Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Kinetics of Anionic Polymerization of ε-Caprolactone (εCL). Propagation of Poly-ε=CL-K Ion Pairs

Stanisl Slashaw Sosnowski[a]; Stanisl Slashaw Slomkowski[a]; Stanisl Slashaw Penczek[a]
[a] Polish Academy of Sciences Centre of Molecular and Macromolecular Studies, Boczna, Poland

To cite this Article Sosnowski, Stanisl Slashaw , Slomkowski, Stanisl Slashaw and Penczek, Stanisl Slashaw(1983) 'Kinetics of Anionic Polymerization of ε-Caprolactone (εCL). Propagation of Poly-ε=CL-K Ion Pairs', Journal of Macromolecular Science, Part A, 20: 9, 979 — 988

To link to this Article: DOI: 10.1080/00222338308060806

URL: http://dx.doi.org/10.1080/00222338308060806

J. MACROMOL. SCI.–CHEM., A20(9), pp. 979-988 (1983)

Kinetics of Anionic Polymerization of ε-Caprolactone (εCL). Propagation of Poly-ε-CL$^-$K$^+$ Ion Pairs

STANISŁAW SOSNOWSKI, STANISŁAW SŁOMKOWSKI,
and STANISŁAW PENCZEK*

Polish Academy of Sciences
Centre of Molecular and Macromolecular Studies
90-362 Łódź, Boczna 5, Poland

ABSTRACT

Kinetics of the anionic polymerization of ϵ-caprolactone (ϵCL) initiated with $(CH_3)_3SiO^-K^+$ and carried out in THF solution has been studied in the temperature range from 0 to 20°C by using a calorimetric method. From the kinetic results and from conductometric measurements of the dissociation constant of the living poly-ϵCL$^-$K$^+$ ion pairs ($K_D^{20} \approx (4 \pm 2) \times 10^{-10}$ mol/L), we concluded that at the conditions indicated above and for concentrations of active centers ranging from 10^{-3} to 3.7×10^{-2} mol/L, propagation proceeds on the ion pairs and is disturbed neither by dissociation nor by the formation of higher aggregates. For the polymerization of ϵCL proceeding on the poly-ϵCL$^-$K$^+$

---

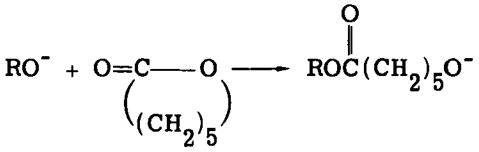
*To whom correspondence should be addressed.

0022-233X/84/2009-0979$3.50/0

ion pairs, the following activation parameters were found: $\Delta H_p^{\ddagger} = 17 \pm 2$ kJ/mol, $\Delta S_p^{\ddagger} = -180 \pm 20$ J/mol·K ($k_p(20°C) = 4.7$ L/mol·s).

INTRODUCTION

Anionic polymerization of ϵ-caprolactone (ϵCL) proceeds with acyl-oxygen bond scission:



and one may expect that active centers, as in the polymerization of ethylene oxide [1-6], can be present in the form of free alkoxide anions, ion pairs, and their higher aggregates. Attempts to initiate polymerization of ϵCL with carboxylates, with subsequent alkyl-oxygen bond scission, were successful only at the much higher temperatures (at 200°C) [7], and thus this mode of polymerization does not take place at the applied conditions.

Alkoxides are known to form aggregates, particularly in media of low polarity [1, 2]. We have recently shown that in the anionic polymerization of ϵCL initiated with $(CH_3)_3SiO^-Na^+$ and carried out in THF solvent at temperatures below 30°C, active centers are aggregated, and in average each aggregate is constituted from three active species—presumably ion pairs [8] forming the corresponding six-membered aggregates. Analysis of the data provided by Yamashita also indicate a considerable aggregation of active centers in the polymerization of ϵCL with Li^+ counterion [9].

In the case of systems in which not only free ions and ion pairs but also various aggregates are formed, determination of the propagation rate constants with participation of free ions and ion pairs is difficult. Hence, we decided to look for a simpler system, expecting to find the conditions for ϵCL polymerization at which formation of aggregates would be suppressed.

In this paper we report on the kinetics of the anionic ϵCL polymerization with K^+ counterion and on the determination (for the first time) of the propagation rate constant for ϵCL on the active centers with a well-defined physical structure (namely, on poly-ϵCL^-K^+ ion pairs).

EXPERIMENTAL PART

Monomer (ϵCL) and solvent (THF) were purified as described previously [8].

The initiator, $(CH_3)_3SiO^-K^+$, was synthesized from $(CH_3)_3SiOH$ and K (mirror) in the same way as was the corresponding Na derivative [8].

The kinetics of polymerization was monitored by using a quasi-adiabatic calorimeter constructed similarly to the apparatus designed by Plesch [10].

The dissociation constant of poly-ϵCL^-K^+ ion pairs was measured conductometrically by using an apparatus described previously [11]. The cell constant was equal to 3.28×10^{-2} cm^{-1}. Conductivity was measured with the semiautomatic bridge BM 484 (Tesla, Czechoslovakia) equipped with an internal generator providing 1592 Hz.

RESULTS

Kinetics of ϵCL Polymerization

Kinetics of the ϵCL polymerization was investigated in the temperature range from 0 to 20°C and for initiator concentrations ranging from 1×10^{-3} to 3.7×10^{-2} mol/L. In all experiments the initial monomer concentration was equal to 5×10^{-1} mol/L.

In Fig. 1 the temperature change recorded during kinetic experiment is shown; Part AB describes the increase of the temperature due to the polymerization process, and part BC the decrease of temperature, after the reaction has been completed, due to the nonideal adiabaticity and the heat transfer to the thermostat.

We did show previously [12] that when the heat evolution during polymerization is much faster than the heat transfer from the calorimeter to the thermostat, and at the same time slow enough to enable the equilibrium between the calorimeter and the reacting mixture to be maintained, the following equation describes the changes of the temperature during the kinetic experiment:

$$T - T_0 = (\Delta H_p M_0/\rho)[\exp(-\beta t) - \exp(-k_p^{app}[I]_0 t)] \qquad (1)$$

where T and T_0 are temperatures of the solution in the calorimeter and of the thermostating bath, respectively, ΔH_p denotes the enthalpy of polymerization, ρ is used for the heat capacity of the solution-calorimeter system, β is the coefficient determining the heat transfer from the calorimeter to the thermostat, M_0 denotes the initial monomer content in moles, $[I]_0$ is the initial concentration of initiator, k_p^{app} is the observed apparent propagation constant, and t denotes time.

The above equation holds for $\beta << k_p^{app}[I]_0$ in the case when the

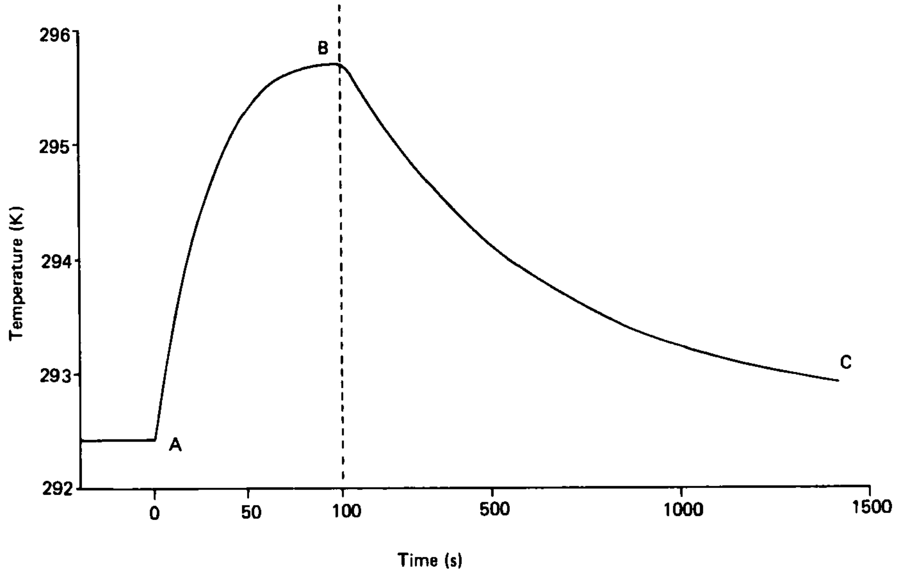


FIG. 1. Temperature change recorded during kinetic experiment. Conditions $[\epsilon CL]_0 = 0.5$ mol/L, $[I]_0 = 7.56 \times 10^{-3}$ mol/L, $T_0 = 292.4$ K. Part AB illustrates the increase of temperature due to the polymerization process; part BC illustrates the cooling of the solution after the completion of polymerization.

opposite inequality holds heat is transferred to the thermostat as fast as it is produced in the course of polymerization and the calorimeter cannot be considered as quasi-adiabatic.

The way in which the discussed equation may be used for the determination of k_p^{app} and ΔH_p will be shown by using the data of the experiment illustrated in Fig. 1.

When the polymerization is completed, i.e., when $\exp(-k_p^{app}[I]_0 t) \approx 0$, the change of the temperature is described by

$$\ln(T - T_0) = \ln(\Delta H_p M_0/\rho) - \beta t \tag{2}$$

The data corresponding to Curve BC in Fig. 1 were used for plotting the dependence of $\ln(T - T_0)$ on time (cf. Fig. 2). From this plot $\beta = 2.03 \times 10^{-3}$ 1/s and $\Delta H_p M_0/\rho = 3.71$ K (by extrapolation to $t = 0$) were determined. Equation (1) can be rearranged to give

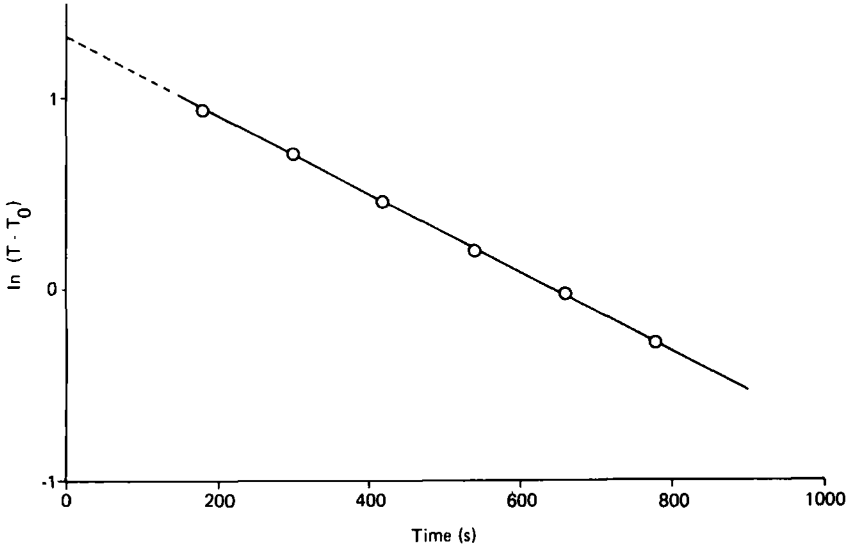


FIG. 2. The dependence of ln $(T - T_0)$ as a function of time for the experiment illustrated in Fig. 1. From the slope, $\beta = 2.03 \times 10^{-3}$ 1/s; and from the intercept, $\Delta H_p M_0/\rho = 3.71$ K were found.

$$-\ln\left[\exp(-\beta t) - (T - T_0)\rho/(\Delta H_p M_0)\right] = k_p^{app}[I]_0 t \qquad (3)$$

Substituting into Eq. (3) the values of β and $\Delta H_p M_0/\rho$ determined previously for the discussed experiment, and plotting the left-hand side of Eq. (3) as a function of time (Fig. 3), the value $\gamma = k_p^{app}[I]_0 = 3.54 \times 10^{-2}$ L/s has been determined. The enthalpy of polymerization ΔH_p was determined from a comparison of $\Delta T_{max} = \Delta H_p M_0/\rho$ with the increase of the temperature ΔT, due to the heating of the solution during time Δt with the electrical heater (Pt thermoresistor), having a power $W = 8.4 \times 10^{-1}$ J/s. In the experiment discussed below, ΔH_p was found equal to 19.7 kJ/mol. In a similar way $\gamma = k_p^{app}[I]_0$ and ΔH_p in other experiments were determined. The corresponding values are given in Table 1.

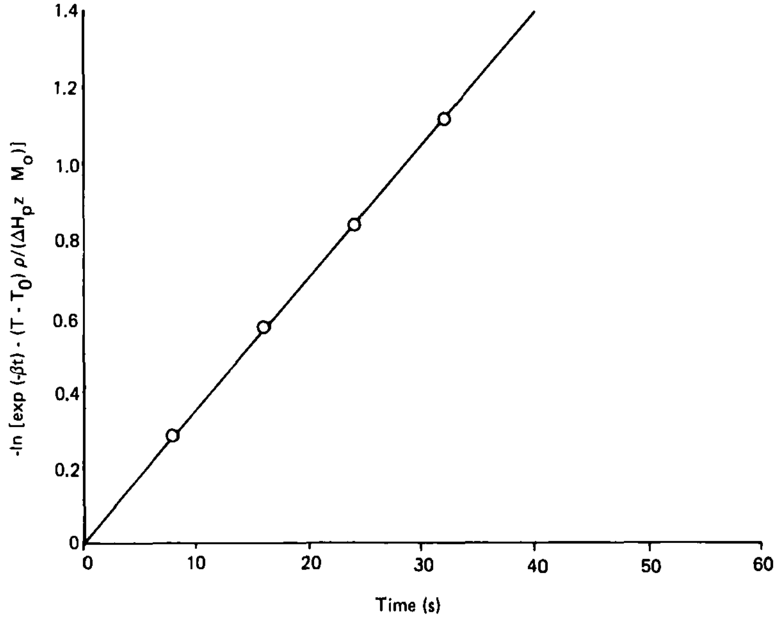


FIG. 3. The dependence of -ln [exp $(2.03 \times 10^{-3}\ s^{-1} \cdot t)$ - $(T - T_0) \cdot$ 0.27] on time for the experiment illustrated in Fig. 1. From the slope, $\gamma = k_p^{app}[I]_0 = 3.54 \times 10^{-2}$ 1/s was found.

Dissociation of Poly-ϵCL-K^+ Ion Pairs

Attempts to measure the dissociation constant (K_D) of the poly-ϵCL^-K^+ ion pairs were complicated by the equilibria between linear macromolecules with active centers and cyclic oligomers. The procedure usually used for the conductometric determination of the dissociation constant consists of examining the dependence of the molar conductance Λ on the concentration of the solute [3, 4]. This procedure can be applied only when the values of the dielectric constant, viscosity, and eventually of the limiting molar conductances of ions are constant.

In the case of poly-ϵCL^-K^+, due to the equilibrium between linear and cyclic macromolecules, the addition of each portion of an ionic active species to the solution is accompanied by the addition of cyclic oligomers. In this way not only is the concentration of ions changed but also the dielectric constant and viscosity of the solution change. Thus, the procedure applied, e.g., for the measurements of the dissociation constant of the ion pairs in the polymerization of ethylene oxide [3, 4], was

TABLE 1. Values of $\gamma = k_p^{app}[I]_0$, k_p^{app}, and ΔH_p Determined for the Polymerization of ϵCL Initiated with $(CH_3)_3SiO^-K^+$(I) in THF Solvent. In All Experiments, $[\epsilon CL]_0 = 0.5$ mol/L.

Temperature (°K)	$[I]_0 \times 10^3$ mol/L	$\gamma \times 10^3$ 1/s	k_p^{app} (L/mol·s)	ΔH_p (kJ/mol)[a]
274	5.34	3.64	0.682	20.6
	13.1	7.96	0.608	18.8
	26.1	12.1	0.464	21.0
	37.3	27.9	0.747	19.2
284	2.19	2.00	0.913	24.6
	4.29	5.13	1.20	20.7
	6.13	7.56	1.23	21.9
	6.54	8.10	1.24	19.1
	22.55	33.7	1.49	20.9
	23.21	32.9	1.42	24.2
293	1.01	4.68	4.65	18.1
	7.56	35.4	4.68	19.6
	25.08	125.8	5.01	20.9

[a] $\Delta\overline{H}_p = 20 \pm 2$ kJ/mol.

not applicable to our investigations. In the case of the poly-ϵCL$^-$K$^+$ ion pairs we could only estimate the dissociation constant on the basis of several assumptions. The limiting molar conductance of K$^+$ ions was calculated from the equation $\eta\Lambda_0^+ = 0.242$ (η in poise units, Λ_0^+ in cm^2/Ω·mol), which in THF at 20°C gives the value $\Lambda_0^+ = 47$ cm^2/Ω·mole used by other investigators [4]. The limiting molar conductance of poly-ϵCL$^-$ anions was estimated from the relation between $\eta\Lambda_0^-$ and $\overline{M}_n$ [13]. $\overline{M}_n$ of the linear fraction of poly-ϵCL was calculated for each concentration of active centers (it was assumed that the concentration of active centers is equal to the initial concentration of initiator $[I]_0$) from the dependence $\overline{M}_n = ([M]_0 - [M_n]_e)MW/[I]_0$, where $[M]_0$ denotes the initial monomer concentration, $[M_n]_e$ the equilibrium concentration of all cyclic oligomers in monomer units (values reported by Yamashita [14], and MW the molecular weight of the monomer. The molar conductances of active centers (Λ) were measured at 20°C for poly-ϵCL equilibrates in THF solvent. Polymerizations were carried out with initial monomer concentration equal to 5×10^{-1} mol/L and with initiator concentrations ranging from 2.5×10^{-3} to 8.5×10^{-3} mol/L. By using values of the calculated limiting molar conductances ($\Lambda_0 = \Lambda_0^- + \Lambda_0^+$) and the measured molar conductances (Λ), the degree of dissociation $\alpha = \Lambda/\Lambda_0$ and the dissociation constant $K_D = \alpha^2 [I]_0/(1 - \alpha)$ were estimated. The following value of the dissociation constant was obtained: $K_D(20°) = (4 \pm 2) \times 10^{-10}$ mol/L. This value is higher than that measured for potassium alkoxide active centers in the polymerization of ethylene oxide (at 20°C $K_D = 1.8 \times 10^{-10}$ mol/L [2]). This may be, at least partially, attributed to the higher dielectric constant of the poly-ϵCL equilibrate in THF than that of THF alone. We found that the value of the dielectric constant of the poly-ϵCL equilibrate in THF containing 5×10^{-1} mol/L of ϵCL mers is equal to 8.1 at 20°C, whereas the value reported in the literature for THF at the same temperature is 7.6 [15].

Conclusions from the Kinetic Measurements and from the Measurements of the Dissociation Constant of Poly-ϵCL$^-$K$^+$ Ion Pairs

The main object of this work is to determine the rate constants of propagation on active centers with well-defined physical structure in the anionic polymerization of ϵCL.

In Fig. 4 the dependence of ln γ ($\gamma = k_p^{app}[I]_0$) on ln $[I]_0$ is shown. For all temperatures the plots obtained are straight lines with slopes

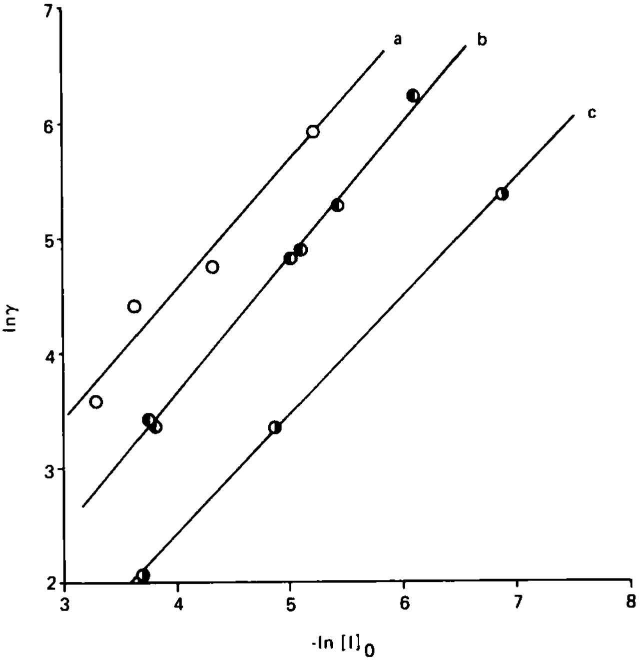


FIG. 4. The dependences of ln γ ($\gamma = k_p^{app}[I]_0$) on ln $[I]_0$. The slopes are (a) 1.1 ± 0.2, (0°C), (b) 1.1 ± 0.2 (10°C), and (c) 1.02 ± 0.01 (20°C).

close to 1. This indicates that k_p^{app} does not depend on the total concentration of active centers.

When the concentration of the active centers is changed from 10^{-3} to 4×10^{-2} mol/L, the calculated fractions of free ions ($K_D(20°) \approx 4 \times 10^{-10}$ mol/L) decrease from $6.3 \times 10^{-2}\%$ to $1.0 \times 10^{-2}\%$. Thus, although the proportion of free ions changes about 6 times, k_p^{app} remains constant. Assuming tentatively that in propagation the total concentration of active centers is equal to 4×10^{-2} mol/L, and free ions constituting a fraction of $1.0 \times 10^{-3}\%$ would contribute no more than 10% of the chain propagation steps, one should expect that lowering the total concentration of active centers to 10^{-3} mol/L (when the fraction of free ions is increased to $6.3 \times 10^{-2}\%$) will cause an increase of k_p^{app} 1.5 times. The experimental results show, however, no increase in rate (cf. Table 1), and hence we have to assume that the free ions do not significantly contribute to propagation in the process investigated.

Moreover, from the observation that k_p^{app} does not depend on $[I]_0$ we can conclude that either ion pairs of living poly-ϵCL do not aggregate at the conditions in which the polymerization was investigated, or that the active centers have the same reactivity regardless from the degree of aggregation. However, this last assumption cannot hold because for the active centers of similar chemical structure in the polymerization of ethylene oxide [1-2] and also for poly-ϵCL^- with Na^+ and Li^+ counterions [8, 14], the reactivity of aggregates is much lower than those of ion pairs. From the above considerations we are inclined to assume that the measured k_p^{app} are indeed equal to the rate constants describing propagation on ion pairs ($k_p^{\mp}$). From the dependence of ln ($k_p^{\mp}$) on the reciprocal absolute temperature, the enthalpy and entropy of activation were calculated and found to be equal to 17 ± 2 kJ/mol and -180 ± 20 J/mol·K, respectively.

REFERENCES

[1] A. A. Solovyanov and K. S. Kazanskii, Vysokomol. Soedin., A12, 2114 (1970).
[2] A. A. Solovyanov and K. S. Kazanskii, Ibid., A14, 1063 (1972).
[3] A. Deffieux and S. Boileau, Polymer, 18, 1047 (1977).
[4] N. V. Ptitsyna, V. K. Kazakevich, and K. S. Kazanskii, Vysokomol. Soedin., A19, 2787 (1977).
[5] J. E. Figueruelo and D. J. Worsfold, Eur. Polym. J., 4, 439 (1968).
[6] A. A. Solovyanov and K. S. Kazanskii, Vysokomol. Soedin., A14, 1072 (1972).
[7] G. A. Estrina, S. P. Davtjan, and B. A. Rozenberg, Ibid., A18, 2438 (1976).
[8] S. Sosnowski, S. Slomkowski, S. Penczek, and L. Reibel, Makromol. Chem., 184, 2159 (1983).
[9] K. Ito and Y. Yamashita, Macromolecules, 11, 68 (1978).
[10] R. H. Biddulph and P. H. Plesch, J. Chem. Soc., p. 3913 (1960).
[11] S. Slomkowski and S. Penczek, Macromolecules, 13, 229 (1980).
[12] S. Sosnowski and S. Slomkowski, Polimery, 27, 149 (1982).
[13] J. Comyn, F. S. Dainton, and K. J. Ivin, Eur. Polym. J., 6, 319 (1970).
[14] K. Ito, Y. Hashizuka, and Y. Yamashita, Macromolecules, 10, 821 (1977).
[15] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Interscience, New York, 1968, Chap. IV, p. 161.

Accepted by editor March 27, 1983
Received for publication May 1, 1983