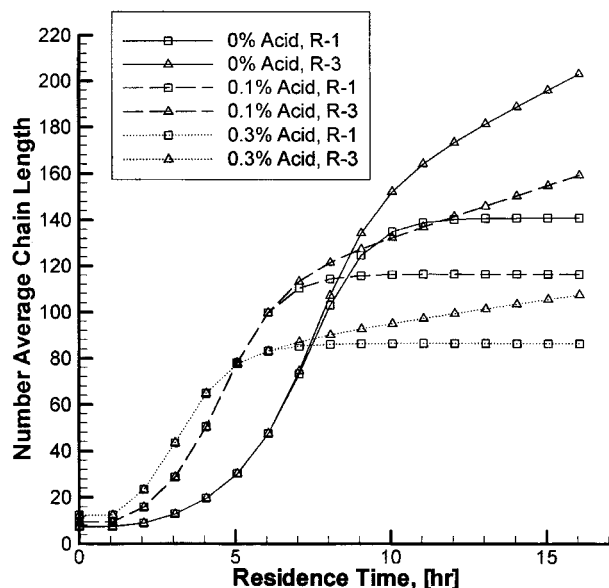


Figure 5 Profiles of the number-average chain length in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

acid promotes a ring-opening reaction where the water molecule is consumed, while in the later step a termination reaction dominates, where water is produced as a by-product. As a result, the conversion is increased in the earlier step by the

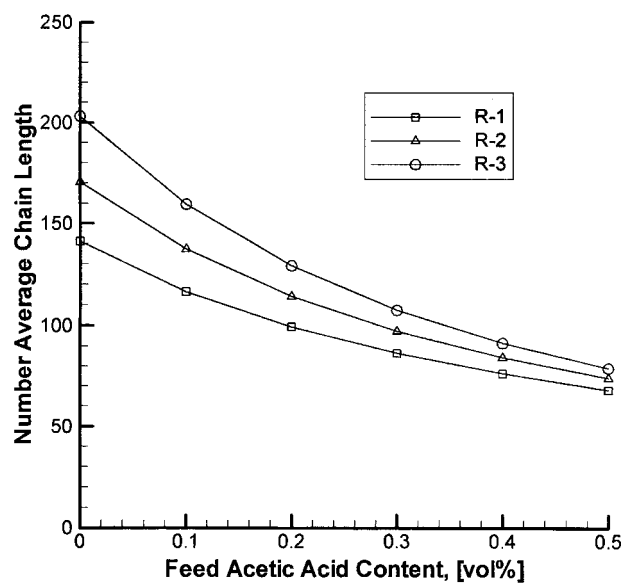


Figure 6 Number-average chain length expressed as functions of the feed acid content and the diffusional water removal.

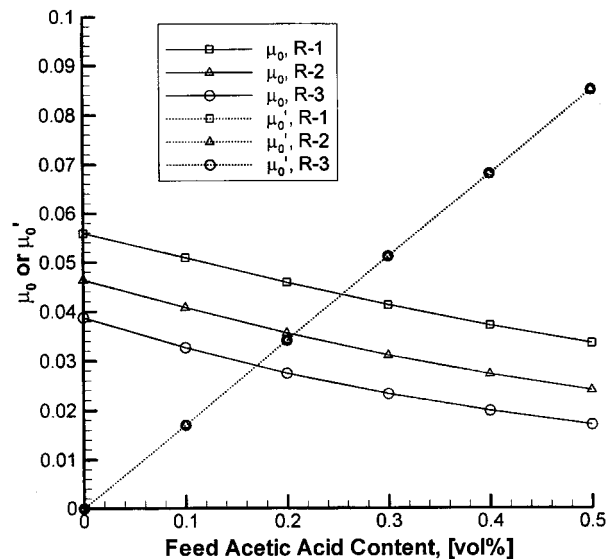


Figure 7 Zeroth moments of the polymers expressed as functions of the feed acid content and the diffusional water removal.

addition of acetic acid as can be seen in Figure 4. However, the final conversion is not much affected by the addition of acetic acid. The diffusional removal of water with the inert gas dramatically decreases the water concentration, but its influence on the monomer conversion is negligible. Thus, regardless of the addition of acetic acid and the diffusional removal of water, the equilibrium conversion of the monomer remains at $\sim 90\%$.

In Figures 5 and 6, it is shown that the number-average chain length becomes smaller as the feed acid content is increased. On the other hand, the number-average chain length increases with the diffusional water removal. Therefore, by a combination of the feed acetic acid content and the diffusional water removal, we can easily modify the end-groups of the polymer without affecting the number-average molecular weight.

To investigate the effects of the feed acid content and the diffusional water removal on the polymer characteristics, the zeroth, first, and second moments of the polymers are plotted in Figures 7–12. It is shown in Figure 7 that the zeroth moment of the polymer with the amine end-group, μ_0 , is decreased by both the addition of acetic acid and the application of diffusional water removal. As can be expected from the structure of acetic acid, the zeroth moment of the polymer with the acetyl end-group, μ'_0 , is increased

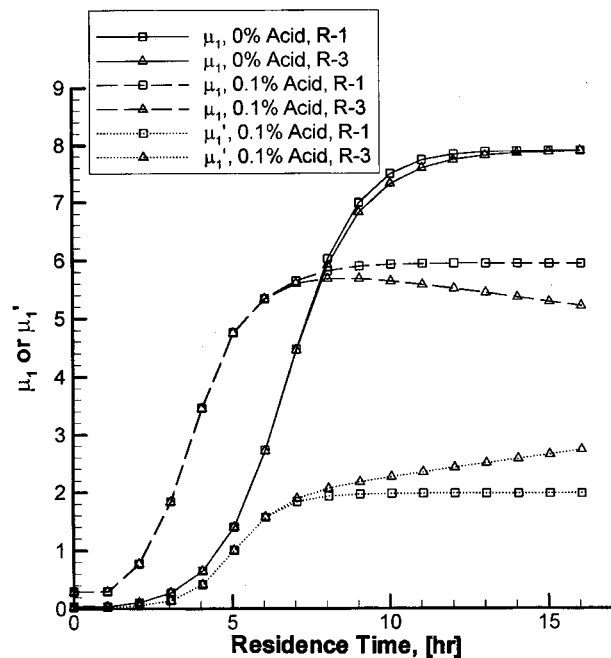


Figure 8 Profiles of the first moments of the polymers in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

linearly by the addition of acetic acid. However, it remains unaffected by diffusional water removal. This is due to the stabilizing effect that is assigned to the polymer by the acetyl end-group.

When the acetic acid is not added, the first moment of the polymer with the amine end-group, μ_1 , is not very sensitive to the diffusional water removal, as shown in Figures 8 and 9. Since the first moment of the polymer means the total chain length, it will not be affected by the polycondensation reaction induced from the water removal. However, when acetic acid is added, μ_1 is decreased as the diffusional water removal is applied, while the first moment of the polymer with the acetyl end-group, μ_1' , is increased. If water is removed, the equilibrium shifts to the forward direction of the polycondensation reaction and the reaction with monofunctional acid [Eqs. (2) and (6) in Table I]. The polycondensation reaction does not affect the total chain length of the polymer whether the polymer has an amine end-group or an acetyl end-group and, as a result, not the first moments either. The reaction that is responsible for the changes of the first moments of the polymer is the reaction with monofunctional acid. In that reaction, the polymer with the amine end-group disap-

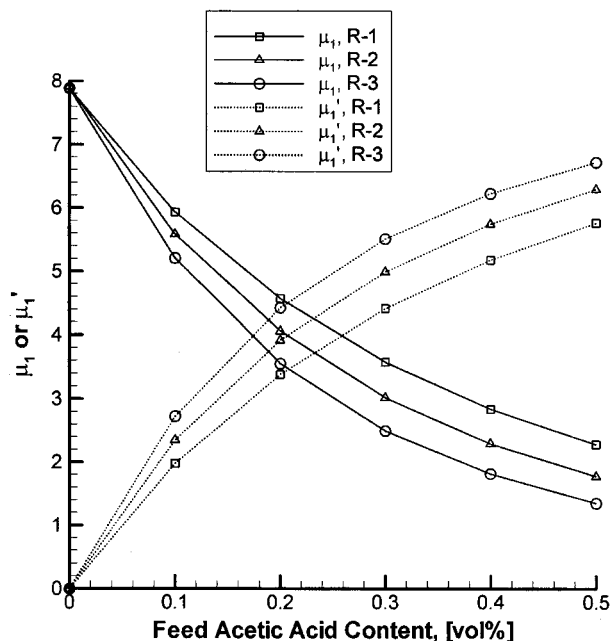


Figure 9 First moments of the polymers expressed as functions of the feed acid content and the diffusional water removal.

pears while the polymer with the acetyl end-group gets as much chain length as that of the disappeared polymer with the amine end-group.

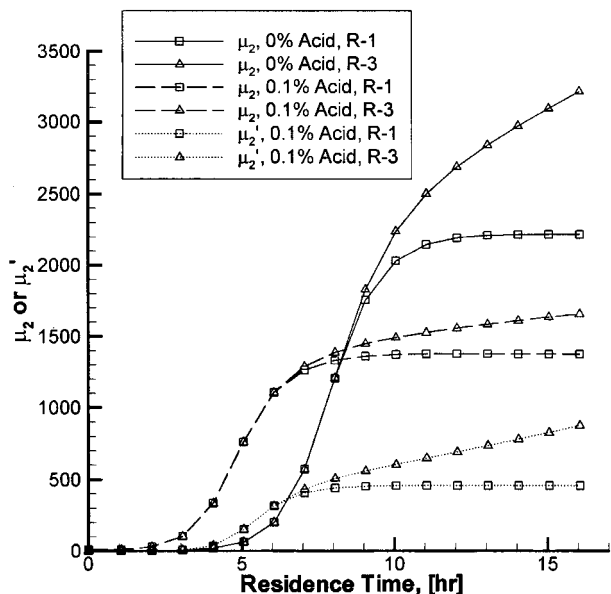


Figure 10 Profiles of the second moments of the polymers in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

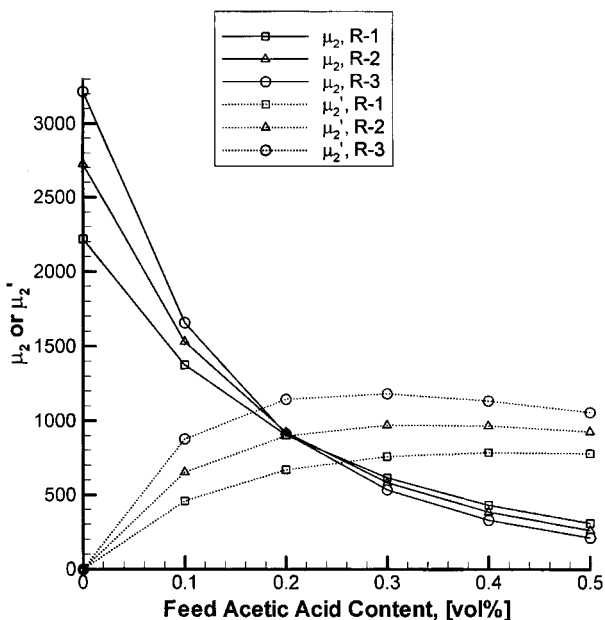


Figure 11 Second moments of the polymers expressed as functions of the feed acid content and the diffusional water removal.

Regardless of the addition of acetic acid, the second moment of the polymer with the amine end-group, μ_2 , is sensitive to the diffusional water removal as shown in Figure 10. It is more interesting to see in Figure 11 that when the feed acid content is less than 0.2 vol %, μ_2 is increased by the diffusional water removal, while when the feed acid content is more than 0.2 vol %, μ_2 is decreased by the diffusional water removal. This is because the polycondensation reaction is relatively more important than is the reaction with monofunctional acid when the feed acid content is less than 0.2 vol % and vice versa. It is also interesting to see that the sensitivity of μ_2 on the moisture content is relatively high when the feed acid content is below 0.2 vol %. The second moment of the polymer with the acetyl end-group, μ_2' , is increased with the application of diffusional water removal when acetic acid is added. This is also because a shift of the equilibrium to the forward direction produces a larger molecular weight polymer with an acetyl end-group, as can be expected from eq. (6) in Table I.

The effects of the feed acid content and the diffusional water removal on the polydispersity index were studied. Profiles of the polydispersity index are shown in Figure 12. At the beginning of the polymerization, in the CSTR, the polydispersity

index is greatly affected by the feed concentration of the acetic acid. It shows values in the range of 1.79–4.78 when the feed acid content is varied from 0 to 0.5 vol %. The increase in the polydispersity index with the acid content is due to the catalytic effect of the acid for the ring-opening and polyaddition reaction. However, as the reaction mass continues to flow through the tubular reactor, the reaction propagates further and then termination by polycondensation will dominate. Thus, irrespective of the feed acid content, the polydispersity indices drop sharply and approach to a value of ~ 2 , which is commonly recognized as the equilibrium value for nylon-6. The figure shows that reducing the moisture content with an inert dry gas does not affect the polydispersity index. Therefore, as far as the polydispersity index of nylon-6 is concerned, both the feed acid and the water content in the reaction mass are not important factors.

CONCLUSIONS

The effects of carboxylic acid on the polymerization characteristics of nylon-6 were numerically investigated in model reactor systems that consist of series connections of a CSTR and a tubular reactor with a diffusional water-removal system.

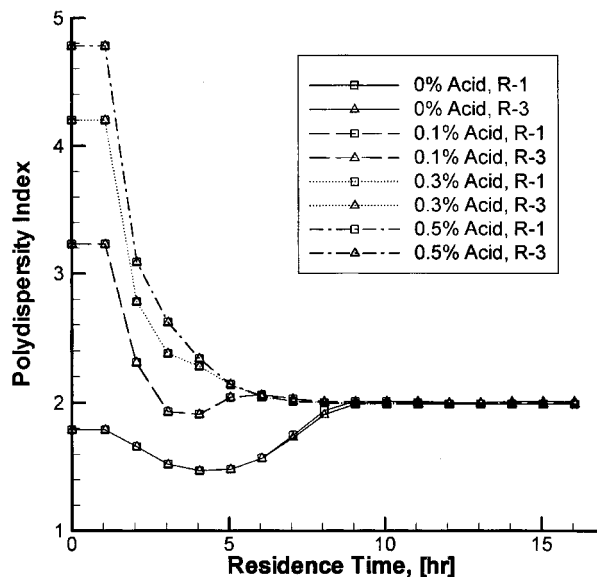


Figure 12 Profiles of the polydispersity index in the polymerization reactor systems obtained for the various feed acid contents with or without diffusional water removal.

In the CSTR, the monomer conversion and the molecular weights increase as the feed acid content is increased. The acid behaves both as a catalyst and as a modifier for the polymerization reaction. Therefore, as the feed acid content is increased, the temperature profile in the tubular reactor is shifted toward upstream and the maximum temperature is lowered. The removal of water had an effect of a temperature increase since it breaks the equilibrium and promotes the polycondensation reaction. The effects of the feed acid content and the diffusional water removal on the zeroth, first, and second moments of the polymers were discussed together with the effects on the polydispersity of the polymer. The moments of the polymers were greatly affected by both the feed acid content and the diffusional water removal. In the CSTR, the polydispersity index is also shown to be greatly affected by the feed concentration of the acetic acid, but approaches to a value of ~ 2 as the polymerization continues further in the tubular reactor. The diffusional water removal has little effect on the polydispersity of the polymer.

NOMENCLATURE

A	molecules with acetyl end-group
A_1	acetic acid
A_m	polymer of chain length m with acetyl end-group
A^*	heat-transfer area for CSTR [m^2]
C_1	ϵ -caprolactam
C_2	cyclic dimer
c_p	specific heat of reaction mixture [$\text{J kg}^{-1} \text{K}^{-1}$]
c_{pW}	specific heat of water [$\text{J kg}^{-1} \text{K}^{-1}$]
D_W	diffusivity of water through the polymeric reaction mass [m^2/h]
F	flow rate of reaction mass [kg/h]
F_i	flow rate of feed [kg/h]
F_v	flow rate of water vapor [kg/h]
ΔH_i	change of enthalpy for reaction i [J/mol]
ΔH_{vap}	latent heat of water vaporization [J/kg]
k	thermal conductivity of the reaction mass [$\text{J h}^{-1} \text{m}^{-1} \text{K}^{-1}$]
k_i	rate constant for reaction i [$\text{kg mol}^{-1} \text{h}^{-1}$]
K_i	equilibrium constant for reaction i
r_1	radius of inert dry-gas bubbles [m]
r_2	half of a center-to-center distance of neighboring inert dry gas bubbles

R_j	rate of formation of component j or rate of reaction j [$\text{mol kg}^{-1} \text{h}^{-1}$]
S	molecules with amine end-group
S_1	aminocaproic acid
S_2	linear dimer
S_c	molecules with carboxylic end-group
S_n	polymer of chain length n with amine end-group
t	residence time [h]
t_0	space time of the CSTR or residence time at the entrance to the tubular reactor [h]
t_1	residence time when the reaction mass starts to contact with inert dry gas bubbles [h]
T	temperature [K]
T_J	jacket temperature [K]
U^*	overall heat transfer coefficient [$\text{J h}^{-1} \text{m}^{-2} \text{K}^{-1}$]
W	water
y	temperature or concentration of all the chemical components
[]	concentration [mol/kg]

Greek Letters

α	thermal diffusivity [m^2/h]
ρ	density [kg/m^3]
μ_ν	ν -th moment of polymer with amine end-group
μ'_ν	ν -th moment of polymer with acetyl end-group
λ_n	number-average chain length or degree of polymerization
λ_w	weight-average chain length or degree of polymerization
δ	polydispersity index

Subscripts

i	feed input
m, n	number of repeating units in a chain molecule
o	feed concentration based on reaction mass
v	vapor

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