

The Kinetics of Hydrolytic Polymerization of ϵ -Caprolactam. IV. Theoretical Aspect of the Molecular Weight Distribution

Poly(ϵ -caprolactam) (PCL; nylon 6) is industrially produced by hydrolytic polymerization of ϵ -caprolactam (CL). The information of the molecular weight distribution (MWD) is indispensable to the process control of various commercial plants and to the control of the physical property of the polymer.

Theoretical representation of MWD was first reported by Tirrell et al.¹ They derived a set of rate equations including a representation of MWD by applying the discrete transform (Z -transform) to the molecular rate equation. As pointed out in the preceding article,² however, some errors were found in their equations.

In this report, a new set of rate equations to describe MWD, which is consistent with the reaction mechanism,²⁻⁵ was derived and a method for solving the set of equations was proposed. The compatibility was inspected between MWD data obtained by GPC and those of the calculations. MWD can therefore be estimated for every commercial plant for every stage of the polymerization by combining the equations with the density distribution function of the respective plants.

DERIVATION OF RATE EQUATIONS

The proposed mechanisms of the polymerization of CL and the set of rate equations representing concentrations of CL, end group (EG), and ϵ -aminocaproic acid (ACA) are summarized in Table I. Here x , y , z , and w are concentrations of CL, EG, ACA, and water, respectively; k_i is the rate constant; K_i ($= k_i/k'_i$) is the equilibrium constant; A_i^j is the frequency factor; E_i^j is the activation energy; S_i is the entropy; H_i is the enthalpy; R is the gas constant; t is the time; T is the temperature; i indicates the kind of reactions; $j = 0$ means noncatalytic reaction; and $j = c$ means catalytic reaction.

TABLE I
Mechanism and Kinetics

	Equilibrium reactions	
(1) Ring Opening	$\text{CL} + \text{H}_2\text{O} \rightleftharpoons \text{ACA}$ $x \quad w \quad C_1 (= z)$	
(2) Polycondensation	$\text{P}_n + \text{P}_m \rightleftharpoons \text{P}_{n+m} + \text{H}_2\text{O}$ $C_n \quad C_m \quad C_{n+m} \quad w$ $-\text{NH}_2 + \text{HOCO}- \rightleftharpoons -\text{NHCO}- + \text{H}_2\text{O}$ $y \quad y \quad x_0 - x - y \quad w$	
(3) Polyaddition	$\text{CL} + \text{P}_n \rightleftharpoons \text{P}_{n+1}$ $x \quad C_n \quad C_{n+1}$ $\text{CL} + \text{H}_2\text{N}- \rightleftharpoons \text{H}_2\text{N}-$ $x \quad y \quad y - z$	
	Rate Equations	
	$\frac{dx}{dt} = -k_1[x(w_0 - y) - z/K_1] - k_3[xy - (y - z)/K_3] \quad (1)$	
	$\frac{dy}{dt} = k_1[x(w_0 - y) - z/K_1] - k_2[y^2 - (x_0 - x - y)(w_0 - y)/K_2] \quad (2)$	
	$\frac{dz}{dt} = k_1[x(w_0 - y) - z/K_1] - 2k_2[yz - (y - z)(w_0 - y)/K_2] - k_3[xz - z/K_3] \quad (3)$	
	Rate and Equilibrium Constants	
	$k_i = k_i^0 + k_i^c y; k_i^j = A_i^j \exp(-E_i^j/R/T); K_i = \exp[(S_i - sH_i/T)/R]$ $(i = 1, 2, 3; j = 0, c)$	

The molecular rate equation for P_n -mer the concentration of which is C_n can be written as follows:

$$dC_n/dt = (k_1xw - k_1' C_1)\delta_{n-1} + k_2 \sum_{m=1}^{n-1} C_{n-m}C_m - 2k_2C_n \sum_{m=1}^{\infty} C_m - k_2'w(n-1)C_n + 2k_2'w \sum_{j=n+1}^{\infty} C_j + k_3xC_{n-1} - k_3xC_n + k_3'C_{n+1} - k_3'C_n + k_3'C_1\delta_{n-1} \quad (4)$$

where δ is the delta function.

Application of the discrete transformation⁶ to eq. (4) yields the following transformed equation:

$$\partial D(Z,t)/\partial t = (k_1xw - k_1' C_1)Z^{-1} + k_2D^2(Z,t) - 2k_2\mu_0D(Z,t) + k_2'w[D(Z,t) + Z\partial D(Z,t)/\partial Z] + 2k_2'w[\mu_0 - ZD(Z,t)]/(Z-1) + k_3x(Z^{-1} - 1)D(Z,t) + k_3'(Z-1)[D(Z,t) - C_1Z^{-1}] \quad (5)$$

where D is the discrete transform of the distribution of polymerization degree and Z is an arbitrary transform variable.

According to the moment generating properties of the transform, the ν th moment is described as

$$\mu_\nu = \sum_n n^\nu C_n = \partial^\nu D(Z,t)/\partial(\ln Z^{-1})^\nu|_{Z=1} \quad (6)$$

Thus the differential equations for the moments obtained were

$$d\mu_0/dt = \partial^0[\partial D(Z,t)/\partial t]/\partial(\ln Z^{-1})^0|_{Z=1} = \partial D(Z,t)/\partial t|_{Z=1} = (k_1xw - k_1' C_1) - k_2\mu_0^2 + k_2'w(\mu_1 - \mu_0) \quad (7)$$

$$d\mu_1/dt = \partial^1[\partial D(Z,t)/\partial t]/\partial(\ln Z^{-1})^1|_{Z=1} = -Z\partial[\partial D(Z,t)/\partial t]/\partial Z|_{Z=1} = (k_1xw - k_1' C_1) + k_3x\mu_0 - k_3'(\mu_0 - C_1) \quad (8)$$

$$d\mu_2/dt = \partial^2[\partial D(Z,t)/\partial t]/\partial(\ln Z^{-1})^2|_{Z=1} = -Z\partial[-Z\partial[\partial D(Z,t)/\partial t]/\partial Z]/\partial Z|_{Z=1} = (k_1xw - k_1' C_1) + 2k_2\mu_1^2 + (1/3)k_2'w(\mu_1 - \mu_3) + k_3x(2\mu_1 + \mu_0) + k_3'(\mu_0 - 2\mu_1 + C_1) \quad (9)$$

Here the following three relations have been found to hold:

$$\mu_0 = \sum_n C_n = w_0 - w = y \quad (10)$$

$$\mu_1 = \sum_n nC_n = x_0 - x \quad (11)$$

$$C_1 = z \quad (12)$$

The substitution of eqs. (10), (11), and (12) into eq. (7) yields an equation identical with eq. (2) in Table I; the substitution of eqs. (10), (11), and (12) into eq. (8) yields an equation identical with eq. (1); and the substitution of eqs. (10), (11), and (12) into eq. (9) yields the following equation:

$$d\mu_2/dt = k_1[x(w_0 - y) - (z/K_1)] + k_2[2(x_0 - x)^2 + (w_0 - y)(x_0 - x - \mu_3)/K_2/3] + k_3[x(2x_0 - 2x + y) + (y - 2x_0 + 2x + z)/K_3] \quad (9')$$

The number-average molecular weight and the weight-average molecular weight can be given as

$$M_n = M(\mu_1/\mu_0) \quad (13)$$

$$M_w = M(\mu_2/\mu_1) \quad (14)$$

where M is the molecular weight of the CL unit. The simplest function to characterize MWD is the polydispersity U , defined by

$$U = M_w/M_n = (\mu_2/\mu_1)/(\mu_1/\mu_0) = \mu_2 y/(x_0 - x)^2 \quad (15)$$

Thus, a new set of equations such as eqs. (1), (2), (3), (9'), (13), (14), and (15), which includes a representation of MWD, was obtained.

NUMERICAL CALCULATION

In order to solve the set of rate equations numerically, it is necessary to represent μ_3 of eq. (9') as a function of x , y , z , and μ_2 . That is, the introduction of the relation is equivalent to assume the type of the distribution function. The Schultz-Zimm^{7,8} distribution function

$$g(P) = [1/\Gamma(b+1)]a^{b+1}P^b \exp(-aP) \quad (16)$$

has been found to be suitable, as a first approximation, for representing the distribution of polymerization degree of PCL. Here, g is the weight fraction of P (degree of polymerization), a and b are parameters of the function, and Γ is the gamma function. U takes the value $U \geq 1$ in variation with b . The most probable distribution is a special case of this distribution and corresponds to $b = 1$. According to the properties of the Schultz-Zimm function, the following relation was derived:

$$\mu_3 = \frac{\mu_2(2\mu_2\mu_0 - \mu_1^2)}{\mu_1\mu_0} = \mu_2 \frac{[2\mu_2 y - (x_0 - x)^2]}{y(x_0 - x)} \quad (17)$$

Thus, the set of rate equations can be solved numerically under the constrained condition of eq. (17).

The equations were integrated numerically using the Runge-Kutta-Gill integration scheme with the time increment of $1/100$ hr. As kinetic and thermodynamic constants, set 4 of ref. 9 was used. The calculation was performed by a HITAC 8250 computer.

GPC EXPERIMENT

Gel permeation chromatography (GPC) of PCL was carried out by using a Toyosoda model HLC-801A GPC apparatus equipped with a refractive index detector. Experimental conditions were as follows: The column was a series of two GMIXH4; carrier liquid was mixed solvent of *m*-cresol (15 wt %), chloroform (84.75 wt %), and a small amount of benzoic acid (0.25 wt %); temperature was 35°C; carrier flow rate was 1 ml/min; sample concentration was 1.5 g/l. A series of polymers was used for the GPC observation, which was made in a sealed glass tube at 240°C using CL containing 0.8 mole/kg water.

RESULTS AND DISCUSSION

The results of the calculation and the experiment are given schematically in Figure 1; the effect of the initial water concentration to the polydispersity U_{calcd} is shown in Figure 1(A), and the effect of the polymerization temperature, in Figure 1(B). These figures revealed that the polydispersity-versus-time curves are affected appreciably by the initial water concentration and the temperature but that equilibrium values are not. The plots (●) in Figure 1(A) are the observed points the U value of which was evaluated from the GPC data. Here, the conversion of polymerization corresponding to the plots are 38, 73, 84, 89, and 90%, respectively. The thick solid line in the figure is the corresponding calculated result. The values of U_{GPC} are larger than U_{calcd} by 9%.

PCL is industrially produced by using autoclave reactor, tubular reactor (TR), or combination of continuous stirred tank reactor (CSTR) and TR. It is one of the desired requirements to add MWD terms (M_n , M_w , and U) to the simulation calculation of the polymerization in the reactors, since to estimate not only concentration terms ([CL], [EG], and [ACA]) but also MWD terms by the theoretical calculations are indispensable to the process control and the control of the polymer property. One can perform the calculation for every commercial plant for every stage of the polymerization by combining the set of rate equations with the density distribution function $E(\theta)$ of the respective reactors. For example, suppose that the polymerization is performed by the combination reactor CSTR + TR. Then (1) an appropriate operation condition for CSTR and TR to obtain the desired polymer can be selected by the calculations of the characteristic data (concentration terms

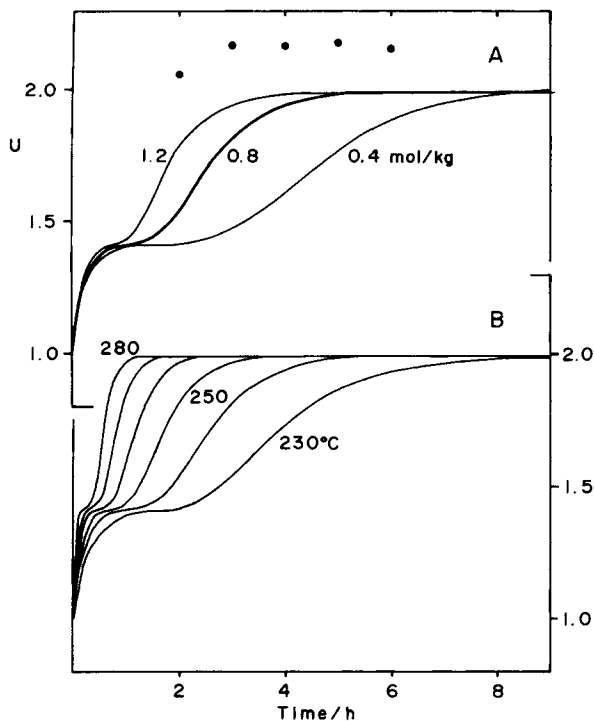


Fig. 1. (A) Effect of initial water concentration on polydispersity U -vs.-time curves for polymerization temperature of 240°C. Solid lines are the calculated data and plots (●) are the data observed by GPC. (B) Effect of temperature on calculated U -vs.-time curves for initial water concentration of 0.8 mole/kg.

and MWD terms) of the polymerization; (2) when the observed value deviates from the target at the outlet of the CSTR, the TR can be controlled to obtain the desired polymer by evaluating the characteristic data of the TR based upon the observed data of the CSTR.

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KAZUO TAI
YOSHIHIRO ARAI
HIROICHI TERANISHI
TAKASHI TAGAWA

Research and Development Center
Unitika Ltd.
23 Kozakura Uji
Kyoto 611, Japan

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