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Polymerization of ϵ-Caprolactone by Divalent Samarium Complexes

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Introduction

Ring-opening polymerization of lactones provides a convenient route to biodegradable polyesters which are of interest for a variety of practical applications.[1-4] ϵ-Caprolactone, $C_6H_{10}O_2$, is one substrate that is currently under investigation in this regard, and it can be polymerized with catalysts containing alkali metals, alkaline earth metals, lanthanides, aluminum, zinc, tin, and early transition metals.[5-12] Recently, it has been reported that yttrium and lanthanide alkoxide complexes generate extremely active, living, ring-opening polymerization systems with this monomer.[12]

Since Sm(II) complexes are reactive species with oxygen-containing substrates due to the strong reduction potential of Sm(II) and the oxophilicity of the metal,[13] we have investigated their utility in the polymerization of ϵ-caprolactone. We report here that these complexes can form active polymerization systems with ϵ-caprolactone, and we describe the variation in reactivity as a function of the ligands attached to Sm(II).

Experimental Section

$SmI_2(THF)_2$,[14] $(C_5Me_5)_2Sm(THF)_x$,[15] $(C_5Me_5)_2Sm$,[16] $[(Me_3Si)_2N]_2Sm(THF)_2$,[17] $(C_9H_7)_2Sm(THF)_x$,[18] and $(C_{13}H_9)_2Sm(THF)_2$[18] (C_9H_7 = indenyl; $C_{13}H_9$ = fluorenyl; x is typically 1.5) were prepared under nitrogen using standard Schlenk, vacuum line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques according to the literature. The THF in all of these complexes is substitutionally labile. Solvents were purified as previously described.[19] ϵ-Caprolactone (Aldrich) was dried over molecular sieves and degassed before use. Molecular weight data are reported versus monodisperse polystyrene calibration samples. The following procedure (Japan Synthetic Rubber Co., Ltd., Yokkaichi) was used. A sample of the polymer was dissolved in THF and filtered through a Teflon filter (1-μm pore size). The resulting solution was analyzed by gel permeation chromatography (GPC). GPC data were recorded on a Waters LC Module with 3 Shodex GPC KF-80M columns. The polycaprolactone was also characterized by ^{13}C-NMR spectroscopy using a JEOL EX-270 spectrometer. A sample of the polymer was dissolved in $CDCl_3$, and tetramethylsilane was used as an internal standard.

Typical Polymerization Procedure. In a glovebox, 0.1 mmol of catalyst precursor and 10 mL of solvent were placed in a 25-mL round-bottom two-neck flask equipped with a stopcock and a magnetic stir bar. ϵ-Caprolactone (1.11 mL, 10 mmol) was added with stirring. After the designated reaction time, the flask was attached to a Schlenk line. HCl (2 M) was added to the mixture under nitrogen to quench the reaction. The resulting mixture was washed twice with dilute HCl and twice with water. The organic layer was separated and added to hexanes (ca. 100 mL) to precipitate the polymer. The polymer was filtered and dried under vacuum. When THF was used as a solvent, toluene was added to the reaction mixture before the HCl wash.

Model Reaction of Polymer Degradation. In the glovebox, 0.1 mmol of catalyst precursor [$(C_5Me_5)_2Sm(THF)_x$ or $(C_5Me_5)_2Sm$] and 20 mL of toluene were placed in a 50-mL round-bottom flask equipped with a stopcock and a magnetic stir bar. ϵ-Caprolactone (1.11 mL, 10 mmol) was added with stirring. After the polymerization reaction was complete (45 min for $(C_5Me_5)_2Sm(THF)_x$, 60 min for $(C_5Me_5)_2Sm$), the mixture was divided into three equal portions. One portion was immediately quenched by addition of dilute HCl as described above. A second portion was stirred for an additional 15 min and then quenched. To the third portion was added the product formed by reacting $(C_5Me_5)_2Sm(THF)_x$ or $(C_5Me_5)_2Sm$ with 2 equiv of caprolactone (i.e., a model for the initially formed samarium complex in the polymerization reaction). The amount of additional samarium added was equal to the amount of samarium originally in the third portion. The third portion was stirred for 15 min and quenched. Each polymer was purified as described above. The total polymer yield for the three portions was 92% for $(C_5Me_5)_2Sm(THF)_x$ and 87% for $(C_5Me_5)_2Sm$.

Reaction of Polymerized Caprolactone with Additional Caprolactone. In the glovebox, 0.1 mmol of $(C_5Me_5)_2Sm(THF)_x$ and 20 mL of toluene were placed in a 50-mL round-bottom flask equipped with a stopcock and a magnetic stir bar. ϵ-Caprolactone (1.11 mL, 10 mmol) was added with stirring. After 1 h, the resulting mixture was divided into two equal portions. One sample was immediately quenched as described above. To the second sample was added caprolactone (0.555 mL, 5 mmol, 100 equiv/equiv of samarium in the sample). The sample was stirred for an additional 1 h and quenched. Both polymers were purified as described above. The total polymer yield was quantitative.

Results and Discussion

As summarized in Table 1, ϵ-caprolactone can be polymerized by a variety of Sm(II) complexes. In each of the successful room temperature polymerizations, the dark color of the Sm(II) reagent immediately changed to a yellow color characteristic of Sm(III) complexes.[13]

The most readily available Sm(II) reagent, $SmI_2(THF)_2$, shows no reactivity for the polymerization of caprolactone over a 6-h period at ambient glovebox temperature (ca. 22 °C). Polymerization does occur in THF at reflux, but the polydispersity (M_w/M_n) of the polymer is higher than with the other systems.

Caprolactone is much more readily polymerized by the more soluble $(C_5Me_5)_2Sm(THF)_x$. The ambient temperature reaction is complete in less than 1 h to give polycaprolactone with low polydispersity. With longer reaction times, the molecular weight decreases and the molecular weight distribution broadens (Table 1 and Figure 1). This suggests that the active samarium complex is catalyzing decomposition of the polymer. In other systems,[1] intramolecular transesterification has been discussed as a route to broader molecular weight distributions.

Caprolactone is also readily polymerized by the unsolvated metallocene $(C_5Me_5)_2Sm$, and the effect of THF in this system is shown in Figure 2. As the amount of THF is increased in the system, the molecular weight increases and a bimodal pattern develops in the molecular weight distribution.

To test the effect of the samarium reagent in degrading the polymer, two reactions in toluene in which the polymerization of caprolactone was complete were treated for 15 min with solutions which modeled the active catalyst in this system. One model was formed by reacting $(C_5Me_5)_2Sm(THF)_x$ with 2 equiv of caprolactone in toluene; the other model was obtained from $(C_5Me_5)_2Sm$ and 2 equiv of caprolactone in toluene. Figure 3a shows that the first model system had no effect on the molecular weight of the polymer during this time period, whereas Figure 3b shows that the second model caused a significant decrease and broadening in the molecular weight of the polymer. These experiments also show that THF can have a significant effect in these samarium-based polymerizations.

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Table 1. Polymerization of ϵ-Caprolactone by Divalent Samarium Complexes[a]

Sm(II) complex	solvent	time	yield (wt %)	M_n	M_w/M_n
$(C_5Me_5)_2Sm(THF)_x$	toluene	1 min	15	9000	1.4
		5 min	61	18000	1.7
		1 h	99	63000	1.4
		6 h	98	29000	2.5
	THF	5 min	70	31000	1.5
	THF	1 h	98	56000	1.3
$(C_5Me_5)_2Sm$	toluene	5 min	55	17000	1.5
$(C_9H_7)_2Sm(THF)_x$	THF	5 min	98	30000	1.7
$(C_{13}H_9)_2Sm(THF)_2$	THF	5 min	94	24000	1.6
$[(Me_3Si)_2N]_2Sm(THF)_2$	toluene	1 min	99	17000	3.0[b]
		5 min	99	48000	2.6[b]
		1 h	99	20000	3.0
		6 h	92	34000	3.0
$SmI_2(THF)_2$	THF	6 h	none		
	THF (reflux)	1 h	95	30000	3.2
		6 h	87	3000	1.7

[a] [Sm] = 0.01 mol/L; caprolactone/Sm = 100/1; at ambient glovebox temperature, 22 °C. [b] Stirring problems occurred due to the speed of the reaction.

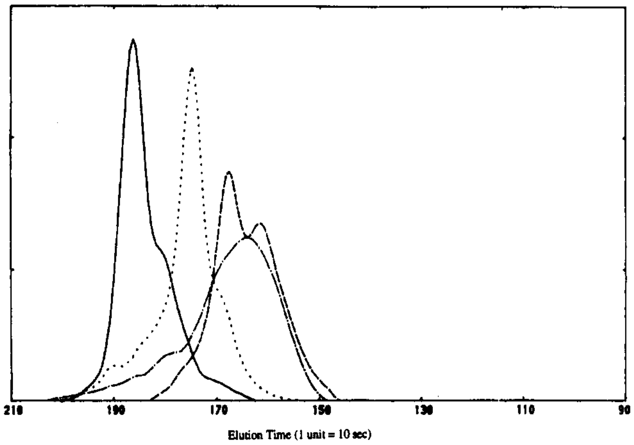

Figure 1. GPC data on the molecular weight distribution of polycaprolactone made from $(C_5Me_5)_2Sm(THF)_x$ with different reaction times: (—) 1 min; (···) 5 min; (- - -) 60 min; (- · · -) 360 min.

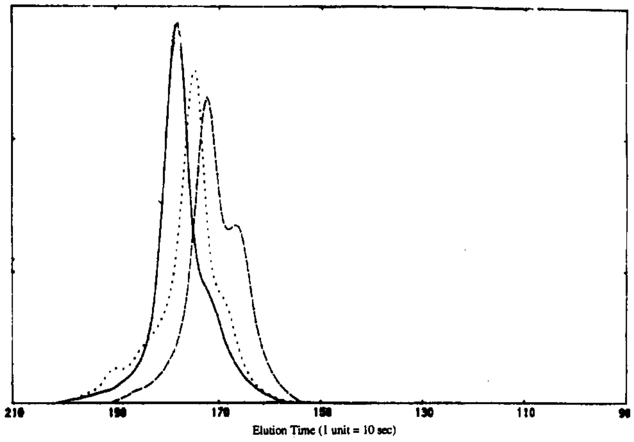

Figure 2. GPC data on the molecular weight distribution of polycaprolactone generated in 5 min from $(C_5Me_5)_2Sm$ in toluene (solid line), $(C_5Me_5)_2Sm(THF)_x$ in toluene (dotted line), and $(C_5Me_5)_2Sm(THF)_2$ in THF (dashed line).

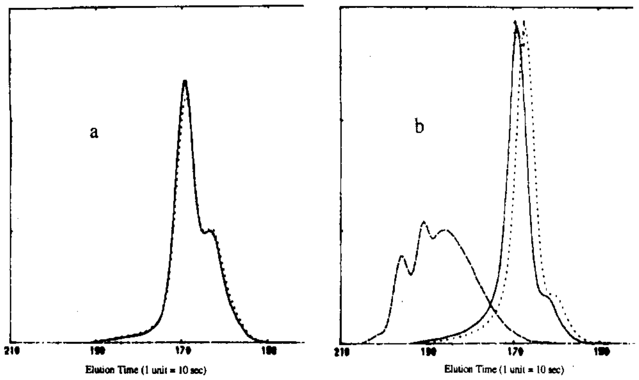

Figure 3. GPC data on the molecular weight distribution of polycaprolactone. (a) Solid line, 45-min polymerization using $(C_5Me_5)_2Sm(THF)_x$; dotted line, same system after 15 min; dashed line, first system 15 min after being treated with the product of reacting $(C_5Me_5)_2Sm(THF)_x$ with 2 equiv of caprolactone. (b) Solid line, 60-min polymerization using $(C_5Me_5)_2Sm$; dotted line, same system after 15 min; dashed line, first system in (b) 15 min after being treated with the product of reacting $(C_5Me_5)_2Sm$ with 2 equiv of caprolactone.

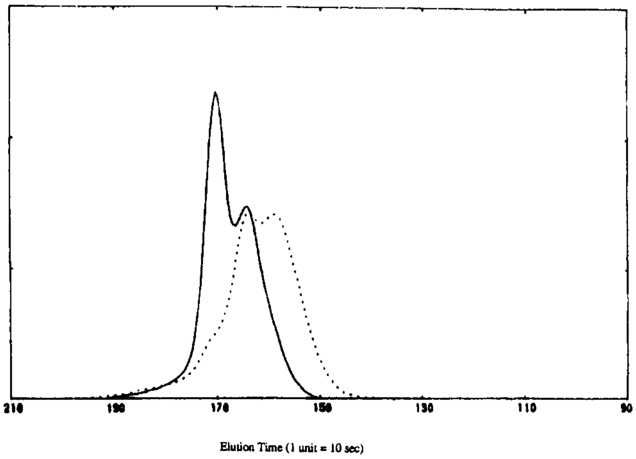

Figure 4. Solid line, GPC data on polymer obtained from $(C_5Me_5)_2Sm(THF)_x$ and caprolactone after 1 h; dotted line, first system treated with 100 equiv of caprolactone/samarium for an additional hour.

To demonstrate that a $(C_5Me_5)_2Sm(THF)_2$-based polymerization system which had consumed all of the substrate was still active for further polymerization, the reaction of a completed polymerization solution with additional caprolactone was examined. Figure 4 shows that the molecular weight distribution of the sample to which additional caprolactone was added has shifted to higher molecular weight compared to the original sample. This indicates that this polymerization system still has active polymerization sites when the initial amount of monomer is consumed and that polymer decomposition is not predominant when there is unreacted monomer present.

The divalent samarium amide $[(Me_3Si)_2N]_2Sm(THF)_2$ was so reactive in caprolactone polymerization that it was difficult to study at ambient temperature. The viscosity of the solutions increased rapidly and interfered with the stirring of the solutions. Quantitative yields could be achieved in 1 min compared to 1 h for $(C_5Me_5)_2Sm(THF)_x$, although under these conditions neither the molecular weight nor the polydispersity was optimal. The activity of the amide complex may arise in part due to the monodentate nature of its ligands compared to the polydentate nature of the cyclopentadienyl groups.

Recently, two new soluble organosamarium reagents have been synthesized using indenyl and fluorenyl ligands.[18] These complexes, $(C_9H_7)_2Sm(THF)_x$ and $(C_{13}H_9)_2Sm(THF)_2$, respectively, showed much higher activity than $(C_5Me_5)_2Sm(THF)_x$ in caprolactone polymerization reactions in THF. This may be caused by the fact that these two complexes have a more open coordination environment around the metal than is found in $(C_5Me_5)_2Sm(THF)_x$. For example, $(C_5Me_5)_2Sm$ complexes typically add two ligands to become formally eight-coordinate, whereas the nine-coordinate $(C_9H_7)_2Sm(THF)_3$ has been crystallographically characterized.[18]

Conclusion

A variety of samarium(II) complexes generate ring-opening polymerization systems with ε-caprolactone in reactions which initially involve oxidation of the metal. The $(C_5Me_5)_2Sm(THF)_x$ reaction has been shown to be an active polymerization system which maintains activity after all of the initial batch of monomer is consumed. The molecular weight, polydispersity, and tendency of the polymer to be degraded by catalyst appear to be sensitive to the nature of the ligands attached to the metal. As a result, these samarium systems may prove to be useful in elucidating details of the ε-caprolactone polymerization.

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