

The Kinetics of Hydrolytic Polymerization of ϵ -Caprolactam. V. Equilibrium Data on Cyclic Oligomers

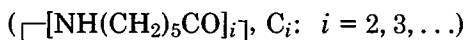
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Synopsis

The concentrations of the cyclic oligomers (C_i ; $i = 3, 4, 5,$ and 6) in the polymeric products of ϵ -caprolactam were determined by high-performance liquid chromatography. The equilibrium data on the oligomers were obtained as a function of the polymerization temperature and initial water concentration. The concentration of each oligomer in the equilibrated polymer was found to increase with the temperature and/or initial water concentration. A set of the kinetic equations to express the oligomer formation during the polymerization was also proposed.

INTRODUCTION

During the hydrolytic polymerization of ϵ -caprolactam (CL), it has been well recognized that cyclic oligomers



are formed as byproducts. These oligomers are undesirable materials for spinning and molding the polymer. Therefore to determine the concentrations of the cyclic oligomers in the polymeric products at equilibrium state for various polymerization conditions and to clarify the formation behavior of the oligomers are very important for the process control and quality control of polymerization, refinery, and recovery plants used in the industry.

Many investigations have been concerned with separation and analytical techniques such as fractional sublimation,¹ thin-layer chromatography,² gel chromatography,³ and high-performance liquid chromatography.⁴ However, there have been few reports which deal with the formation behavior of the cyclic oligomers, except one⁵ in which the mechanism and kinetics of the cyclic dimer ($i = 2, C_2$) formation were investigated.

In this work, a rapid and reliable method of quantitative analysis to determine the concentrations of the cyclic oligomers (cyclic i -mer; $i = 3, 4, 5, 6$) by high-performance liquid chromatography is established. The concentration data of the cyclic oligomers are obtained for the equilibrated polymers produced under various polymerization conditions and effects of the temperature and initial water concentration on the cyclic oligomer formation are examined. The mechanism and kinetics of the cyclic oligomer formation are also discussed.

EXPERIMENTAL

Material

Cyclic trimer (C_3), cyclic tetramer (C_4), and cyclic pentamer (C_5) were prepared from a product obtained by the hot-water extraction of the polymeric mixtures. Fractional sublimation of which the experimental method was reported by Heikens¹ was used. The purity of the isolated materials was examined by high performance liquid chromatography and the following values were observed: C_3 ; [C_3] = 95.8 wt %, impurities, [C_2] = 1.0 and [C_4] = 3.2; C_4 ; [C_4] = 91.5 wt %, impurity, [C_5] = 8.5; C_5 ; [C_5] = 99.9 wt %.

A set of the polymer samples (18 kinds) was used for the analysis, which was made by polymerizing CL in sealed glass tubes under the following conditions^{5,6}: polymerization temperatures ($^{\circ}\text{C}$): 230, 240, 250, 260, 270, and 280; initial water concentrations (mol/kg): 1.18, 0.82, and 0.42; polymerization time: 10 h. Under these conditions, as described in a preceding paper⁶ (cf. Figures 2–5 of that paper), the polymerization reaction attains the equilibrium.

Analysis

The rod-shaped polymer samples were shaved to thin films by a drill. The weighted samples were then extracted with 20 times their weight of freshly distilled water at 90°C for 6 h using sealed extraction tubes, after which they were filtered onto weighted glass filters and dried to constant weight by heating to 70°C under vacuum. The total hot-water-soluble content is equal to the loss in weight of the sample caused by the extraction.

The cyclic oligomers (C_3 , C_4 , C_5 , and cyclic hexamer C_6) were analyzed by high-performance liquid chromatography. The aqueous solution of the water-soluble components was chromatographed by using a Shimadzu Model LC-3A liquid chromatograph apparatus equipped with an ultraviolet spectrometer. A 210-nm wavelength was selected. The separation column was a μ -Bondapak C_{18} (Waters Associate), and the mobile phase was the mixed solvent of 35 vol % methanol and 65 vol % water. The temperature of the column oven was controlled to 40°C and the flow rate of the mobile phase was 1 mL/min.

The peak area of the chromatograph was counted by a Shimadzu Chromatopack El-A digital data analyzer. The determination of the amount of the cyclic oligomers was carried out by the absolute calibration method. The calibration curve for each oligomer showed good linearity and the weight sensitivities were found as follows: C_3 ; $0.669 \times 10^5 \mu\text{V}\cdot\text{s}/\mu\text{g}$; C_4 ; 0.641×10^5 ; C_5 ; 0.685×10^5 . The value for C_6 was assumed as $0.680 \times 10^5 \mu\text{V}\cdot\text{s}/\mu\text{g}$ because of lack of the standard sample of C_6 available for the calibration.

RESULTS AND DISCUSSION

Experimental Results

Figure 1 is an example of the chromatograph which shows a good separation of the cyclic oligomers except the first unresolved strong peak (CL + C_2). The average retention times of the cyclic oligomers were obtained as: C_3 , 8.4 min; C_4 , 12.4; C_5 , 19.2; and C_6 , 30.9. Cyclic higher oligomers than C_6 such as heptamer

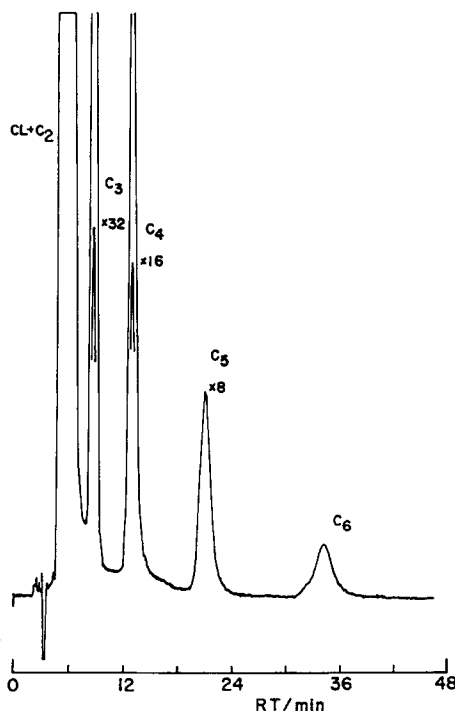


Fig. 1. High performance liquid chromatography of cyclic oligomers.

(C_7), octamer (C_8), etc. were not analyzed in this work, though their trace peaks were observed on the positions with longer retention time (C_7 , 70 min and C_8 , 113 min).

In Figure 2 are shown the observed concentrations of the cyclic oligomers in the polymer samples as a function of the polymerization temperature. Here u_i ($=[C_i]$) signifies the concentration of C_i (mmol/kg) and the plots of \circ , \square , and \triangle express the initial water concentrations of 1.18, 0.82, and 0.42 mol/kg, respectively.

Mori and Takeuchi³ and Mochizuki and Ito⁷ have analyzed the cyclic oligomers by gel chromatography and their reported values are listed in Table I. As for a reference, typical representative data of this work for the polymer sample whose polymerization temperature and initial water concentration are 259°C and 0.82 mol/kg are also given in the table. Although the comparison of these three sets of the data is essentially impossible since the details of the polymerization conditions for the former two sets are not clear, it is found from the table that the values of $[C_3]$ and the values of $[C_4]$ have a same order among the three, while the value of $[C_5]$ by Mochizuki and Ito and the value of $[C_6]$ by Mori and Takeuchi seem to have rather high value compared to the others.

Effects of Temperature and Initial Water Concentration

From Figure 2, it is revealed that the concentrations of C_3 , C_4 , C_5 , and C_6 in the polymeric mixture at equilibrium state of the polymerization increase monotonically with increasing the polymerization temperature and/or initial

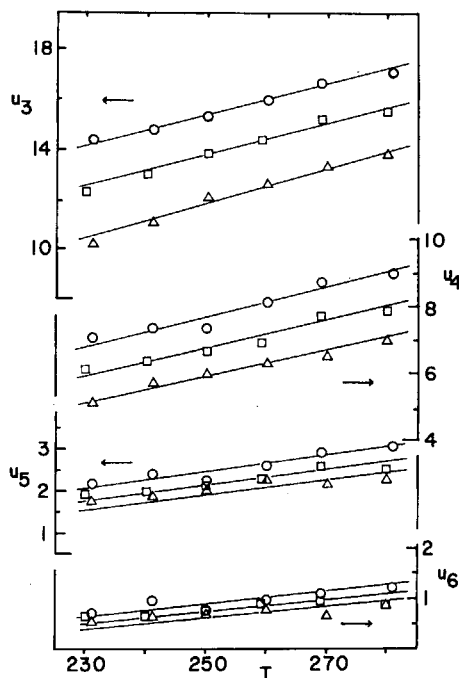


Fig. 2. Concentration vs. temperature plots for the cyclic oligomers, where u_i ($= [C_i]$) is the concentration of cyclic i -mer (mmol/kg) and T is the polymerization temperature ($^{\circ}\text{C}$). The plots of \circ , \square , and Δ correspond to the initial water concentrations of 1.18, 0.82, and 0.42 mol/kg, respectively.

water concentration. Good linear relationships are found for the $[C_3]$ and $[C_4]$ vs. temperature plots, while the $[C_5]$ and $[C_6]$ plots have some scatters. The slopes of the linear plots and the spacings of the plots with regard to the initial water concentration decrease with increasing the molecular weight of the respective oligomers from C_3 to C_6 , so that the effects of the polymerization temperature and initial water concentration on the concentration of the oligomers become small with increasing the molecular size of the oligomers. These data are beneficial for the process control and quality control of polymerization, refinery, and recovery plants and for the control of physical properties of the polymer.

TABLE I
Concentrations of Cyclic Oligomers

No.	Origin	T^a	w_0^a	$[C_3]^a$	$[C_4]^a$	$[C_5]^a$	$[C_6]^a$
1	Mori and Takeuchi ³	—	—	13.8	6.6	3.0	2.4
2	Mochizuki and Ito ^{7,b}	—	—	15.9	8.2	5.5	—
3	This work	259	0.82	14.3	6.9	2.2	0.9

^a T is the polymerization temperature ($^{\circ}\text{C}$), w_0 is the initial water concentration (mol/kg), and $[C_i]$ is the concentration of cyclic i -mer (mmol/kg).

^b The values were estimated from Figure 5 of the Ref. 7.

TABLE II
Rate Equations

$$dx/dt = -k_1[x(w_0 - y) - z/K_1] - k_3[xy - (y - z)/K_3] \quad (1)$$

$$dy/dt = k_1[x(w_0 - y) - z/K_1] - k_2\left[y^2 - \left(x_0 - x - y - \sum_{i=2}^i u_i\right)(w_0 - y)/K_2\right] \quad (2)$$

$$dz/dt = k_1[x(w_0 - y) - z/K_1] - 2k_2[yz - (y - z)(w_0 - y)/K_2] - k_3(xz - z_2/K_3) - \sum_{i=2}^i k_{2i+1}(u_i z - z_{i+1}/K_{2i+1}) \quad (3)$$

$$du_2/dt = -k_4[u_2(w_0 - y) - z_2/K_4] - k_5[u_2 y - (y - z - z_2)/K_5] \quad (4)$$

...

$$du_i/dt = -k_{2i}[u_i(w_0 - y) - z_i/K_{2i}] - k_{2i+1}\left[u_i y - \left(y - z - \sum_{i=2}^i z_i\right)/K_{2i+1}\right] \quad (2+i)$$

Mechanism and Kinetics of Cyclic Oligomer Formation

It is well known that three main equilibrium reactions, i.e., (1) ring-opening reaction of CL, (2) condensation reaction, and (3) addition reaction of CL, are undergone during the polymerization. In the preceding paper,⁵ we dealt with the mechanism and kinetics of the cyclic dimer formation, where two equilibrium reactions concerned with C₂: (4) Ring-opening reaction of C₂ and (5) addition reaction of C₂ were taken into consideration in addition to the above three main reactions, and the good compatibility was found between the calculated kinetic data and observed ones.

In analogy to the treatment of C₂, it can be expected that the formation mechanism of the cyclic oligomers is described as: (6) ring-opening reaction of C_i with water to form linear *i*-mer and (7) addition reaction of C_i to the terminal of a polymer molecule followed by the increase of *i* CL units. The direct reaction between two cyclics such as C_i + C_j ⇌ C_{i+j} and the intramolecular cyclization except at the terminal are not to be taken into account,⁵ since the amide exchange reaction is not caused by the direct reaction between amide linkages but by the aminolysis and acidolysis reactions.⁸

A set of the rate equations can be derived from the mechanism and is summarized in Table II. Here the notations of the variables and constants are as follows: *w*, *x*, *y*, *z*, *z_i*, and *u_i* are the concentrations (mol/kg) of water, CL, endgroup, ε-aminocaproic acid, linear *i*-mer, and cyclic *i*-mer, respectively. *k₁*, *k₂*, and *k₃* and *K₁*, *K₂*, and *K₃* are the rate constants and equilibrium constants for the three main reactions. *k_{2i}* and *k_{2i+1}* and *K_{2i}* and *K_{2i+1}* are those for the ring-opening reaction and addition reaction of the cyclic *i*-mer (*i* ≥ 2). All the reactions considered here are accepted to be catalyzed by the carboxyl end group, so that the rate constants can be expressed as *k* = *k*⁰ + *k*^{*c*}, where 0 and *c* mean the noncatalytic and catalytic, respectively. The set of the rate equations listed in the table is valid, provided that the variables satisfy the following constrained conditions based on the material valance:

$$w_0 = w + y(5)$$

$$x_0 = (1000.0 - 18.015 \times w_0)/113.16$$

$$= x + z + \sum_{i=2}^i iu_i + \sum_{i=2}^{\infty} iz_i$$

Here the $\sum_{i=2}^i iu_i$ terms means the concentration of CL converted to the cyclic oligomers and the $\sum_{i=2}^{\infty} iz_i$ term means the concentration of CL converted to the polymers.

The set of these rate equations can be solved numerically, if an adequate set of the rate and equilibrium constants concerning the cyclic oligomers ($i \geq 3$) is available. The addition of the cyclic oligomer terms to the simulation calculation of the polymerization in various reactors⁹ will make very important contributions to the process control and quality control of the plants used in the industry.

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