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Polymerization of ϵ-Caprolactone Initiated by Aluminum Isopropoxide Carried Out in the Presence of Alcohols and Diols. Kinetics and Mechanism

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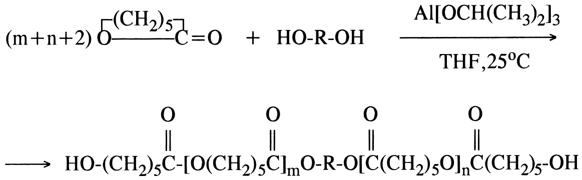
ABSTRACT: The mechanism of polymerization of ϵ-caprolactone (ϵCL) initiated with aluminum isopropoxide ($Al(O^iPr)_3$) trimer (A_3) and/or tetramer (A_4) carried out in the presence of ethanol, 2-propanol, 1,2-ethanediol, 1,5-pentanediol (PD), and poly(ethylene glycol) as chain-transfer agents was studied. It has been established, by the kinetic studies, that the low-molecular-weight alcohols and diols, introduced purposely into the polymerization mixture, operate not only as the chain-transfer agents but also either as inhibitors, in polymerization initiated with A_3, or as accelerators, in polymerizations initiated with A_4. Thus, the kinetic curves are practically identical for different compositions of the A_3/A_4 mixture in the feed, under the otherwise comparable conditions. At the early stages of polymerization the relative polymerization rate ($r_p = -d \ln [\epsilon CL]/dt$) increases, and at higher conversions, after complete consumption of the starting alcohol or diol, r_p becomes constant; i.e. polymerization becomes first-order (internally) in monomer. These kinetic effects were explained by assuming the complete disruption of any aggregate present, followed by a coordination of the resulting nonaggregated (monomeric) Al−tris(macroalkoxide) active species with the *low-molecular-weight* alcohol or diol. Analysis of the ^1H and ^{27}Al NMR spectra of the polymerizing mixtures confirmed that both A_3 and A_4 are consumed quantitatively. This is in contrast to the polymerization conducted without alcohols, in which only A_3 is reacted fast, whereas A_4 mostly remains unreacted when the polymerization is over. Moreover, the ^1H NMR spectra show that the equilibrium $>Al-O^iPr + HO(CH_2)_5OH \rightleftharpoons >Al-O(CH_2)_5-OH + {}^iPrOH$ is shifted to the right-hand side. The kinetic scheme taking into account both propagation, $P_n^* + \epsilon CL \rightarrow P_{n+1}^*$, and the temporary deactivation of the growing species, $P_n^* + PD \rightleftharpoons P_n^*{\cdot}PD$ (where the complex $P_n^*{\cdot}PD$ does not propagate), was proposed. A set of the resulting differential equations was solved numerically. The computed kinetic plots, $\ln([\epsilon CL]_o/[\epsilon CL])$ and [PD] vs time, reproduce well the respective plots obtained experimentally.

Introduction

Although the high-molecular-weight, linear poly(ϵ-caprolactone) (poly(ϵCL)) was obtained with aluminum trialkoxides as initiators a long time ago,[1,2] the fully controlled process became possible with the monofunctional dialkylaluminum alkoxides (R_2AlOR').[3−5] Since the reactivity differences of various aggregates of aluminum isopropoxide ($Al(O^iPr)_3$) are understood[6−8] and the trimer was found to initiate fast and quantitatively, this initiator has become an attractive alternative to R_2AlOR' initiators. On the other hand, in spite of a few claims indicating that initiators based on lanthanides lead to faster polymerization,[9−13] it has more recently been observed that they are less selective than the Al-based initiators.[14]

The telechelic poly(ϵCL)'s were also prepared with aluminum alkoxides.[15−17] The products of the ϵ-caprolactone (ϵCL) polymerization initiated by the difunctional monoalkoxides $R_2AlO-R'-OAlR_2$, followed by the hydrolysis of the growing ends, were shown to be linear, well-defined HO−poly(ϵCL)−OH, having molecular weights ($\bar{M}_n$) controlled by the $[monomer]_o/[initiator]_o$ ratio and narrow molecular-weight distributions ($\bar{M}_w/\bar{M}_n \leq 1.13$),[15] provided that pure initiator was prepared. Otherwise, mixtures with broader molecular-weight distributions result.[16]

More recently, $Al(O^iPr)_3$ has been applied as initiator for the controlled synthesis of HO−poly(ϵCL)−OH by the chain-transfer polymerization of ϵCL:[17]



$$(m+n+2)\,\overset{\ulcorner (CH_2)_5 \urcorner}{O\text{———}C}{=}O \;+\; HO\text{-}R\text{-}OH \xrightarrow[THF, 25^{o}C]{Al[OCH(CH_3)_2]_3}$$

$$\longrightarrow HO\text{-}(CH_2)_5\overset{O}{\overset{\|}{C}}\text{-}[O(CH_2)_5\overset{O}{\overset{\|}{C}}]_m O\text{-}R\text{-}O[\overset{O}{\overset{\|}{C}}(CH_2)_5O]_n\overset{O}{\overset{\|}{C}}(CH_2)_5\text{-}OH \quad (1)$$

where R = $(CH_2)_5$, $O[(CH_2)_2O]_n$, and $O[(CH_2)_4O]_n$.

Moreover, it was shown that ϵCL polymerization initiated with $Al(O^iPr)_3$ and conducted in the presence of 1,5-pentanediol (PD) is, at its early stages, almost completely inhibited.[17]

In the present work the mechanism and kinetics of polymerization in the ϵCL/alcohol (or diol) system initiated with $Al(O^iPr)_3$ trimer (A_3) and/or tetramer (A_4) are studied. The structure of the involved active centers is analyzed with ^1H and ^{27}Al NMR spectra of the polymerizing mixtures. Finally, the kinetic plots reproduced numerically are compared with those obtained experimentally.

Experimental Section

Materials. ϵ-Caprolactone (from Aldrich) was purified and stored as was already described.[5,17]

Aluminum isopropoxide (from POCh, Poland) was purified by three consecutive distillations under reduced pressure (150 °C, 2 mbar) and stored at −12 °C, giving a mixture of A_3 and A_4. Its composition was determined using ^1H NMR as described in ref 7. A_3 and A_4 were prepared by starting from this A_3/A_4 mixture, according to the procedures given in ref 7 and similar to those already described in refs 18 and 19.

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1,5-Pentanediol (from Aldrich), 2-propanol, and ethanol (from POCh, Poland) were dried by reacting with a Na metal and distilled under reduced pressure into ampules equipped with breakseals. Poly(ethylene glycol) 1000 (from Riedel De Haën, Germany) was dried under high vacuum at 90−100 °C for 8 h and additionally purified by dissolving in dry toluene (distilled from Na−K alloy), which thereafter was evaporated at 50 °C under reduced pressure.

THF, benzene (from POCh, Poland), and benzene-d_6 (from Świerk/Warsaw, Poland) were kept, after the usual purification, over liquid Na−K alloy from which they were distilled into the reaction vessel, using a high-vacuum manifold via the glass vacuum buret.

Procedures. Polymerizing mixtures were prepared in sealed glass ampules, using standard high-vacuum techniques.

The kinetics of ϵCL polymerization was studied using the vacuum dilatometric method, according to the procedure described in our earlier work.[20]

GPC analyses were performed using an LKB 2150 HPLC pump, a set of HPLC Waters ultrastyragel columns (10^3, 5×10^2, and 10^2), and a RIDK 102 (Praha, Czechoslovakia) detector. THF was used as an eluent.

^{1}H NMR spectra were registered in dry benzene-d_6 on Bruker AC 200 or Bruker MSL 300 operating at 200 or 300 MHz, respectively.

^{27}Al NMR spectra were recorded in dry benzene-d_6 on a Bruker MSL 300, equipped with a multinuclear probe head and operating at 75 MHz; as the external standard a 0.1 mol·L^{-1} benzene-d_6 solution of Al[CH(C(O)CH$_3$)$_2$]$_3$ was used. The living polymerization mixtures and the initiator solutions were prepared and transferred into the NMR tubes under the high-vacuum conditions. The NMR tubes were sealed off after freezing in liquid nitrogen.

Results and Discussion

Kinetics of Polymerization. In the preceding work[17] polymerization of ϵ-caprolactone (ϵCL) initiated with Al(O^{i}Pr)$_3$ was studied in the presence of 1,5-pentanediol (PD). Al(O^{i}Pr)$_3$ was purified by distillation before use. Thus prepared initiator, as has recently been reconfirmed,[7,8] consists mostly of a mixture of Al(O^{i}Pr)$_3$ trimer (A$_3$) and tetramer (A$_4$). Therefore, it was decided to see, in the present work, how the individual aggregates of Al(O^{i}Pr)$_3$ behave in the presence of a diol, since it became known that they differ considerably in their reactions with ϵCL. The starting concentrations of monomer ([ϵCL]$_o$) and initiator ([Al(^{i}OPr)$_3$]$_o$) were equal to 2.0 and 3.5×10^{-3} mol·L^{-1}, respectively, in all kinetic experiments.

Results of the measurements, in THF as solvent at 25 °C, are given in Figure 1 in the semilogarithmic coordinates: ln([ϵCL]$_o$/[ϵCL]) versus time. Plots obtained for the polymerizations without introduced transfer agent (points marked by filled circles and triangles for A$_3$ and A$_4$, respectively) illustrate the vast difference of reactivities between A$_3$ and A$_4$. Introduction of PD into the reaction mixture, under the otherwise identical conditions, leads either to inhibition (A$_3$ initiation, Figure 1, hollow circles) or to acceleration (A$_4$ initiation, Figure 1, hollow triangles) of the ϵCL polymerization.

Interestingly, A$_3$, A$_4$, and the equimolar A$_3$/A$_4$ mixture gave, in the presence of PD, almost identical kinetic plots (Figure 1). Thus, in further kinetic studies we exclusively used the A$_3$/A$_4$ mixtures, obtained from the crude commercial alkoxide by distillation, to initiate the chain-transfer polymerization of ϵCL. The results are collected in Figures 2 and 3.

In polymerizations without introduction of a transfer agent (Figure 2a, points marked by filled triangles) first-order (internally) kinetics in ϵCL is observed, which is in agreement with the already published results.[2,7,8]

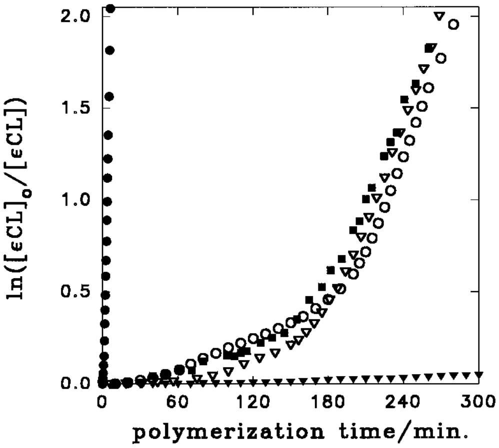


Figure 1. Kinetics of ϵCL polymerization initiated with Al(O^{i}Pr)$_3$ trimer (A$_3$) and/or tetramer (A$_4$). Polymerization conditions: [ϵCL]$_o$ = 2 mol·L^{-1}, [Al(O^{i}Pr)$_3$]$_o$ = 3.5×10^{-3} mol·L^{-1}, THF as solvent, 25 °C. Key: (●) 95% A$_3$, no transfer agent; (▼) "100%" A$_4$, no transfer agent; (○) 95% A$_3$, [PD]$_o$ = 0.2 mol·L^{-1}; (▽) "100%" A$_4$, [PD]$_o$ = 0.2 mol·L^{-1}; (■) A$_3$/A$_4$ equimolar mixture, [PD]$_o$ = 0.2 mol·L^{-1}.

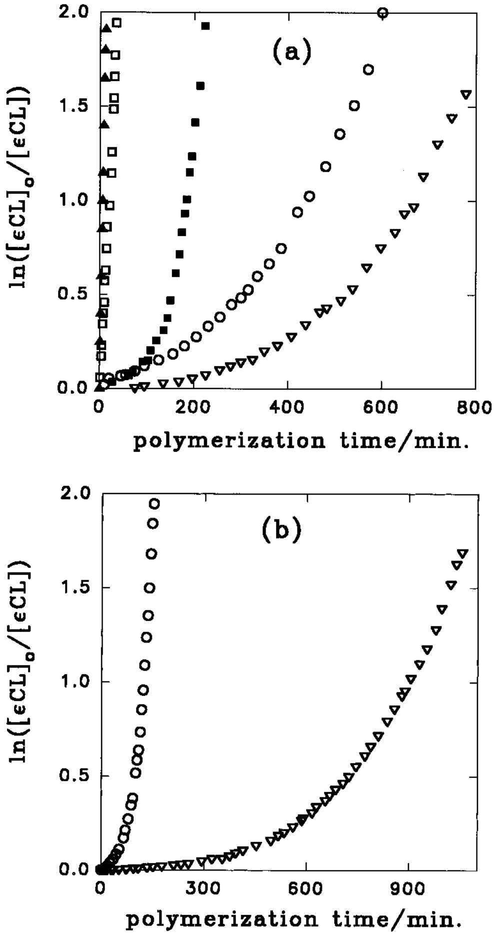


Figure 2. Kinetics of ϵCL polymerization initiated with an equimolar A$_3$/A$_4$ mixture and conducted in the presence of various alcohols as the transfer agents. Polymerization conditions: [ϵCL]$_o$ = 2 mol·L^{-1}, [Al(O^{i}Pr)$_3$]$_o$ = 3.5×10^{-3} mol·L^{-1}, 25 °C. (a) THF as solvent, [transfer agent]$_o$ = 0.100 mol·L^{-1}: (▲) no alcohol, (□) poly(ethylene glycol) (M_n = 890), (■) PD, (○) 2-propanol, (▽) ethanol. (b) Benzene as solvent, transfer agent and its starting concentration: (○) [PD]$_o$ = 0.220 mol·L^{-1}, (▽) [2-propanol]$_o$ = 0.220 mol·L^{-1}.

Figure 2a gives also kinetic data obtained for various transfer agents introduced at the same starting concentrations (i.e. 0.1 mol·L^{-1}). For PD (filled squares)

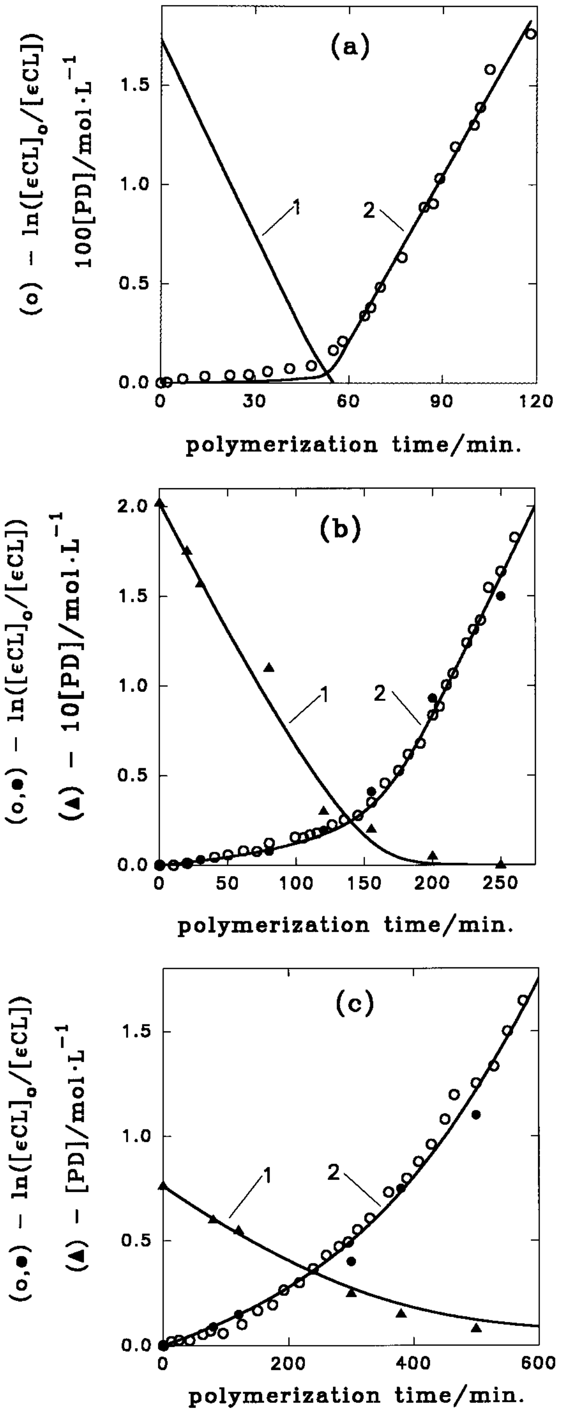


Figure 3. Kinetics of ϵCL polymerization initiated with an equimolar A_3/A_4 mixture and conducted in the presence of PD. Polymerization conditions: $[\epsilon CL]_o = 2$ mol·L^{-1}, $[Al(O^iPr)_3]_o =$ 3.5×10^{-3} mol·L^{-1}; $[PD]_o$/mol·L^{-1} = 0.018 (a), 0.200 (b), 0.760 (c); THF as solvent; 25 °C. Instantaneous concentrations measured by dilatometry and by GPC (points marked by (○) and by (●, ▲), respectively). Lines computed numerically by means of eqs 21 and 22 substituting $k_p = 0.15$ mol^{-1}·L·s^{-1}, K_c = 3603 mol^{-1}·L, $r = 1$ (a); $k_p = 0.075$ mol^{-1}·L·s^{-1}, $K_c = 49.2$ mol^{-1}·L, $r = 1$ (b); $k_p = 0.069$ mol^{-1}·L·s^{-1}, $K_c = 8.40$ mol^{-1}·L, $r = 1$ (c). Lines 1 and 2 are plots of [PD] and ln([ϵCL]$_o$/[ϵCL]) vs polymerization time, respectively.

polymerization accelerates, after the initial inhibition period, eventually becoming first-order in monomer. Moreover, as shown in Figure 3, the higher the starting concentration of diol, the longer the polymerization half-life time.

Monoalcohols, such as 2-propanol or ethanol, led to much more significant inhibition (Figure 2a, hollow circles and triangles, respectively). The inhibiting effect of 2-propanol on the polymerization rate was already reported for the ϵCL/aluminum alkoxide system.[21,22]

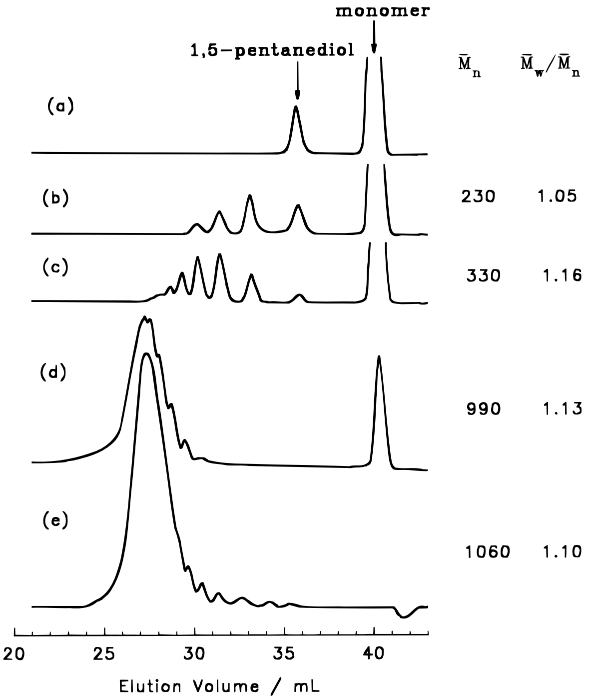


Figure 4. GPC traces of the $\epsilon CL/PD/A_3/A_4$ polymerizing mixtures. Polymerization conditions: $[\epsilon CL]_o = 2$ mol·L^{-1}, $[Al(O^iPr)_3]_o = 3.5 \times 10^{-3}$ mol·L^{-1}, $[PD]_o = 0.20$ mol·L^{-1}, THF as solvent. Polymerization time (min): 0 (a), 80 (b), 155 (c), 250 (d), 1000 (e). Waters Ultrastyragel columns: 10^3, 5×10^2, and 10^2. Eluent: THF. Flow rate: 0.7 mL·min^{-1}.

Apart from the kinetics of the ϵCL consumption, independently, the disappearance of PD was also measured. This is illustrated in Figure 3b,c. Concentrations of ϵCL were determined dilatometrically (experimental points marked by hollow circles) and by gel permeation chromatography (GPC, filled circles), whereas PD was determined exclusively by GPC (filled triangles). The representative GPC traces, given in Figure 4, show that for $[\epsilon CL]_o = 2$ mol·L^{-1} and $[PD]_o = 0.2$ mol·L^{-1} the PD transfer agent is consumed quantitatively before polymerization is completed.

Direct comparison of the kinetic plots obtained for ϵCL and PD (Figure 3b,c) reveals that the relative polymerization rate; $r_p = -d \ln [\epsilon CL]/dt$, increases with the decreasing instantaneous concentration of PD. Once PD disappears, r_p becomes first-order with respect to ϵCL. Apparently, only the low-molecular-weight diols are the inhibiting agents.

Indeed, application of the oligomeric poly(ethylene glycol) (PEG, $\bar{M}_n \approx 900$) in place of PD as the transfer agent, under comparable conditions, eliminates the inhibition period (Figure 2a, hollow squares). The dihydroxytelechelic poly(ϵCL) having $\bar{M}_n = 1300$ (cf. Figure 8 in ref 17) behaves the same way.

The model NMR studies were performed in benzene-d_6 solution. Therefore, some kinetics were monitored in the same solvent. Replacing THF by benzene did not change the concave shape of the semilogarithmic plots (Figure 2b).

^{1}H and ^{27}Al NMR Spectra of the Polymerizing Mixtures. The ^{1}H and ^{27}Al NMR spectra of the $Al(O^iPr)_3$ initiator and the $Al(O^iPr)_3/\epsilon CL$ polymerizing mixtures were already discussed.[6-8] It has been concluded that in the A_3/A_4 mixture the "true" initiator is the

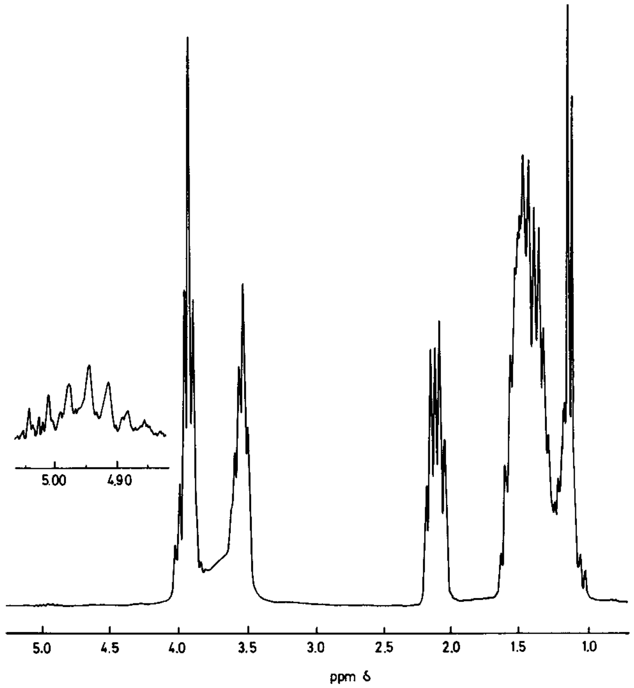


Figure 5. ^{1}H NMR (200 MHz) spectra of the living poly(ϵCL)/HO−poly(ϵCL)−OH reaction mixture. Conditions of polymerization: $[\epsilon CL]_o = 1.6$ mol·L^{-1}, $[Al(O^iPr)_3]_o = 0.085$ mol·L^{-1} (equimolar A_3/A_4 mixture), $[PD]_o = 0.85$ mol·L^{-1}, benzene-d_6 as solvent, 20 °C.

trimeric $Al(O^iPr)_3$, whereas A_4 remains intact, at least within the time required for the complete ϵCL polymerization initiated by A_3. Moreover, each of the three $-O^iPr$ groups, linked to one Al atom, starts the growth of one macromolecule.[8]

However, the kinetic data given in Figure 1 suggest that in the presence of PD the A_3/A_4 mixture behaves differently and that both A_3 and A_4 are consumed. The same conclusion comes from the analysis of the ^{1}H NMR spectrum of the living poly(ϵCL)/HO−poly(ϵCL)−OH reaction mixture prepared with PD as the transfer agent (Figure 5). The starting conditions were the following: $[\epsilon CL]_o = 1.6$ mol·L^{-1}, $[Al(O^iPr)_3]_o = 0.085$ mol·L^{-1} (the equimolar A_3/A_4 mixture), $[PD]_o = 0.85$ mol·L^{-1}, C_6D_6, 25 °C. The $>Al-O-CH(CH_3)_2$ signals ($\delta = 4.2-4.8$ ppm), corresponding to both A_3 and A_4, are practically absent. Also the signal ($\delta \approx 5.00$ ppm) related to the polymer end groups ...$-C(O)OCH(CH_3)_2$ has a relatively small intensity. The concentration of these end groups can be estimated as being less than 5 mol % of $[-O^iPr]_o$. On the other hand, the intensity of the doublet at $\delta = 1.1$ ppm corresponds approximately to all of the $-CH_3$ groups, coming from the starting initiator (both A_3 and A_4). The chemical shift of this doublet is characteristic for 2-propanol. Apparently, the 2-propanolate groups of the initiator have been interchanged with the 1,5-pentanediolate groups (cf. next section, equilibrium 2 shifted to the right-hand side) and at least a part of the 2-propanol was left in the reaction mixture.

A multiplet in the vicinity of $\delta = 3.6$ ppm is due to the ...$-CH_2-OH$ end groups, and the remaining multiplets centered at $\delta = 1.4$, 2.1, and 3.95 ppm correspond to the main-chain protons of HO−poly(ϵCL)−OH (for details see refs 2, 5, and 17).

In the ^{27}Al NMR spectrum, of the same polymerizing mixture, the sharp and narrow peak at δ 1.8 ppm, characteristic for A_4, and the broad band at $\delta = 33$ ppm, due to A_3,[8,23−25] are absent (Figure 6). Two bands, at $\delta \approx 5$ ppm and the broader one centered at $\delta \approx 60$ ppm are ascribed to the aluminum alkoxide growing species. The pertinent structures are briefly discussed in the next section. Thus, the ^{27}Al NMR data agree well with the results from the ^{1}H NMR spectra.

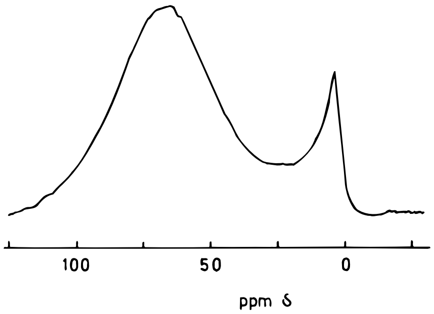
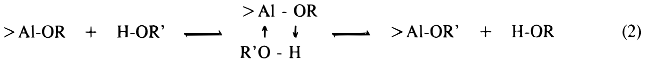


Figure 6. ^{27}Al NMR (75 MHz) spectra of the living poly(ϵCL)/HO−poly(ϵCL)−OH reaction mixture. Conditions of polymerization given in the caption for Figure 5.

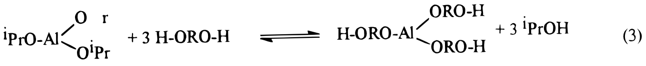
Mechanism of ϵ-Caprolactone Polymerization Initiated by $Al(O^iPr)_3$ and Conducted with $HO(CH_2)_5OH$ as a Transfer Agent. (a) Exchange of the Alcoholate Ligands at Active Centers. It is known that in the $Al(OR)_3/HOR'$ mixture, the RO− and R′O− alcoholate groups interchange relatively easily:[26]



$$>Al\text{-}OR + H\text{-}OR' \rightleftharpoons \begin{matrix} >Al\text{-}OR \\ \uparrow\downarrow \\ R'O\text{-}H \end{matrix} \rightleftharpoons >Al\text{-}OR' + H\text{-}OR \qquad (2)$$

The $>Al-OR$ alcoholate could be quantitatively transformed into the $>Al-OR'$ alcoholate by removing one of the components from the reacting mixture. For instance, either by distilling off ROH or by precipitation of $>Al-OR'$.

Aluminum trialkoxides and diols, due to their polyfunctionality, may form networks if the $[diol]/[Al(OR)_3]$ ratio is close to 2. When a large excess of diol is used, the simpler structures are formed, e.g.



$$^iPrO\text{-}Al\begin{matrix} O^iPr \\ O^iPr \end{matrix} + 3\ H\text{-}ORO\text{-}H \rightleftharpoons H\text{-}ORO\text{-}Al\begin{matrix} ORO\text{-}H \\ ORO\text{-}H \end{matrix} + 3\ ^iPrOH \qquad (3)$$

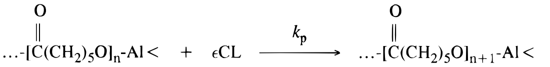
which, however, may form the sparingly soluble, oligomeric aggregates.

Various diols as chain-transfer agents were used, namely, 1,2-ethanediol, 1,5-pentanediol, HO−poly(ϵCL)−OH ($\bar{M}_n \geq 1000$), and $HO-[(CH_2)_xO]_n-OH$ ($x = 2$ or 4, $\bar{M}_n \approx 1000$).[17] In the case of the low-molecular-weight diols, the reaction mixtures were heterogeneous even for $[diol]_o/[Al(O^iPr)_3]_o$ ratios as high as 300. The Al−alkoxide prepared from $Al(O^iPr)_3$ and $HO-CH_2CH_2-OH$ precipitated out, after the monomer introduction, and the polymerization did not proceed. Substitution of $HO(CH_2)_5OH$ for $HO(CH_2)_2OH$ led first to a gel-like adduct. The polymerization started almost from the very begining of the mixing the components and the resulting reaction mixtures became homogeneous.

The ^{1}H NMR spectrum of the living poly(ϵCL) prepared in the presence of PD (Figure 5) shows that even for the relatively low excess of the transfer agent ($[PD]_o/[Al(O^iPr)_3]_o = 10$) the interchange equilibrium 2 is shifted to the 2-propanol side; i.e. it results in almost quantitative substitution of the 2-propanolate by the 1,5-pentanediolate groups at the Al atoms. This is, apparently, not only due to the law of mass action. Another factor could be related to the higher acidity of the primary alcohols and diols, in comparison with that of 2-propanol. The respective pK_a values (from 15 to

16 vs 17.1),[27] although determined in aqueous alcohols indicate a trend which also could be expected for another, less polar media.

The starting PD, as was shown in the preceding paper[17] and as is illustrated in Figure 4, is transferred into the growing macromolecules of poly(ϵCL). Therefore, we assume that apart from propagation



$$\ldots\text{-}[\overset{\displaystyle \text{O}}{\overset{\|}{\text{C}}}(\text{CH}_2)_5\text{O}]_n\text{-Al}< \;+\; \epsilon\text{CL} \xrightarrow{k_p} \ldots\text{-}[\overset{\displaystyle \text{O}}{\overset{\|}{\text{C}}}(\text{CH}_2)_5\text{O}]_{n+1}\text{-Al}< \qquad (4)$$

the reversible exchange of the alkoxide ligands takes place, not only at the Al atoms of the initiator (eq 2) but also at any stage of the propagating active centers:

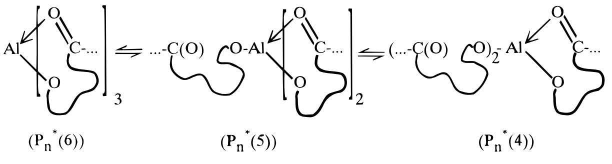
$$>\text{Al-O-R-OH} \;+\; \text{HO-R'-OH} \underset{k_{\text{-ex}}}{\overset{k_{\text{ex}}}{\rightleftharpoons}} >\text{Al-O-R'-OH} \;+\; \text{HO-R-OH} \qquad (5)$$

(where R and R′ denote fragments of the polymer or PD molecules and k_p, k_{ex}, and k_{-ex} are the rate constants of the propagation and the exchange of alkoxide groups, respectively).

The Poissonian molecular-weight distribution of the growing oligodiols, observed during polymerization (see Table 1 in ref 17 and Figure 4 in the present work), suggests that this chain transfer is reversible indeed and fast, in comparison with propagation (k_{ex}, $k_{-ex} > k_p$). Results reported by Inoue et al.[28] for the (tetraphenylporphinato)aluminum alkoxide/CH_3OH or $HOCH_2CH_2OH$/ϵCL system lead to similar conclusions for their systems called "immortal" because of this observation.

(b) Structure of Active Species. Since the ^1H NMR and the molecular-weight data for the ϵCL/Al(O-$^iPr)_3$ system have shown that in the Al–trialkoxide active center all three alkoxide groups propagate and that the active species have the nonaggregated (monomeric) structure,[6−8] the same may be assumed for the polymerization conducted in the presence of the transfer agent. The trifunctional structure of the propagating species is additionally supported by the $\bar{M}_n$ data, for the poly(ϵCL) prepared in the presence of 2-propanol.[2,22] The measured $\bar{M}_n$ values, for the polymerizations with the comparable starting concentrations of $Al(O^iPr)_3$ and HO^iPr, indicate that the concentration of the poly(ϵCL) macromolecules formed is equal to the sum of the concentration of O^iPr groups, from both the Al–alkoxide and the added alcohol.

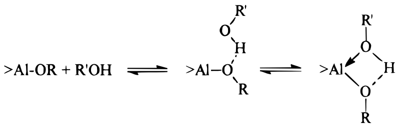
Recently, it has been observed[8] that $(\ldots-C(O)CH_2CH_2CH_2CH_2CH_2O)_3Al$ active centers gave two signals in ^{27}Al NMR: at 5 and 60 ppm, i.e. in the regions characteristic for the hexa- and tetracoordinated Al atoms, respectively. These coordination numbers, in the trivalent, monomeric species, were attributed to the coordination with the acyl oxygen atoms of two or three polymer repeating units. Thus, the species responsible for the ^{27}Al NMR absorption (Figure 6) may assume structures P_n^*, participating in the interchange equilibria 6, in which the tetra- and hexacoordinated species dominate:



(6)

In the presence of alcohols or diols at least some of the >C=O ligands, coordinating with Al atoms, can be substituted by the ROH ligands, as in the structures shown schematically below (eqs 7−9).

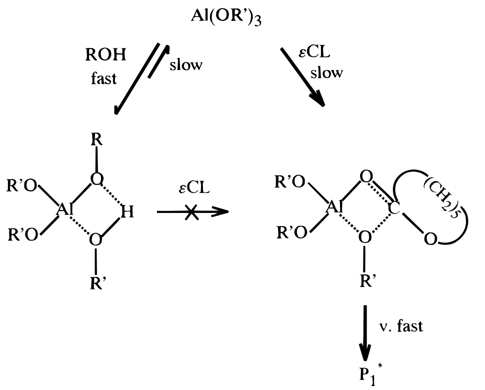
(c) Kinetic Scheme and Its Solution. The kinetic data discussed above suggest that the low initial rate of the ϵCL polymerization conducted in the presence of alcohols or diols may be related to the relatively strong complexation of the monomeric aluminum trialkoxide species by the *low-molecular-weight* alcohol or diol, in comparison with that by an ester group. A large difference of basicities, expressed by the pK_a values of the corresponding conjugated acids (from −3 to −4 for hydroxyl and −7 for the ester group),[29] although related to the phenomena which may be distant from the complexation of the aluminum alkoxides, suggests that the complexation ability of the hydroxyl group is stronger than that of the ester group. Moreover, alcohols may form hydrogen bonds with the Al–alkoxide oxygen atoms, e.g.



(7)

(self-coordination by the acyl oxygen atoms from the poly(ϵCL) repeating units is omitted). Thus, the more effective filling out of the Al atoms solvation shell by the low-molecular-weight alcohol than by the monomer molecules leads eventually to the observed decrease of the propagation rate.

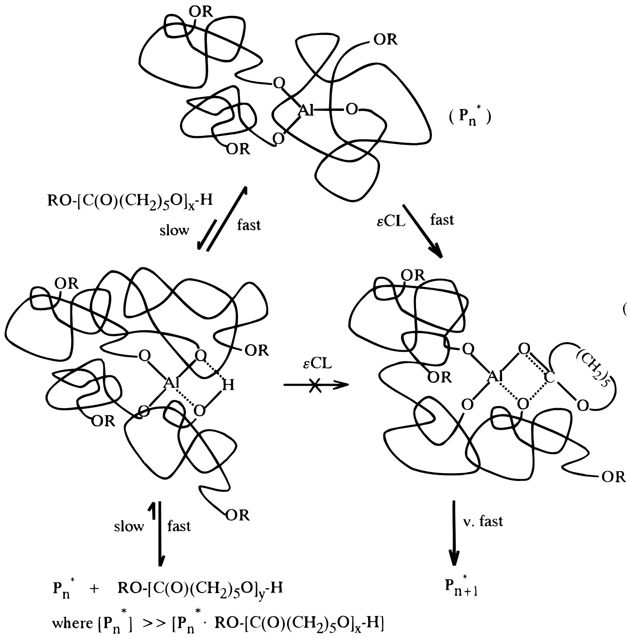
At the very begining of polymerization both ϵCL and ROH molecules diffuse readily to a vicinity of the >Al–O– active species. However, formation of the unreactive Al(OR′)$_3$·ROH complex proceeds much faster than that of the ϵCL-coordinated species: Al(OR′)$_3$·ϵCL (followed by the very fast opening of the lactone ring). Schematically



(8)

where Al(OR′)$_3$ denotes the first monomeric active species formed from the aggregated initiator and [Al(OR′)$_3$] ≪ [Al(OR′)$_3$·ROH].

During ϵCL polymerization, however, the growing alkoxide ligands linked to Al atoms increase their molecular weight. The starting alcohol, due to the relative fast exchange reactions (eq 2), also transforms from the low- into the high-molecular-weight compound. Then, the hydroxyl end groups of the resulting macroalcohol (or macrodiol) molecules become engaged in the intra- and/or intermolecular hydrogen bonds with the ester groups of the poly(ϵCL) repeating units; a similar phenomenon has been reported for the hydroxytelechelic poly(ethylene oxide)s.[30−32] Thus, the polyester chains linked to one Al atom may hinder diffusion of the macroalcohol hydroxyl groups, whereas the monomer molecules are still able to approach the active species, which leads to an increase of the ϵCL propagation rate as the net effect. Schematically



(9)

(self-coordination by the acyl oxygen atoms from the poly(ϵCL) repeating units is omitted).

However, the apparent propagation rate constants, determined from the straight linear parts of the kinetic semilogarithmic plots, are still lower then those obtained without the transfer agent. This result indicates that the oligomeric alcohols or diols ($\bar{M}_n \approx 10^3$) are also able to afford some complexation of the Al−alkoxide active species. Indeed, the chain transfer, requiring this kind of −OH group−active species interactions proceeds effectively also for the oligodiols.

The pertinent kinetic scheme is given below:

$$P_n^* + r\mathrm{R{-}OH} \xrightarrow{K_c} P_n^{\,d}\ (P_n^*{\cdot}r\mathrm{HO{-}R}) \qquad (10)$$

$$P_n^* + \mathrm{M} \xrightarrow{k_p} P_{n+1}^* \qquad (11)$$

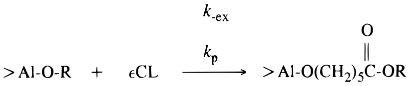
where ROH denotes the transfer agent (low-molecular-weight monoalcohol or diol), P_n^* and P_n^d are the propagating and dormant (complexed) active centers, respectively, K_c is the equilibrium constant of complexation, r is the average number of hydroxyl groups coordinating one Al atom, and M is the monomer. In further analysis it is also assuemd that both the interchange (2) and complexation (10) equilibria are established at rates higher than that of propagation.

Propagation rate:

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_p[P_n^*][\mathrm{M}] \qquad (12)$$

The starting alcohol (or diol) ROH is consumed in the following reactions:

$$>\!\mathrm{Al{-}OR'} + \mathrm{ROH} \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} >\!\mathrm{Al{-}O{-}R} + \mathrm{R'OH} \qquad (13)$$



$$>\!\mathrm{Al{-}O{-}R} + \epsilon\mathrm{CL} \xrightarrow{k_p} >\!\mathrm{Al{-}O(CH_2)_5\overset{\overset{\displaystyle O}{\|}}{C}{-}OR} \qquad (14)$$

Assuming, that $k_{ex} = k_{-ex}$ and $k_{ex} \gg k_p$ the ROH consumption rate reads

$$-\frac{\mathrm{d[ROH]}}{\mathrm{d}t} = -\frac{\mathrm{d[{>}Al{-}O{-}R]}}{\mathrm{d}t} = k_p[\mathrm{{>}Al{-}O{-}R}][\mathrm{M}] \qquad (15)$$

On the basis of eq 13

$$[\mathrm{{>}Al{-}O{-}R'}][\mathrm{ROH}] = [\mathrm{{>}Al{-}O{-}R}][\mathrm{R'OH}] \qquad (16)$$

Moreover

$$[\mathrm{{>}Al{-}O{-}R'}] + [\mathrm{{>}Al{-}O{-}R}] = [P_n^*] \qquad (17)$$

and when $[\mathrm{ROH}]_o \gg [\mathrm{{>}Al{-}}]$

$$[\mathrm{ROH}] + [\mathrm{R'OH}] = [\mathrm{ROH}]_o \qquad (18)$$

Finally, after rearranging eqs 15−18, one obtains

$$-\frac{\mathrm{d[ROH]}}{\mathrm{d}t} = ([\mathrm{ROH}]/[\mathrm{ROH}]_o)k_p[P_n^*][\mathrm{M}] \qquad (19)$$

The proportion between the concentrations of the propagating and dormant active centers can be calculated from the expression for the complexation equilibrium:

$$K_c = \frac{[P_n^{\,d}]}{[P_n^*](f[\mathrm{ROH}])^r} \qquad (20)$$

(where f is a functionality (the number of hydroxyl groups) of the transfer agent molecule).

In the absence of termination: $[P_n^*] + [P_n^d] = [\mathrm{Al(O^iPr)_3}]_o$. Thus, rearranging eqs 12, 19, and 20, we eventually obtain two differential equations describing the kinetics of consumption of both monomer and transfer agent:

$$-\frac{\mathrm{d[M]}}{\mathrm{d}t} = k_p\frac{[\mathrm{Al(O^iPr)_3}]_o[\mathrm{M}]}{1 + K_c(f[\mathrm{ROH}])^r} \qquad (21)$$

$$-\frac{\mathrm{d[ROH]}}{\mathrm{d}t} = k_p\frac{[\mathrm{ROH}][\mathrm{Al(O^iPr)_3}]_o[\mathrm{M}]}{[\mathrm{ROH}]_o(1 + K_c(f[\mathrm{ROH}])^r} \qquad (22)$$

A set of these kinetic equations have been numerically integrated using the EPISODE procedure.[33] The starting value of k_p has been determined from the slop of the straight linear part of the ln([M]$_o$/[M]) versus time plot; that of K_c has been chosen, for a given starting k_p, using the trial-and-error approach—the first approximation was obtained this way. Then the values of K_c and k_p have been adjusted by the nonlinear least squares minimization, until the best fit between the experimental and simulated kinetic curves was obtained. All numerical calculations have been performed using the Scientist (MicroMath, USA) program. The solid lines in Figure 3 are plotted according to the integrated eqs 21 and 22. There is fairly good agreement of the reconstructed kinetic dependencies and the experimental points, both for the monomer and transfer agent, particularly for the polymerizations with high enough $[\mathrm{PD}]_o/[\mathrm{Al(O^iPr)_3}]_o$ ratios (approximately ≥40) (Figure 3b,c). For the lower starting concentrations of PD some deviations from the experimentally determined curves were observed (Figure 3a). The best fit, independent

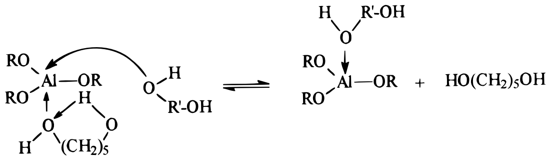
Table 1. Calculated [$\bar{M}_n$(calcd)] and Measured [$\bar{M}_n$(GPC)] Number-Average Molecular Weights and Polydispersity Indexes ($\bar{M}_w/\bar{M}_n$) of the Resulting Oligomers [Conditions: $[\epsilon CL]_o = 2$ mol·L^{-1}, $[Al(O^iPr)]_o = 3.5 \times 10^{-3}$ mol·L^{-1}, 25 °C]

				$\bar{M}_n$		$\bar{M}_w/\bar{M}_n$		
sample no.	solvent	alcohol	[alcohol]$_o$, 10^{-3} mol·L^{-1}	calcd[a]	GPC[b]	calcd[c]	GPC[b]	β[d]
1	THF	^{i}PrOH	101	2107	3200	1.03	1.18	0.62
2	THF	^{i}PrOH	171	1317	2300	1.05	1.17	0.54
3	THF	EtOH	106	2059	2250	1.05	1.16	0.88
4	toluene	^{i}PrOH	234	993	2180	1.05	1.16	0.41

[a] $\bar{M}_n(\text{calcd}) = \{[\epsilon CL]_o 114.14/(3[Al(O^iPr)_3]_o + [ROH]_o)\} + MW_{ROH}$, where 114.14 and MW_{ROH} are molecular weights of ϵCL and alcohol, respectively. [b] $\bar{M}_n$(GPC), $\bar{M}_w/\bar{M}_n$(GPC): molecular weight and its distribution, respectively, measured by gel permeation chromatography with calibration on the poly(ϵCL) standards. [c] $\bar{M}_w/\bar{M}_n(\text{calcd}) = 1 + \bar{n}/(1 + \bar{n})^2$, where $\bar{n}$ is the number-average polymerization degree. [d] β is the efficiency of the alcohol consumption; $\beta = [ROH]_{consumed}/[ROH]_o$, $[ROH]_{consumed} = \{114.4[\epsilon CL]_o/(\bar{M}_n(\text{GPC}) - MW_{ROH})\} - 3[Al(O^iPr)_3]$.

of the $[PD]_o/[Al(O^iPr)_3]_o$ ratio, was achieved for $r = 1$, i.e. assuming the temporary deactivation of the active center by only one diole molecule. Values of k_p and K_c ensuring the best fit are given in the caption for Figure 3. It has to be stressed, however, that these are the apparent values, valid only for a given composition of the reaction mixture. This is related to the fact that the kinetic scheme (10)–(22) gives only the net equations, describing general features of the ϵCL/PD/Al(O^{i}Pr)$_3$ polymerization. Further work would be needed to determine the dependencies of K_c on the oligodiol polymerization degree, the rates of interconversions, and the actual instantaneous concentration of the growing species.

Attempts of reconstructing the kinetic plots, obtained with 2-propanol and ethanol, similar to how we did for polymerizations with 1,5-pentanediol, failed. Equations 21 and 22 have been derived by assuming dynamic and reversible exchange between the "free" alkoxide and macroalkoxide groups and those located at the Al atoms of the active centers. However, monoalcohols, in contrast to 1,5-pentanediol, were not consumed quantitatively, at least during the time required for the complete ϵCL polymerization, and polydispersities of the resulting oligomers were apparently higher than that predicted by the Poisson distribution (Table 1). These results may indicate that in the case of simple alcohols (at least CH_3CH_2OH and $(CH_3)_2CHOH$) the rate of propagation exceeds that of the chain transfer. This may be because the bidentate structure of PD facilitates the exchange reaction by forming the intramolecular hydrogen bond, e.g.



(23)

(self-coordination by the acyl oxygen atoms from the poly(ϵCL) repeating units is omitted). This kind of anchimeric assistance, existing for diols, is not possible for monoalcohols. The considerably weaker inhibiting effect given by 1,5-pentanediol (Figure 2) can be explained in a similar way.

Conclusions

It has been shown that in the polymerization of ϵ-caprolactone (ϵCL) initiated with Al(O^{i}Pr)$_3$ and carried out in the presence of alcohols or diols (ROH), both Al(O^{i}Pr)$_3$ trimer (A_3) and tetramer (A_4) are consumed quantitatively and fast in the initiation step. This behavior is in contrast to the already studied[7,8] ϵCL polymerization, conducted without the purposely introduced ROH, where the initiation rates with A_3 and A_4 differ up to 10^3 times. Thus, in the absence of alcohols

$$aA_3 + bA_4 + m\epsilon CL \rightarrow 3a\ Al\{[O(CH_2)_5C(O)]_nOCH(CH_3)_2\}_3 + bA_4 \qquad (9a\bar{n} = m) \quad (24)$$

whereas in the presence of an alcohol or a diol

$$aA_3 + bA_4 + pROH + m\epsilon CL \rightarrow (3a + 4b)\ Al\{[O(CH_2)_5C(O)]_nOCH(CH_3)_2\}_3 + pH[O(CH_2)_5C(O)]_qOR \qquad (3(3a{+}4b)\bar{n} + p\bar{q} = m) \quad (25)$$

Usually, $[ROH]_o \gg [Al(O^iPr)_3]_o$ and therefore $p\bar{q} \approx m$.

Thus, the propagating species, the monomeric aluminum tris(macroalkoxide)s: Al–(O–poly(ϵCL)–OR)$_3$ are formed fast and quantitatively, from a mixture of A_3 and A_4 in the presence of ROH. It does not mean, however, that A_3 and A_4 react with similar rates but only that ROH facilitates transformation of the otherwise low-reactive A_4 into A_3 or other more reactive initiating species, therefore making the rate of initiation with A_4 (formally) at least comparable with the rate of propagation. It means that ROH, in the polymerizations initiated with A_3, behaves kinetically as an inhibitor, whereas in those with A_4, it acts as an accelerator. This conclusion can be supported by the already reported observation[19] that 2-propanol increases the $A_4 \rightarrow A_3$ conversion rate.

Therefore, polymerization carried out in the presence of ROH can be described by the same scheme for any A_3 and A_4 concentration ratio: the initial rate of the polymerization ($r_p = -d \ln [\epsilon CL]/dt$) is very low, then $\bar{r}_p$ slowly increases, and eventually it becomes constant—this moment coincides with the complete consumption of ROH. This kinetic behavior can be explained by assuming deactivation of a large majority of the involved active species due to a reversible complexation by the low-molecular-weight ROH. During polymerization ROH is transformed into the oligomeric poly(ϵCL)–OH, unable apparently to effectively complex the growing species, which results eventually in the polymerization rate increase. The solution of the pertinent kinetic scheme (eqs 10 and 11) for the polymerizing system, ϵCL/1,5-pentanediol (PD)/Al(O^{i}Pr)$_3$, leads to dependency of both [ϵCL] and [PD] on time, reconstructing well the respective experimental kinetics plots (Figure 3).

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