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A Versatile and Highly Efficient Catalyst System for the Preparation of Polyesters Based on Lanthanide Tris(2,6-di-*tert*-butylphenolate)s and Various Alcohols

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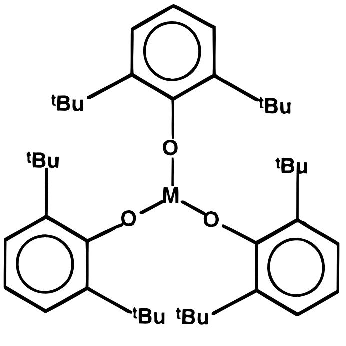
Introduction. Polyesters are widely used polymeric materials. Development of simple, convenient initiators for controlled ring-opening polymerization of cyclic esters is important from a practical as well as a fundamental point of view. Recently, it was reported that trivalent rare earth alkoxides can initiate living polymerization of monomers such as ϵ-caprolactone, lactide, and β-butyrolactone with activities unprecedented in coordination polymerization of these monomers.[1−5] We now report a highly efficient catalyst system for the preparation of polyesters based on lanthanide tris(2,6-di-*tert*-butylphenolate)s and various alcohols, allowing excellent control over molecular weight and end-group identity. Lanthanide tris(2,6-di-*tert*-butylphenolate)s are easy to prepare from cheap reagents, easy to purify, and thermally very stable and structurally well characterized.[6−8] The system allows the synthesis of block copolymers, either by sequential polymerization of monomers or by using hydroxy-functionalized prepolymers as macroinitiators. Also, L-lactide is conveniently polymerized without racemization or transesterification, a problem frequently encountered in polymerizations using highly basic alkaline earth metal alkoxides as initiators.[9−11]

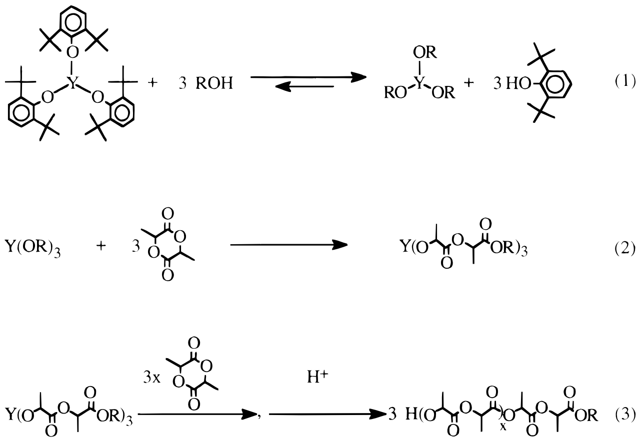
Results and Discussion. The polymerization of L-lactide (L-LA), ϵ-caprolactone (ϵ-CL), and δ-valerolactone (δ-VL) in the presence of yttrium tris(2,6-di-*tert*-butylphenolate) (**1a**) and 2-propanol proceeded smoothly to the equilibrium conversion in dichloromethane at 22 °C to yield a narrow molecular weight distribution polyester (entries 1−3, Table 1).[12]



1a: M = Y

1b: M = La

For example, when a toluene solution of **1a** was added to a mixture of 2-propanol and L-lactide at an inital molar ratio $[\text{L-LA}]_0/[\text{2-PrOH}]_0/[\mathbf{1a}]_0$ of 50/1/0.3, instantaneous polymerization occurred and within minutes maximum conversion was reached. After workup by washing against 0.1 N HCl solution in water and precipitation in methanol, the polymer is recovered in good yield (typically 85−90%) along with a number average molecular weight close to the value calculated from the molar monomer to alcohol ratio. Similar experiments were carried out for ϵ-CL and δ-VL. Polymers isolated had polydispersities of 1.05−1.24. The identity of the end groups was determined by ^{1}H NMR spectroscopy, and it appeared that only poly(ester)s with isopropoxycarbonyl end groups on one side and hydroxyl groups on the other side were obtained. This reveals that the 2,6-di-*tert*-butylphenolate moieties are not incorporated in the polymer chain and that the polymerization of these lactones proceeds through acyl−oxygen cleavage only. We propose a mechanism in which the bulky phenoxide ligands are exchanged for the smaller alcohol followed by coordination and insertion of the first monomer. The reaction mechanism is schematized for lactide and some alcohol ROH by eqs 1−3.



During the progress of this work a similar mechanism was proposed for the polymerization of ϵ-CL using alcohol/methylaluminum diphenolate systems, although the polymerization proceeds much slower in this case.[13] If a polymerization of L-LA is attempted in the presence of **1a** without the addition of a sterically less hindered alcohol, slow conversion of monomer does occur, but after workup no specific end groups can be detected and a high molecular weight, broad polydispersity polymer is isolated. In this case initiation seems to occur by a different mechanism, e.g. proton transfer from monomer or solvent, but again no direct insertion of monomer into the yttrium−oxygen bond of **1a** is possible. It is of interest to note that poly(lactide)s with nearly identical characteristics can be prepared by using commercially available yttrium tris(isopropoxide) ($\mathrm{Y_5(\mu\text{-}O)(O^iPr)_{13}}$, (**2**)), but in this case complete conversion is only reached in 5 days.[5] The addition of 2,6-di-*tert*-butylphenol to a mixture of **2** and L-lactide did not affect the kinetics of the polymerization or the characteristics of the polymer prepared. This indicates that the active catalyst system prepared by mixing **1** and 2-propanol has a structure different from **2**.

To investigate the scope of the reaction, a number of different alcohols were used to co-initiate polymerization (Table 1, entries 4−9) of L-LA. In the cases of *tert*-butanol, due to steric hindrance, and 1,2-ethanediol, due to the limited solubility in dichloromethane, propagation was so much faster than initiation that only part of the added alcohol was consumed in the initiation process. Polymerizations could also be carried out using the lanthanum compound **1b** (Table 1, entry 10) in combi-

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Table 1. Polymerization of L-LA, ϵ-CL, and δ-VL Initiated with the Alcohol/Lanthanide Tris(2,6-di-*tert*-butylphenolate)s ($[M]_0/[ROH]_0/[1]_0$ of 50/1/0.3)[a]

no.	monomer	co-initiator	reacn time (min)	conversion (%)	$10^{-3}\bar{M}_{n,calc}$	$10^{-3}\bar{M}_{n,NMR}$	$10^{-3}\bar{M}_{n,GPC}$	$\bar{M}_w/\bar{M}_n$
1	L-LA	^{i}PrOH	2	100	7.2	8.4	12.3	1.24
2	ϵ-CL	^{i}PrOH	5	100	5.7	6.0	7.4	1.14
3	δ-VL[b]	^{i}PrOH	20	81	8.1	8.6	10.3	1.10
4	L-LA	^{n}BuOH	5	100	7.2	6.6	8.6	1.16
5	L-LA	^{t}BuOH	5	99	7.2	13.0	18.4	1.21
6	L-LA	HOEtOH	5	92	14.4	25.2	26.1	1.28
8	L-LA	Me_2NEtOH	3	99	6.5	6.9	8.4	1.11
9	L-LA	MeOEtOH	3	99	6.5	5.6	7.9	1.04
10	L-LA	^{i}PrOH	5	98	7.2	7.1	10.8	1.14
11	L-LA[c]	^{i}PrOH	8	96	7.2	6.8	9.6	1.05
12	L-LA[d]	^{i}PrOH	8	99	19.2	24.0	21.0	1.37[e]

[a] All reactions were carried out using **1a** as an initiator, except no. 10 which was carried out using **1b**. [b] Carried out at $[\delta\text{-VL}]_0/[\text{2-PrOH}]_0/[\mathbf{1a}]_0$ of 100/1/0.3. [c] Carried out in dioxane. [d] Carried out in dioxane with $[\text{L-LA}]_0/[\text{2-PrOH}]_0/[\mathbf{1a}]_0$ of 150/1/1. [e] This sample was quenched after 18 h, which could explain the relatively large polydispersity index.

nation with 2-propanol. The use of different lanthanide atoms might provide a tool to fine tune the reactivity of a particular initiating system, because the ionic radius of the lanthanides varies nearly continuously over the whole of the series and the size of the lanthanide atom is expexted to influence the propagation rate. Dioxane could also be used as the solvent for the polymerization of L-LA by **1a** and 2-propanol (Table 1, entry 11), although the reaction seemed a little slower in this case. Additionally, an experiment was carried out in which only one of three possible bulky phenoxide ligands was replaced by 2-propanol (Table 1, entry 12). The resulting polymer had a M_n 3 times as high as in the previous experiment. This shows that substoichiometric amounts of alcohol can be used to initiate polymerization and even in this case the molecular weight of the polymer is determined only by the amount of added alcohol.

Two strategies for the preparation of block copolymers were evaluated. In a first experiment a toluene solution of **1a** was added to a mixture of 2-propanol and ϵ-CL at a molar ratio $[\epsilon\text{-CL}]_0/[\text{2-PrOH}]_0/[\mathbf{1a}]_0$ of 50/1/0.3. After 3 min an amount of L-LA at a molar ratio $[\epsilon\text{-CL}]_0/[\text{L-LA}]_0$ of 1/1 was introduced. The reaction was quenched after 8 min. It appeared after analysis that a block copolymer had formed with an ϵ-CL isopropoxycarbonyl end group on one side and a PLLA hydroxyl end group on the other side with a molecular weight close to the calculated value ($M_{n,calc} = 12\,900$ and $M_{n,found} = 13\,900$) and a low polydispersity ($M_w/M_n = 1.16$). An attempt to prepare a block copolymer by adding ϵ-CL to a living PLLA solution failed, in line with observations made previously.[14] If both ϵ-CL and L-LA were introduced simultaneously, only polymerization of L-LA occurred, although at a much slower rate than in the absence of ϵ-CL. Probably, initiation of L-LA is preferred over initiation of ϵ-CL, but its polymerization rate is decreased in the presence of ϵ-CL because it competes for metal coordination sites with L-LA.

In a second approach, poly(ethylene glycol) ($M_n = 1000$, two hydroxyl end groups, PEG1000) was used as a model polymer for preparing triblock copolymers by using a difunctional central block as co-initiator for lactone polymerization. A toluene solution of **1a** was added to a mixture of PEG1000 and L-LA at a mole ratio $[\text{L-LA}]_0/[\text{OH}]_0/[\mathbf{1a}]_0$ of 50/1/0.3, and the polymerization was allowed to proceed for 2 min. During this period gelation occurred, but after quenching, the reaction mixture became fluid again. The gelation is attributed to the difunctional co-initiator in combination with the trifunctional catalyst. Nevertheless, monomer conversion was still high (94%). It appeared after analysis that a triblock copolymer had formed with PLLA hydroxyl end groups, a molecular weight rather close to the calculated value ($M_{n,calc} = 15\,400$ and $M_{n,found} = 18\,500$), and a low polydispersity ($M_w/M_n = 1.16$).

In conclusion, a versatile and highly efficient catalyst system for the preparation of polyesters based on lanthanide tris(2,6-di-*tert*-butylphenolate)s and various alcohols was introduced. Good control over molecular weight, molecular weight distribution, and end groups groups can be exerted. Further study is now in progress in our laboratories to establish the scope, mechanism, and kinetics of this new initiating system.

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(12) All reactions were carried out under an inert atmosphere at 22 °C using previously dried glassware and reagents. Initial concentrations of the compounds used in the polymerizations are denoted by a zero subscript, e.g. $[M]_0$. ^{1}H-NMR spectra were recorded on a Bruker AC 250 operating at 250 MHz (^{1}H) or 62.5 MHz (^{13}C) in chloroform-d_1. Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions (M_w/M_n). GPC measurements were carried out with THF as the eluent (2.0 mL/min) using a Waters 510 pump, a HP 1050 autosampler, four Waters μStyragel columns (10^5, 10^4, 10^3, 5×10^2) in series, a Waters 410 differential refractometer, and a Viscotek Viscometer Detector H502. The columns were calibrated with poly(styrene) standards using the universal calibration technique.

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