# Kinetics of the Dispersion Ring-Opening Polymerization of ϵ-Caprolactone Initiated with Diethylaluminum Ethoxide

**Mariusz Gadzinowski, Stanislaw Sosnowski, and Stanislaw Slomkowski***

*Center of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Lodz, Poland*

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ABSTRACT: Dispersion polymerization of ϵ-caprolactone initiated with diethylaluminum alkoxide, carried out in the 1,4-dioxane:heptane (1:9 v/v) mixture at room temperature in the presence of poly(dodecyl acrylate)-*g*-poly(ϵ-caprolactone) used as the surface active agent, proceeds in two stages. In the first stage the growth of the poly(ϵ-caprolactone) chains is initiated in solution and, when the molecular weight of growing macromolecules comes close to 1000, the primary particles are nucleated and all propagating chains become incorporated into growing microspheres. In the second stage the polymerization process consists of propagation taking place inside microspheres into which monomer molecules diffuse from solution. During the first stage the apparent propagation rate constant is low and does not exceed $1 \times 10^{-2}$ L·mol$^{-1}$·s$^{-1}$. In the second stage, due to the high local concentration of growing species confined in polymer particles, the apparent propagation rate constant becomes much higher. For monomer concentrations in the region from $3.9 \times 10^{-1}$ mol·L$^{-1}$ to $4.3 \times 10^{-1}$ mol·L$^{-1}$ and for initiator concentrations ranging from $3.4 \times 10^{-3}$ mol·L$^{-1}$ to $2.6 \times 10^{-2}$ mol·L$^{-1}$ the apparent propagation rate constant ($k_p^{app}$) varied from $4.79 \times 10^{-1}$ L·mol$^{-1}$·s$^{-1}$ to $6.5 \times 10^{-2}$ L·mol$^{-1}$·s$^{-1}$.

## Introduction

Recently, we reported on the dispersion polymerization of ϵ-caprolactone (CL) leading to microspheres with the number average diameter $\bar{D}_n = 0.628\ \mu$m and with the low diameter polydispersity ($\bar{D}_v/\bar{D}_n = 1.038$, where $\bar{D}_v$ denotes the volume average diameter).[1] The advantage of the dispersion polymerization, in comparison with polymerizations in solution, consists of the convenient isolation of produced polymer, which quickly sediments from suspension under gravitational force, without the need to use centrifuges.

Extensive studies of the anionic and coordination-insertion polymerization of CL in solution carried out during the last 20 years provided rather comprehensive knowledge of the structure of various kinds of active species, equilibria between them, and their contribution to the overall propagation and side reactions (e.g. intra- and intermolecular transesterification).[2−25] In contrast to the relatively well-investigated polymerization of CL in solution, essentially nothing is known on the mechanism and kinetics of the dispersion ring-opening polymerization of this monomer. In this paper we present the first results on the kinetics of the dispersion polymerization of CL initiated with diethylaluminum ethoxide.

## Experimental Part

ϵ-Caprolactone (CL) was purified and stored as described in our earlier papers.[1,7]

1,4-Dioxane (Aldrich) was dried over Na wires and then distilled on the vacuum line into an ampule equipped with a Teflon stopcock and containing Na−K alloy. From this ampule the required amounts of 1,4-dioxane were distilled on the vacuum line to ampules in which the reaction mixture was prepared for the polymerization.

Heptane (Aldrich) was distilled, dried over Na wires, and then transferred by distillation on the vacuum line to similar ampules as in the case of 1,4-dioxane.

Diethylaluminum ethoxide (Aldrich) was transferred under Ar to glass ampule with a Teflon stopcock. The required amounts of initiator were transferred to thin glass vials by distillation on the vacuum line.

Poly(dodecyl acrylate)-*g*-poly(ϵ-caprolactone) (poly(DA−CL)), used as the surface active agent, was synthesized by radical copolymerization of dodecyl acrylate and poly(ϵ-caprolactone) macromonomers. The detailed description of the synthesis was given in our earlier paper.[1] For kinetic experiments we used poly(DA−CL) with $\bar{M}_n = 28\,800$, 15% (wt) content of poly(CL), and the average number of poly(CL) grafts per one copolymer macromolecule equal $\overline{NG} = 1.20$.

Polymerizations were performed in the following way. Poly(DA−CL) (80 mg) was placed into a glass vessel with an attached ampule containing the required amount of CL. The vessel was equipped with the Teflon stopcock. Heptane (36 mL) and 1,4-dioxane (4 mL) were distilled into this vessel on the vacuum line. After dissolution of poly(DA−CL) the glass break-seal was broken and CL was added. A solution of initiator ($(CH_3CH_2)_2AlOCH_2CH_3$) was prepared in the second vessel. For this purpose the thin-walled glass vial, with the known amount of initiator, was placed inside of the vessel and thereafter 1 mL of 1,4-dioxane and 9 mL of heptane were distilled into it on the vacuum line. The vial was then broken and the solution was ready to initiate polymerization. Polymerization was carried out in a 100 mL reactor equipped with a magnetic stirrer and thermostated at 25 °C. The reactor was purged with dry Ar. A solution containing monomer was introduced into the reactor. Then 0.60 mL of dodecane (dried over Na−K alloy), which served as a reference in gas chromatography analysis, was added, and finally the solution of initiator was introduced. The content was stirred with 60 revolutions per minute. Samples of reacting mixture were collected during 1 h. An example of the scanning electron micrograph of the finally formed microspheres is shown in Figure 1. Each sample collected during kinetic experiments was added to THF containing acetic acid ($[CH_3COOH] = 4 \times 10^{-4}$ mol·L$^{-1}$). In experiments, in which the changes of monomer concentration were monitored, samples were frozen in liquid $N_2$ and evacuated for 10 min. After melting, the whole liquid content was quantitatively distilled on the vacuum line into vials and thereafter analyzed by GLC. Concentrations of unreacted monomer were determined from the GLC traces, using the signal of dodecane as the reference. The accuracy of this method was checked in the independent experiments, in which the earlier synthesized poly(CL) microspheres were suspended in a solution containing a known amount of CL and dodecane. It has been found that the described above procedure affords a measurement of the

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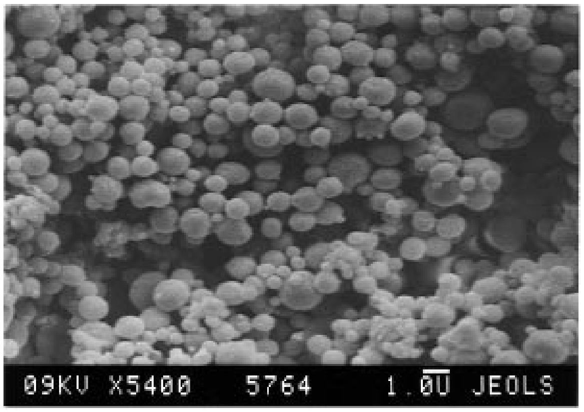


**Figure 1.** SEM microphotograph of poly(CL) microspheres. Polymerization conditions: $[CL]_o = 4.2 \times 10^{-1}$ mol·L$^{-1}$, $[(CH_3CH_2)_2AlOCH_2CH_3] = 1.0 \times 10^{-2}$ mol·L$^{-1}$. The number average diameter of microspheres $\bar{D}_n = 0.94$ $\mu$m, and the polydispersity factor $\bar{D}_v/\bar{D}_n = 1.26$ ($\bar{D}_v$ denotes the volume average diameter).

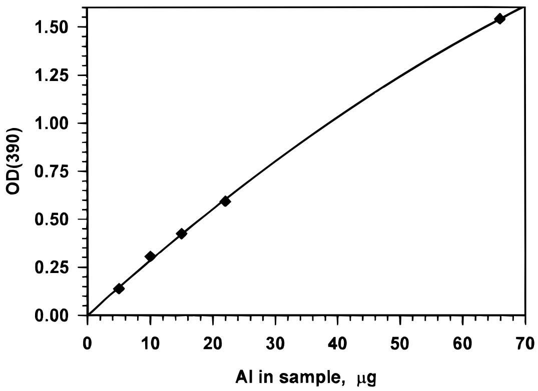
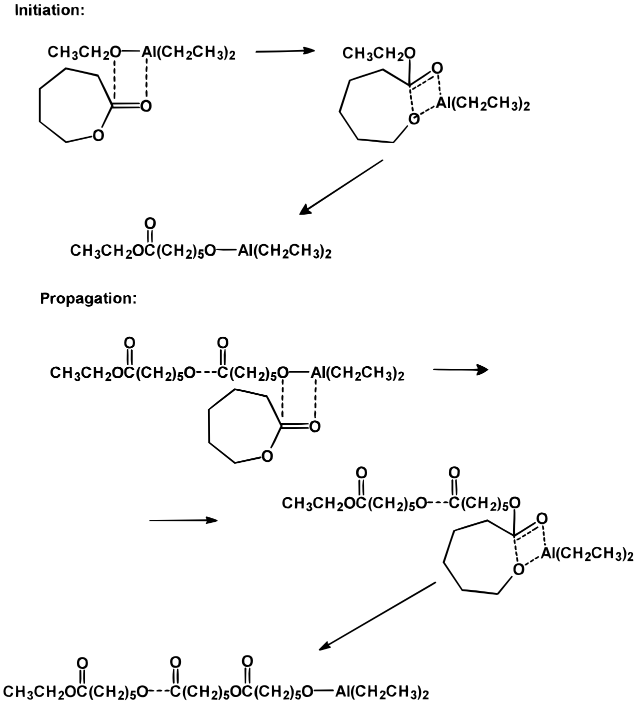


**Figure 2.** Calibration curve for determination of Al based on samples with known amounts of $(CH_3CH_2)_2AlOCH_2CH_3$ in 2.5 mL of 1,4-dioxane:heptane (1:9 v/v) solvent.

**Scheme 1**



concentration of CL in such a mixture down to $5 \times 10^{-3}$ mol·L$^{-1}$ with 1% accuracy.

GLC analyses were done using a Hewlett-Packard 5890A gas chromatograph equipped with HP-17 columns ($\Phi = 0.53$ mm and 10 m length) and a FID detector. During analysis columns were heated from 85 to 260 °C with the heating rate 20 °C/min.

The molecular weight of poly(CL) in microspheres was determined by gel permeation chromatography using a system of an LKB 2150 pump, a set of Ultrastyragel columns 100, 100, 500, 1000, and a Wyatt Optilab 903 interferometric refractometer. Tetrahydrofuran was used as eluent with a flow of 0.7 mL/min. The polymer concentrations in the analyzed solutions were in the region from 0.8 to 1 g/l. Calibration was done by using poly(CL) with known $\bar{M}_n$ and low polydispersity, synthesized earlier in our laboratory.[16,26,27]

## Results and Discussion

**Partition of Active Centers between the Solution and Condensed Phase.** Polymerization of CL initiated with dialkylaluminum alkoxides proceeds according to Scheme 1 with dialkylaluminum groups at the growing center.[16,28] The monomer molecule is first coordinated with the aluminum containing initiator and/or active species via the carbonyl group. Subsequent rearrangement within this complex results in breaking of the acyl−oxygen bond in the monomer molecule, accompanied with monomer insertion and re-creation of the structure of the active center. Thus, monitoring of the changes in the concentration of organoaluminum compounds in solution allows us to establish the proportion of growing species in solution and in microspheres. Samples of the polymerizing mixture containing microspheres were collected in the period of 1 h. Each sample was added to heptane containing acetic acid. Microspheres were isolated by centrifugation (centrifugal force 2000*G*), and the content of Al in the supernatant was determined using 8-hydroxyquinoline as the specific reagent.[29−32] In each determination of Al containing compounds in the supernatants, the solvents were distilled off. Then, 20% KOH was added to the solid residue and the content was heated to boiling. After cooling, the pH of solution was adjusted with HCl ($5 \times 10^{-1}$ mol·L$^{-1}$) to 7.4, and from this solution the Al ions were extracted twice with a 1% (wt) solution of 8-hydroxyquinoline in chloroform. The overall volume of this extract was adjusted to 50 mL by addition of the required amount of 1 wt % of chloroform solution of 8-hydroxyquinoline. Formation of the $Al(C_9H_6ON)_3$ complex was monitored by UV spectroscopy (maximum of absorption of $Al(C_9H_6ON)_3$ at 390 nm). Solutions with known concentrations of $(CH_3CH_2)_2AlOCH_2CH_3$ in heptane were used for calibration. The calibration curve is shown in Figure 2.

Measurements were made for polymerization with $[CL]_o = 4.1 \times 10^{-1}$ mol·L$^{-1}$ and $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 1.66 \times 10^{-2}$ mol·L$^{-1}$. Changes of the concentration of organoaluminum compounds in solution (in mol/L of Al) vs the polymerization time are illustrated in Figure 3. The molecular weight ($\bar{M}_n$) of poly(CL) in microspheres formed during this polymerization were determined by GPC. The dependence of $\bar{M}_n$ on time is also illustrated in Figure 3. From the plots in Figure 3 it follows that at a polymerization time of 150 s the concentration of organoaluminum compounds in solution is reduced to about 5% of its initial value. After ca. 250 s from the onset of the polymerization, the $\bar{M}_n$ of poly(CL) comes close to 1000. At this moment more than 90% of the growing species has already disappeared from the solution. After 500 s the concentration of active centers in solution was lower than $2 \times 10^{-4}$ mol·L$^{-1}$ corresponding to the limit of the analytical method which was used in these determinations. The molecular weight of poly(CL) in microspheres growths

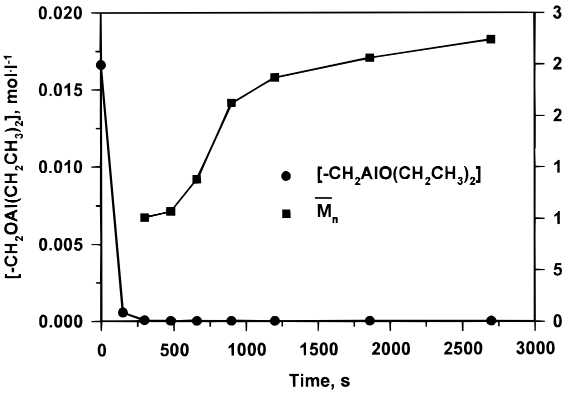


**Figure 3.** Dispersion polymerization of CL. Changes in concentration of $-CH_2OAl(CH_2CH_3)_2$ species in solution and of $\bar{M}_n$ of poly(CL) with time. Conditions of polymerization: $[CL]_o = 4.1 \times 10^{-1}$ mol·L$^{-1}$, $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 1.66 \times 10^{-2}$ mol·L$^{-1}$.

steadily during the subsequent time period, indicating that after initiation the propagation proceeds principally on macromolecules in microspheres.

**Kinetics of the Polymerization.** The kinetics of the dispersion polymerization of CL was investigated for monomer concentrations over the narrow range, of $3.9 \times 10^{-1}$ mol·L$^{-1}$ $4.3 \times 10^{-1}$ mol·L$^{-1}$, and for the initiator concentrations between $3.4 \times 10^{-3}$ and $2.6 \times 10^{-2}$ mol·L$^{-1}$. For analysis of the collected data we formally applied the equation used for the studies of the polymerization of CL in solution:[21]

$$\ln\{[CL]_o/[CL]\} = k_p^{app}[I]_o t \qquad (1)$$

where $k_p^{app}$ denotes the apparent propagation rate constant, $[CL]_o$ and $[I]_o$ correspond to the initial concentration of monomer and $(CH_3CH_2)_2AlOCH_2CH_3$, [CL] is used for the actual monomer concentration, and $t$ denotes time.

We are fully aware that such phenomenological treatment does not reflect the complexity of all elementary reactions and processes combined in this polymerization (e.g. equilibria between various aggregates of active centers known to exist in solution[7,23,25] and possibly also in the condensed state, transport of monomer molecules from solution to microspheres, changes in segmental mobility of poly(CL) macromolecules in microspheres during polymerization). However, this simplified treatment might be only useful for comparison of the dispersion polymerization and the polymerization in solution.

A plot of $\ln\{[CL]_o/[CL]\}$ versus time, shown in Figure 4, indicates the presence of a short induction period, corresponding to the time required for formation of primary particles containing almost all macromolecules with growing centers (cf. Figure 3). After the induction period the dependence of $\ln\{[CL]_o/[CL]\}$ on time can be approximated with a straight line. The slope of this line divided by the initial concentration of initiator is equal to the apparent propagation rate constant ($k_p^{app}$). Values of $[(CH_3CH_2)_2AlOCH_2CH_3]_o$, $k_p^{app}$, and of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(CL) in microspheres isolated at the end of polymerization are collected in Table 1. Data given in Table 1 demonstrate that the apparent propagation rate constant decreases with the increasing initial concentration of initiator. Similar dependence, observed earlier for the polymerization of CL initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ and carried out in solution, was found to be due to the changes of the position of equilibrium between the monomeric and the nonreactive aggregated species.[23] On the basis of the available experimental data it would be premature to speculate on the role of such equilibria in the polymerization in the condensed state; however, there are no reasons which preclude the formation of the nonreactive aggregates in microspheres.

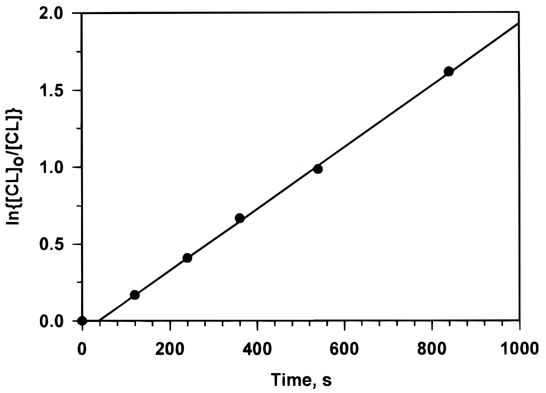


**Figure 4.** Kinetics of the dispersion polymerization of CL. Conditions of the polymerization: $[CL]_o = 4.3 \times 10^{-1}$ mol·L$^{-1}$, $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 1.6 \times 10^{-2}$ mol·L$^{-1}$.

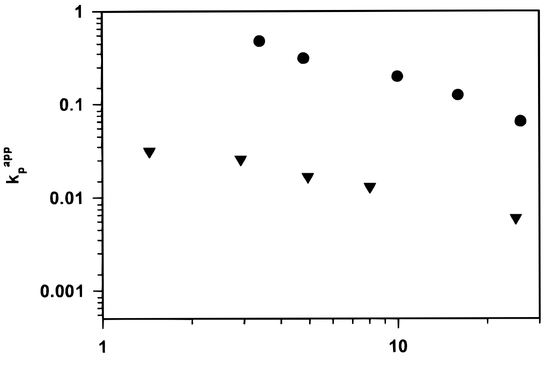


**Figure 5.** Dependence of $k_p^{app}$ on the concentration of initiator for the polymerization of CL in dispersion (circles) and in solution (triangles) initiated with $(CH_3CH_2)_2AlOCH_2CH_3$. The dispersion polymerization was in 1,4-dioxane:heptane (1:9 v/v) mixture, and the polymerization was in solution in THF. Data for the polymerization in solution are from ref. 23.

**Table 1. Rates and Apparent Propagation Rate Constants ($k_p^{app}$) of the Dispersion Polymerization of CL Initiated with $(CH_3CH_2)_2AlOCH_2CH_3$ (Values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of Poly(CL) after Complete Monomer Conversion)**

| $[(CH_3CH_2)_2AlOCH_2CH_3]_o$, mol·L$^{-1}$ | $10[CL]_o$, mol·L$^{-1}$ | Rate of polymerization, $10^{-3}$ s$^{-1}$ | $k_p^{app}$, L·mol$^{-1}$·s$^{-1}$ | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|
| $3.4 \times 10^{-3}$ | 3.9 | 1.63 | $4.97 \times 10^{-1}$ | 6760 | 1.17 |
| $4.8 \times 10^{-3}$ | 3.9 | 1.50 | $3.13 \times 10^{-1}$ | 5210 | 1.27 |
| $1.0 \times 10^{-2}$ | 4.2 | 1.9 | $1.98 \times 10^{-1}$ | 3460 | 1.30 |
| $1.6 \times 10^{-2}$ | 4.3 | 2.02 | $1.25 \times 10^{-1}$ | 2860 | 1.37 |
| $2.6 \times 10^{-2}$ | 4.1 | 1.69 | $6.50 \times 10^{-2}$ | 2930 | 1.29 |

Plots of the dependence of $k_p^{app}$ on the initial concentration of $(CH_3CH_2)_2AlOCH_2CH_3$, for the dispersion polymerization of CL and for the polymerization of CL in solution, are shown in Figure 5. From these plots it follows that the apparent propagation rate constants for the dispersion polymerization are much higher. This difference is due, at least in part, to the following: In the dispersion polymerization active centers are located inside of growing particles. The volume of these particles constitutes only a small fraction the overall volume of the reaction mixture. Thus, in the dispersion polymerization the local concentration of active centers is much higher than in the polymerization carried out in solution. In the dispersion polymerization it is difficult to determine the actual volume of microreactors (swollen microspheres) in which the polymerization takes place. However, from a rough estimate, on the basis of the assumption that in the dispersion polymerization the volume in which the active centers are concentrated is of the order of the volume of the monomer, one could conclude that in the dispersion polymerization with $[CL]_o = 4 \times 10^{-1}$ mol·L$^{-1}$, i.e. with volume fraction of monomer ca. 0.044, the local concentration of active centers would be 22 times higher than the average concentration related to the total volume of the polymerization mixture. Thus, the real propagation rate constants in the growing microspheres should be 22 times lower than values of $k_p^{app}$ given in Table 1, i.e. equal to ca. 50% of the propagation rate constants for the analogous polymerization of CL in solution. However, from the practical point of view it is important to compare the effective rates characterizing the polymerizations of CL in dispersion and in solution and times required for the given monomer conversion. For the same initial concentrations of $(CH_3CH_2)_2AlOCH_2CH_3$ the effective rates of the dispersion polymerization, described in this paper, are ca. 10 times faster than for the polymerizations in solution. For example, the polymerization in solution requiring about 8 h for a 90% monomer conversion (according to the data from ref 23 for $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 4.95 \times 10^{-3}$ mol·L$^{-1}$, $\ln\{[CL]_o/[CL]\} = 8.33 \times 10^{-5}\ s^{-1}t$) could be replaced with the dispersion polymerization initiated with the similar concentration of initiator and lasting only ca. 25 min (from Table 1 it follows that for $[(CH_3CH_2)_2AlOCH_2CH_3]_o = 4.80 \times 10^{-3}$ mol·L$^{-1}$, $\ln\{[CL]_o/[CL]\} = 1.50 \times 10^{-3}\ s^{-1}t$).

Another important advantage of the dispersion polymerization of CL over the polymerization in solution consists of the easy isolation of produced polymer. Whereas after the polymerization in solution poly(CL) has to be isolated by precipitation requiring organic nonsolvents (e.g. ethanol or hexane), the polymer in the form of microspheres could be separated by sedimentation in the field of gravitational force, without centrifugation.

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