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Mechanism and kinetics of the hydrochloric acid initiated polymerization of ε-caprolactam

2. Identification of the kinetic model*

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Summary

A quantitative description of the hydrochloric acid initiated polymerization of caprolactam (CL) based on the previously proposed mechanism is given. Essential parameters were identified by strategy mainly based on principal component analysis. Our kinetic model is in good agreement with experiments and describes specific features of the kinetics of the process with the suggested parameters.

Introduction

The reaction mechanism of the protonic acid initiated CL polymerization was described in our previous communication[1]. The mechanism encompassed also earlier proposals for the mechanism of amine salt initiated[2] and hydrolytic[3] polymerization. Based both on polymerchemical, stereochemical and thermodynamic considerations and experimental evidences a set of reactions was selected supposed to have an essential role. Although our kinetic model is already built upon a reduced mechanism, it comprises 10 differential and 23 algebraic equations with a large number of unknown parameters. Unfortunately only a few of the latter can be extracted from available experimental data. Since the partly intuitive approach applied previously to identify the model parameters was not suitable in this case, a combination of principal component analysis of kinetic models[4] and the indirect method for estimating parameters in differential models[5] seemed useful.

RESULTS AND DISCUSSION

Kinetic model of protonic acid initiated CL polymerization

Mechanism of polymerization initiated by HCl can be described by 28 equations[1]. Neglecting reactions having only negligible influence on kinetics 16 equations have been invoked for formulation of the kinetic model (cf.Table 1, equations 27-42, for the corresponding chemical structures Table 2). Rates - except for (28),(32) and (35), involving fast equilibria - can be expressed by kinetic equations given adjacent to the equations. (Order and indexing is in conformity with those in our preceding papers[1,2].)

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Table 1 Algorithm of the kinetic model of cationic lactam polymerization

$$W = B + Bh + Bah + Bhp - S \quad (1)$$

$$CL = [(K_{14}c1 - 1) + \sqrt{(K_{14}c1-1)^2 + 4(K_{14}c1-1)(c1+c2)}]/2K_{14} \quad (2)$$

$$CLh = CL - c1 \quad (3)$$

$$CLah1 = c2 - CLh \quad (4)$$

$$Ah = CLho - (Bh + Bah + Bhp + CLh) \quad (5)$$

$$CLa = A + B + Ah + Bh + Bhp - S \quad (6)$$

$$R = CLo - (CL + CLa + B + Bah + Bh + Bhp) \quad (7)$$

$$Pn = (R + Bah + S + CLa)/(S - Bhp + CLa) \quad (8)$$

$$A2 = A1\,(1 - 1/\bar{P}n) \quad (9)$$

$$Ah2 = Ah1\,(1 - 1/\bar{P}n) \quad (10)$$

$$B1 = B/\bar{P}n \quad (11)$$

$$Bh1 = Bh/\bar{P}n \quad (12)$$

$$CLah2 = CLah1\,(1 - 1/\bar{P}n) \quad (13)$$

$$Th*** = CLah2/K2 \quad (14)$$

$$Th1 = Ah2/K2 \quad (15)$$

$$Bah* = (A - Ah1 - CLah1)\,Bah/(R + Bhp + Bah) \quad (16)$$

$$Bhp* = (A - Ah1 - CLah1)\,Bhp/(R + Bhp + Bah) \quad (17)$$

$$Bah** = (S - Ah1 - Bh1)\,Bah/(R + Bhp + Bah) \quad (18)$$

$$Bhp** = (S - Ah1 - Bh1)\,Bhp/(R + Bhp + Bah) \quad (19)$$

$$Th = (Ah - Ah1 - CLah1 - Bah** - Bhp**)/K2 \quad (20)$$

$$Tah* = [k15\,CLah1\,Ah + l16\,CLh\,(Ah - Ah1 - CLah1 - Bah* - Bhp*) + l17\,Bah*W]/(l15 + k16 + k17) \quad (21)$$

$$Tah** = k15\,CLa\,Ah1 + l16\,CLh\,(S - Ah1 - Bah** - Bhp**) + l17\,Bah**W/(l15 + k16 + k17) \quad (22)$$

$$Tah = (k15\,CLa\,Ah + l16\,RCLh + l17\,Bah\,W)/(l15 + k16 + k17) \quad (23)$$

Rate constants of catalyzed reactions:

$$k8 = k8o + k8*S + k8**Ah \quad (24)$$

$$k8 = k8*S \quad (25)$$

$$k12 = k12*S \quad (26)$$

Reactions and their rates:

$Ah + CL \rightleftharpoons Th$	$v1 = k1\,CLAh - l1\,Th$	(27)
$Th \rightleftharpoons R + Ah$	$K2 = Ah/Th$	(28)
$Th \rightleftharpoons Bh + W$	$v3 = k3\,Th - l3\,Bh\,W$	(29)
$CL + W \rightleftharpoons A1$	$v6 = k6\,(CLW - A1/K8)$	(30)
$A + CL \rightleftharpoons Te$	$v8 = k8\,(ACL - (A - A1)/K8\,K9)$	(31)
$Te \rightleftharpoons R + A$	$K9 = A/Te$	(32)
$Te \rightleftharpoons B + W$	$v10 = l10\,[(A - A1)K10/K9 - BW]$	(33)
$B + S \rightleftharpoons R + R$	$v12 = k12\,SB - l12\,[R - (A - A1) - (Ah - Ah1) - (B - B1) - (Bh - Bh1)]$	(34)
$CLh + CL \rightleftharpoons CLah1$	$K14 = CLah1/(CL.CLh)$	(35)
$Ah + CLa \rightleftharpoons Tah$	$v15 = k15\,CLa\,Ah - l15\,Tah$	(36)
$Tah \rightleftharpoons R + CLh$	$v16 = k16\,Tah - l16\,RCLh$	(37)
$Tah \rightleftharpoons Bah + W$	$v17 = k17\,Tah - l17\,Bah\,W$	(38)
$CLh + W \rightleftharpoons Ah1$	$v18 = k18\,CLh\,W - l18\,Ah1$	(39)
$CLa + W \rightleftharpoons R + S$	$v19 = k19\,CLa\,W - l19\,(S - A1 - B1 - Ah1 - Bh1 - Bah** - Bhp**)$	(40)
$S + CL \rightleftharpoons S + R$	$v20 = k20\,CLS - l20\,(S - A1 - B1 - Ah1 - Bh1 - Bah** - Bhp**)$	(41)
$Bah + W \rightleftharpoons Bhp + S$	$v21 = k21\,Bah\,W - l21\,Bhp**$	(42)

Differential equation system:

$$d(CL-CL_h)/dt=-v_1-v_{20}-v_{16}+v_{18}-v_6-v_8 \quad (43)$$

$$dB_h/dt=v_3 \quad (44)$$

$$dB_{ah}/dt=v_{17}-v_{21} \quad (45)$$

$$dS/dt=v_{18}+v_{19}+v_{21}+v_6-v_{12} \quad (46)$$

$$dB_{hp}/dt=v_{21} \quad (47)$$

$$dA_{h1}/dt=-k_1A_{h1}CL+l_1T_{h1}-k_{15}A_{h1}CL_a+l_{15}T_{ah}^{**}+v_{18}-k_{20}A_{h1}CL+ +l_{20}A_{h2} \quad (48)$$

$$d(CL_{ah1}+CL_h)/dt=-k_1CL_{ah1}CL+l_1T_h^{***}-k_{15}CL_{ah1}A_h+l_{15}T_{ah}^{*}- -k_{19}CL_{ah1}W+l_{19}A_{h2}+v_{16}-v_{18} \quad (49)$$

$$dB/dt=v_{10}-v_{12} \quad (50)$$

$$dA/dt=-k_{20}A_1CL+l_{20}A_2+v_6-v_{10}-k_{12}A_1B+l_{12}(A-A_1-A_2) \quad (51)$$

$$dA_1/dt=-k_{20}A_1CL+l_{20}A_2+v_6-k_8(A_1CL-A_2/K_8K_9)- -k_{12}A_1B+l_{12}(A-A_1-A_2) \quad (52)$$

$$c1=CL-CL_h \quad \text{(at initial concentration) } c1=CL_o-CL_{ho} \quad (53)$$

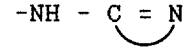
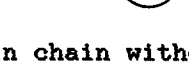
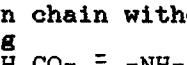
$$c2=CL_{ah1}+CL_h \quad \text{(at initial concentration) } c2=CL_{ho} \quad (54)$$

Computation of observed values:

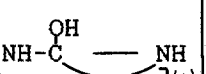
$$[\text{conversion}]=(CL-CL_o)/CL_o \quad (55)$$

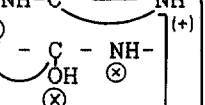
$$[\text{total basicity}]=[A_h+A+B+B_h+B_{ah}+B_{hp}] \quad (56)$$

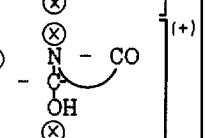
Table 2 Compounds and groups involved in kinetic model

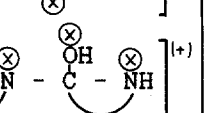
Name	structure	symbol (concentration)
monomer		CL
water	H_2O	W
Basic groups		
amine	$-NH_2$	A
amidine		B
C-terminal groups		
carboxyl	$-COOH$	S
acyllactam		CLa
Groups in chain without branching		
amide		R
Groups in chain with branching		
acyl-amidine		Ba
amidine in polymer chain		Bp

Tetrahedral intermediates:

Te = A + CL 

Th = Ah + CL 

Tah = Ah + CLa 

Th*** = Th + CLa 

⊗ sites of protonation

 denotes: $-(CH_2)_5-$

Subscriptes:
h = hydrochlorides of resp.groups(e.g. A_h=amine hydrochloride)
o = initial concentrations
1,2 first and second members of polymer homologue series
* denotes the concentrations of groups adjacent to A_h and
** adjacent to S in case of B_{ah}, B_{hp} and T_{ah}
(e.g. $B_{hp}^{*} = H_3N\frown\overset{NH}{\overset{(+)}{C}}{=}NH-$ and $B_{hp}^{**} = S\frown\overset{NH}{\overset{(+)}{C}}{=}NH-$)
T_{h1} = T_h adjacent to S
$\bar{P}_n$ = number average degree of polymerization

Determination of rate constants in the equations requires the knowledge of concentrations. Concentration of CL-CL_h, B_h, B_{ah}, S, B_{hp}, A_{1h}, CL_{ah1}+CL_h, B and A_1 can be calculated by means of differential equations (43)-(52) (Table 1). Concentration of CL can be obtained from equation (35) written for K_{14} as well as from the solutions of the differential equation (43) and (49) according to the Eq.(2). Concentration of intermediates figuring in the differential equations - assuming small steady state values for them - can be given by relationships (14),(15),(20)-(23) (Table 1). Concentrations for the amidine groups adjacent A_h and S -i.e. B_{ah}^{*} and B_{hp}^{*}, as well as B_{ah}^{**} and B_{hp}^{**} - can be estimated by Eqs.(16)-(19). Concentration of some additional components were assessed by the Flory distribution, using the Eq.(8) for the number average degree of polymerization. Accordingly values for A_2, A_{h2}, B_1, B_{h1} and CL_{ah2} can be given by equations (9)-(13). Equations, rate constants of the catalytic reactions (24)-(26), initial conditions (53)-(54) and expressions to compute the observed conversion, total basicity, carboxyl and amidine group concentrations from the model variables are given in Table 1 in the logical order directly suitable for computer programming. A more detailed description of the kinetic model will be given in a forthcoming publication. The model describes the time dependence of 32 concentrations and of the number average degree of polymerization. For ten components differential equations are solved, the other variables are computed from 23 algebraic equations. There are 30 kinetic parameters (rate and equilibrium constants) in the model. The aim of identification was to find parameter values which (i) yield a satisfactory description of CL conversion, total basicity, amidine and carboxyl concentrations; (ii) are in a good agreement with parameter values suggested in previous investigation of simpler systems; (iii) describe well the inflection of the conversion curve at low initiator concentration; (iv) can yield N- and C-terminal group concentrations exceeding the initial initiator concentration. To satisfy these partly contradictory requirements a suitable identification strategy was chosen. First the parameter sensitivities of the observed kinetic variable were computed at a set of nominal parameter values selected on the basis of polymerkinetic analogy. Identifiability studies were carried out using principal component analysis discussed in some detail as follows.

Principal component analysis
The variables investigated (e.g. the conversion at observation time "t") depend on the kinetic parameters. The semi-logarithmic sensitivity of the i-th observed $y_i(t)$ with respect to the j-th parameter k_j is defined as[6]

$$s_{ij}(t) = \frac{\partial y_i(t)}{\partial \ln k_j} = k_j \frac{\partial y_i(t)}{\partial k_j}$$

Let S denote the matrix of semi-logarithmic sensitivities. The j-th column of matrix S contains all the sensitivities with respect to parameter k_j. The S^TS cross-product matrix is of dimension p x p where p is the number of investigated parameters. The eigenvalue-eigenvector decomposition of investigated cross-product matrix contains important information on the identifiability of the parameters[4]. For a given set of observation the number of identifiable parameters or parameter combinations is limited by the number of eigenvalues exceeding a certain threshold value. The threshold value is taken from information available on error of measurement. A straightforward way to eliminate eigenvalues below the given threshold is to fix the same number of parameters at their nominal values. The selection of parameters to be fixed is not unique, but the investigation of the eigenvectors corresponding to the small eigenvalues supplies a framework for possible candidates[4]. Final selection is carried out taking into account additional chemical information and practical considerations.

Model identification
The model was fitted by the aid of program package REPROCHE[8] written in FORTRAN 77 for IBM PC. The package consists of the following parts:
- semi-implicit Runge-Kutta method[7] to solve a system of stiff differential equations and the sensitivity equations
- principal component analysis of cross-product sensitivity matrix
- direct and indirect method of nonlinear parameter estimation (Gauss-Newton-Marquardt method)[5]
- statistical interpretation of the results, graphic output.

Because of the complexibility of the model the three sets corresponding to different initiator concentrations were analyzed separately. According to principal component analysis a suitable description of the observations could be hoped too if parameters known previously were fixed except for $K_8 \cdot K_9$ (cf.Table 3, column 1). The number of identifiable parameters were between 6-8 in each case. So further parameters had to be fixed. The final selection is shown in Table 3, column 2. Whenever a choice had to be made between a rate constant and equilibrium constant, the former was fixed. The estimated parameters are shown in Table 3, column 3. The parameter estimation algorithm had no difficulty to fit the

model when only these parameters were estimated. The parameter estimates were, however, different for the data of separate measured series. To obtain a unique and consistent parameter set the information provided by principal component analysis was applied again. The main idea was to fix a parameter if it proved to be well identifiable for any of three data sets. Such an iterative refinement yielded a consistent set of parameter estimates. A further improvement for any of the data sets would cause deterioration of the fit of another one. Optimal values are shown in Table 3, column 3. The lower number of digits is in accordance with the parameter uncertainty.

Comparison of observed and computed values

The curves computed with optimal parameter values are shown in Fig.1. The terminal group concentration - unlike in our previous communication[1] - is normalized relatively to the initial initiator concentration.

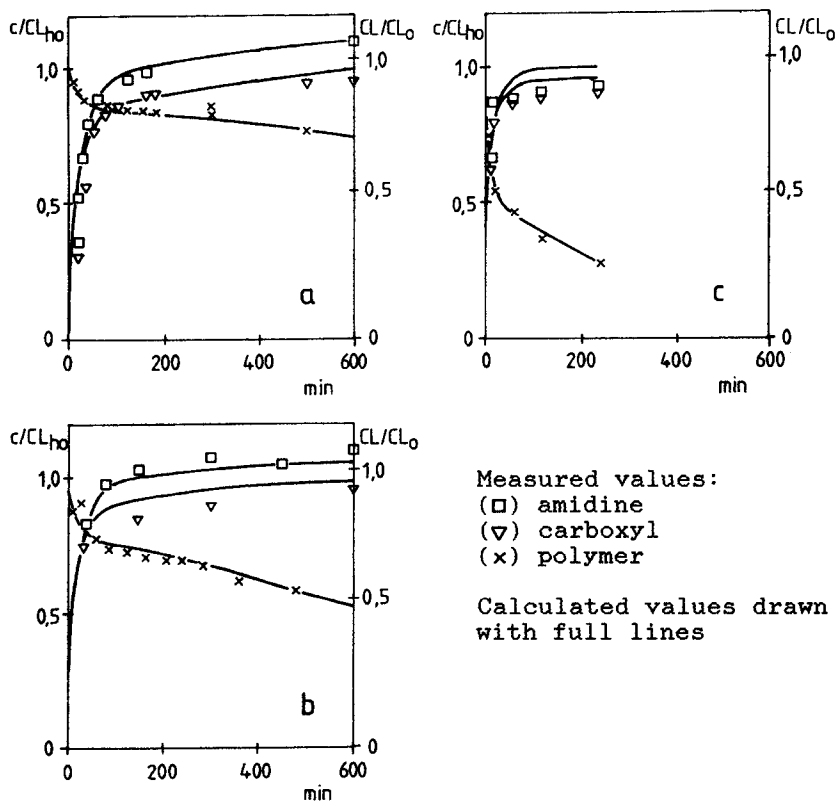


Figure 1 Relative concentration of functional groups (c/CL_{ho}) and monomer (CL/CL_o) in ∈-caprolactam polymerization at 256°C
a., 0.005mol/molCL; b.,0.01mol/molCL; c.,0.035mol/molCL

Table 3 **Numerical values of rate constants k and l and equilibrium constants K of HCl initiated ∈-caprolactam polymerization $K_i = k_i\ l_i^{-1}$**

Parameters taken from amine salt initiated lactam polymerization[2]		Parameters fixed at the starting nominal values		Parameters determined by the least squares curve fitting	
K_1	0.1 g mmol^{-1}	K_{14}	1.0 g mmol^{-1}	K_{15}	1.836 g mmol^{-1}
l_1	1.2 min^{-1}	l_{15}	5.525 min^{-1}	K_{16}	492 mmol g^{-1}
K_2	15	l_{16}	0.1 g mmol^{-1}min^{-1}	K_{17}	2.557 mmol g^{-1}
K_3	8.25 mmol g^{-1}	l_{17}	2.0 g mmol^{-1}min^{-1}	K_{19}	1000 g mmol^{-1}
l_3	0.05 g mmol^{-1}min^{-1}	K_{18}	600 g mmol^{-1}	K_{20}	0.01506 g mmol^{-1}
k_{60}	6.10^{-5} g mmol^{-1}min^{-1}	l_{18}	0.1 min^{-1}	K_{10}/K_9	0.01 mmol g^{-1}
k_6*	0.013 g^{2}mmol^{-2}min^{-1}	l_{19}	0.1 min^{-1}		
k_6**	0.06 g^{2}mmol^{-2}min^{-1}	l_{20}	0.0067 min^{-1}		
K_6	$2.727.10^{-3}$ g mmol^{-1}	K_{21}	2000 g mmol^{-1}		
k_8*	1.7 g^{2}mmol^{-2}min^{-1}	l_{21}	0.05 min^{-1}		
K_8K_9	1.5 g mmol^{-1}				
l_{10}	1.0 g mmol^{-1}min^{-1}				
K_{12}	10^5 g mmol^{-1}				
k_{12}*	0.8 g^{2}mmol^{-2}min^{-1}				

$k_8 = k_{60} + k_8 * S + k_6 ** Ah$
$k_8 = k_8 * S$
$k_{12} = k_{12} * S$
k_{i0} - rate constant of the non-catalysed reaction
S - concentration of carboxyl groups
Ah - concentration of amine hydrochloride

The agreement of observed and computed values is satisfactory although the deviations are not of statistical character probably due to neglected reactions. The inflection character of the computed curve of lactam concentration at low initiator concentration is obvious from the figure. With increasing initiator concentration the inflection is gradually disappearing. The model is also capable of describing the situation where the concentration of the N- or C-terminal groups exceed the initiator concentration.

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