

Figure 1 Gel permeation chromatographs of polymers from crown ether catalysed reaction of *m*-xylylene dibromide and dipotassium sebacate at (a) 60° (b) 80°C; reaction time 4 days; reaction conditions as in Table 1

each case the acetonitrile-benzene mixture (20 ml) was used, with 3.8 mmol of K_2CO_3 and the dibromide, and 0.19 mmol of 18-crown-6. After stirring at 80°C for three days the polycarbonates were recovered as before. From the *m*- and *p*-xylylene dibromides respectively the yields were 27 and 12%, and the molecular weights (by g.p.c.) were 1.8×10^3 and 1.0×10^3 .

Clearly there are advantages to be gained by using the *m*-isomer in these systems, though it is not entirely clear why this should be so. If the reaction involved a simple nucleophilic substitution then one would expect the *p*-isomer to react slightly faster⁵ than the *m*-compound. Our results suggest that the *p*-isomer is more prone to interfering side reactions.

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Kinetics of hydrolytic polymerization of ϵ -caprolactam:

3. Formation of cyclic dimer

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INTRODUCTION

The authors have investigated the mechanism and kinetics of the hydrolytic polymerization of ϵ -caprolactam¹ (CL) and proposed improved sets of kinetic and thermodynamic constants necessary to formulate the rate equations². In these studies, the three main equilibrium reactions, i.e. ring-opening of CL, polycondensation of chains, and poly-addition of CL, are taken into account. However, cyclic oligomers, $[NH(CH_2)_5CO]_x$ with $x=2, 3, \dots$, exist in polymeric equilibrates as by-products. This study deals with the formation of cyclic dimer (CD, $x=2$), the major portion of the cyclic oligomers.

Many investigations have been concerned with separation and analytical techniques such as fractional sublimation³, thin-layer chromatography⁴, infrared spectrometry⁵, gas chromatography⁶, and gel permeation chromatography^{6,7}, the cyclization equilibria^{6,8,9}, and the formation of cyclic oligomers¹⁰. But there have been few reports of kinetic studies of the hydrolytic polymerization of ϵ -caprolactam for a variety

of polymerization conditions because of the lack of either rapidity or accuracy in the analysis of CD. Thus, the effects of temperature and initial water concentration on the behaviour of CD formation during the reaction have not yet been clarified.

A rapid quantitative analysis to determine the concentration of CD by gas chromatography is established. The kinetic data for CD formation are obtained in various reaction conditions, and the mechanism and the kinetics of CD formation are discussed.

EXPERIMENTAL

Material

A molten ϵ -caprolactam of fibre grade was used as the reactant without further purification, and the concentration of water contained was determined by the Karl-Fisher method.

Cyclic dimer of ϵ -caprolactam, $[NH(CH_2)_5CO]_2$, was prepared from the product of the refining process of

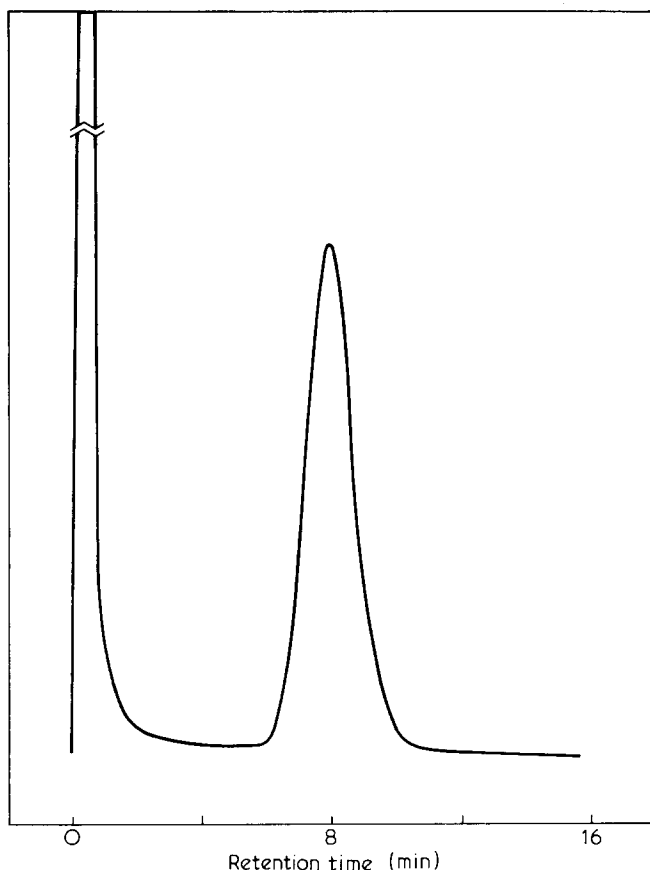


Figure 1 Gas chromatogram of cyclic dimer of ϵ -caprolactam

nylon-6 as follows.

Any remaining ϵ -caprolactam was removed by decanting off from aqueous solution, and cyclic dimer was obtained by re-crystallizing the precipitate from methanol followed by drying in an oven under vacuum. The purity was confirmed by high pressure liquid chromatography.

Polymerization of ϵ -caprolactam

Cyclic dimer formation in the course of the hydrolytic polymerization of ϵ -caprolactam was investigated by analyzing the polymeric products obtained previously¹. Details of the polymerization procedures were given in reference 1.

Polymerization of cyclic dimer

Molten ϵ -caprolactam containing a prescribed concentration of water was introduced into a previously weighed glass ampoule, and the required amount of cyclic dimer was added. The reaction mixture was cooled in a dry ice-methanol bath, degassed under high vacuum, and sealed off. Reaction was carried out homogeneously by heating the ampoule in a salt bath maintained at the required temperature. After the required time, the reaction was quenched by cooling the ampoule in water.

Extracting procedure

The ampoule was broken open and the reaction product was crushed by a hammer or shaved by an electric pencil shaver prior to the extraction of cyclic dimer. The weighed sample was extracted with freshly distilled water in such a manner that the preliminary estimated concentration of cyclic dimer did not exceed the saturated

value at room temperature (0.1 wt %), and the weight ratio of added water to sample changed its value from 20 to 400.

Determination of cyclic dimer concentration

The concentration of cyclic dimer was determined by gas chromatography using a Shimadzu GC-6A gas chromatograph. The aqueous sample solution was chromatographed using a 1 m stainless steel column packed with Tenax GC of 60/80 mesh (AKZO). A flame ionization detector and nitrogen carrier gas (60 ml/min) was used, and the column temperature was kept at 305°C. A chromatogram for an aqueous solution containing cyclic dimer is shown in Figure 1. In Figure 1, the extremely sharp peak at first is that of ϵ -caprolactam, and the second one at a retention time of eight minutes is that of the cyclic dimer. A calibration curve was prepared from a chromatogram of known concentration of the cyclic dimer, and the concentration of cyclic dimer in the reactant was determined from the value of the peak area considering the extraction efficiency.

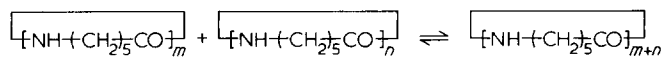
RATE EQUATIONS AND CALCULATION

Mechanism and kinetics

For this polymerization, three main equilibrium reactions have been proposed, (1) ring-opening reaction of CL with water to produce ϵ -aminocaproic acid (ACA), (2) condensation reaction between amino and carboxyl end-groups to form amide linkage and water, (3) an addition reaction of CL to a polymer molecule followed by increasing one CL unit. These reactions are shown in Table I. The reaction concerning the cyclic monomer is not included in the mechanism mentioned above owing to difficulty in quantitative analysis and the complication of the equation representing the cyclics. In order to clarify the details of this polymerization, it seems to be important, however, to incorporate a reaction concerning CD, the major portion of the cyclics except the monomer, into the mechanism.

Adding the above reactions, the following equilibrium reactions concerning CD can be considered; (4) ring-opening reaction of CD with water to produce a linear dimer, (5) addition reaction of CD to a polymer molecule followed by increasing two CL units. These equilibrium reactions are listed in Table I.

It is reported that the amide exchanging reaction is not caused by the direct reaction between amide groups but by the aminolysis and acidolysis¹¹, and for this reason the two equilibrium reactions, (6) direct reaction between cyclics,



and (7) the intramolecular amide exchanging reaction

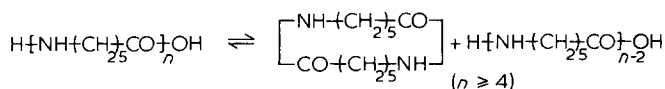


Table 1 Mechanisms and kinetics

Equilibrium reactions	
Ring-opening of CL	
$\text{HN}-(\text{CH}_2)_5\text{CO} \xrightleftharpoons[w_0-y]{x} \text{H}_2\text{N}-(\text{CH}_2)_5\text{COOH}$	
Polycondensation	
$\text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_m\text{OH} + \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_n\text{OH} \rightleftharpoons \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_{m+n}\text{OH} + \text{H}_2\text{O}$	$x_0 - x - y - u \quad w_0 - y$
Polyaddition of CL	
$\text{HN}-(\text{CH}_2)_5\text{CO} + \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_n\text{OH} \rightleftharpoons \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_{n+1}\text{OH}$	$y \quad y-z$
Ring-opening of CD	
$\left[\text{NH}-(\text{CH}_2)_5\text{CO} \right]_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_2\text{OH}$	$u \quad w_0 - y \quad z_2$
Polyaddition of CD	
$\left[\text{NH}-(\text{CH}_2)_5\text{CO} \right]_2 + \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_n\text{OH} \rightleftharpoons \text{H}-(\text{NH}-(\text{CH}_2)_5\text{CO})_{n+2}\text{OH}$	$u \quad y \quad y-z-z_3$
Rate equations	
$\begin{aligned} dx/dt &= -k_1[x(w_0 - y) - z/K_1] - k_3[xy - (y - z)/K_3] \\ dy/dt &= k_1[x(w_0 - y) - z/K_1] - k_2[y^2 - (x_0 - x - y - u)(w_0 - y)/K_2] \\ dz/dt &= k_1[x(w_0 - y) - z/K_1] - 2k_2[yz - (y - z)(w_0 - y)/K_2] \\ &\quad - k_3[xz - z_2/K_3] - k_5[uz - z_3/K_5] \\ du/dt &= -k_4[u(w_0 - y) - z_2/K_4] - k_5[uy - (y - z - z_3)/K_5] \end{aligned}$	

Notation of corresponding concentration: x , CL; y , endgroup; z , ACA; z_2 linear dimer; z_3 , linear trimer; u , cyclic dimer; w , water

seem to be negligible except at the terminal. In conclusion, the five equilibrium reactions are adopted to discuss the behaviour of CD in the polymerization. These are summarized in Table 1 corresponding concentrations.

The rate equations are derived from the reaction mechanism, and summarized in Table 1. These reactions are accelerated by endgroups and consequently the rate constant k_i is represented by the following equation:

$$k_i = k_i^0 + k_i^c \cdot y$$

Here 0 and c stand for non-catalytic and catalytic reactions, respectively. The rate and equilibrium constants are represented using these kinetic and thermodynamical constants; frequency factor A , activation energy E , entropy S , and enthalpy H , as follows:

$$k_i^0 = A_i^0 \exp(-E_i^0/RT)$$

$$k_i^c = A_i^c \exp(-E_i^c/RT)$$

$$K_i = \exp(S_i/R - H_i/RT)$$

($i = 1, 2, 3, 4, 5$).

In these equations, $i = 1$ means ring-opening of CL, $i = 2$ means polycondensation, $i = 3$ means poly-addition of CL, $i = 4$ means ring-opening of CD, and $i = 5$ means poly-addition of CD, respectively.

Calculation

The rate equations proposed above were integrated numerically using the Runge-Kutta-Gill integration scheme with a time increment of 1/100 h. A HITAC 8250 computer was used for this calculation.

In a numerical calculation process, it was necessary to represent z_2 and z_3 as a function of x , y , z , and u , and the assumption that z_2 and z_3 are equal to z was adopted in the actual calculation. This assumption was confirmed to be correct as no detectable change was found in varying z_2 and z_3 in the neighbourhood of z .

As for the kinetic and thermodynamic constants of the three equilibrium reactions; ring-opening of CL, polycondensation, and polyaddition of CL, a set of evaluated constants applicable for this range of the initial water concentration concerning CL, ACA, and end group concentrations were used directly (set 4 of reference 2). To evaluate the constants of the remaining two equilibrium reactions, ring-opening of CD, and polyaddition of CD, the following computation method was adopted: the values of two equilibrium constants were calculated using the corresponding equilibrium concentrations at ten h, and from the plots of $\ln K$ versus $1/T$ the approximate values of entropy (S_4, S_5), and enthalpy (H_4, H_5) were evaluated. For the other constants ($A_i^0, E_i^0/j = 0, c; i = 4, 5$), those of ring-opening of CL and polyaddition of CL ($A_i^0, E_i^0/j = 0, c; i = 1, 3$) were used as first approximate values. Starting from these approximate values, an improved set of kinetic and thermodynamic constants of these two

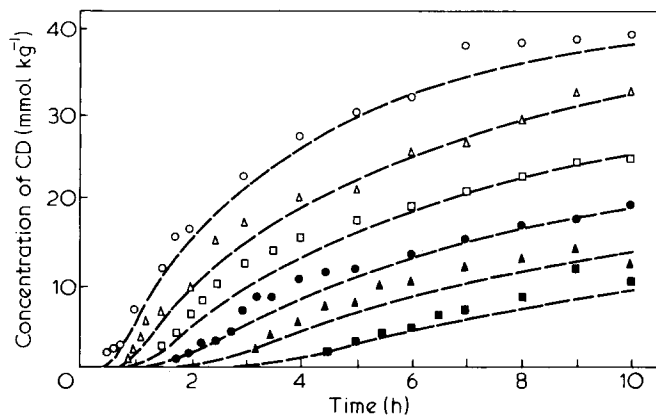


Figure 2a Effect of the temperature on CD formation for the initial water concentration of 0.42 mol kg^{-1} . Temperatures: \blacksquare , 231°C ; \blacktriangle , 241°C ; \bullet , 250°C ; \square , 260°C ; \triangle , 270°C ; \circ , 280°C . Calculated data are indicated in broken lines.

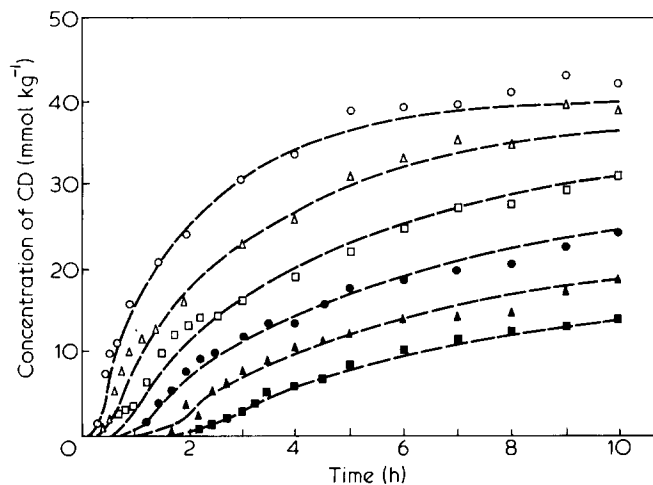


Figure 2b Effect of the temperature on CD formation for the initial water concentration of 0.82 mol kg^{-1} . Temperatures: \blacksquare , 230°C ; \blacktriangle , 240°C ; \bullet , 249°C ; \square , 259°C ; \triangle , 269°C ; \circ , 280°C . Calculated data are indicated in broken lines.

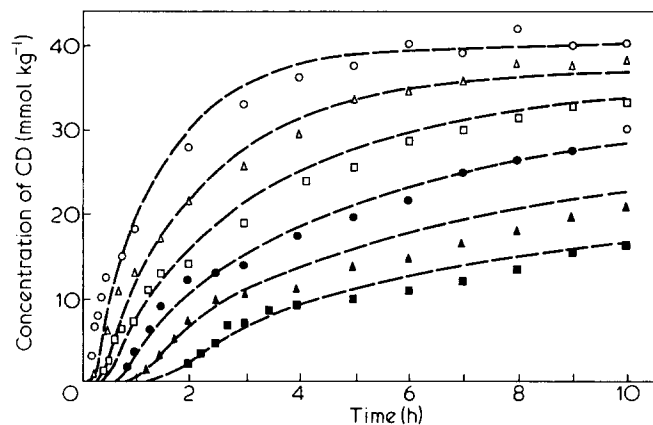


Figure 2c Effect of the temperature on CD formation for the initial water concentration of 1.18 mol kg^{-1} . Temperatures: \blacksquare , 231°C ; \blacktriangle , 241°C ; \bullet , 250°C ; \square , 260°C ; \triangle , 269°C ; \circ , 281°C . Calculated data are indicated in broken lines.

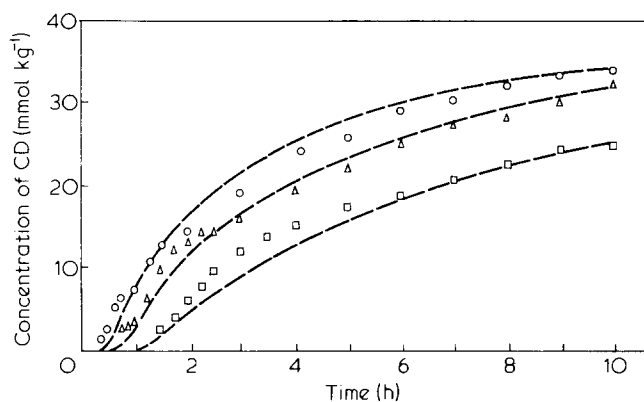


Figure 3 Effect of the initial water concentration on CD formation for the temperature of 260°C . Initial water concentrations: \square , 0.42 mol kg^{-1} ; \triangle , 0.82 mol kg^{-1} ; \circ , 1.18 mol kg^{-1} . Calculated data are indicated in broken lines.

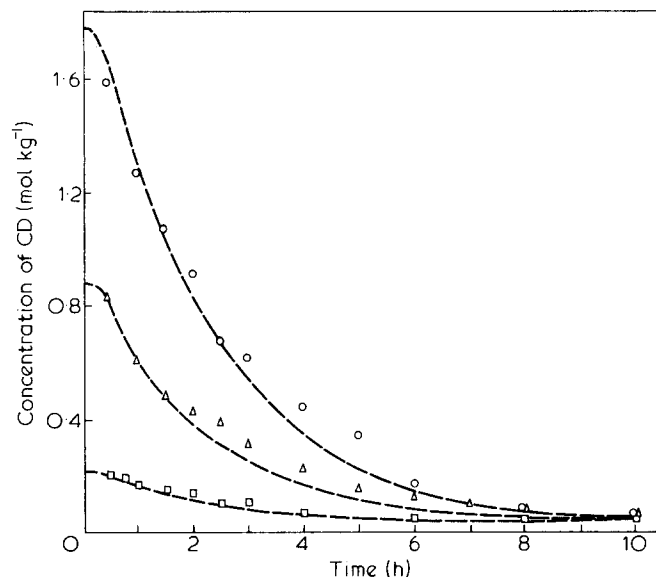


Figure 4 Concentration versus time curve of CD in the polymerization system where a mixture of CL and CD is the starting material. Reaction conditions: initial water concentration; 0.82 mol kg^{-1} . Temperature: 280°C . Initial CD concentrations: \square , 0.21 mol kg^{-1} ; \triangle , 0.88 mol kg^{-1} ; \circ , 1.77 mol kg^{-1} . Calculated data are indicated in broken lines.

the polymerization, the reaction was carried out at various temperatures; 230° , 240° , 250° , 260° , 270° , and 280°C , and with a variety of initial water concentrations; 0.42 , 0.82 , and 1.18 mol kg^{-1} . The results obtained were shown in Figures 2a, 2b, 2c, and 3. From these figures, it was revealed that the formation of CD proceeds gradually with the time, attains equilibrium in ten h, and the rate of formation and the equilibrium concentration of CD increases with temperature and the initial water concentration.

The kinetic and thermodynamic constants

The constants of the rate equations were calculated by the method described above. The values thus obtained were summarized in Table 2. As shown in Table 2, the values of non-catalytic and catalytic activation energy for the ring-opening of CD are 42.0 and $37.4 \text{ kcal mol}^{-1}$, respectively, which are in good agreement with the values of the apparent activation energy of ring-opening reported in the hydrolytic polymerization of CD catalyzed

equilibrium reactions was obtained by trial curve fitting methods.

RESULTS AND DISCUSSION

Effects of temperature and initial water concentration

To clarify the effects of the temperature and the initial water concentration on the behaviour of CD formation in

Table 2 Kinetic constants

Reaction	A^0	E^0	A^C	E^C	H	S
Ring-opening of CL	5.9874×10^5	1.9880×10^4	4.3075×10^7	1.8806×10^4	1.9180×10^3	-7.8846×10^0
Polycondensation	1.8942×10^{10}	2.3271×10^4	1.2114×10^{10}	2.0670×10^4	-5.9458×10^3	9.4374×10^{-1}
Polyaddition of CL	2.8558×10^9	2.2845×10^4	1.6377×10^{10}	2.0107×10^4	-4.0438×10^3	-6.9457×10^0
Ring-opening of CD	8.5778×10^{11}	4.2000×10^4	2.3307×10^{12}	3.7400×10^4	-9.6000×10^3	-1.4520×10^1
Polyaddition of CD	2.5701×10^8	2.1300×10^4	3.0110×10^9	2.0400×10^4	-3.1691×10^3	5.8265×10^{-1}

Dimensions: $A^0 = (\text{kg mol}^{-1} \cdot \text{h})$, $A^C = (\text{kg}^2 \text{mol}^{-2} \cdot \text{h})$, $E^0 = (\text{cal mol}^{-1})$, $E^C = (\text{cal mol}^{-1})$, $S = (\text{e.u.})$, $H = (\text{cal mol}^{-1})$

by phosphoric acid¹², which are greater than that in the ring-opening of CL. For this reason, CD seems to have a poorer reactivity for this reaction than CL.

However, non-catalytic activation energy for the addition of CD, 21.3, and 20.4 kcal mol⁻¹, are almost same as evaluated in the addition of CL, and for this reaction CD seems to have similar reactivity as CL.

The calculated data from numerical solutions of the rate equations taking the evaluated kinetic and thermodynamical constants in Table 2 for various reaction temperatures and initial water concentrations are indicated by broken lines in Figures 2a, 2b, and 2c. A close agreement between observed and calculated data was recognized in a variety of reaction conditions as shown in the figures.

Polymerization of cyclic dimer

The behaviour of CD in the polymerization system where a mixture of ϵ -caprolactam and cyclic dimer are the starting materials was investigated to test the applicability of the proposed mechanism and the evaluated kinetic and thermodynamic constants. The cyclic dimer was initially added to the reaction mixture of ϵ -caprolactam and water, and the concentration of CD was followed with the time. The reaction conditions were as follows: the reaction temperature (280°C) and initial water concentration (0.82 mol kg⁻¹) were kept constant, and initial CD concentration was varied (0.21, 0.88, and 1.77 mol kg⁻¹). The

experimental data and the calculated data from the numerical solutions of the rate equations proposed by this work were shown in Figure 4. Figure 4 shows a reasonable agreement between the observed and the calculated CD concentration *versus* time curves and indicates the good applicability of the proposed mechanism and the evaluated kinetic and thermodynamic constants in clarifying the behaviour of CD in the polymerization system.

In conclusion the present study suggests that the proposed mechanism and the evaluated constants are useful to simulate the behaviour of CD in the hydrolytic polymerization of CL and the mixture of CL and CD in various kinds of reactors.

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