Kinetics and Mechanism of ϵ-Caprolactone Polymerization Using Yttrium Alkoxides as Initiators

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ABSTRACT: ϵ-Caprolactone polymerization using an initiating system comprising tris(2,6-di-*tert*-butylphenoxy)yttrium and 2-propanol was first-order in monomer and initiator. A propagation rate constant of 1.65 $L \cdot mol^{-1} \cdot s^{-1}$ was determined in dichloromethane. The reaction proceeds via a three-step mechanism. In the first step the large 2,6-di-*tert*-butylphenoxy ligands are exchanged for the smaller 2-propanol. In the second step the polar alkoxide is able to attack the carbonyl group and form the thermodynamically favored ring-opened product. After the first two initiating steps, the polymerization can proceed until complete conversion of monomer is reached. Evidence for these three steps is provided by ^1H and ^{13}C NMR spectroscopy of the reaction products of each single step. The kinetic behavior of commercially available yttrium isopropoxide was more complicated. 2-Propanol could be used as an effective chain transfer agent for this initiator.

Introduction

Ring-opening polymerization of ϵ-caprolactone using lanthanide alkoxide based initiators is a relatively recent discovery.[1] Meanwhile, it has been shown that high molecular weight, low polydispersity poly(ϵ-caprolactone)s can be prepared by initiators of the $(C_5Me_5)_2$-LnR (Ln = Y or lanthanide series element, R = alkyl fragment) and $(C_5H_5)_2$LnOR type.[2] Successful synthesis at a reasonable rate of such polymers by other initiating systems has not been reported. Also, the synthesis of several new macromolecular architectures, incorporating poly(ϵ-caprolactone) segments initiated by lanthanide elements, has been demonstrated. Examples include, e.g., poly(tetrahydrofuran)−poly(ϵ-caprolactone) di- and triblock copolymers,[3,4] difunctional poly(ϵ-caprolactone)s,[5] poly(ethylene)−poly(ϵ-caprolactone)[6] block copolymers, and poly(methyl methacrylate)−poly(ϵ-caprolactone) block copolymers.[7] Furthermore, it was reported that trivalent rare earth alkoxides can initiate living polymerization of monomers such as lactide,[8−11] δ-valerolactone,[2,11] β-propiolactone,[2] and β-butyrolactone,[9] with activities unprecedented in coordination polymerization of these monomers. The polymerization activity of lanthanide alkoxides is not restricted to the polymerization of lactone type monomers, and monomers such as isocyanates,[12] ethylene oxide,[13] and cyclic carbonates[14] can be satisfactorily (co)polymerized.

In contrast to the rapidly increasing number of papers dealing with the exciting synthetic aspects of these initiators, there is only poor understanding of the fundamental aspects of these polymerizations. In the past, anionic ring opening polymerization of lactones has been studied and examples of ϵ-caprolactone[15−17] and δ-valerolactone[18−20] polymerization are available. Apart from propagation, these polymerizations are characterized by transesterification reactions, either intermolecular with concomitant broadening of the polydispersity or intramolecular, leading to the formation of macrocycles or depolymerization. In coordination or pseudoanionic polymerization, kinetic studies are available for ϵ-caprolactone polymerizations by dialkylaluminum alkoxides[21−23] and aluminum tris(alkoxide)s.[24−28] The transesterifications mentioned above are mainly absent in these polymerizations, at the expense of much longer reaction times. We have recently shown that for L-lactide polymerization, yttrium alkoxides combine the high propagation rate of anionic polymerization with the high selectivity of the aluminum compounds toward propagation.[29]

Yttrium compounds containing yttrium−hydrogen, yttrium−carbon, and yttrium−nitrogen bonds are very reactive toward substrates containing activated hydrogen atoms, predominantly by acid−base type reactions.[30] For the synthesis of well-defined poly(caprolactone)s, lanthanide catalysts with strong basic properties have to be avoided, because the side reactions encountered in traditional anionic polymerization of lactides can be expected for these compounds as well.[29] Alkoxides are ligands of potential interest, because the highly electropositive lanthanide elements are stabilized by the electronegative oxygen atoms and thus decrease the reactivity of these elements in acid−base reactions.

In this study, the kinetics and mechanism of ϵ-caprolactone polymerization initiated by a commercially available yttrium alkoxide, $Y_5(\mu\text{-}O)(O^iPr)_{13}$ (**1**), and by a novel catalyst system comprising tris(2,6-di-*tert*-butylphenoxy)yttrium (**2**) and 2-propanol are discussed. The elementary reactivity of **1** was studied in the pioneering work of McLain and Drysdale.[1] More insight into the characteristics of lactone polymerization by lanthanide alkoxide based initiators is provided in this work.

Experimental Section

Materials. ϵ-Caprolactone (Merck-Schuchardt, Darmstadt, Germany) and 2-propanol were dried over CaH_2 prior to distillation. L-(−)-Lactide (Purac Biochem b.v., the Netherlands) was used as received. Tris(2,6-di-*tert*-butylphenoxy)-yttrium ($Y(OAr'')_3$) was prepared as described previously.[31] Stannous(II) ethylhexanoate (stannous octoate, $Sn(Oct)_2$) (Sigma Chemical Co., St. Louis, MO) was used as received. Toluene-d_8 and dichloromethane-d_2 (Merck-Schuchardt, Darmstadt, Germany) were dried by stirring over CaH_2 and vacuum transferred in a special grease free distillation apparatus. Chloroform-d_1 (Merck-Schuchardt, Darmstadt, Germany) was used as received. All glassware for the preparation of living oligomers was dried before use and reactions were carried out in a Braun 150 GI drybox under nitrogen.

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Preparation of Living Oligomers. In a typical experiment 50 mg (0.071 mmol) of $Y(OAr'')_3$ was dissolved in 250 μL of the appropriate NMR solvent in a 2 mL mixing vessel with a Teflon-coated magnetic stirrer. In a separate vessel 16.3 μL (0.213 mmol) of 2-propanol was added to a solution of a 2- or 8-fold molar excess of ϵ-caprolactone relative to 2-propanol in 250 μL of the NMR solvent. The $Y(OAr'')_3$ solution was added to the monomer/co-initiator solution, and the resulting solution was stirred for 2 min and transferred to a Pyrex NMR tube with vacuum adapter. The solution was frozen in liquid nitrogen, and the NMR tube was flame sealed under a pressure of 0.06 mbar and gently warmed to room temperature.

Preparation of Hydroxyl-Terminated Oligomers. A solution of 1 g (16.6 mmol) of 2-propanol was refluxed in the presence of a 2- or 8-fold molar excess of ϵ-caprolactone and 100 mg of $Sn(Oct)_2$ in 15 mL of toluene for 3 h. All volatiles were removed by means of a rotavapor, and the resulting oligomers were characterized by ^1H and ^{13}C NMR spectroscopy.

Kinetic Experiments. Glassware was dried overnight in an oven at 130 °C. A hot reaction vessel was connected to a high vacuum line, cooled under argon outflow, evacuated to 10^{-5} mmHg, and flushed with argon again. UV spectra were recorded with a MCPD Spectro Multi Channel Photo Detector (Otsuka Electronics). Spectra were measured directly in the reaction mixture by means of an immersed fiber optics probe. The probe had been fitted to the reaction vessel in order to allow experiments in a perfectly closed system. The sampling time of the spectra was varied according to the progress of the reaction with a minimum of 1 s per spectrum and with a maximum of 80 spectra in total. An optical path length of 5.75 mm was used, which was calculated on the basis of the absorption of styrene in hexane at 280 nm.[32] Reference and background spectra were recorded with a solution containing 2,6-di-*tert*-butylphenol (HOAr″) in the same concentration as calculated for the final polymerization mixture.

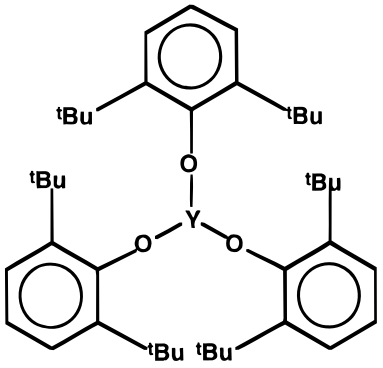
To a solution of monomer and co-initiator of known concentration, prepared in a drybox, an appropriate amount of catalyst was added and the optical density was followed in time. The final conversion was established by ^1H NMR spectroscopy after quenching the polymerization with a 10-fold excess of acetic acid. The optical densities were related to the conversion by assuming a linear relationship between the variation of optical density and conversion.[29] This method was not applicable to the polymerization of ϵ-caprolacone using the $Y(OAr'')_3$/2-propanol system. In this case the conversion in time was monitored by manual sampling of polymerizations carried out in a drybox followed by NMR analysis to determine conversions. Reactions were quenched by adding a 1 mL sample to a small amount of acetic acid in a small round-bottomed flask capped by a rubber septum.

Characterization. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 operating at 250 MHz (^1H) or 62.5 MHz (^{13}C) with 60 and 2400 scans, respectively, for the living oligomers and 16 and 160 scans, respectively, for the hydroxyl-terminated model oligomers. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions (M_w/M_n). A Waters 6000A GPC apparatus equipped with three Waters μStyragel (10^3, 10^4, 10^5 Å pore diameter) columns was used, combined with a H502 viscometer detector (Viscotek Corp.) for determination of absolute values of molecular weights. Polymers were dissolved in tetrahydrofuran (1.0 wt %), and elution was performed at 25 °C at a flow rate of 2.0 mL/min using THF as eluent.

Results and Discussion

The use of commercially available yttrium isopropoxide, a cluster compound in which five yttrium atoms are attached to a single central oxygen atom,[33] $Y_5(\mu\text{-}O)(O^iPr)_{13}$ (**1**), as an initiator for ϵ-caprolactone polymerization was evaluated.[1,8] Complexes containing bridging oxide and chloride ions are abundant in lanthanide alkoxide chemistry,[34] and **1** could be an interesting example of the reactivity of this class of compounds. The results of this study were reported elsewhere and will not be repeated here.[8] Foremost, it was concluded that all isopropoxide groups are active as initiators in the polymerization of ϵ-caprolactone and the polymerization proceeds in a living manner.

The use of tris(2,6-di-*tert*-butylphenoxy)yttrium ($Y(OAr'')_3$, **2**) as a catalyst in the ring opening polymerization of ϵ-caprolactone was evaluated,[11,29] because this compound, in contrast to **1**, does not contain a



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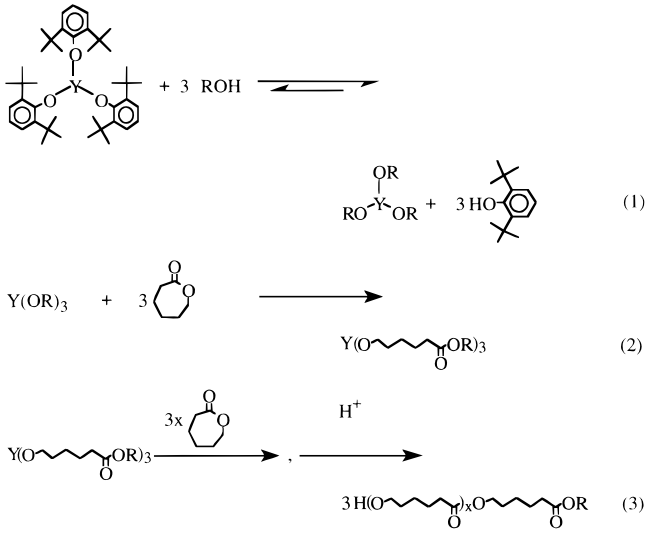
bridging oxide anion and is known to be unassociated in solution (NMR, cryoscopy) and the solid state (single crystal X-ray diffraction).[31,35]

We have reported that addition of an alcohol as co-initiator is necessary to initiate lactone polymerization in a controlled way, because no direct reaction with the sterically very hindered yttrium−oxygen bond in this compound is possible.[11]

Addition of **2** to a reaction mixture containing ϵ-caprolactone and 2-propanol, functioning as co-initiator, resulted in the fast and quantitative formation of polymer. The presence of 2,6-di-*tert*-butylphenol did not affect the polymerization, and this compound was easily removed from the polymer by precipitation. The end group of the resulting polymer consisted only of the alkyl ester group of the added 2-propanol and caproyl hydroxyl groups. On the basis of these findings, a three-step mechanism is proposed for the polymerization of ϵ-caprolactone using the tris(2,6-di-*tert*-butylphenoxy)-yttrium ($Y(OAr'')_3$, (**2**))/2-propanol system (Eqs 1−3).



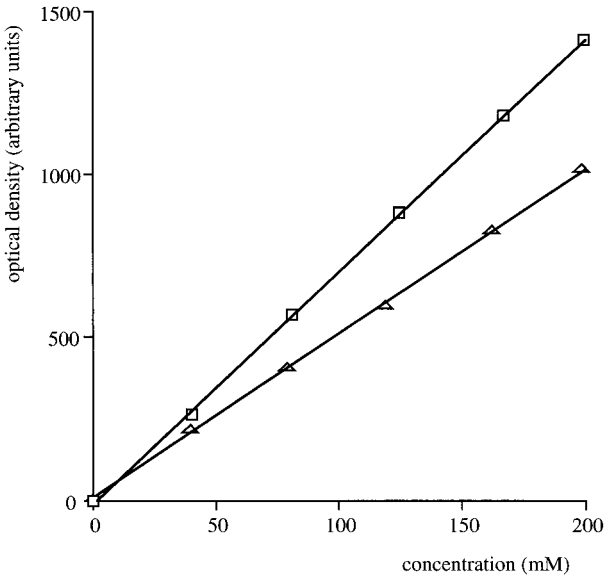


Figure 1. Dependence of the optical density of ϵ-caprolactone (squares) and poly(ϵ-caprolactone) (triangles) as a function of molar ester concentration at λ_{max} 240 nm in dichloromethane.

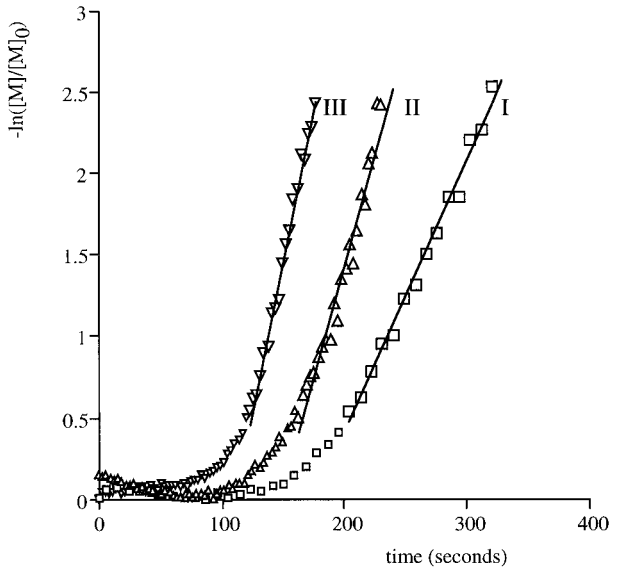


Figure 2. Semilogarithmic plots of ϵ-caprolactone ($[M]_0 = 175$ mM) conversion in time initiated by **1** at various initiator concentrations (I, $[\mathbf{1}]_0 = 0.58$ mM; II, $[\mathbf{1}]_0 = 1.16$ mM; III, $[\mathbf{1}]_0 = 2.33$ mM) in dichloromethane at 22 °C, as determined by in situ UV spectroscopy.

In the first step, the large 2,6-di-*tert*-butylphenoxy ligands are exchanged for the smaller 2-propanol. In the second step, the polar alkoxide is able to attack the carbonyl group and form the thermodynamically favored ring-opened product. After the first two initiating steps, the polymerization can proceed until complete conversion of monomer is reached. During the progress of this work a catalyst system for the polymerization of ϵ-caprolactone and 2,2-dimethyltrimethylene carbonate was described, based on methylaluminum diphenolates and 2-propanol, using the same inert bulky phenoxide/alcohol exchange principle.[36] Thus, the inertness of the phenolic proton of 2,6-di-*tert*-butylphenol in these reactions is well established. We showed that a similar mechanism was operative in the polymerization of L-lactide and it thus appears to be quite general for ring-opening of lactones.

Kinetics of ϵ-Caprolactone Polymerization. Even in dilute solution at room temperature, the polymerization of ϵ-caprolactone was complete within a few minutes using **1** as an initiator. We have shown that rapid lactone polymerizations can be monitored by in situ UV spectroscopy.[29] The UV extinction coefficient of the carbonyl groups of ϵ-caprolactone is lower in the linear polymer than in the cyclic monomer (Figure 1).

Details of the method were given in a previous paper.[29] The conversion in time at various initiator concentrations was monitored for ϵ-caprolactone polymerization using **1** as an initiator in dichloromethane. The corresponding first-order kinetic plots for the polymerization are shown in Figure 2.

An induction period is observed, followed by a linear relationship. In related polymerizations of ϵ-caprolactone and 2,2-dimethyltrimethylenecarbonate initiated by aluminum alkoxides, it was suggested that this induction period is related to structural rearrangement processes of the initiator to form the actual active sites.[37] In all cases we observed a slight increase in intensity directly after addition of the initiator. This can be attributed to coordination of monomer to the (pre)-initiator, leading to a more polarized carbonyl group and to higher extinction coefficients. Coordination of carbonyl groups to electron deficient compounds is a well-known phenomenon for lactones and has been established by IR spectroscopy[38] and single crystal X-ray diffraction.[39] If apparent rate constants are calculated from the linear parts of the curve, it is evident that the reaction is not first-order in initiator. This was established for L-lactide polymerization initiated by **1** as well. Apparent rate constants for ϵ-caprolactone and L-lactide polymerization are plotted as a function of initiator concentration in Figure 3.

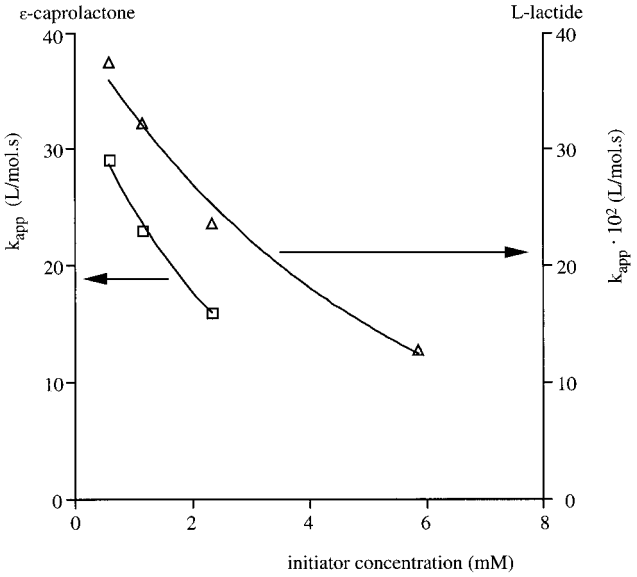


Figure 3. Apparent rate constants of ϵ-caprolactone (squares) and L-lactide (triangles) polymerization initiated by **1** at various initiator concentrations in dichloromethane at 22 °C.

In the concentration range studied, apparent rate constants of 16 $L \cdot mol^{-1} \cdot s^{-1}$ ($[I]_0 = 2.33$ mM) to 29 $L \cdot mol^{-1} \cdot s^{-1}$ ($[I]_0 = 0.58$ mM) were determined. The curved nature of this plot indicates that species of different activities are present during polymerization, possibly generated by partial or complete disassembly of **1** upon coordination of monomer and/or polymer. However, identification of these species is not straightforward. Remarkably, the apparent rate constants for ϵ-caprolactone and L-lactide polymerization differ by 2

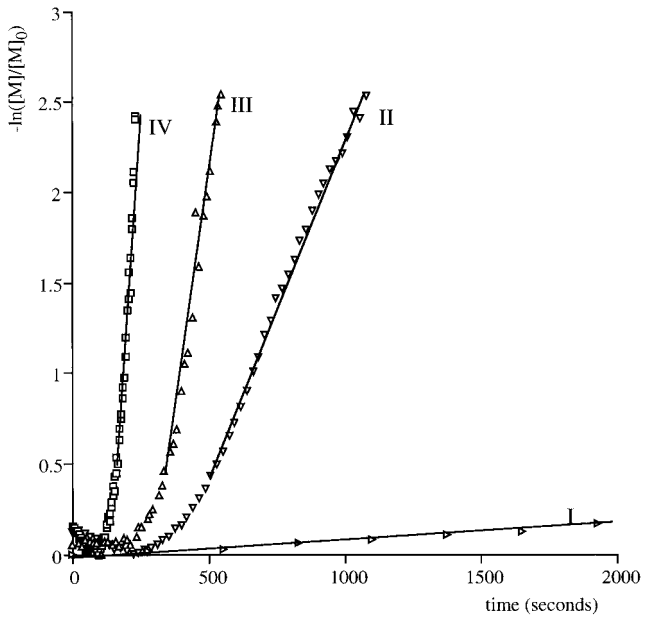


Figure 4. Semilogarithmic plots of ϵ-caprolactone ($[M]_0 = 175$ mM) conversion in time initiated by **1** ($[\mathbf{1}]_0 = 1.16$ mM) with addition of various amounts of alcohol (I, $[^i\text{PrOH}]_0 = 21$ mM; II, $[^i\text{PrOH}]_0 = 14$ mM; III, $[^i\text{PrOH}]_0 = 7.0$ mM; IV, no ^{i}PrOH added) in dichloromethane at 22 °C, as determined by in situ UV spectroscopy.

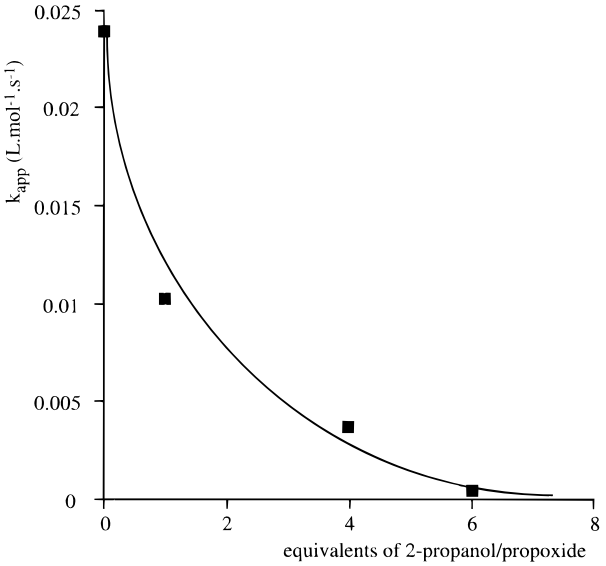


Figure 5. Apparent rate constant of ϵ-caprolactone polymerization initiated by **1** with addition of various amounts of free alcohol in dichloromethane at 22 °C.

orders of magnitude, which is remarkable. Probably, ϵ-caprolactone polymerization is not restricted by the presence of aggregates, whereas L-lactide polymerization is.

The effect of addition of 2-propanol on the polymerization kinetics of ϵ-caprolactone initiated by **1** was studied as well. If effective exchange of alcohol groups can be achieved, formation of low molecular weight hydroxyl-functionalized poly(ϵ-caprolactone)s with low metal content is possible. Graft copolymers and star-shaped polymers are easily accessible by this method as well, if hydroxyl-functionalized prepolymers are used. The first-order kinetic plots obtained for ϵ-caprolactone polymerization by **1** in the presence of different amounts of 2-propanol are represented in Figure 4.

It was found that the experimental number average molecular weight could be calculated from the starting concentrations of free 2-propanol and 2-propoxide as present in **1**. Polymerization conducted in the presence of 2-propanol is very slow at its early stages, then gradually increases, and eventually becomes first-order with respect to ϵ-caprolactone. Also, the low polydispersity of the polymers was maintained. Alcohols are thus effective chain transfer agents. Apparent rate constants were calculated from the linear parts of the curve and plotted as a function of free alcohol concentration, as shown in Figure 5.

Apparent rate constants at high 2-propanol concentrations were more difficult to determine, because of the low rate of the polymerization process. Similar experiments were carried out using $Al(O^iPr)_3$ and various alcohols by Duda.[24,40] It was shown that the effect of excess alcohol on the kinetics of ϵ-caprolactone polymerization can be simulated by assuming that alcohols reversibly coordinate to the active species to form dormant species. Also, the interchange and complexation equilibria must be faster than propagation. For a quantitative solution of the model, two of the three independent variables (propagation rate, equilibrium constant of dormant and propagating species, and number of alcohols coordinating to a dormant species) must be known, but none of these is experimentally easily accessible. Qualitatively, the model seems to apply. Since it is presently unknown what is the structure of the active centers in the case of ϵ-caprolactone polymerization in the presence of **1** and additional 2-propanol, it would be hard to interpret the results obtained by application of the model to this system.

The retardation of ϵ-caprolactone polymerization by alcohols allowed us to compare the UV method we applied for determining conversions with a method using manual sampling for a direct validation of the former method. The polymerization of ϵ-caprolactone initiated by **1** in the presence of 6 equiv of 2-propanol (per 2-propoxide ligands as present in **1**) was carried out and monitored in time by UV spectroscopy and manual sampling at similar conditions (temperature, concentration of reagents). The resulting kinetic plots are shown in Figure 6.

Especially if the additional intensity due to coordination of monomer is taken into account, the results are similar for two different experiments using two very different techniques. The values found for the induction period and the slopes of the kinetic curves in the linear regime used for determining apparent rate constants are somewhat different. Nevertheless, the UV technique can be a valuable tool in determining the kinetics of fast lactone polymerizations if manual sampling is problematic.

Polymerizations of ϵ-caprolactone initiated by the **2**/2-propanol system were monitored in time by manual sampling followed by ^{1}H NMR analysis to determine conversions. The UV method is not applicable in this case, because the intensity at 240 nm is much higher than can be expected for the combination of HOAr″, monomer, and polymer present. Probably, this is due to a coordinative interaction of one of the chromophores with the yttrium atoms present in solution. It is likely that the coordination of monomer or polymer carbonyl groups enhances their UV absorption capability, which could explain the difficulty in monitoring the polymerization by UV spectroscopy. The intensity of the UV source used was too low to study this process in detail, because saturation of the UV absorption occurred (at

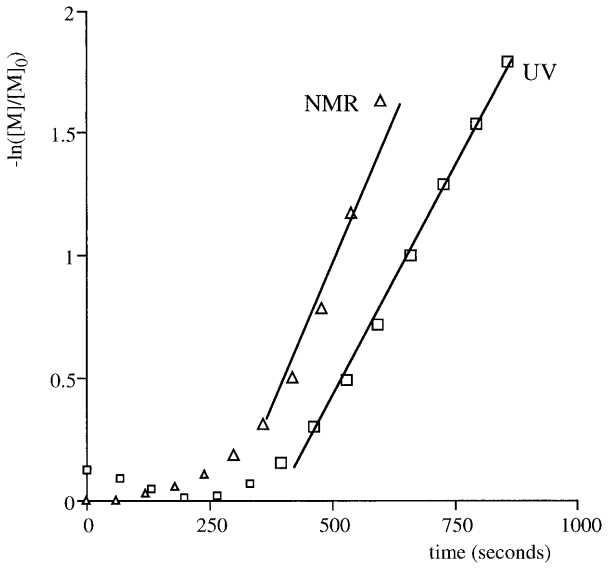


Figure 6. Semilogarithmic plots of ϵ-caprolactone ($[M]_0 = 175$ mM) conversion in time initiated by **1** ($[\mathbf{1}]_0 = 1.16$ mM) with addition of alcohol ($[^i\text{PrOH}] = 14$ mM) in dichloromethane at 22 °C, as monitored by in situ UV spectroscopy (UV) and by manual sampling followed by ^{1}H NMR analysis to determine conversions (NMR). In the former case only one out of every three points measured is shown for clarity.

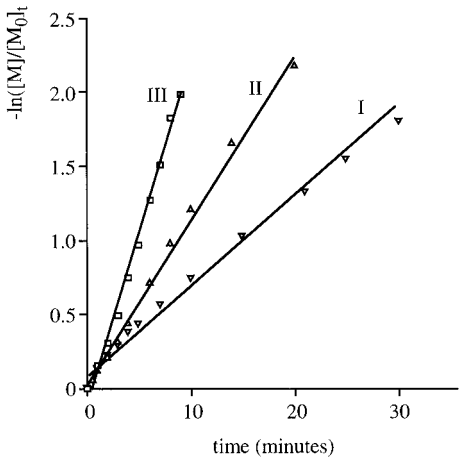


Figure 7. Semilogarithmic plots of ϵ-caprolactone ($[M]_0 = 175$ mM) conversion in time initiated by the **2**/2-propanol system at various initiator concentrations (I, $[\mathbf{2}]_0 = 0.58$ mM; II, $[\mathbf{2}]_0 = 1.16$ mM; III, $[\mathbf{2}]_0 = 2.33$ mM and $[\mathbf{2}]_0 = [^i\text{PrOH}]_0$ in these experiments) in dichloromethane (22 °C).

practical path lengths). The resulting kinetic plots are shown in Figure 7.

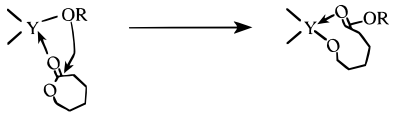
The polymerization is first-order in monomer and in initiator and no induction period is observed. From the slope of the curves, a propagation rate constant of 1.65 $L \cdot mol^{-1} \cdot s^{-1}$ was calculated. This value can be compared with values determined for various aluminum or sodium alkoxide based initiators, and these are summarized in Table 1.

The activity of the catalyst is higher than any of the aluminum systems studied in detail so far. The active centers act as unassociated species in the presence of monomer or polymer. In this case, coordination of the active centers to polymer carbonyl groups might slow down polymerization, because these compete with monomer for coordination sites. It was suggested that *in the absence of monomer* the carbonyl groups coordinating to the active sites are the first ones in the polymer chain for entropic reasons, although the formation of a nine-membered ring is required which would restrict the conformational space available to such a polymer chain segment.[46] The occurrence of transesterification reactions after complete conversion of monomer[1] is an indication that carbonyl groups which are somewhere in the middle of a chain are able to interact with metal centers. Such an interaction would not require extensive bending of polymer fragments. On the other hand *during propagation*, immediately after ring-opening, the carbonyl group of the first ester moiety is already in a favorable position for coordination without the need for rearrangement (Eq 4).

Table 1. Propagation Rate Constants for ϵ-Caprolactone Polymerization Initiated by Various Metal Alkoxides[a]

no.	structure of active centers	solvent	temp (°C)	k_p ($L \cdot mol^{-1} \cdot s^{-1}$)	ref
1	RONa	THF	20	1.7	41
2	$ROAl(Et)_2$	THF	25	0.039	42
3	$ROAl(Et)_2$	benzene	25	0.14	43
3	$ROAl(^iBu)_2$	THF	20	0.03	43
4	$(RO)_3Al$	THF	25	0.5	44
5	$(RO)_3Y$	CH_2Cl_2	22	1.65	this work

[a] It has been shown that the propagation rate can also depend on the presence of functional groups in the initiator.[45]



(4)

The effect of such a coordination on the polymerization rate is expected to be strongly dependent on the coordination properties of the monomer, solvent, and the degree of association of the active sites.

NMR Experiments. To elucidate the structure of the active centers in solution and to provide evidence for the mechanism proposed, living oligomers were studied in various solvents. No differences were observed in spectra of oligomers initiated by **1** or **2**/2-propanol. This illustrates the difficulty of developing structure activity relationships in lanthanide alkoxides. ^{1}H NMR spectra of living oligomers of ϵ-caprolactone and hydroxyl-terminated oligomers, both with a number average molecular weight of 1000, were recorded in dichloromethane-d_2, toluene-d_8, and tetrahydrofuran-d_8 as the spectra of the living oligomers proved very sensitive to the nature of the solvent, as shown in Figure 8. The spectra of the hydroxyl-terminated oligomers were essentially similar in all solvents studied.

If recorded in CD_2Cl_2, which was the solvent used for the kinetic studies, spectra of the living oligomers initiated by the **2**/2-propanol system and the model hydroxyl-terminated oligomers are similar except for the distinct signals of the $HOCH_2-$ (3.65 ppm, CD_2Cl_2) end group signal upfield relative to the polymer backbone signals, which are absent in the living oligomers. In tetrahydrofuran-d_8, a separate signal can be discerned for the first methylene group in the yttrium-bonded alkoxide at 4.10 ppm ($(RO)_2YOCH_2-R$), near the polymer backbone signal. The experiments were repeated in toluene-d_8, and in this solvent additional signals for the living oligomer were observed at 4.05, 2.30, and 1.75 ppm, respectively, as shown in Figure 8. Similar results were obtained in benzene-d_6, for yttrium[1] and aluminum[25] alkoxide initiated polymerization of ϵ-caprolactone. This set of signals is assigned to the ultimate repeating unit linked directly to the yttrium atom. The integration of these signals corresponds well with the

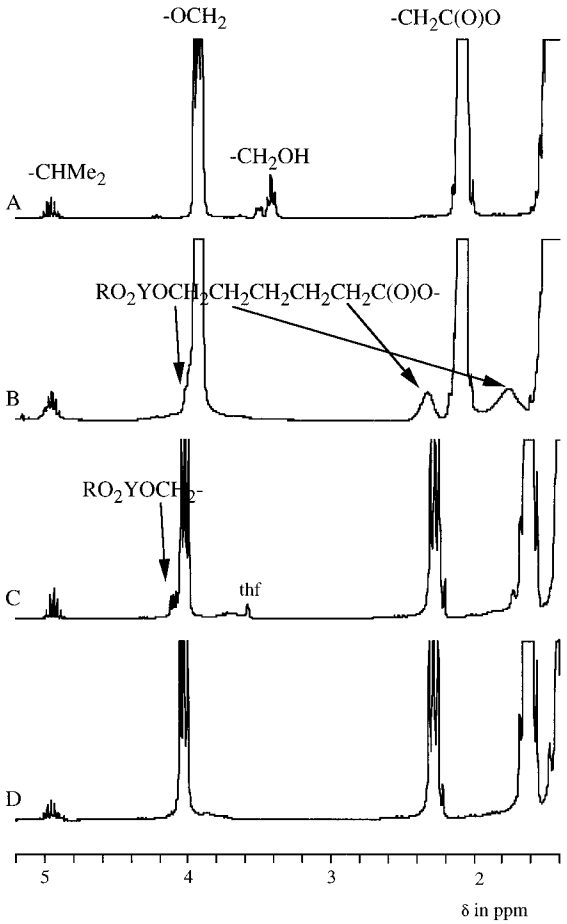


Figure 8. Detail of ^{1}H NMR spectra of a hydroxyl-terminated oligo(ϵ-caprolactone) in toluene-d_8 (A) and living oligo(ϵ-caprolactone)s initiated with **2**/2-propanol in toluene-d_8 (B), tetrahydrofuran-d_8 (C), and dichloromethane-d_2 (D). The small signal in spectrum A at 3.55 ppm is due to residual ϵ-caprolactone, which was not removed from the hydroxyl-terminated oligo(ϵ-caprolactone).

integration of the isopropyl end group. The chemical shift differences found for this ultimate unit in toluene cannot be explained by inductive effects of the yttrium atom alone. In general, yttrium alkoxides are never three-coordinate except for complexes with sterically very demanding ligands, such as 2,6-di-*tert*-butylphenoxy. Coordination numbers of 6−8 are much more common for this metal, and these can be achieved by coordination of acyl oxygen atoms, in this case of the first acyl oxygen atoms in the polymer chain. The fact that in the more polar solvents only inductive shifts are observed is an indication that in these solvents coordination of the first acyl oxygen atom in the chain is less favorable, because the solvent interacts preferentially with the metal center or with the extended polymer chain. The former case is probable for tetrahydrofuran, while the latter case is probable for dichloromethane.

The ^{13}C NMR spectra of living oligomers prepared by the **2**/2-propanol system and the model hydroxyl-terminated oligomers appeared less sensitive to the nature of the solvent than the corresponding ^{1}H NMR spectra. The living oligomers and model hydroxyl-terminated polymers with degrees of polymerization of approximately 2 and 8 that had been prepared made it possible to fully assign the signals in the ^{13}C NMR spectra.

For the oligo(ϵ-caprolactone)s, three signals are visible in the carbonyl (171−173 ppm), α-oxygen (62−65 ppm), and α-carbonyl (32−35 ppm) region. A full assignment of the ^{13}C NMR spectra of hydroxyl-terminated and living oligomers of ϵ-caprolactone initiated with the **2**/2propanol system in dichloromethane-d_2 is given in Figure 9.

The NMR spectra of hydroxyl-terminated oligomers are obviously different from those of the living oligomers. From the sharp signals of the yttrium-terminated chain ends, as well as from the HOAr″ signals (data not shown), it can be concluded that HOAr″ does not interact with the metal centers.

Living poly(ϵ-caprolactone)s initiated by Al(O^{i}Pr)$_3$ were recently studied by ^{13}C spectroscopy.[27] Using this initiator, the ^{13}C NMR signal for the carbonyl carbon of the ultimate unit was found at 172.2 ppm in benzene-d_6, while the backbone signal was observed at 172.6 ppm. It was claimed for the living oligomers initiated by Al(O^{i}Pr)$_3$ that upon addition of a large excess of inert Lewis base (tetrahydrofuran) the signal at 172.2 ppm disappeared, which would show the reversibility of this coordination in the case of aluminum.[47] However, for oligomers initiated by the **2**/propanol system, the ^{13}C NMR spectra in toluene-d_8, dichloromethane-d_2, tetrahydrofuran-d_8, and even pyridine-d_5 are very similar. Details of the carbonyl region of the spectra recorded in these solvents are shown in Figure 10.

Clearly, the shift of the carbonyl atom in the ultimate caproyl unit linked to the yttrium atom is not very solvent dependent. One explanation could be that the interaction of the yttrium atoms with the acyl oxygens is much stronger than for aluminum. However, it is more likely that the small shift differences between the three peaks are just an effect of the different sequences present in the polymer chain and are not a result of coordination of the acyl oxygens to yttrium. In this respect, it is important to note that the difference between the chemical shifts of a caproyl unit attached to the hydroxyl chain end and a nonterminating caproyl unit are larger than for a caproyl unit attached to an yttrium atom. The same was observed for living and hydroxyl-terminated oligo(lactide)s. We are aware of only one example of a compound in which an ester coordinates to a lanthanide atom and which is characterized by ^{13}C NMR spectroscopy.[30] In this case, the signal of the carbonyl carbon atom shifted from approximately 172 ppm for a noncoordinating aliphatic ester to 184.8 ppm in benzene-d_6 upon coordination.[30] The observed shift differences in living oligomers of ϵ-caprolactone initiated by yttrium and aluminum alkoxides are much smaller. In noncoordinating solvents there is very likely an interaction between the yttrium atoms and the carbonyl groups of the esters, but this process is probably too fast to observe on the ^{13}C NMR time scale.

A tentative explanation for the fact that the necessary coordination (from a coordination chemistry point of view) of ester groups is visible in the ^{1}H NMR spectrum in toluene but not in the ^{13}C NMR spectrum is that the ^{1}H NMR shift differences are due to conformational changes in a whole segment, which is slow, as opposed to a single ester group, which could be fast.

So far the oligomers prepared were described as "living", and to investigate if this is indeed a proper designation, the activity of the living ϵ-caprolactone oligomers in lactide polymerization was determined. The reactions were carried out at room temperature by adding the contents of an NMR tube to an L-lactide solution in dichloromethane in such a way that if the

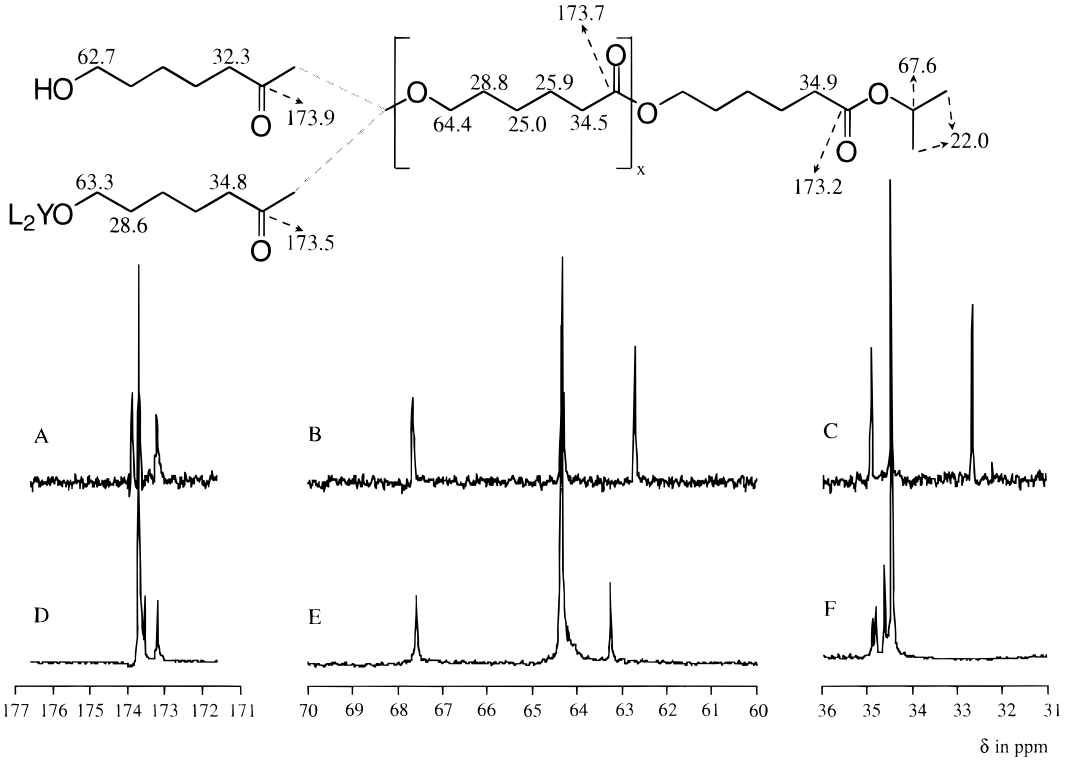


Figure 9. Full assignment of ^{13}C NMR spectra of hydroxyl-terminated and living oligomers of ϵ-caprolactone inititated with the **2**/2-propanol system in dichloromethane-d_2 and details of ^{13}C NMR specta of a hydroxyl-terminated oligo(ϵ-caprolactone) [(A) carbonyl region, (B) α-oxygen region, and (C) α-ester region] and a living oligo(ϵ-caprolactone) [(D) carbonyl region, (E) α-oxygen region, and (F) α-ester region] initiated with **2**/2-propanol in dichloromethane-d_2. A signal for the quarternary carbon atom of the *tert*-butyl groups of the 2,6-di-*tert*-butylphenol ligand can be discerned at 34.6 ppm in spectrum F.

block copolymer would form in a living fashion, it would have a molecular weight of approximately 8000. The time elapsed between the preparation of a solution for NMR analysis and the activity test was at least 10 days. All living oligomers of ϵ-caprolactone were able to initiate L-lactide polymerization and reached near complete conversion of lactide monomer ($t_{1/2}$ between 5 and 30 min) with formation of poly(caprolactone)−poly(lactide) block copolymer. The activity of the initiator solutions thus has decreased in time compared to the activity of a freshly prepared initiator solution. In view of the fact that the activities are still at least comparable to those reported for other yttrium-based systems such as $Y(OEtNMe_2)_3$,[9] the oligomers prepared can be regarded as living systems.

Conclusions

The kinetic behavior of **1** and the **2**/2-propanol system in lactone polymerization is very different. Polymerization of lactones by the latter initiator could be described by assuming a simple kinetic scheme with a first-order dependence on the monomer and initiator concentration. For ϵ-caprolactone a propagation rate constant of 1.65 $L \cdot mol^{-1} \cdot s^{-1}$ was established. The **2**/2-propanol system is thus a very active initiator/catalyst system for the polymerization of ϵ-caprolactone. The kinetic behavior of **1** is more complicated and still poorly understood. Alcohols are effective chain transfer agents in the polymerization of ϵ-caprolactone in the presence of **1**.

It was shown that the polymerization of ϵ-caprolactone initiated by the **2**/2-propanol system proceeds via a three-step mechanism. In the first step the large 2,6-di-*tert*-butylphenoxy ligands are exchanged for the smaller 2-propanol. In the second step the polar alkoxide is able to attack the carbonyl group and form the

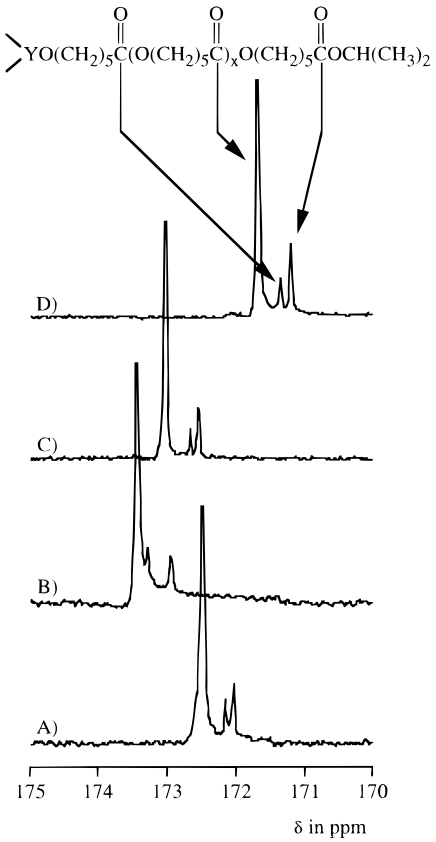


Figure 10. Carbonyl region of the ^{13}C NMR spectra of living oligo(ϵ-caprolactone)s initiated with **2**/2-propanol in (A) toluene-d_8, (B) dichloromethane-d_2, (C) tetrahydrofuran-d_8, and (D) pyridine-d_5.

thermodynamically favored ring-opened product. After the first two initiating steps, the polymerization can proceed until the equilibrium conversion of the monomer is reached. ^{1}H NMR spectroscopy indicated that for ϵ-caprolactone a coordinative interaction between the polymer carbonyl groups and the active polymerization sites exists and that this interaction is solvent dependent. Kinetic experiments indicated that this interaction is important during propagation as well.

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(47) The interpretation of the spectra presented in ref 27 may not be maintained completely without further evidence. Personal communication with Ph. Dubois.

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