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A NUMERICAL STUDY ON THE EFFECTS OF ACIDIC CATALYST ON THE POLYMERIZATION OF NYLON-6

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Abstract – The effects of acetic acid on the polymerization characteristics of nylon-6 are investigated in a reactor model that consists of a continuous flow stirred tank reactor (CSTR) and a tubular reactor connected in series. Mathematical models for the CSTR and the tubular reactor have been established and solved by numerical methods. In the CSTR, the monomer conversion and the molecular weights are increased as the feed acetic acid concentration is increased. In the tubular reactor, the acid acts as both a catalyst and a modifier for the polymerization reaction. The effects of the feed acetic acid content on the zeroth, first and second moments and the polydispersity index of the polymer have been discussed.

Key words : Acid, Nylon-6, Polymerization, Modeling, CSTR, Tubular Reactor

INTRODUCTION

Significant research in the area of 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 et al. [1972, 1977] initially suggested the following three major reversible reactions for the mechanism of the nylon-6 polymerization : (a) ring opening reaction, in which the ring of the monomer, ε-caprolactam, is opened by water molecules to form aminocaproic acid ; (b) polycondensation reaction in which the amine and carboxylic end-groups react to form large polymer chains via amide linkages, with water formed as a condensation product ; (c) polyaddition reaction in which monomer adds on to the growing polymer chain. Later, Tirrell et al. [1975] incorporated the reaction with monofunctional acid (modifier) in their kinetic scheme. Arai and co-workers [1981] have coupled the ring-opening and polyaddition reaction of cyclic dimer into Reimschuessel et al.'s basic reactions. A better set of rate constants for nylon-6 polymerization has been obtained by them.

Gupta et al. [1982] studied the design of three-stage nylon-6 reactors with intermediate mass transfer by solving the mass transfer equations numerically. Their study considered only the diffusional mass transfer of water through the reaction mass. Tai et al. [1983] used their kinetic constants data to simulate the thermal effects for a plug flow reactor. They reviewed the effects of the position of the heat exchanger on the temperature profile and the reactor performance for a commercial VK-column reactor. In particular, the research group led by S. K. Gupta has published many research papers concerning the polymerization of nylon-6. Among them are researches on the optimum temperature profile of nylon-6 polymerization in a plug flow reactor [Ramagopal et al., 1983], optimization of the reactor with respect to the controlled degree of polymerization [Ray and Gupta, 1986], modelling of a counter-current flow reactor [Gupta and Tjahjadi, 1987], optimization of a reactor with velocity distribution of laminar flow [Srivastava and Gupta, 1991] and modelling of a semi-batch nylon-6 reactor [Gupta and Gupta, 1992]. Recently, Ahn [1997a] 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. Ahn [1997b] also modelled the top portion of a commercial atmospheric nylon-6 reactor by a continuous flow stirred tank reactor. He showed that keeping the reaction temperature and the water concentration constant by reducing both water content in the feed and jacket temperature is a positive way of saving energy without affecting the reaction characteristics.

Two types of commercial reactors are used for nylon-6 polymerization : pressurized and atmospheric. In a pressurized reactor, a suitable amount of water is mixed together with reactants and the mixture is fed to the reactor under a pressurized condition. On the other hand, in an atmospheric reactor more than a sufficient amount of water is mixed with reactants and fed to the reactor where, according to Raoult's law, only the equilibrated amount of water participates in the reaction and the excess water is vented out as vapor. Therefore, the top portion of the atmospheric reactor can be modelled by a continuous flow stirred tank reactor because of the mixing effects caused by boiling of the excess water.

In this study, the nylon-6 polymerization reactor that is operated under atmospheric pressure is to be modelled as a continuous flow stirred tank reactor and a tubular reactor connected in series ; the effect of acetic acid on the performance of the reactor system will be studied in terms of the molecular

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Table 1. Kinetic scheme for nylon-6 polymerization

1. Ring opening : $C_1 + W \underset{k_1/K_1}{\overset{k_1}{\rightleftarrows}} S_1$
2. Polycondensation : $S_n + S_m \underset{k_2/K_2}{\overset{k_2}{\rightleftarrows}} S_{n+m} + W$
3. Polyaddition : $S_n + C_1 \underset{k_3/K_3}{\overset{k_3}{\rightleftarrows}} S_{n+1}$
4. Ring opening of cyclic dimer : $C_2 + W \underset{k_4/K_4}{\overset{k_4}{\rightleftarrows}} S_2$
5. Polyaddition of cyclic dimer : $S_n + C_2 \underset{k_5/K_5}{\overset{k_5}{\rightleftarrows}} S_{n+2}$
6. Reaction with monofunctional acid : $S_n + A_m \underset{k_2/K_2}{\overset{k_2}{\rightleftarrows}} A_{n+m} + W$

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

weight and its distribution.

PROCESS MODELLING

The basic reactions, as briefly mentioned in the **Introduction**, are coupled together to form a complete reaction system. The kinetic scheme used is summarized in Table 1. The rate constants are those corresponding to the reaction between functional groups. The polymerization reaction is well described by an autocatalytic reaction, and the forward reaction rate constant k_i (i=1, 2, 3, 4, 5) is expressed in terms of the acid end-group concentration (in g-mole/kg mixture) as

$$k_i = k_i^0 + k_i^c \left(\sum_{n=1}^{\infty} [S_n] + \sum_{m=1}^{\infty} [A_m] \right) \equiv k_i^0 + k_i^c (\mu_0 + \mu_0') \tag{1}$$

where $[S_n]$ is the concentration of polymer of chain length n with amine end-group, $[A_m]$ is the concentration of polymer of chain length m with acetyl end-group, μ_0 is the zeroth moment of polymers with amine end-group, and μ_0' is the zeroth moment of polymers with acetyl end-group. The ν-th moments of polymers are generally expressed by

$$\mu_\nu = \sum_{n=1}^{\infty} n^\nu [S_n] \tag{2}$$

$$\mu_\nu' = \sum_{m=1}^{\infty} m^\nu [A_m] \tag{3}$$

The values of ν are 0, 1, 2, and 3 for the eight different kinds of moments used in the formulation. k_i and k_i^0 have units of kg/mol-hr, while k_i^c has units of kg^2/mol^2-hr. Both k_i^0 and k_i^c are functions of temperature expressed by an Arrhenius-type relation as follows :

$$\ln k_i^* = \ln A_i^* - \frac{E_i^*}{RT} \tag{4}$$

where superscript $*$ is to be replaced by 0 or c for each corresponding rate constant. A and E are the frequency factor and the activation energy, respectively. R is the gas constant and T is the absolute temperature expressed in units of K. The equilibrium constant, K_i, is similarly given as a function of temperature :

$$\ln K_i = \frac{\Delta S_i}{R} - \frac{\Delta H_i}{RT} \tag{5}$$

Here, ΔS and ΔH denote the change of entropy and enthalpy, respectively. Values of A_i^*, E_i^*, ΔS_i and ΔH_i for the various reactions have been given by Arai et al. [1981] and are summarized in Table 2. The ring opening of ε-caprolactam is endothermic since the enthalpy of linear aminocaproic acid produced is higher than that of ε-caprolactam. On the other hand, the ring opening of cyclic dimer is exothermic since the equilibrium concentration of cyclic dimer increases with increasing temperature as observed by Arai et al. [1981].

In the polymerization of nylon-6, the content of water participating in the reaction is determined in two ways. One is to add an adequate amount of water into the reactants in the mixing stage considering the desired degree of polymerization. The other is to add an excessive amount of water into the reactants and evaporate the excess water by heating the mixture to the desired temperature. Then, the water content that participates in the reaction is determined by Raoult's law according to the temperature of the mixture. The former method is adopted in a pressurized reactor, while the latter is a method used in an atmospheric reactor. In the latter, a heat exchanger is located at the top portion of an atmospheric reactor so that the reaction mixture is heated to the boiling point and the vapor is condensed and refluxed by a condenser located over the top of the reactor. This will increase the efficiency of mixing and promote the ring opening reaction of ε-caprolactam with sufficient amount of water at the initial stage of polymerization. This top portion of the reactor can be modelled by a continuous flow stirred tank reactor (CSTR) and the remaining portion of the reactor can be treated as a tubular reactor [Ahn, 1997b].

Thus, in the top portion that is to be modelled by a CSTR, the equilibrium concentration of water in liquid phase is determined by Raoult's law. Jacobs and Schweigman [1972] obtained the water concentration by experiment as follows.

Table 2. Kinetic constants and thermodynamic constants

i	A_i^0	E_i^0	A_i^c	E_i^c	ΔS_i	ΔH_i
1	5.9874×10^{5}	1.9880×10^{4}	4.3075×10^{7}	1.8806×10^{4}	-7.8846×10^{0}	1.9180×10^{3}
2	1.8942×10^{10}	2.3271×10^{4}	1.2114×10^{10}	2.0670×10^{4}	9.4374×10^{-1}	-5.9458×10^{3}
3	2.8558×10^{9}	2.2845×10^{4}	1.6377×10^{10}	2.0107×10^{4}	-6.9457×10^{0}	-4.0438×10^{3}
4	8.5778×10^{11}	4.2000×10^{4}	2.3307×10^{12}	3.7400×10^{4}	-1.4520×10^{1}	-9.6000×10^{3}
5	2.5701×10^{8}	2.1300×10^{4}	3.0110×10^{9}	2.0400×10^{4}	5.8265×10^{-1}	-3.1691×10^{3}

Dimensions : A^0 $[kg\cdot mol^{-1}\cdot hr^{-1}]$; A^c $[kg^2\cdot mol^{-2}\cdot hr^{-1}]$; E $[cal\cdot mol^{-1}]$; ΔS [eu] ; ΔH $[cal\cdot mol^{-1}]$

$$[W] = \frac{1}{1.8}[1.76 - 0.0060(T - 273.15)] \tag{6}$$

where T is the absolute temperature expressed in units of K.

The following expressions for the calculation of density, ρ, and specific heat, c_p, of reaction mass have been reported by Jacobs and Schweigman [1972] and adopted in this study.

$$\rho = 10^3\{1.0065 + 0.0123[C_1] + (T - 495)(0.00035 + 0.00007[C_1])\}^{-1} \tag{7}$$

$$c_p = 238.09\left(2.76\frac{[C_1]}{[C_1]_0} + \frac{[C_1]_0 - [C_1]}{[C_1]_0}(2.035 + 0.00141T)\right) \tag{8}$$

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

For the part of CSTR, the analysis has been performed by establishing the material and energy balance equations and solving them by Newton-Raphson method [Ahn, 1997b]. The reaction rates in the model are expressed in terms of concentrations as follows.

$$R_1 = k_1[C_1][W] - k_1'[S_1] \tag{9}$$

$$R_2 = k_2[S]^2 - k_2'([C_1]_0 - [C_1] - 2[C_2] - [S])^*[W] \tag{10}$$

$$R_3 = k_3[C_1][S] - k_3'([S] - [S_1]) \tag{11}$$

$$R_4 = k_4[C_2][W] - k_4'[S_2] \tag{12}$$

$$R_5 = k_5[C_2][S] - k_5'([S] - [S_2] - [S_1]) \tag{13}$$

$$R_6 = k_2[S][A] - k_2'([C_1]_0 - [C_1] - 2[C_2] - [S])^*[W] \tag{14}$$

Here, the subscript 0 means initial value and superscript $*$ means a part of the total amide group concentration that belongs to polymers with amine or acetyl end-groups. S and A are polymers with amine and acetyl end-groups, respectively. The summation of [S] and [A] is equal to the carboxylic end-group concentration $[S_c]$, that is,

$$[S_c] = [S] + [A] \tag{15}$$

The material and energy balances have been set up for the CSTR as follows.

$$F_i - F - F_v = 0 \tag{16}$$

$$F_i[C_1]_i - F[C_1] + \rho V(-R_1 - R_3) = 0 \tag{17}$$

$$F_i[W]_i - F[W] - \frac{1000}{18}F_v + \rho V(-R_1 + R_2 + R_6 - R_4) = 0 \tag{18}$$

$$\begin{aligned} F_i[S_1]_i - F[S_1] &+ \rho V(R_1 - 2k_2[S][S_1] + 2k_2'([S] - [S_1])[W] \\ &- k_3[S_1][C_1] + k_3'[S_2] - k_5[S_1][C_2] + k_5'[S_3] - k_2[S_1][A] \\ &+ k_2'([A] - [A_1])[W]) = 0 \end{aligned} \tag{19}$$

$$F_i[S_c]_i - F[S_c] + \rho V(R_1 - (R_2 + R_6) + R_4) = 0 \tag{20}$$

$$F_i[C_2]_i - F[C_2] + \rho V(-R_4 - R_5) = 0 \tag{21}$$

$$F_i[A_1]_i - F[A_1] + \rho V(-k_2[S][A_1] + k_2'([A] - [A_1])[W]) = 0 \tag{22}$$

$$\begin{aligned} Fc_p(T_i - T) &+ F_v c_{pW}(T_i - 373.15) - F_v \Delta H_{vap} \\ &+ \rho V\{(-\Delta H_1)R_1 + (-\Delta H_2)(R_2 + R_6) \\ &+ (-\Delta H_3)R_3 + (-\Delta H_4)R_4 + (-\Delta H_5)R_5\} \\ &+ U^*A^*(T_J - T) = 0 \end{aligned} \tag{23}$$

where F_i is the flow rate of feed [kg/hr], F the flow rate of reaction mass [kg/hr], F_v the flow rate of vapor [kg/hr], c_{pW} the specific heat of water [cal/kg·K], ΔH_{vap} the latent heat of vaporization [cal/kg], U^* the overall heat transfer coefficient [cal/hr·m^2·K], A^* the heat transfer area [m^2], T_J the jacket temperature [K], and the subscript i means the feed. The above balance Eqs. (16)-(23), and Eqs. (6)-(8) and Eq. (15) constitute twelve simultaneous equations for twelve unknowns, since the linear components $[S_2]$ and $[S_3]$ are related to $[S_1]$ by the following closure condition [Reimschuessel, 1977],

$$[S_1] = [S_2] = [S_3] \tag{24}$$

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

$$[C_1]_0 = \frac{[C_1]_i F_i}{F} \tag{25}$$

$$[A] = \frac{[A_1]_i F_i}{F} \tag{26}$$

The simultaneous equations have been solved by Newton-Raphson method for the unknown solution vector

$$\underline{x} = [F, F_v, C_1, W, S_1, S, S_c, C_2, A_1, T, c_p, \rho]^T \tag{27}$$

The balance equations for the first and second moments can also be established for the CSTR and solved by Newton-Raphson method [Ahn, 1997b].

The mass and energy balance equations for the tubular reactor are given in Table 3, where μ_v and μ_v' (v=0, 1, 2, 3) are the v-th moments of polymers defined by Eqs. (2) and (3). The balance equations for the moments μ_v and μ_v' (v=0, 1, 2) can be obtained through differentiation with respect to time of the following relations

$$\mu_v = \left.\frac{\partial^v D(z, t)}{\partial(\ln z^{-1})^v}\right|_{z=1} \tag{28}$$

$$\mu_v' = \left.\frac{\partial^v F(z, t)}{\partial(\ln z^{-1})^v}\right|_{z=1} \tag{29}$$

where D(z, t) and F(z, t) are the z-transforms defined by

$$D(z, t) = \sum_{n=1}^{\infty} z^{-n}[S_n] \tag{30}$$

$$F(z, t) = \sum_{m=1}^{\infty} z^{-m}[A_m] \tag{31}$$

The differential equations governing the time change of D and F are first obtained from Eqs. (30) and (31) by using exact expressions of $\partial[S_n]/\partial t$ and $\partial[A_m]/\partial t$. These equations are subsequently differentiated using Eqs. (28) and (29) in order to obtain the balance equations for the various moments. In order to break the hierarchy of equations regarding the components $[S_2]$, $[S_3]$, μ_3 and μ_3', the closure condition and the Schultz-Zimm distribution function are introduced. The closure condition is expressed by Eq. (24). According to the properties of the Schultz-

Table 3. Mass and energy balance equations for tubular reactor model

$$R_1 = k_1[W][C_1] - k_1'[S_1]$$

$$R_2 = k_2\mu_0^2 - k_2'[W](\mu_1 - \mu_0)$$

$$R_3 = k_3[C_1]\mu_0 - k_3'(\mu_0 - [S_1])$$

$$R_4 = k_4[W][C_2] - k_4'[S_2]$$

$$R_5 = k_5[C_2]\mu_0 - k_5'(\mu_0 - [S_1] - [S_2])$$

$$R_6 = k_2\mu_0\mu_0' - k_2'[W](\mu_1' - \mu_0')$$

$$\frac{\partial \mu_0}{\partial t} = R_1 - R_2 + R_4 - R_6$$

$$\frac{\partial \mu_1}{\partial t} = R_1 + R_3 + 2R_4 + 2R_5 - k_2\mu_1\mu_0' + k_2'[W]\frac{\mu_2' - \mu_1'}{2}$$

$$\begin{aligned}\frac{\partial \mu_2}{\partial t} &= R_1 + 2k_2\mu_1^2 + \frac{k_2'}{3}[W](\mu_1 - \mu_3) + k_3[C_1](\mu_0 + 2\mu_1)\\ &\quad + k_3'(\mu_0 - 2\mu_1 + [S_1]) + 4R_4 + 4k_5[C_2](\mu_0 + \mu_1)\\ &\quad + 4k_5'(\mu_0 - \mu_1 + [S_2]) - k_2\mu_2\mu_0' + k_2'[W]\frac{2\mu_3' - 3\mu_2' + \mu_1'}{6}\end{aligned}$$

$$\frac{\partial \mu_0'}{\partial t} = 0$$

$$\frac{\partial \mu_1'}{\partial t} = k_2\mu_1\mu_0' - \frac{k_2'[W]}{2}(\mu_2' - \mu_1')$$

$$\frac{\partial \mu_2'}{\partial t} = k_2(2\mu_1\mu_1' + \mu_2\mu_0') - k_2'[W]\frac{4\mu_3' - 3\mu_2' - \mu_1'}{6}$$

$$\frac{\partial [C_1]}{\partial t} = - R_1 - R_3$$

$$\frac{\partial [C_2]}{\partial t} = - R_4 - R_5$$

$$\begin{aligned}\frac{\partial [S_1]}{\partial t} &= R_1 - 2k_2[S_1]\mu_0 + 2k_2'[W](\mu_0 - [S_1]) - k_3[S_1][C_1] + k_3'[S_2]\\ &\quad -k_5[S_1][C_2] + k_5'[S_3] - k_2[S_1]\mu_0' + k_2'[W](\mu_0' - [A_1])\end{aligned}$$

$$\frac{\partial [A_1]}{\partial t} = - k_2[A_1]\mu_0 + k_2'[W](\mu_0' - [A_1])$$

$$\frac{\partial [W]}{\partial t} = - R_1 + R_2 - R_4 + R_6$$

$$\begin{aligned}\frac{\partial T}{\partial t} &= \frac{1}{c_p}[(-\Delta H_1)R_1 + (-\Delta H_2)R_2 + (-\Delta H_3)R_3\\ &\quad + (-\Delta H_4)R_4 + (-\Delta H_5)R_5 + (-\Delta H_6)R_6]\end{aligned}$$

k' (=k/K)=backward reaction constants

Zimm distribution function, the following relations can be derived [Tai et al., 1980]:

$$\mu_3 = \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0} \tag{32}$$

$$\mu_3' = \frac{\mu_2'(2\mu_2'\mu_0' - \mu_1'^2)}{\mu_1'\mu_0'} \tag{33}$$

The set of differential equations in Table 3 is solved along with the above relations. The tubular reactor has been assumed to be a plug flow reactor with adiabatic insulation, in which the initial condition is

$$t = t_0 : y = y_0 \tag{34}$$

where y denotes concentrations of chemical components or temperature, and the subscript 0 denotes the entrance to the tubular reactor. The t_0 is the time the reactants from the CSTR enter the tubular reactor, which is equal to the space time of the CSTR. The differential equations in Table 3 can be solved explicitly using Euler method with a time increment Δt of 0.005 hr.

From the zeroth, first and second moments solved, the number- and weight-average chain lengths are computed as follows:

$$\lambda_n = \frac{\mu_1 + \mu_1'}{\mu_0 + \mu_0'} \tag{35}$$

$$\lambda_w = \frac{\mu_2 + \mu_2'}{\mu_1 + \mu_1'} \tag{36}$$

Then, the polydispersity index, δ, is given by

$$\delta = \frac{\lambda_w}{\lambda_n} \tag{37}$$

RESULTS AND DISCUSSION

For the analysis, the size of the reactor has been selected in reference to a commercial reactor that is frequently used for nylon-6 polymerization. It has the scale of producing 12 tons per day (=500 kg/hr) based on ε-caprolactam with volume of 0.6 m^3 for the top portion where the reactants are mixed by boiling. The top portion has a heat exchanger, the heat transfer area of which has been assumed to be 46 m^2. This top portion can be modelled by a continuous flow stirred tank reactor. Based on ε-caprolactam consumption, the amount of water to be mixed with ε-caprolactam is set to be 4.0 vol% and the amount of acetic acid is set to range from 0 to 0.5 vol%. The feed and jacket temperatures are set to be 85 °C and 260 °C, respectively. The remaining part of the reactor can be assumed to be a plug flow reactor that does not have a heat exchanger. Thus, the whole reactor has been modelled by series of a CSTR and a plug-flow reactor as shown schematically in Fig. 1.

Nylon-6 that is produced by a ring-opening reaction of ε-caprolactam has both amine and carboxylic end-groups at each end of the chain. The amine end-group is known to be the site that is attacked by monomer. Therefore, in order to control the degree of polymerization, monofunctional acid such as acetic acid is used to substitute an acetyl end-group for the amine end-group. In this research, acetic acid has been chosen as the acidic catalyst and its effect on the polymerization of nylon-6 has been investigated.

As for the CSTR, the calculated results for the given process conditions are summarized in Table 4 in terms of the effects of acetic acid content on the polymerization characteristics. The temperature is maintained at about 237 °C and the water concentration is slightly more than 0.18 mole/kg.

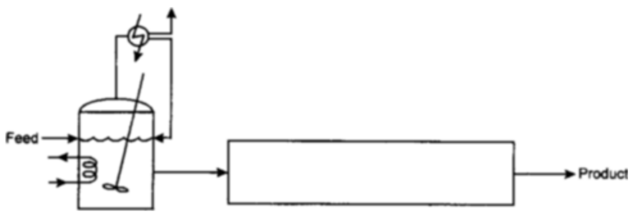

Fig. 1. Schematic diagram of the nylon-6 polymerization reactor system.

Table 4. Effects of acetic acid content on the polymerization reaction in CSTR

Feed acetic acid content, [vol%]	0.0	0.1	0.2	0.3	0.4	0.5
F, [kg/hr]	501.741	502.360	502.935	503.485	504.020	504.546
F_v, [kg/hr]	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, [cal/kg·K]	657.14	657.10	657.06	657.03	657.01	656.99
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

The conversion increases from 0.46 to 15.39% as the feed acetic acid content is increased from 0 to 0.5 vol%. The number average and weight average chain lengths are also affected by the feed acetic acid content. The number average chain length increases from 7.39 to 12.89 and the weight average chain length increases from 13.24 to 61.62 as the feed acetic acid content is increased. As a result, we can see that in the CSTR the polydispersity increases from 1.79 to 4.78 as the feed acetic acid content is increased from 0 to 0.5 vol%. It can be said that in the CSTR the conversion and the polymer characteristics are greatly affected by acetic acid content.

The reactants from the CSTR flow into the tubular reactor where polymerization reactions proceed further to complete. The temperature profiles of the reactor system are shown in Fig. 2. The acid promotes initiation of the polymerization and shifts the temperature profiles toward upstream. This is because the acetic acid has a carboxylic end-group that behaves like a catalyst in an autocatalytic reaction according to Eq. (1). On the other hand, the maximum temperature is lowered compared to that obtained without acid since the acid also acts as a modifier to prohibit chain growth. In Fig. 3, we can

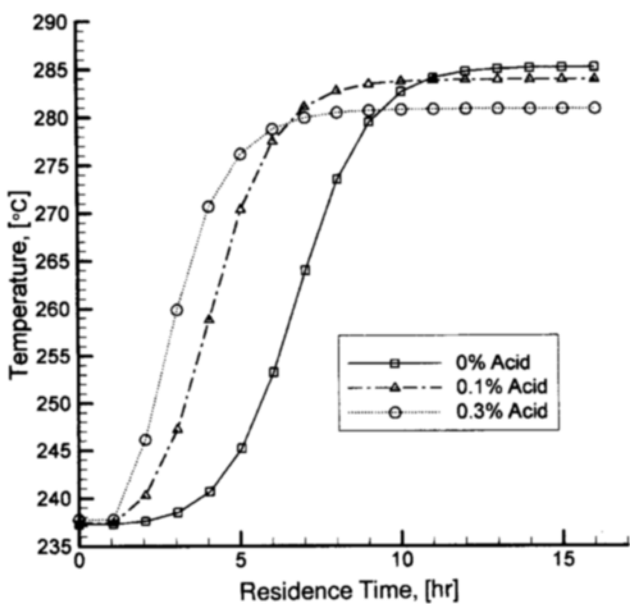

Fig. 2. Effects of the feed acetic acid content on the temperature profiles of the polymerization reactor system.

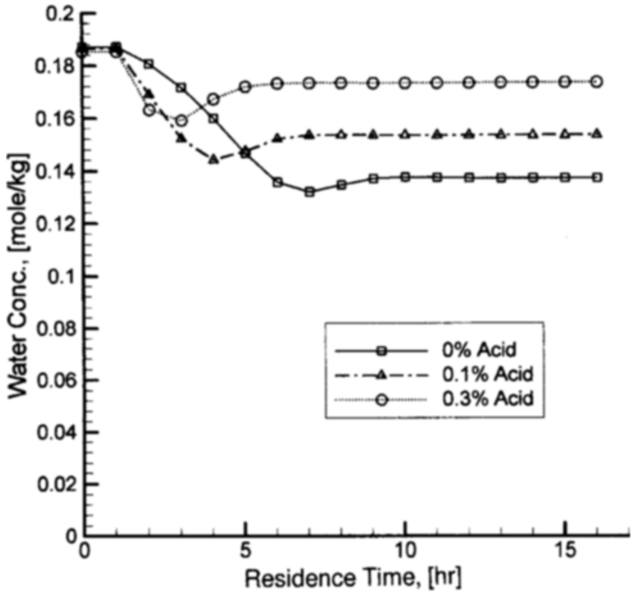

Fig. 3. Effects of the feed acetic acid content on the profiles of water concentration for the polymerization reactor system.

see that the addition of acetic acid promotes consumption of water at the earlier stage of polymerization, but it eventually increases the water concentration. This is related to the dual characteristics of the acetic acid both as a catalyst and as a modifier. That is, at the earlier stage the acid promotes a ring-opening reaction which consumes water, while at the later stage the termination reaction prevails and produces water as a by-product. As a result, the conversion is increased by addition of acetic acid at the earlier stage, as can be seen in Fig. 4. However, the equilibrium conversion is about 90% regardless of the acid concentration.

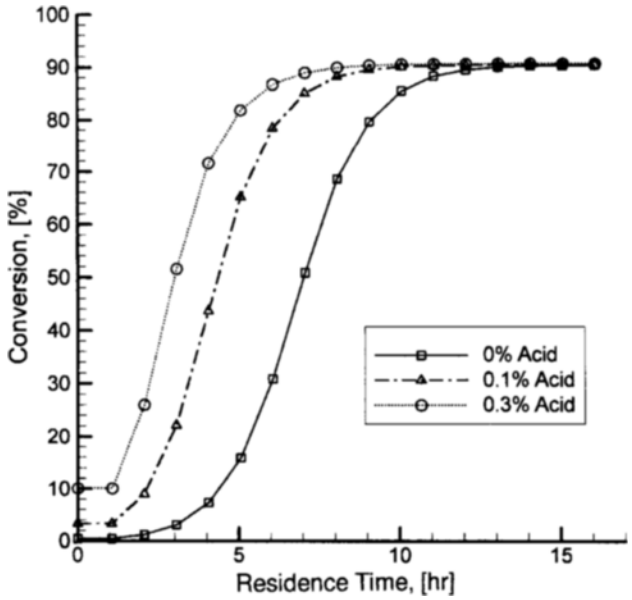

Fig. 4. Effects of the feed acetic acid content on the profiles of monomer conversion for the polymerization reactor system.

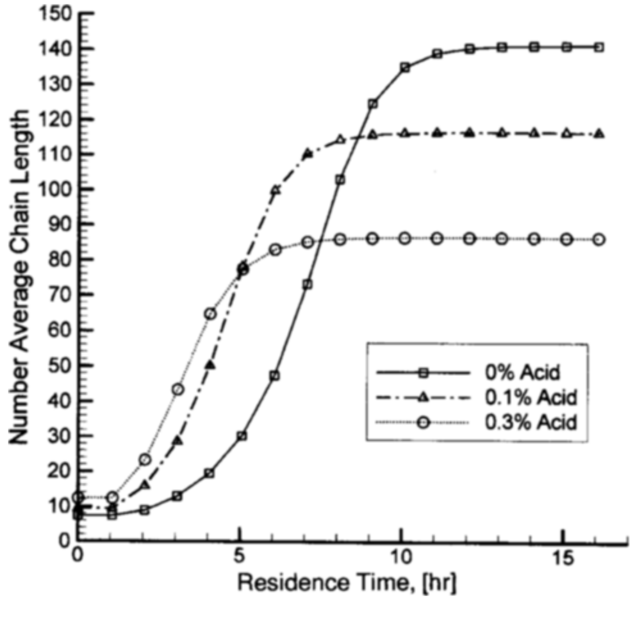

Fig. 5. Effects of the feed acetic acid content on the profiles of number average chain length for the polymerization reactor system.

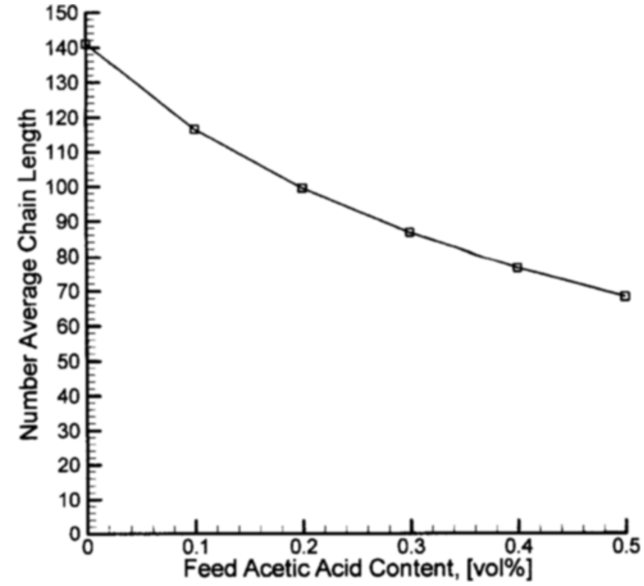

Fig. 6. Effects of the feed acetic acid content on the number average chain length of the polymers.

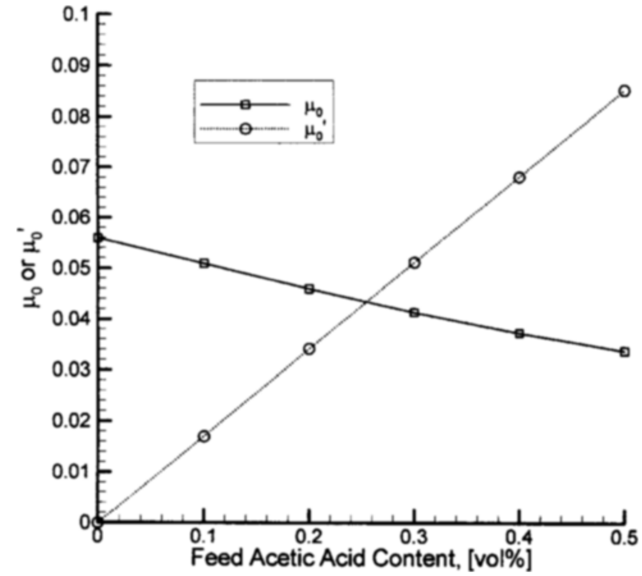

Fig. 7. Effects of the feed acetic acid content on the zeroth moments of the polymers.

Since acetic acid acts like a prohibitor for chain growth, we can expect a lowered chain length with addition of the acid in the feed. This can be seen in Figs. 5 and 6, where the number average chain length becomes lower as the feed acetic acid content is increased.

The effects of the feed acetic acid content on the zeroth, first, and second moments are shown in Figs. 7-9. The zeroth moment of the polymer with amine end-group, μ_0, is decreased by the addition of acetic acid. However, the zeroth moment of the polymer with acetyl end-group, μ_0', is increased linearly by the addition of acetic acid. The first and second moments of the polymers have the similar trends as the zeroth moment.

The polydispersity index changes with time as shown in Fig. 10. In the CSTR, the polydispersity index is greatly affected by

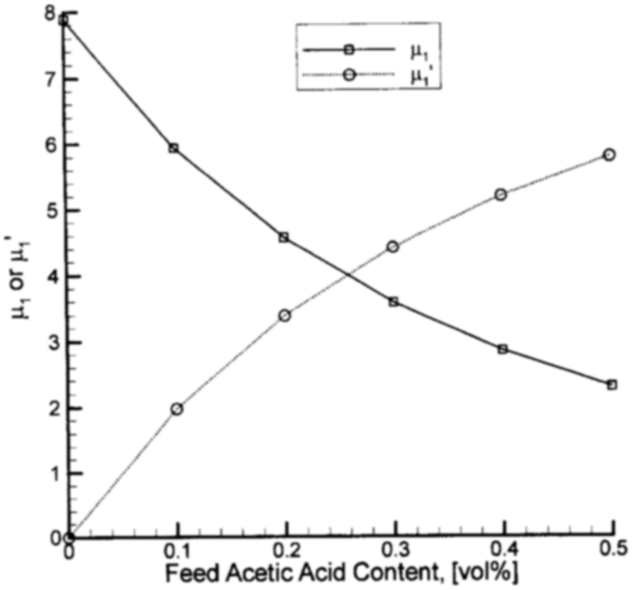

Fig. 8. Effects of the feed acetic acid content on the first moments of the polymers.

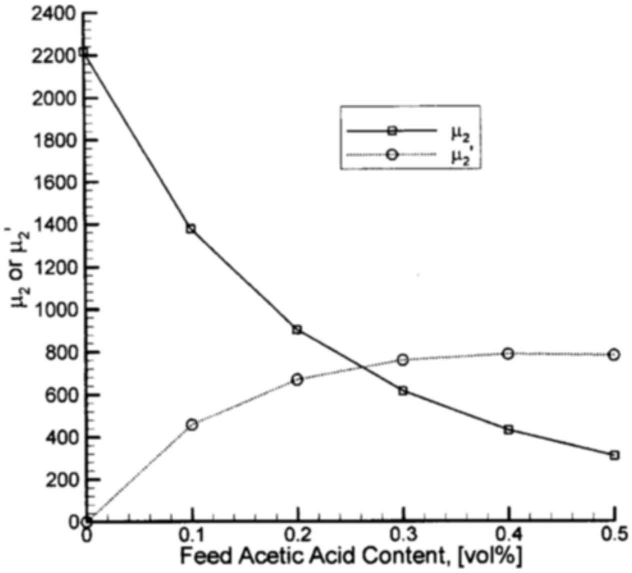

Fig. 9. Effects of the feed acetic acid content on the second moments of the polymers.

the feed concentration of the acetic acid. It ranges from 1.79 to 4.78 when the content of acetic acid in the feed ranges from 0 to 0.5 vol%. As the reaction mixture flows through the tubular reactor, the polydispersity index drops rapidly and approaches to a value of ~2 that is recognized as the equilibrium polydispersity index for nylon-6.

CONCLUDING REMARKS

The effects of acetic acid on the polymerization characteristics of nylon-6 have been investigated in a reactor system that consists of a continuous flow stirred tank reactor and a tubular reactor connected in series. Mathematical models for the continuous flow stirred tank reactor and the tubular reactor have been established and solved by numerical methods. In the CSTR, the monomer conversion and the molecular weights increase as the feed acetic acid concentration is increased. The acid behaves like both a catalyst and a modifier for the polymerization reaction. Therefore, the temperature profile in the tubular reactor is shifted toward upstream and the maximum temperature is lowered as the feed acetic acid concentration is increased. The effects of the feed acetic acid content on the zeroth, first and second moments of the polymers have been discussed together with the effects on the polydispersity index. The polydispersity index is greatly affected by the feed concentration of acetic acid in the CSTR, but approaches a value of ~2 in the tubular reactor.

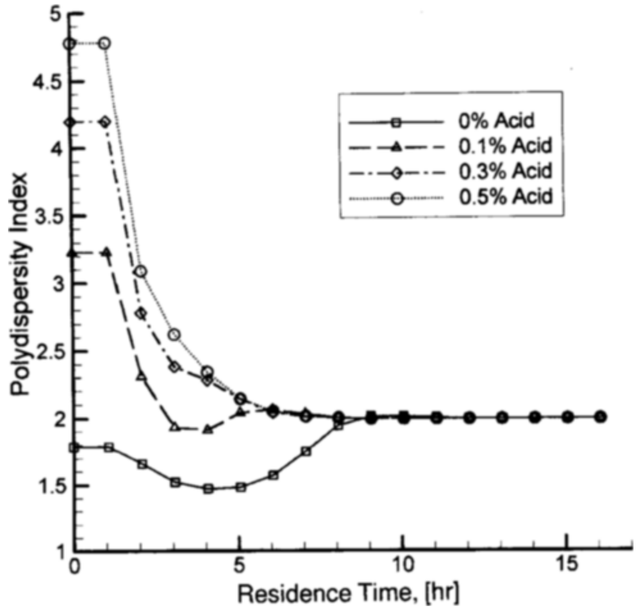

Fig. 10. Effects of the feed acetic acid content on the profiles of polydispersity index for the polymerization reactor system.

ACKNOWLEDGMENTS

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NOMENCLATURE

A : molecules with acetyl end-group
A_1 : acetic acid
A_i^c : frequency factor of autocatalytic rate constant for reaction i [$kg^2/mol^2 \cdot hr$]
A_i^o : frequency factor of pure rate constant for reaction i [$kg/mol \cdot hr$]
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 [cal/kg·K]
c_{pW} : specific heat of water [cal/kg·K]
E_i^c : activation energy of autocatalytic rate constant for reaction i [cal/mol]
E_i^o : activation energy of pure rate constant for reaction i [cal/mol]
F : flow rate of reaction mass [kg/hr]
F_i : flow rate of feed [kg/hr]
F_v : flow rate of water vapor [kg/hr]
ΔH_i : change of enthalpy for reaction i [cal/mol]
ΔH_{vap}: latent heat of water vaporization [cal/kg]
k_i : rate constant for reaction i [kg/mol·hr]
k_i^c : autocatalytic rate constant for reaction i [kg^2/mol^2·hr]
k_i^o : pure rate constant for reaction i [kg/mol·hr]
K_i : equilibrium constant for reaction i
R_i : rate of reaction i [mol/kg·hr]
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
ΔS_i : change of entropy for reaction i [eu]
t : residence time [hr]
t_0 : space time of CSTR or entrance time to tubular reactor [hr]
T : temperature [K]
T_J : jacket temperature [K]
U^* : overall heat transfer coefficient [cal/hr·m^2·K]
W : water
y : concentrations of chemical components or temperature
[ ] : concentration [mol/kg]

Greek Letters

ρ : density [kg/m^3]
μ_ν : ν-th moment of polymers with amine end-group
μ_ν' : ν-th moment of polymers 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

Superscripts

c : autocatalytic reaction
0 : pure reaction
* : part of total amide group concentration that belongs to polymers with amine or acetyl end-groups

Subscripts

i : reaction number or feed
m, n : number of repeating units in a chain molecule
0 : initial concentration based on reaction mass
v : vapor

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