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The Kinetic Equation for the Initiated, Anionic Polymerization of ϵ-Caprolactam

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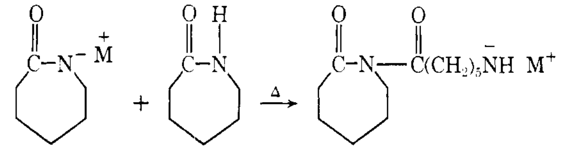
ABSTRACT: The general kinetic equation that describes the low temperature, initiated, anionic polymerization of ϵ-caprolactam has been derived and experimentally satisfied. The kinetics allow the simultaneous formation of two polymer chains from one catalyst molecule.

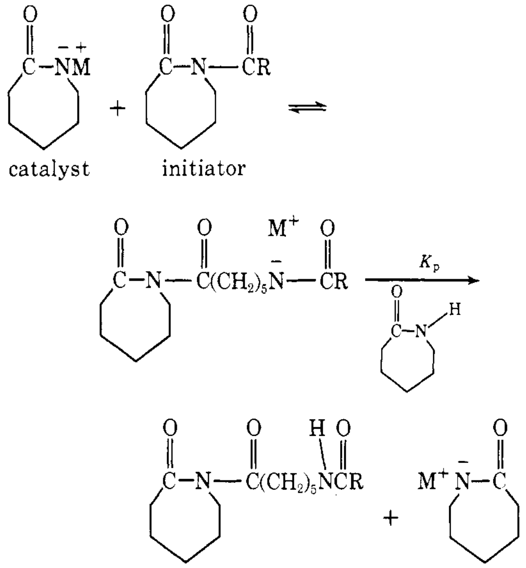
Of the three techniques developed for the polymerization of ϵ-caprolactam, *viz.*, condensation, high-temperature anionic, and initiated, low-temperature anionic, the latter method has received considerable attention recently as it allows rapid polymerization at temperatures below 225°, the melting point of the polymer. Champetier and Sekiguchi[1] derived a kinetic model which fit the high-temperature anionic polymerization. In this system, a lactam imide initiator is formed by the reaction of a caprolactam metal salt catalyst with monomer.



In the area of the low-temperature, anionic polymerization, where a known concentration of an initiator or initiator precursor is added to the monomer, attempts to derive the kinetic equation have been less rewarding. The use of an adiabatic calorimeter by Wittmer and Gerrens[2] and Wichterle, Tomka, and Sebenda[3] to follow the course of the polymerization afforded precise results which were confounded, however, by the superposition of the heat of crystallization on the heat of polymerization. Sittler and Sebenda[4] recently published conversion data obtained by a sampling technique. They were unable to arrive at a satisfactory kinetic equation.

Derivation of the Kinetic Equation

The reaction path which is now generally accepted for the initiated, anionic polymerization of ϵ-caprolactam was first proposed by Mottus, Hedrick, and Butler[5] and, subsequently, Sebenda and Kralicek,[6] in 1958.



(1)

Recently this type of reaction has been termed an "activated monomer polymerization."[7] The polymerization of caprolactam has been characterized as an equilibrium reaction in that there is a definite temperature dependent concentration of residual monomer[8] and there is no known termination reaction other than that which can occur with impurities.

Champetier and Sekiguchi[1] showed the following

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[1] G. Champetier and H. Sekiguchi, *J. Polym. Sci.*, **48**, 309 (1960).

[2] P. Wittmer and H. Gerrens, *Makromol. Chem.*, **89**, 27 (1965).

[3] O. Wichterle, J. Tomka, and J. Sebenda, *Collect. Czech. Chem. Commun.*, **29**, 610 (1964).

[4] E. Sittler and J. Sebenda, *ibid.*, **33**, 270 (1968).

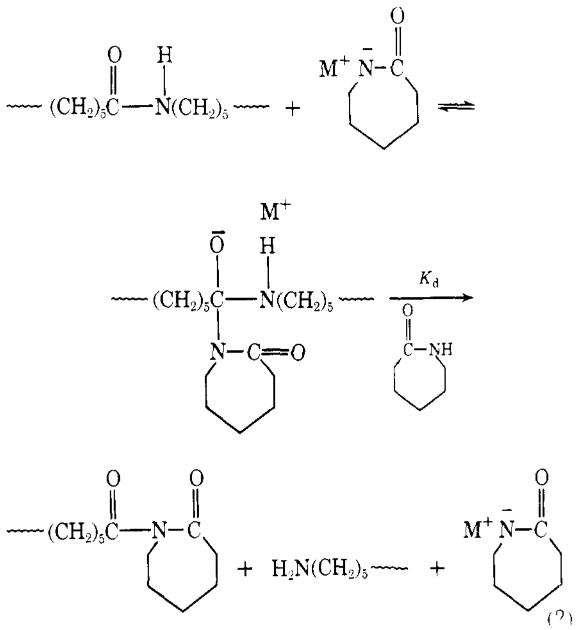
[5] Italian Patent 580,069 (1958), Monsanto Chemical Co.; E. H. Mottus, R. M. Hedrick, and J. M. Butler, French Patent 1,194,451 (1959); U. S. Patent 3,017,391 (1962), filed Dec 13, 1956; U. S. Patent 3,017,392 (1962), filed Aug 5, 1957.

[6] J. Sebenda and J. Kralicek, *Collect. Czech. Chem. Commun.*, **23**, 766 (1958).

[7] M. Szwarc, *Polym. Preprints*, **7**, 11 (1966). Papers presented at the Phoenix Meeting of the American Chemical Society, Jan 1966.

[8] Z. Bukac, *et al.*, *Collect. Czech. Chem. Commun.*, **29**, 2615 (1964).

degradative reaction to be kinetically significant in the high-temperature, anionic polymerization of caprolactam. This reaction path should also be applicable to the rate of the initiated, anionic polymerization of ε-caprolactam.



(2)

Rate equations for the two reactions were readily formulated. In the first derivation of the kinetic equation the rate of polymerization was assumed to be a first-order function of catalyst, initiator, and monomer concentrations. Subsequently, our data indicated that the assumed reaction paths were incorrect with regard to the catalyst and initiator stoichiometry. It was found experimentally that the rate of polymerization is a half-order function of the catalyst concentration and a first-order function of the initiator and monomer concentrations. To avoid repetition the following derivation uses this latter condition which will be justified in the Discussion.

From eq 1, the polymerization reaction is dependent upon the catalyst (C), initiator (I), and monomer (M) concentrations with proton abstraction from the monomer as the rate-determining step. For the degradative

$$\nu_p = K_p[I][C]^{1/2}[M] \tag{3}$$

reaction, eq 2, the rate is dependent upon the polymer (P), catalyst, and monomer concentrations with proton abstraction from the monomer again the rate-determining step. Since the polymer concentration is equivalent

$$\nu_d = K_d[P][C]^{1/2}[M] \tag{4}$$

to 1 − M, eq 4 may be expressed as

$$\nu_d = K_d[C]^{1/2}[M] - K_d[C]^{1/2}[M]^2$$

The differential rate equation for polymerization is then

$$\frac{dP}{dt} = \frac{-dM}{dt} = \nu_p - \nu_d = K_p[I][C]^{1/2}[M] - K_d[C]^{1/2}[M] + K_d[C]^{1/2}[M]^2$$

Integration between limits leads to the kinetic equation

$$\int_0^t dt = -\int_{M_0=1}^{M} \frac{dM}{(K_pIC^{1/2} - K_dC^{1/2})M + K_dC^{1/2}M^2}$$

for the initiated, anionic polymerization of ε-caprolactam

$$t = \frac{1}{C^{1/2}(K_pI - K_d)} \ln\left(\frac{1}{M} - \frac{K_d}{K_pIM} + \frac{K_d}{K_pI}\right) \tag{5}$$

Previous attempts to obtain the kinetic equation had assumed that K_d was negligible at lower conversions and could be ignored in the derivation. This is not valid in that the correct relationship between the polymerization rate and the catalyst and initiator concentrations would not be obtained.

As it stands, eq 5 cannot be solved graphically. To overcome this barrier K_d was assumed to be much smaller than K_p as a first approximation. Therefore, the sum of the terms $-K_d/K_pIM$ and $+K_d/K_pI$ in the logarithmic part of eq 5 becomes insignificant compared to $1/M$. Thus, a plot of ln $1/M$ *vs.* time should be linear with the

$$\text{slope} = C^{1/2}(K_pI - K_d) \tag{6}$$

By rearranging eq 6 to

$$I = K_d/K_p + 1/K_p(\text{slope}/C^{1/2}) \tag{7}$$

a plot of I *vs.* slope/$C^{1/2}$ affords a straight line of slope $1/K_p$ and an intercept of K_d/K_p.

Results

Two different catalyst/initiator systems, sodium caprolactam/N-carbanilinocaprolactam and bromomagnesium caprolactam/N-acetylcaprolactam, were studied. Also, the published data of Sittler and Se-

Table I

Slopes from Sodium Caprolactam/N-Carbanilinocaprolactam Polymerizations at 100°

	Imide, mol	Catalyst, mol	Slope, min^{-1}
A	0.022	0.011	0.0337
	0.018	0.011	0.0287
	0.014	0.011	0.0261
	0.010	0.011	0.0196
	0.006	0.011	0.0128
	0.018	0.009	0.0237
	0.014	0.009	0.0169
	0.014	0.009	0.0172
	0.010	0.009	0.0122
	0.007	0.009	0.0097[a]
	0.006	0.009	0.0104
	0.014	0.007	0.0185
	0.009	0.007	0.0097[a]
	0.0055	0.0055	0.0044[a]
	0.010	0.005	0.0086
	0.0035	0.0045	0.0030[a]
	0.002	0.004[b]	0.0019[a]
	0.002	0.002[b]	0.0015[a]
	0.002	0.002[b]	0.0013[a]
B	0.011	0.011	0.0100[a]
	0.010	0.007	0.0148
	0.006	0.007	0.0119
	0.003	0.011	0.0014[a]
C	0.022	0.009	0.0154
	0.018	0.007	0.0154
	0.014	0.005	0.0118

[a] Initiator from phenyl isocyanate. [b] J. Stehlicek, K. Gehrke, and J. Sebenda, *Collect. Czech. Chem. Commun.*, **32**, 370 (1967).

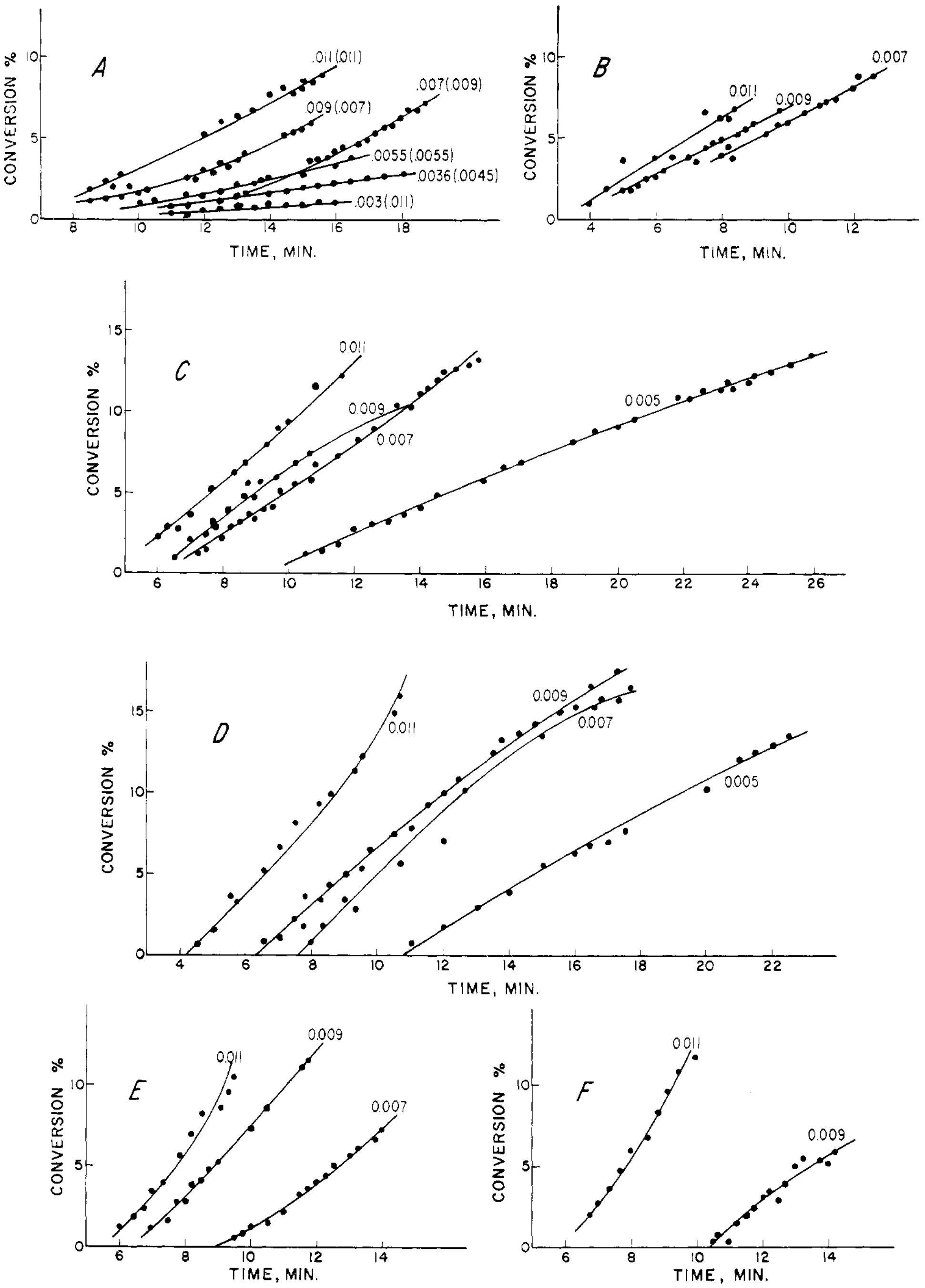
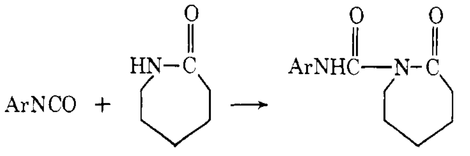


Figure 1. Conversion data for the sodium caprolactam/N-carbanilinocaprolactam system at 100°: A, phenyl isocyanate derived initiator designated as moles of imide (moles of catalyst); B–F, toluene diisocyanate derived initiator; moles of catalyst shown (moles of imide—B 0.006, C 0.010, D 0.014, E 0.018, F 0.0221).

benda[4] for the sodium caprolactam/N-acetylcaprolactam system were evaluated. Except for the polymerizations run to obtain Arrhenius data, the polymerization temperature employed was 100°. This temperature best mated the speed of polymerization with the sampling technique (see Experimental Section).

Sodium Caprolactam/N-Carbanilinocaprolactams. The imidic initiator was formed *in situ* by the addition of an aryl isocyanate to the monomer. Both a difunctional, toluene diisocyanate, and a monofunctional, phenyl isocyanate, initiator precursor were employed. The conversion data for these polymerizations are shown in Figure 1. During most of these runs a conversion was reached at which a sharp viscosity increase was observed. This behavior was attributed to either high molecular weight polymer at low initiator concentration or the start of gelation due to cross-linking at higher concentrations of the difunctional initiator. Therefore, the kinetic calculations were restricted to data obtained before the viscosity increase.



The least square slopes of the straight lines resulting from the pseudo-first-order plot of ln $1/M$ *vs.* time were

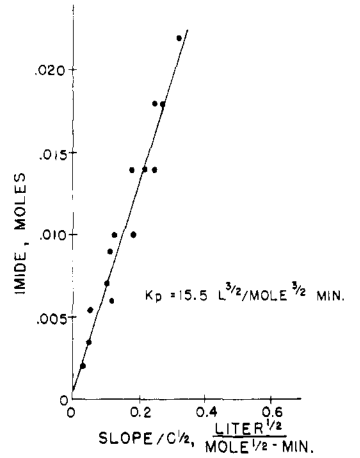


Figure 2. Determination of K_p at 100° for the sodium caprolactam/N-carbanilinocaprolactam system from eq 7.

determined and are listed in Table I. Equation 7 was employed to evaluate K_p. A plot of initiator concentration *vs.* slope/$C^{1/2}$ gave a least squares slope of 0.0638 mol$^{3/2}$ min/l.$^{3/2}$ and a resultant K_p value of 15.5 l.$^{3/2}$/mol$^{3/2}$ min (Figure 2). The value of K_d was estimated to be 7 × 10^{-3} mol$^{5/2}$ min/l.$^{5/2}$ from the intercept of 0.0005 mol/l. The slope values in Table IB were not included in the determination as they were outside experimental error (±0.0020 min^{-1}). The data in Table IC are from polymerizations in which the initiator concentration was greater than twice that of the catalyst. Under these conditions, the polymerization rate was lower than predicted and a gas, thought to be carbon dioxide, was evolved.

A subsequent evaluation of eq 5 in its entirety with a nonlinear regression program[9] verified that K_d was insignificant with respect to K_p at these low conversions and could be ignored in the logarithmic portion of eq 5 without significantly affecting the value of K_p.

Inspection of Figure 1 shows that a significant induction period occurred in all of the polymerizations. An empirical dependence of the induction period on $I^{1/2}/C$, Figure 3, for the difunctional initiator at 100° was established from a conventional technique for determining the order of reactants.[10] No relationship could be found for the monofunctional initiator even though the polymerizations resulting from the two types of initiators were equivalent. This behavior is thought to be the result of the formation of a catalyst–initiator–monomer complex with various stoichiometries of catalyst and initiator. No attempt has been made to verify this hypothesis.

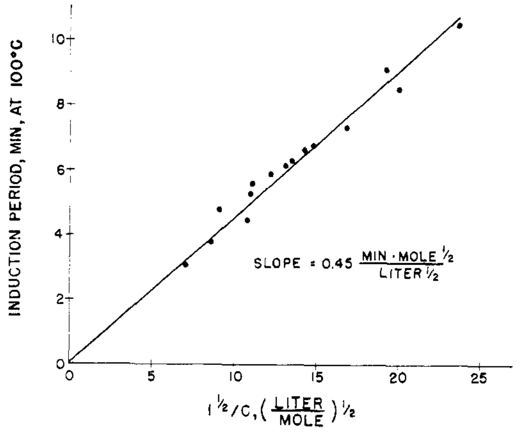


Figure 3. Effect of initiator and catalyst concentration on the induction period at 100° for the sodium caprolactam catalyst and the initiator derived from toluene diisocyanate.

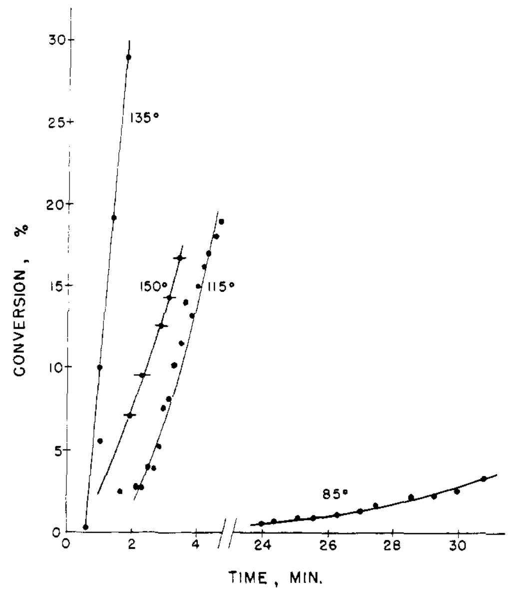


Figure 4. Conversion data at various polymerization temperatures for the sodium caprolactam/N-carbanilinocaprolactam system; moles of imide/moles of catalyst: ●, 0.014/0.009; -●-, 0.002/0.002.

The activation energy for the polymerization was determined in the usual manner from runs at 85, 115, 135, and 150° (Figure 4) in addition to the above 100° data. Since the results at 100° showed K_p to be approximately 1500 times larger than K_d, eq 6 with K_d set equal to zero was used to approximate K_p values from these single polymerizations. The results are listed in Table II. The least squares slope from the plot of log K_p *vs.* $1/T$ gave an activation energy of 22.1 kcal/mol for the polymerization of ε-caprolactam with an aryl isocyanate derived initiator and sodium caprolactam as the catalyst.

Bromomagnesium Caprolactam/N-Acetylcaprolactam.

Table II

Data for the Determination of the Activation Energy for the Sodium Caprolactam/N-Carbanilinocaprolactam Polymerization

Temp, °C	Initiator, equiv	Catalyst, mol	Slope, min^{-1}	K_p, l.$^{3/2}$ mol$^{-3/2}$ min^{-1}
85	0.014	0.009	0.0039	2.9
100	(Equation 7)			15.5
115	0.014	0.009	0.0815	61.4
135	0.014	0.009	0.2961	223
150	0.002	0.002	0.0716	804

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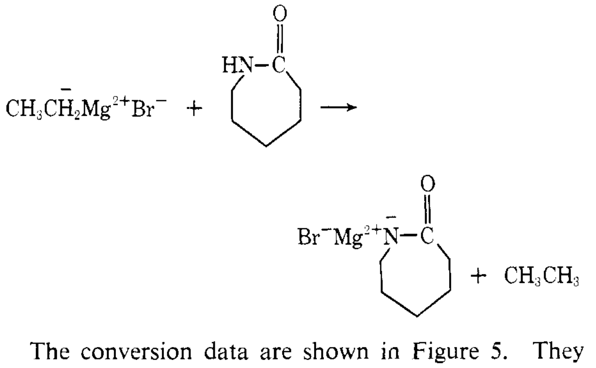
[9] Performed on an IBM 360/35 computer by A. W. Dickinson of the Monsanto Company.

[10] W. J. Moore, "Physical Chemistry," 2nd ed, Prentice-Hall, Englewood Cliffs, N. J., 1955, p 541.

This system was studied to determine the applicability of the kinetic equation to other catalysts and initiators. In these polymerizations, the catalyst rather than the initiator was formed *in situ*.



The conversion data are shown in Figure 5. They were evaluated using eq 7 with the same restriction concerning viscosity changes employed in the previous section. The slopes obtained from the least-squares pseudo-first-order plots are shown in Table III.

TABLE III
SLOPES FROM BROMOMAGNESIUM CAPROLACTAM/N-ACETYLCAPROLACTAM POLYMERIZATIONS AT 100°

Initiator, mol	Catalyst, mol	Slope, min^{-1}
0.009	0.007	0.0528
0.007	0.005	0.0345
0.003	0.003	0.0125

TABLE IV
DATA FOR THE DETERMINATION OF THE ACTIVATION ENERGY FOR THE BROMOMAGNESIUM CAPROLACTAM/N-ACETYLCAPROLACTAM POLYMERIZATION (EQUATION 6)

Temp, °C	Initiator, mol	Catalyst, mol	Slope, min^{-1}	K_p, $\text{l.}^{3/2}\ \text{mol}^{-3/2}\ \text{min}^{-1}$
90	0.003	0.003	0.0084	51
100	(Equation 7)			82.6
110	0.002	0.002	0.0115	129

A plot of initiator concentration *vs.* slope/$C^{1/2}$ (eq 7, Figure 6) gave a least-squares slope of 0.0121 $\text{mol}^{3/2}$ min/$\text{l.}^{3/2}$ and a corresponding rate constant, K_p, of 82.6 $\text{l.}^{3/2}/\text{mol}^{3/2}$ min. A value of 0.01 for K_d was estimated from the intercept of 0.0002 mol/l. These data were coupled with those obtained at 90 and 110° (Figure 7), for which values of K_p (Table IV) were obtained in the same manner as the previous section to arrive at an activation energy of 11.0 kcal/mol for the polymerization of ε-caprolactam with N-acetylcaprolactam as an initiator and an ethylmagnesium bromide derived catalyst.

Although only one experiment was run, it appeared that the particular halide anion used does affect the polymerization. When a chloride-containing catalyst was used, an increase in the induction period and a slight decrease in polymerization rate were observed.

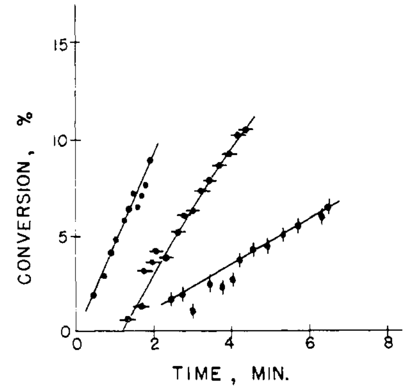
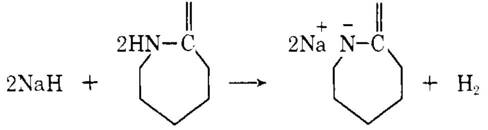
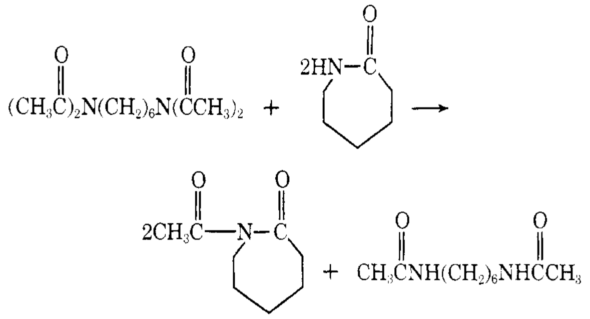


Figure 5. Conversion data for the bromomagnesium caprolactam/N-acetylcaprolactam system at 100°; moles of imide/moles of catalyst: ●, 0.007/0.009; -●-, 0.005/0.007; ɸ, 0.003/0.003.

Sodium Caprolactam/N-Acetylcaprolactam (Sittler and Sebenda[4]). These data were treated in the same manner as the previous systems. In this case, both the catalyst



and the initiator



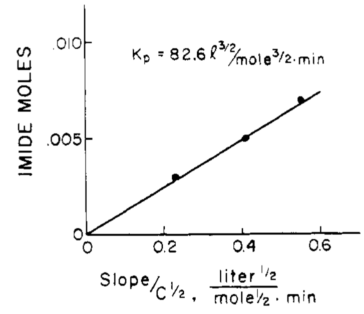


Figure 6. Determination of K_p at 100° for the bromomagnesium caprolactam/N-acetylcaprolactam system from eq 7.

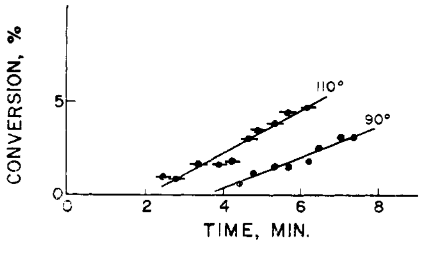


Figure 7. Conversion data at other temperatures for the bromomagnesium caprolactam/N-acetylcaprolactam system; moles of imide/moles of catalyst: ● 0.003/0.003; -●-, 0.002/0.002.

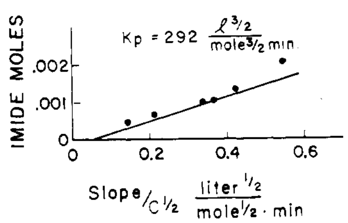


Figure 8. Determination of K_p at 150° for the sodium caprolactam/N-acetylcaprolactam system[4] from eq 7.

are formed *in situ*. The value of K_p at 150° was evaluated from the pseudo-first-order slopes (Table VA) according to eq 7 as 292 $\text{l.}^{3/2}/\text{mol}^{3/2}$ min (Figure 8). In this instance, the least-squares plot had a negative intercept, −0.0001 mol/l., and K_d was assumed to be negligible. Sittler and Sebenda[4] showed that at initiator concentrations greater than twice that of the catalyst, the polymerization rate was slower than expected. In this present analysis of their data, these same runs (Table VB) were also found to give rate constants outside the experimental error of the slope in Figure 8. The Arrhenius plot, again using eq 6 with K_d equal to zero to evaluate K_p for the 140, 160, and 170° (Table VI) polymerizations, afforded an activation energy of 16.0 kcal/mol. This agrees fairly well with their reported value of 16.8 kcal/mol obtained from apparently unpublished adiabatic calorimeter experiments.

Experimental Section

The reactor was a 3-l. four-necked flask, to the bottom of which an 8-mm stopcock had been attached. The reactor was equipped with a mechanical stirrer, positive nitrogen pressure inlet, vacuum pump, a heating mantle modified to accommodate the stopcock, and a thermocouple. The monomer temperature was maintained through a Wheelco temperature controller. The flask was charged with a known amount of ϵ-caprolactam (900–1200 g). The monomer was dried by distilling off water and a known amount of ϵ-caprolactam (50–100 g) at 175° (25 mm) using dry nitrogen to maintain the pressure. The monomer was then cooled to *ca.* 150° and the isocyanate added. The solution was degassed three times and then cooled to the polymerization temperature. The sodium caprolactam was then added. This was taken as time zero. In the case of the other system, the ethereal solution of 3 *M* ethylmagnesium bromide was added to the dried monomer a 130°. The N-acetylcaprolactam was added at the polymerization temperature.

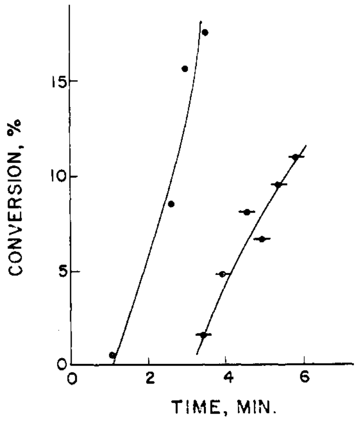


Figure 9. Conversion data for the sodium caprolactam/N-acetylcaprolactam system at 100°; moles of imide/moles of catalyst: ●, 0.014/0.009; -●-, 0.007/0.007.

Table V

Slopes from Sodium Caprolactam/N-Acetylcaprolactam Polymerizations at 150°

	Initiator, mol	Catalyst, mol	Slope, min^{-1}
A	0.0007	0.001	0.0068
	0.001	0.001	0.0108
	0.001	0.001	0.0114
	0.0013	0.001	0.0136
	0.002	0.001	0.0174
	0.0005	0.0005	0.0031
	0.001	0.0005	0.0083
B	0.0015	0.0005	0.0090
	0.002	0.0005	0.0104
	0.004	0.0005	0.0110

Table VI

Data for the Determination of the Activation Energy for the Sodium Caprolactam/N-Acetylcaprolactam Polymerization (Equation 6)

Temp, °C	Initiator, mol	Catalyst, mol	Slope, min^{-1}	K_p, $\text{l.}^{3/2}$ $\text{mol}^{-3/2}$ min^{-1}
140	0.001	0.001	0.0048	155
150	(Equation 7)			292
160	0.001	0.001	0.0142	458
170	0.001	0.001	0.0218	703

Reagents. The toluene diisocyanate, an 80:20 mixture of the 2,4 and 2,6 isomers, respectively (Mondur TD-80, Mobay Chemical Co.), phenyl isocyanate, 3 *M* ethylmagnesium bromide in diethyl ether, and 2.41 *M* phenylmagnesium chloride in tetrahydrofuran were used as received. The N-acetylcaprolactam[11a] and the sodium caprolactam[11b] were synthesized by conventional techniques.

Linear least square determinations were performed with an Olivetti-Underwood Programma 101.

Discussion

Catalyst Functionality. The kinetic equation was initially derived with the polymerization rate taken as a first-order function of the catalyst, initiator, and monomer concentrations. When the data were evaluated according to this equation, negative values for K_d were always obtained. Since these negative values are not possible, the stoichiometry of the reaction components was reassessed.

The experimental fact that concentrations of initiator greater than twice that of the catalyst did not give the expected increase in polymerization rate for the two catalyst/initiator systems examined led to the conclusion that the catalyst molecule is difunctional in this system and will allow initiation of polymerization by two or less imidic functions. This new stoichiometry, which was expressed as $[\text{catalyst}]^{1/2}$ [initiator] to simplify the integration, was substituted into rate equations, eq 3 and 4.

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[11] (a) R. E. Benson and T. L. Cairns, *J. Amer. Chem. Soc.*, **70**, 2115 (1948); (b) F. Bayerlein, K. Dachs, and H. Wolhelm, German Patent 1,204,821 (1965).

TABLE VII
THE EFFECT OF CATALYST/INITIATOR STOICHIOMETRY ON INTERCEPT VALUES FOR EQUATION 7

	—Intercept,	mol/l. × 10^3—
Catalyst (initiator)	[C] [I]	$[C]^{1/2}$ [I]
Bromomagnesium caprolactam (N-acetylcaprolactam)	−6.7	+0.2
Sodium caprolactam (N-carbanilinocaprolactam)	−0.3	+0.5
Sodium caprolactam (N-acetylcaprolactam)	−2.5	+0.1

Reevaluation of the data using eq 7 resulted in positive intercepts and K_d values. As further verification, two sodium caprolactam catalyzed polymerizations were run at 100° with N-acetylcaprolactam as the initiator (Figure 9). The resulting changes in intercept values are summarized in Table VII.

These facts suggest that two imide functions occupy coordination sites around one catalyst molecule and lead to the conclusion that there may be simultaneous growth of two polymer molecules from a catalyst site if an initiator/catalyst ratio of 2 is employed. If ratios of less than 2 are employed or the polymer chain with its imide end group is removed from the catalyst, degradative and branching[12] processes should be enhanced due to the ability of the polymer amide groups to compete more favorably with monomer for coordination sites than they could with imide functions.

Activation Energies. From the reaction path scheme it is expected that polymerization activation energies should be essentially identical for a given catalyst after the initial addition to an initiator species. This was not found to be true for sodium caprolactam with N-carbanilinocaprolactams and N-acetylcaprolactam. This anomaly may be explained in part by a coordination mechanism. The urea end group formed from the carbanilinoimide would more readily coordinate with the catalyst than the amide end group resulting from the N-acyllactam. At temperatures higher than 120° it has been shown[13] that disubstituted ureas react with the catalyst to form an imide and an amine, the latter acting as a polymerization modifier.

Conclusions

Although this kinetic equation does not specifically account for all of the many possible side reactions and equilibria,[1,4] it does satisfactorily describe the initiated, anionic polymerization of ε-caprolactam with regard to the rate-determining steps.

Acknowledgment. We wish to thank Dr. R. M. Hedrick for his encouragement.

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[12] E. H. Mottus, R. M. Hedrick, and J. M. Butler, *Polym. Preprints*, **9**, 390 (1968). Papers presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

[13] E. H. Mottus and R. M. Hedrick, U. S. Patent 3,086,962 (1963).

Polyimides. Synthesis and Polymerization of 4-Carboxy-2-piperidone

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ABSTRACT: A new polyimide, poly[(2,5-dioxo-1,3-pyrrolidinediyl)dimethylene], has been obtained by thermal polymerization of 4-carboxy-2-piperidone, which was synthesized from dialkyl itaconate *via* cyanomethyl succinate. A possible mechanism of polymerization is discussed that involves isomerization of the 4-carboxy-2-piperidone and step-growth polymerization of the isomerization product.

Recent reports from this laboratory have been concerned with synthesis and polymerization of β-carboxymethylcaprolactam.[1-4] The corresponding polymer was identified as a poly[(2,6-dioxo-1,4-piperidonediyl)trimethylene],[2] the formation of which has been explained by a mechanism that involved an initial isomerization of the caprolactam derivative to a reactive species and subsequent polymerization of the latter by condensation.[3] Since to our knowledge this type of mechanism was unique in the area of condensation polymerization, it was of interest to determine the scope of this new polymerization process. A research program concerned with the study of lactams containing carboxylic functions has therefore been initiated. In this paper we shall report on the synthesis and polymerization of 4-carboxy-2-piperidone.

Discussion

Monomer. The synthesis of 4-carboxy-2-piperidone (IV) consisted of the addition of hydrogen cyanide to dialkyl itaconate I and reductive cyclization of the resulting dialkyl cyanomethylsuccinate II to afford

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