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Living Pseudoanionic Polymerization of ϵ-Caprolactone. Poly(ϵ-caprolactone) Free of Cyclics and with Controlled End Groups

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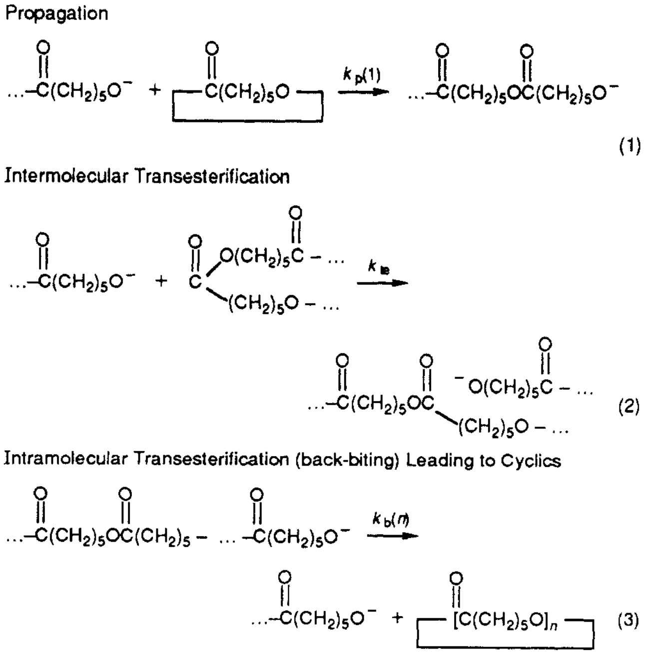
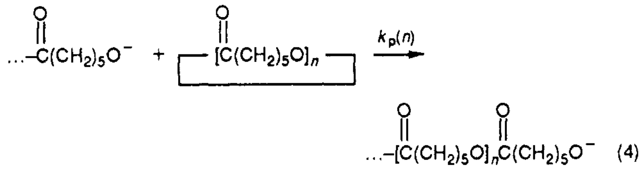
ABSTRACT: In the polymerization of ϵ-caprolactone (ϵCL) initiated with $(CH_3CH_2)_2AlOCH_3$, $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$, or $[(CH_3)_2CHCH_2]_2AlOCH_3$ and carried out in THF solvent at 20 or 25 °C linear poly(ϵCL) with $1.03 < M_w/M_n < 1.13$ and free of macrocyclics was obtained. Comparison of $\bar{M}_n$, calculated and measured, indicated that each initiator molecule starts one macromolecule and that during polymerization transfer reactions, including cyclization, are practically absent. ^1H and ^{13}C NMR studies of the end-group structures revealed that only alkoxy groups (OR′) from initiator (R_2AlOR') were directly involved in initiation. The described polymerization of ϵCL can be considered as the living process, yielding linear polyesters free from cyclics within the polymerization time required to reach 99% of monomer conversion. Cyclics are produced after much longer time from the linear polymer already formed. The ratios of propagation rate constant ($k_p(1)$) to the rate constants of back-biting, leading to the cyclic dimer ($k_b(2)$), have been used as a measure of kinetic enhancement in linear polymer. For ϵCL polymerizations carried out in THF at 20 °C and initiated with $(CH_3CH_2)_2AlOCH_3$ and $[(CH_3)_2CHCH_2]_2AlOCH_3$ $k_p(1)/k_b(2) = 4.6 \times 10^4$ and 7.7×10^4 L·mol^{-1}, respectively. These values are substantially higher than for the anionic polymerization of ϵCL with Na^+ counterion ($k_p(1)/k_b(2) = 1.55 \times 10^3$ L·mol^{-1}).

Introduction

In the anionic polymerization of ϵ-caprolactone (ϵCL) propagation is accompanied with side reactions, namely intermolecular and intramolecular transesterifications (eqs 1-3). These processes are shown below schematically for macroanions. The macrocycles, formed in the back-biting reaction, participate further in propagation in a manner similar to that of the monomer. Due to these side reactions MWDs of the polymers are above 1.3 and the product is a mixture of both linear and cyclic molecules. The total concentration of monomeric units, incorporated into the macrocycles, is equal at equilibrium to 0.25 mol·L^{-1}.[1] As it is shown for initial monomer concentrations lower than this critical concentration, finally only cyclic oligomers are produced. When the initial monomer concentration is increased, fraction of cyclic oligomers in the overall product can be decreased but cannot be eliminated. Polymerization in bulk sets the limit.





In our previous studies we found that modification of the structure of active centers, leading to the change of the mechanism of propagation and to decreasing of their reactivity, results in even more pronounced slowing down macrocyclization with respect to propagation.[2] This extent of the relative enhancement of the rate of propagation, when compared with the rate of cyclization, has been expressed in our work by the ratio $k_p(1)/k_b(2)$, where $k_p(1)$ and $k_b(2)$ denote rate constants of propagation involving monomer and back-biting with formation of a cyclic dimer, respectively. Variation of the nature of counterion in the anionic polymerization, although influencing the relative rate of cyclization, is not leading to elimination of macrocyclization and other transesterification reactions.[1,3,4] Recently, we found that polymerization of ϵCL initiated with diethylaluminum methoxide proceeds with kinetic enhancement in linear polymer.[5] Similar initiator was used by Cherdron, but cyclization phenomena were not studied at that time.[6] Pseudoanionic polymerization of ϵCL with kinetic enhancement in linear polymer, yielding polyester with low polydispersity

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Table I
Measured and Calculated Molecular Weights of Poly(εCL)

$[\epsilon CL]_0$, mol·L^{-1}	$[I]_0$, ×10^2 mol·L^{-1}	$\bar{M}_n$(calcd)	$\bar{M}_n$ (osmometry)	GPC $\bar{M}_n$	GPC $\bar{M}_w$	GPC $\bar{M}_w/\bar{M}_n$
		I = $(CH_3CH_2)_2AlOCH_3$[a]				
0.255	1.04	2790	3030	3140	3220	1.03
0.984	4.10	2740	3010	3135	3220	1.03
0.520	1.79	3330	3425	3370	3540	1.05
0.925	3.37	3130	3840	3440	3580	1.04
0.500	1.08	5280	3910	4110	4440	1.08
0.510	0.894	6510	4130	4480	4810	1.07
1.00	1.92	5950	4130	4790	5250	1.10
0.520	0.999	6050	4850	4250	4560	1.07
0.987	1.78	6330	6600	5300	5750	1.08
0.510	0.578	9730	8450			
0.986	0.813	13800	9500			
1.22	1.00	13970	10200			
0.506	0.456	12420	10800			
3.00	1.08	31800	27100			
1.90	0.444	48960	45900			
3.00	0.500	68480	63770			
2.00	0.363	62880	62890			
1.94	0.229	96670	97900			
		I = $[(CH_3)_2CHCH_2]_2AlOCH_3$[b]				
2.00	4.87	4690	7410	6510	7350	1.13
2.00	2.83	8070	10390	8780	9930	1.13
0.98	0.920	12210	13100	15910	17640	1.11
1.00	0.560	20380	19500	21030	23260	1.11
2.00	0.598	38170	39580			
2.00	0.242	94330	86010			
		I = $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$[b]				
0.918	12.25	855	935	1035	1150	1.11
0.499	2.12	2680	2680	2980	3080	1.03
1.06	2.44	4960	3645	5080	5760	1.13
0.974	1.75	6360	6510	5680	6430	1.13
0.956	1.34	8140	7060	6420	7090	1.10

[a] Polymerization temperature 20 °C. [b] Polymerization temperature 25 °C.

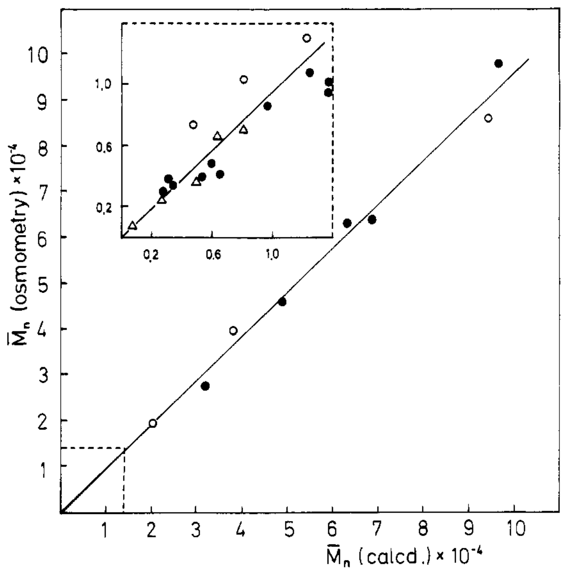


Figure 1. Relationship between measured ($\bar{M}_n$(osmometry)) and calculated ($\bar{M}_n$(calcd)) molecular weights of poly(εCL). Initiators: (●) $(CH_3CH_2)_2AlOCH_3$; (○) $[(CH_3)_2CHCH_2]_2AlOCH_3$; (△) $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$.

and essentially free from cyclics, has also been observed by Inoue when (5,10,15,20-tetraphenylporphyrinato)aluminum methoxide–methanol mixture was used for initiation.[5]

In the present studies we applied dialkylaluminum alkoxides related to the initiators already used by Teyssié,[8] Hsieh,[9] and Kricheldorf[11] as well in their studies of εCL polymerization.

Teyssié[8a–d] and then other authors cited above indicated that at certain conditions polymerization initiated with $(iC_3H_7O)_3Al$ or bimetallic initiators proceeds with an invariant number of the growing species. Moreover, Teyssié stated that for $(iC_3H_7O)_3Al$ "...polymerization equilibrium is shifted to open chains to the extent more than 99%...".[8a,d] Apparently, what is meant by this statement is not the equilibrium, which could hardly be affected, but the fact that the system is under kinetic control.

In this paper, by using the enhancement coefficient $(k_p(1)/k_b(2)$ introduced by us earlier,[5] we have been able to compare quantitatively the ability of various initiators (and, therefore, the active chain ends) to enhance formation of linear or cyclic poly(ε-caprolactones).

Experimental Part

εCL was purified according to the procedure described earlier.[4] The known amounts of monomer were distilled on the vacuum line into ampules equipped with break-seals. Ampules were stored in a refrigerator at −12 °C.

THF, used as solvent, was purified in the usual way and was stored over sodium–potassium alloy in ampules equipped with Teflon stopcocks. The required portions of solvent were distilled into the reaction vessel on the vacuum line.

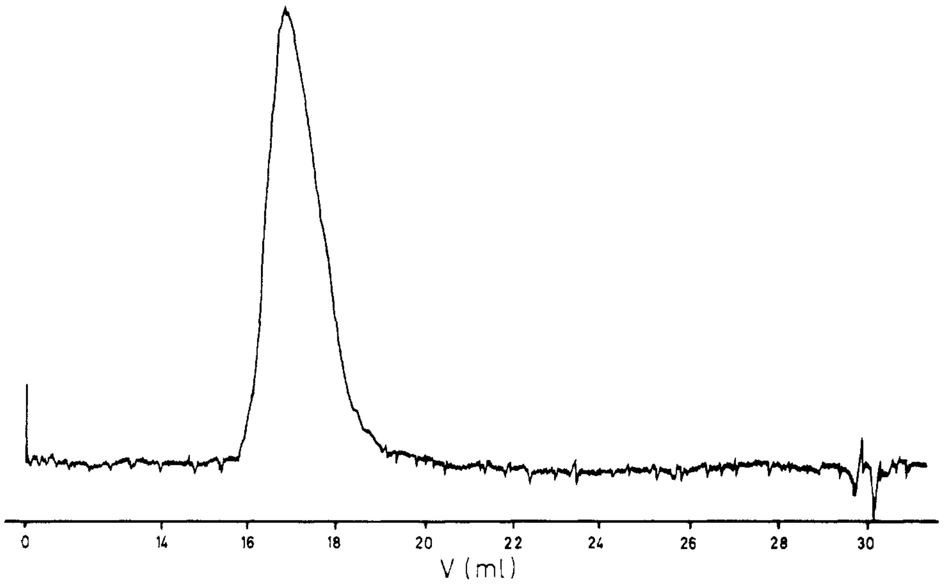


Figure 2. GPC trace of the polymerizing mixture. Conditions of polymerization: $[\epsilon CL]_0 = 5.06 \times 10^{-1}$ mol·L^{-1}, $[(CH_3CH_2)_2AlOCH_3]_0 = 4.56 \times 10^{-3}$ mol·L^{-1}, THF solvent at 20 °C. Waters 10^3, 5×10^2, and 10^2 columns; eluent flow rate 0.9 mL·min^{-1}.

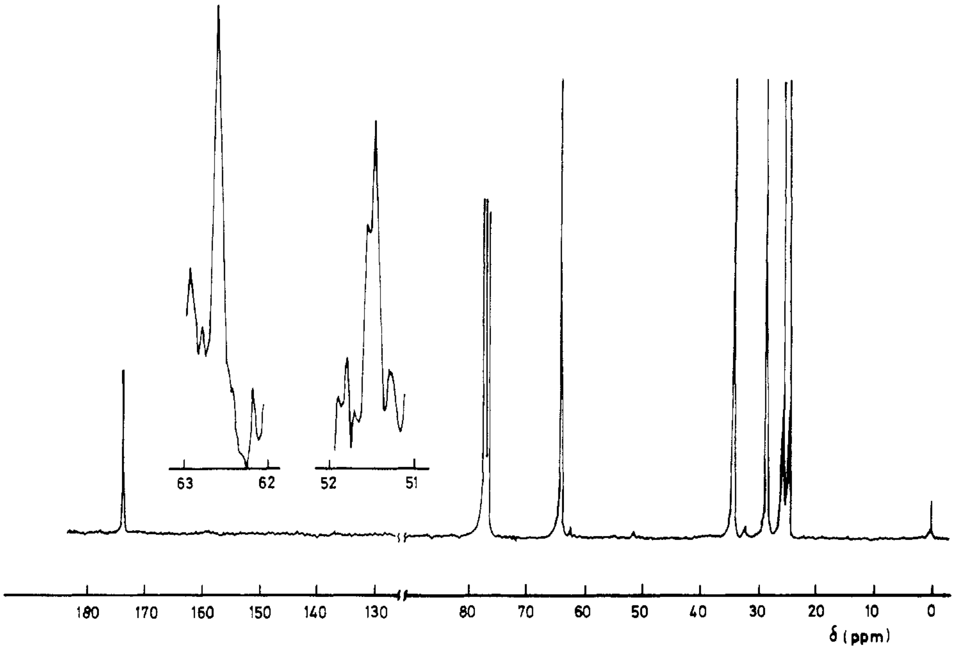
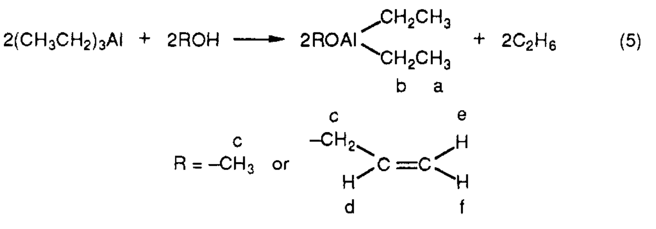


Figure 3. ^{13}C NMR spectrum of poly(εCL). Conditions of polymerization: $[\epsilon CL]_0 = 5.29 \times 10^{-1}$ mol·L^{-1}, $[(CH_3CH_2)_2AlOCH_3]_0 = 9.99 \times 10^{-3}$ mol·L^{-1}, in THF at 25 °C.

Diethylaluminum alkoxides were obtained in reactions of triethylaluminum with the corresponding alcohols. All operations were carried out under nitrogen using freshly distilled triethylaluminum (Fluka) and dried toluene as a solvent. The organoaluminum compound (0.1 mol) was dissolved in 100 mL of toluene in a glass vessel equipped with a stirrer and connected through a liquid seal to a gas burette. An equimolar amount of the required alcohol in 50 mL of toluene was then slowly dropped in with vigorous stirring at −78 °C. When the evolution of ethane stopped, the reaction mixtures were slowly warmed up and kept at room temperature for about 1 h. After evaporation of the toluene solvent the diethylaluminum alkoxides were isolated by distillation.



$$2(CH_3CH_2)_3Al + 2ROH \longrightarrow 2ROAl\begin{matrix}CH_2CH_3\\CH_2CH_3\end{matrix} + 2C_2H_6 \qquad (5)$$

Product Identification. Diethylaluminum methoxide: bp 67–68 °C (0.4 mmHg); ^1H NMR (toluene-d_8) δ 1.25 (t, 6 H_a), 0.21 (q, 4 H_b), 3.33 (s, 3 H_c); J_{a-b} = 8.93 Hz. Anal. Al: calcd, 23.2; found, 22.8.

Diethylaluminum allyloxide: bp 82–83 °C (0.3 mmHg); ^1H NMR (toluene-d_8) δ 1.17 (t, 6 H_a), 0.04 (q, 4 H_b), 3.91 (d, 2 H_c), 5.72 (m, 1 H_d), 5.05 (d, 1 H_e), 4.96 (d, 1 H_f); J_{a-b} = 8.19 Hz, J_{c-d} = 6.32 Hz, J_{c-e} = −1.40 Hz, J_{c-f} = −0.95 Hz, J_{d-e} = 17.00 Hz, J_{d-f} = 10.20 Hz, J_{e-f} = 1.35 Hz. Anal. Al: calcd, 19.0; found, 18.9. Coupling constants were calculated accord-

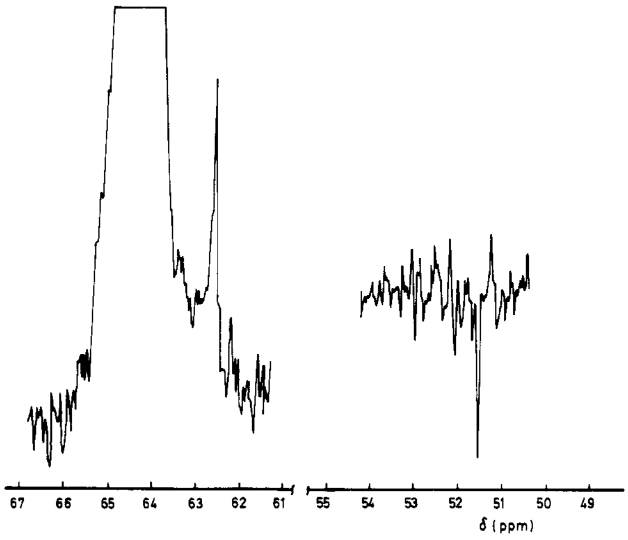
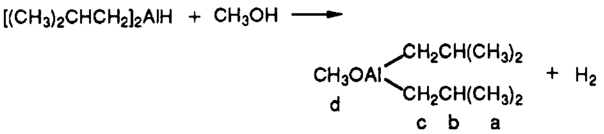


Figure 4. ^{13}C DEPT 135° NMR spectrum of poly(ϵCL). The same polymerization conditions as given in the caption for Figure 3.

ing to the LAOCN 3 method.[10] Diisobutylaluminum methoxide was obtained in reaction of diisobutylaluminum hydride with methanol.



$$\mathrm{[(CH_3)_2CHCH_2]_2AlH + CH_3OH \longrightarrow \underset{d}{CH_3O}Al\begin{matrix}CH_2CH(CH_3)_2\\ \underset{c\quad b\quad\ a}{CH_2CH(CH_3)_2}\end{matrix} + H_2} \qquad (6)$$

Diisobutylaluminum methoxide: bp 108–110 °C (0.3 mmHg); ^{1}H NMR (toluene-d_8) δ 1.23 (d, 12 H_a), 2.11 (q, 2 H_b), 0.33 (d, 4 H_c), 3.42 (s, 3 H_d); J_{a-b} = 7.74 Hz, J_{b-c} = 5.95 Hz. Anal. Al: calcd, 15.5; found, 15.4.

Polymerizations were carried out in dilatometers and/or in a glass apparatus described in our previous paper.[4] Active centers were deactivated by addition of acetic acid (3-4-fold molar excess with respect to the initiator used). Polymers were isolated by precipitation in the cold (ice-bath) heptane and dried at room temperature under high vacuum during several days.

GPC analyses of the polymerization mixtures and of the isolated polymers were performed using an LKB 2150 HPLC pump, a set of Waters ultrastyragel columns 10^3, 5×10^2, and 10^2 and/or Toyo Soda columns G4000HXL and G2000HXL, and a Hewlett Packard 1031A RI detector. THF was used as an eluent.

Molecular weight measurements were performed using a Hewlett Packard 302B VPO and Hewlett Packard 502 high-speed membrane osmometers.

^{1}H and ^{13}C NMR spectra of poly(ϵCL) were registered in $CDCl_3$ on Bruker MSL 300. ^{1}H NMR spectra of initiators were recorded with JEOL C-100H and Bruker AM 300.

Results and Discussion

Molecular Weights of Poly(ϵ-caprolactone). Polymerizations were carried out at 20 and/or 25 °C until monomer conversion reached at least 99%. The extent of polymerization was determined from the dilatometric measurements or from the polymer and monomer peaks in GPC chromatograms of the withdrawn samples of the polymerization mixture. Propagation was terminated by mixing the polymerizing mixture with a THF solution containing CH_3COOH. Polymerizations were performed for $[\epsilon CL]_0/[I]_0$ ratios ranging from 8 to 850. Conditions of polymerization and results of molecular weight ($\bar{M}_n$) measurements are presented in Table I. For each experiment $\bar{M}_n$ has also been calculated, assuming that every initiator molecule (R_2AlOR') initiates the growth of one macromolecular chain

$$\bar{M}_n(\text{calcd}) = \frac{[\epsilon CL]_0 M_{\epsilon CL}}{[R_2AlOR']_0} \qquad (7)$$

where $M_{\epsilon CL}$ = 114.14 (MW of the monomer). Plot of $\bar{M}_n$(osmometry) versus $\bar{M}_n$(calcd) is given in Figure 1.

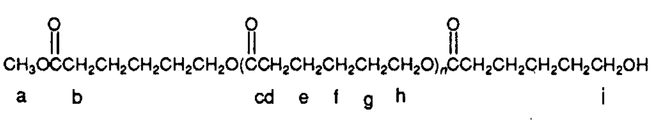
The linear relationship between $\bar{M}_n$(osmometry) and $\bar{M}_n$(calcd) with a slope of 0.964, i.e., close to 1, justifies an assumption that only one substituent at the aluminum atom in $(CH_3CH_2)_2AlOCH_3$, $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$, and $[(CH_3)_2CHCH_2]_2AlOCH_3$ is involved in initiation.

Molecular Weight Distribution of Poly(ϵCL). GPC measurements have shown that macrocycles could not be detected in the polymerization mixtures up to the monomer conversion approaching 99.9%. Thus, if any cyclic oligomers would be present in the system, they should constitute less than 0.1% of the linear polymer. On the other hand, isolation of poly(ϵCL) by precipitation in n-heptane or methanol did not affect the shape and position of the polymer peaks, indicating that this procedure did not change the molecular weight distribution. The residue after evaporation of n-heptane (supernatant) did not contain any cyclics, as evidenced from the GPC analysis of this fraction.

Results of independent measurements of $\bar{M}_n$ (VPO) were used for "self-calibration" of GPC chromatograms. The dependence of ln $\bar{M}_n$ on elution volume (V) gave a first approximation of the calibration curve and was used for calculating of $\bar{M}_n'$, $\bar{M}_w'$, and $\sigma'^2 = \bar{M}_w'/\bar{M}_n'$ (polydispersity). The value of σ'^2 was used for calculation of $M_p = \sigma'\bar{M}_n'$, where M_p denotes the molecular weights corresponding to the peak maximum. Eventually, the relation between ln M_p and V was used for calibration. Values of $\bar{M}_n$, $\bar{M}_w$, and $\bar{M}_w/\bar{M}_n$ determined from the GPC chromatograms are collected in Table I. The polydispersity ($\bar{M}_w/\bar{M}_n$) of poly(ϵCL) samples with $\bar{M}_n \leqslant 10^4$ equals 1.03–1.13.

The Poisson distribution indicates the living character of polymerization, additionally backed by the close proximity of measured and calculated $\bar{M}_n$'s. On top of these findings, an additional argument comes from the linearity of the semilogarithmic kinetic plots.[12]

Determination of the End-Group Structure in Poly(ϵCL) by ^{13}C and ^{1}H NMR Spectroscopy. ^{13}C NMR spectrum of poly(ϵCL), obtained with use of $(CH_3CH_2)_2AlOCH_3$ as initiator and after the deactivation–isolation procedure, is shown in Figure 3. Signals in this spectrum were assigned in the following way. Chemical



$$\mathrm{\underset{a}{CH_3}O\underset{b}{\overset{O}{\overset{\|}{C}}}CH_2CH_2CH_2CH_2CH_2O(\underset{c}{\overset{O}{\overset{\|}{C}}}\underset{d}{CH_2}\underset{e}{CH_2}\underset{f}{CH_2}\underset{g}{CH_2}\underset{h}{CH_2}O)_n\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\underset{i}{CH_2}OH}$$

shifts in $^{13}C\{^1H\}$ NMR: δ = 51.47 (C_a), 32.25 (C_b), 173.49 (C_c), 34.19 (C_d), 25.56 (C_e), 24.60 (C_f), 28.39 (C_g), 64.14 (C_h), 62.63 (C_i). Assignment of absorption at δ 51.47 to the $CH_3OC(O)$–... end group was verified by a DEPT 135° pulse experiment, giving spectra in which phases of CH_3– and $-CH_2-$ signals were opposite. A ^{13}C DEPT 135° NMR spectrum of poly(ϵCL) is shown in Figure 4. In this spectrum a signal at δ 51.47 is "negative" in comparison with signals of $-CH_2-$ groups.

The CH_3O–... end group is derived directly from the initiator (cf. eqs 9 and 10). The second end group, namely

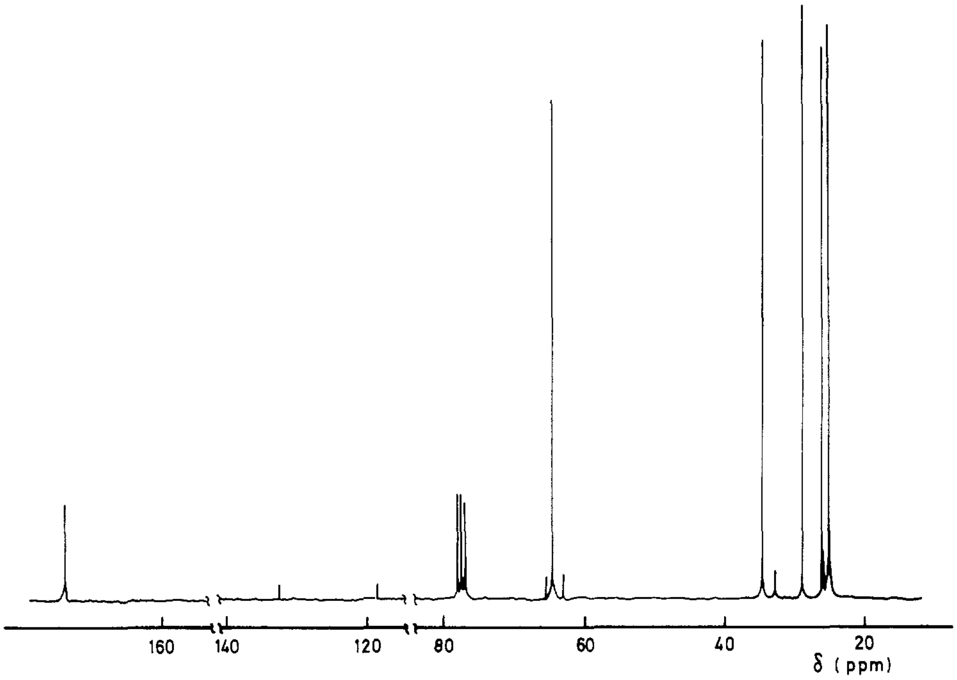


Figure 5. ^{13}C NMR spectrum of poly(εCL). Conditions of polymerization: $[\epsilon CL]_0 = 1.0$ mol·L^{-1}, $[(CH_3CH_2)_2AlOCH_2CH{=}CH_2]_0 = 6.62 \times 10^{-2}$ mol·L^{-1}, THF solvent at 25 °C.

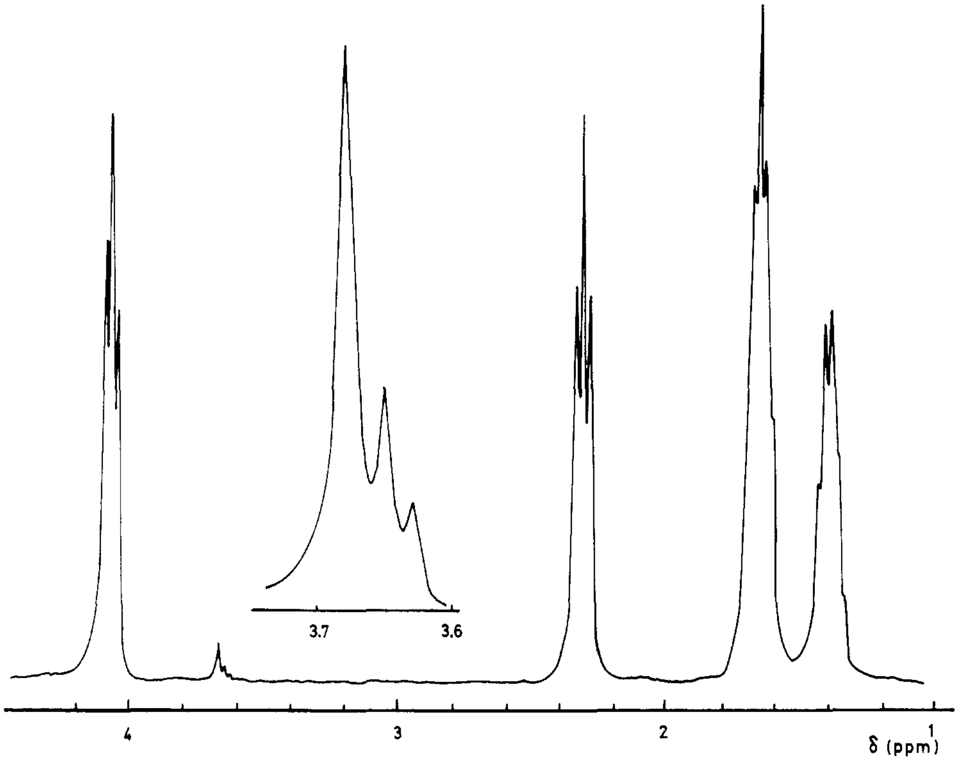
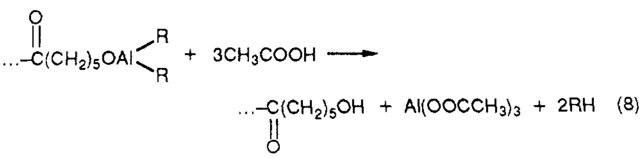


Figure 6. ^1H NMR spectrum of poly(εCL). Conditions of polymerization: $[\epsilon CL]_0 = 5.29 \times 10^{-1}$ mol·L^{-1}, $[(CH_3CH_2)_2AlOCH_3]_0 = 9.99 \times 10^{-3}$ mol·L^{-1}, THF solvent at 25 °C.

the ...–CH_2OH end-group, is a product of the reaction of the active centers with the deactivating agent, e.g.:



$$...\text{–}C(=O)(CH_2)_5OAlR_2 + 3CH_3COOH \rightarrow ...\text{–}C(=O)(CH_2)_5OH + Al(OOCCH_3)_3 + 2RH \quad (8)$$

Chemical shifts in ^{13}C NMR spectra of poly(εCL) synthesized by using $[(CH_3)_2CHCH_2]_2AlOCH_3$ as an initiator, and deactivated with acetic acid, were the same as for $(CH_3CH_2)_2AlOCH_3$, indicating that in both cases polymers with the same end groups were formed. Signals from ethyl or isobutyl end groups, which would be formed by involving alkyl groups from the corresponding initiators, were not observed.

In the $^{13}C\{^1H\}$ NMR spectrum of poly(εCL), obtained in εCL polymerization initiated with $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$ (cf. Figure 5), besides those signals due to the main-chain atoms, signals of allyl end groups were also

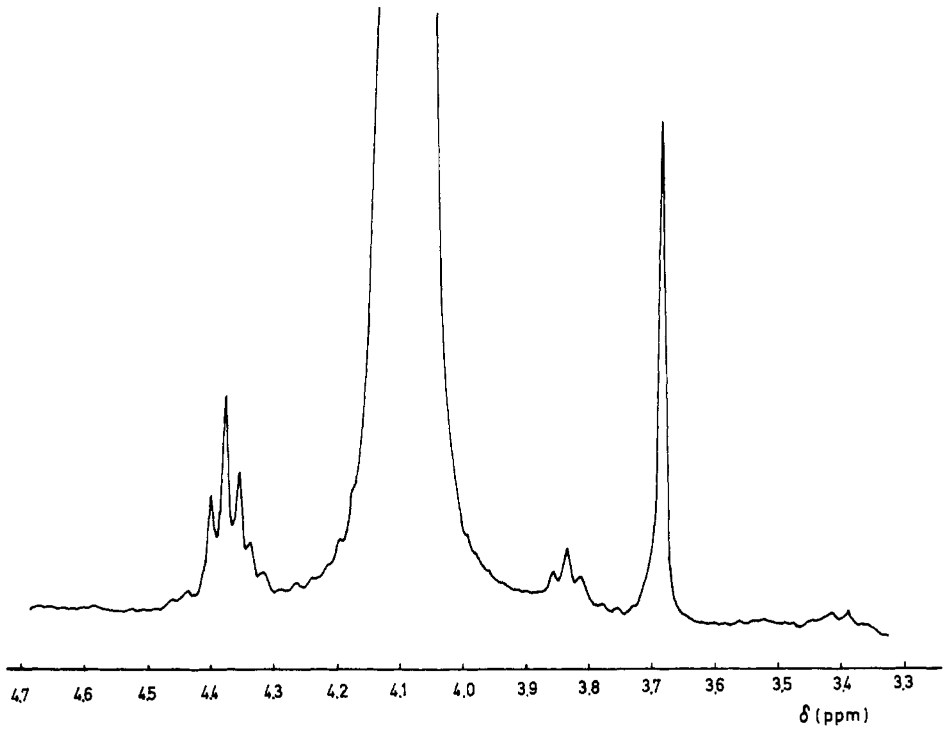


Figure 7. ^{1}H NMR spectrum of poly(εCL) (polymerization conditions given in the caption for Figure 6) after reaction with $(CF_3CO)_2O$.

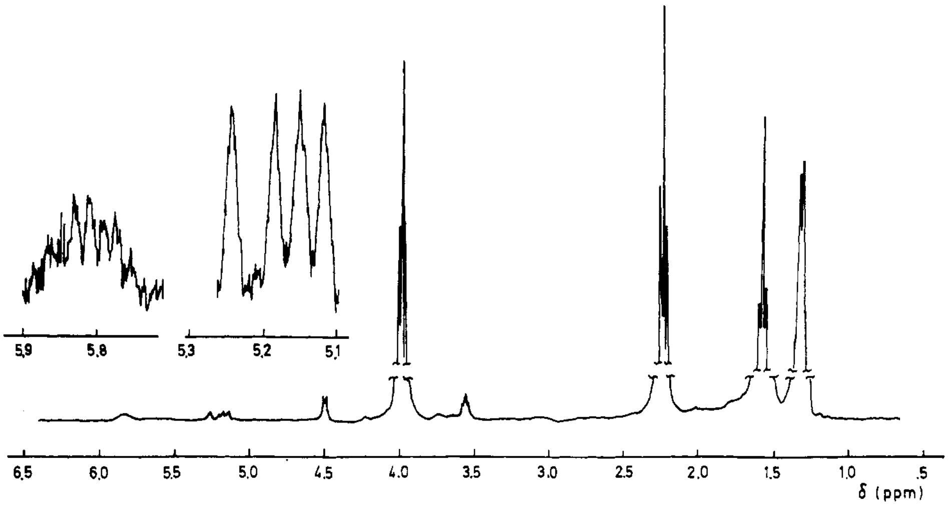
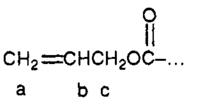
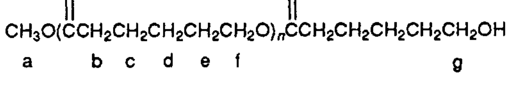


Figure 8. ^{1}H NMR spectrum of poly(εCL). Conditions of polymerization: $[\epsilon CL]_0 = 5.0 \times 10^{-1}$ mol·L^{-1}, $[(CH_3CH_2)_2AlOCH_2CH{=}CH_2]_0 = 2.12 \times 10^{-2}$ mol·L^{-1}, THF solvent at 25 °C.

observed. Chemical shifts in ^{13}C NMR: δ 118.1 (C_a), 132.3 (C_b), 65.0 (C_c).

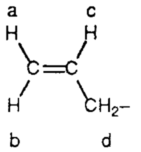

$\underset{a}{CH_2}{=}\underset{b}{CH}\underset{c}{CH_2}O\overset{O}{\overset{\|}{C}}-\ldots$

The ^{1}H NMR spectra of poly(εCL) initiated with $(CH_3CH_2)_2AlOCH_3$ and/or $[(CH_3)_2CHCH_2]_2AlOCH_3$ and deactivated with acetic acid contain signals with the same chemical shifts. In these spectra, in addition to the signals of $-CH_2-$ groups of the main chain, the overlapping singlet (at δ 3.68) and triplet (at δ 3.65) are present. Chemical shifts in ^{1}H NMR: δ 3.68 (s, H_a), 2.32 (t, H_b), 1.66 (m, H_c + H_e), 1.39 (m, H_d), 4.07 (t, H_f), 3.65 (t, H_g).


$\underset{a}{CH_3}O(\overset{O}{\overset{\|}{C}}\underset{b}{CH_2}\underset{c}{CH_2}\underset{d}{CH_2}\underset{e}{CH_2}\underset{f}{CH_2}O)_n\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_2\underset{g}{CH_2}OH$

Absorption at δ 3.68 (s) is due to the $CH_3OC(O)CH_2-\ldots$ terminal end groups (Figure 6; for $CH_3OC(O)CH_3$ absorption at δ 3.65 is observed). A triplet at δ 3.65 was assigned to the $\ldots-CH_2CH_2OH$ end group. This has been confirmed by esterification of the $\ldots-CH_2OH$ end groups, with $(CF_3CO)_2O$ leading to $\ldots-CH_2CH_2OC(O)CF_3$. After esterification a triplet at δ 3.65 disappeared and a new one at δ 4.28, due to an ester end group, was formed (cf. Figure 7). A triplet, due to the terminal $\ldots-CH_2CH_2OH$, was earlier observed for oligo εCL obtained by using aluminum triisopropoxide.[11]

^{1}H NMR spectrum of poly(εCL) initiated with $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$, and deactivated with acetic acid, is shown in Figure 8. In addition to the signals due to the main-chain $-CH_2-$ groups and signals due to the terminal $\ldots-CH_2CH_2OH$ groups, the spectrum contains signals due to the allyl end groups: Chemical shifts in ^{1}H NMR: δ 5.16 (d, H_a), 5.21 (d, H_b), 5.83 (m, H_c), 4.49 (d, H_d).



End groups from alkyl substituents at aluminum are absent in the studied polymer samples.

Formation of Macrocycles after Complete (99.9%) Monomer Conversion. When the living polymerization mixture was allowed to react further after the complete monomer conversion was reached, two phenomena were observed; the MWD of the linear fraction broadened (intermolecular reaction leading to scrambling) and peaks due to macrocyclics appeared (intramolecular backbiting). Formation of linear polymer and cyclic oligomers was monitored by GPC for polymerizations initiated with $(CH_3CH_2)_2AlOCH_3$ and $[(CH_3)_2CHCH_2]_2AlOCH_3$. In order to correlate the influence of the initiator structure, i.e., the structure of the growing species, with the rates of propagation and formation of cyclic oligomers, the ratio $k_p(1)/k_b(2)$ ($k_p(1)$ is the propagation rate constant involving a monomer, $k_b(2)$ is the rate constant of back-biting leading to cyclic dimer) was estimated. For polymerization initiated with $(CH_3CH_2)_2AlOCH_3$ (all data for 20 °C), $k_p(1)/k_b(2) = 4.6 \times 10^4$ L·mol^{-1}, and for $[(CH_3)_2CHCH_2]_2AlOCH_3$ $k_p(1)/k_b(2) = 7.7 \times 10^4$ L·mol^{-1}. In our previous studies of the anionic polymerization of εCL with Na^+ counterion, we found $k_p(1)/k_b(2) = 1.55 \times 10^3$ L·mol^{-1}.[4] Thus, the kinetic enhancement in linear polymer is highly pronounced for pseudoanionic polymerization of εCL. On the other hand, formation of linear polymer is more enhanced with more bulky (isobutyl compared with ethyl) substituents at Al atom.

Conclusions

Measurements of the molecular weights, molecular weight distributions, and determination of the chemical structure of the end groups in the polymer samples indicate the following:

a. Each molecule of R_2AlOR' initiates one macromolecule.

b. Only CH_3O– groups from $(CH_3CH_2)_2AlOCH_3$ or $[(CH_3)_2CHCH_2]_2AlOCH_3$ and $CH_2{=}CHCH_2O$– groups from $(CH_3CH_2)_2AlOCHCH{=}CH_2$ are involved in initiation and transferred to the polymer chain quantitatively as the head end groups.

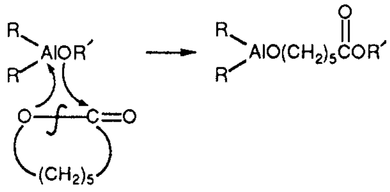
c. Addition of the monomer molecules to the growing centers proceeds with acyl–oxygen bond scission.

d. Side reactions, leading to macrocyclization and intermolecular transesterification, are not important at least during the time required for almost complete (over 99%) monomer conversion.

e. Kinetic enhancement in linear polymer is more efficient for initiator with bulkier alkyl substituents at the Al atom.

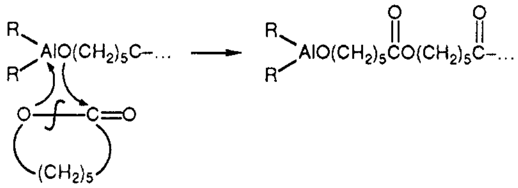
The absence of cyclics strongly suggests that the mechanism of propagation does not involve ions. This is another indication of the already postulated pseudoanionic process. Thus, the following scheme of the polymerization initiated with R_2AlOR' can be proposed:

Initiation



(9)

Propagation



(10)

The scheme above is a crude, tentative presentation. Further work on the elementary step of propagation should reveal mechanistic details, the role of the carbonyl oxygen atom (the strongest nucleophile in εCL molecule) in preliminary complexation, being or not being a component of an insertion.

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References and Notes

(1) Ito, K.; Hashizuka, Y.; Yamashita, Y. *Macromolecules* **1977**, *10*, 821.

(2) Słomkowski, S. *Makromol. Chem.* **1985**, *186*, 2581.

(3) Ito, K.; Yamashita, Y. *Macromolecules* **1978**, *11*, 68.

(4) Sosnowski, S.; Słomkowski, S.; Penczek, S.; Reibel, L. *Makromol. Chem.* **1983**, *184*, 2159.

(5) Hofman, A.; Słomkowski, S.; Penczek, S. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 387.

(6) Cherdron, H.; Ohse, H.; Korte, F. *Makromol. Chem.* **1962**, *56*, 187.

(7) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.

(8) (a) Ouhadi, T.; Stevens, Ch.; Teyssié, Ph. *Makromol. Chem. Suppl.* **1975**, *1*, 191. (b) Ouhadi, T.; Hamitou, A.; Jerome, R.; Teyssié, Ph. *Macromolecules* **1976**, *9*, 927. (c) Hamitou, A.; Ouhadi, T.; Jerome, R.; Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 865. (d) Teyssié, Ph. In *Comprehensive Polymer Science*; Allen, G., et al., Eds.; Pergamon Press: Oxford, 1989; Vol. 3, Part I, p 509.

(9) Hsieh, H. L.; Wang, I. W. *ACS Symp. Ser.* **1985**, *286*, 161.

(10) Bother-By, A. A.; Castellano, S. M. *Computer Program for Chemistry*; De Tar, D. F., Ed.; Benjamin: New York, 1968; Vol. 1, Chapter 3.

(11) Kricheldorf, H. R.; Mang, T.; Jonte, J. M. *Macromolecules* **1984**, *17*, 2173.

(12) Duda, A.; Penczek, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *34* (1), in press.

Registry No. $(CH_3CH_2)_2AlOCH_3$, 6076-62-6; $(CH_3CH_2)_2AlOCH_2CH{=}CH_2$, 124287-75-8; $[(CH_3)_2CHCH_2)_2AlOCH_3$, 3183-64-0; poly(εCL) (homopolymer), 24980-41-4; poly(εCL) (SRU), 25248-42-4; εCL, 502-44-3.