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Notes

Copolymerization of Ethylene Carbonate and ε-Caprolactone Using Samarium Complexes

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Introduction

Lactones undergo ring-opening polymerization to form polyesters with useful properties particularly in applications in which biodegradability is important.[1-12] Although a variety of lactones have been polymerized, those containing five-membered rings have proven more difficult.[13] For example, ethylene carbonate ($\overline{OCH_2CH_2OC}{=}O$) is not polymerized by the reactive Sm(II) reagents which we have found to generate active ring-opening polymerization systems with ε-caprolactone ($\overline{O(CH_2)_5C}{=}O$).[14] We report here, however, that, by combining ethylene carbonate with caprolactone, polymers containing both ethylene carbonate and caprolactone can be obtained using samarium reagents.

Experimental Section

$SmI_2(THF)_2$,[15] $(C_5Me_5)_2Sm(THF)_2$,[16] $[(Me_3Si)_2N]_2Sm(THF)_2$,[17] $(C_9H_7)_2Sm(THF)_{1.5}$,[18] and $(C_{13}H_9)_2Sm(THF)_2$[18] were prepared under nitrogen using standard Schlenk, vacuum-line, and glovebox (Vacuum/Atmospheres HE-553 Dri-Lab) techniques according to the literature. 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 copolymer 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 Copolymerization Procedure. In the glovebox, 0.1 mmol of catalyst precursor and 20 mL of solvent were placed in a 50-mL round-bottomed, two-neck flask equipped with a stopcock and a magnetic stir bar. Ethylene carbonate (0.88 g, 10 mmol) in 2 mL of THF was added to the rapidly stirred solution. After 1 h, 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. The ethylene carbonate content was estimated by ^{13}C-NMR spectroscopy (vide infra). When THF was used as a solvent, toluene was added to the reaction mixture before the HCl wash.

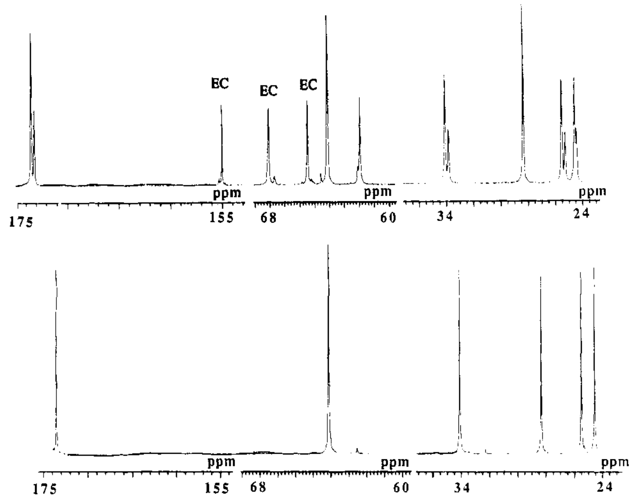

Figure 1. ^{13}C-NMR spectra of polycaprolactone (bottom) and of an ethylene carbonate/caprolactone copolymer (top). Peaks arising from the ethylene carbonate component are labeled EC.

Stepwise Addition of Caprolactone. In the glovebox, 0.1 mmol of the Sm(II) reagent and 20 mL of solvent were placed in a 50-mL round bottomed, two-neck flask equipped with a stopcock and a magnetic stir bar. Ethylene carbonate (0.88 g, 10 mmol) in 2 mL of THF was added to the rapidly stirred solution. After 1 h, ε-caprolactone (0.55 mL, 5 mmol) was added. After the designated time, another 0.55 mL of caprolactone was added. The reaction was quenched, and the polymer was purified as described above.

Ethylene Carbonate Content Determination by ^{13}C-NMR Spectroscopy. The ^{13}C-NMR peaks of a typical EC/CL copolymer were assigned as shown in Figure 1[14] which also contains a spectrum of polycaprolactone for comparison. The amount of ethylene carbonate was calculated from the ratio of the area of the 155.0 ppm peak (the carbonyl carbon of ethylene carbonate) to peaks at 173.5 and 173.2 ppm (carbonyl carbons of caprolactone).

Results and Discussion

Ethylene carbonate is not homopolymerized by $(C_5Me_5)_2Sm(THF)_2$ or $[(Me_3Si)_2N]_2Sm(THF)_2$ in toluene or THF even at reflux. These reactions contrast sharply with the reaction of these reagents with ε-caprolactone which readily forms polycaprolactone at ambient temperature.[14]

However, when ε-caprolactone is added to the ethylene carbonate/Sm(II) system, polymers are formed which contain components derived from both ethylene carbonate and caprolactone as shown in Table 1. The polymers derived from the ethylene carbonate/caprolactone reactions differ from the pure caprolactone homopolymers in that they are rubbery materials. As shown in Table 1, the copolymer yield increased with time but never exceeded 70% even after 48 h when a 1/1 ratio of ethylene carbonate/caprolactone was used. In contrast, caprolactone polymerizations were found to be quantitative after 1 h with these reagents (for $[(Me_3Si)_2N]_2Sm(THF)_2$ the caprolactone polymerization was over in minutes).[14] It is interest-

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Table 1. Ethylene Carbonate (EC)/ϵ-Caprolactone (CL) Copolymerization by Divalent Samarium Complexes[a]

					GPC		EC content (mol %)	
catalyst	solvent	EC/CL	time (h)	yield (wt %)	M_n	M_w/M_n	calcd[b]	found[c]
$(C_5Me_5)_2Sm(THF)_x$	toluene	100/100	1	12	6 000	1.9		22
			6	54	43 000	2.0		22
			24	68	82 000	1.9	21	22
			48	70	82 000	1.8	23	22
		40/160	24	94	95 000	1.9	13	11
	THF	100/100	6	30	19 000	1.7		12
			24	59	34 000	1.9		
$(C_9H_7)_2Sm(THF)_{1.5}$	THF	100/100	6	14	18 000	1.9		10
$(C_{13}H_9)_2Sm(THF)_2$	THF	100/100	6	63	28 000	2.3	13	14
$[(Me_3Si)_2N]_2Sm(THF)_2$	toluene	100/100	1	30	7 000	4.7		23
			6	68	53 000	2.2	21	21
			24	66	11 000	5.8	19	20
		40/160	6	93	84 000	1.8	12	8
$SmI_2(THF)_2$	THF (reflux)	100/100	1	55	6 000	1.8	0	5
			6	55	4 000	1.7	0	6

[a] [Sm] = 0.005 M; EC/CL/Sm = 100/100/1; ambient temperature. [b] Based on yield assuming all available CL was polymerized. [c] By ^{13}C NMR.

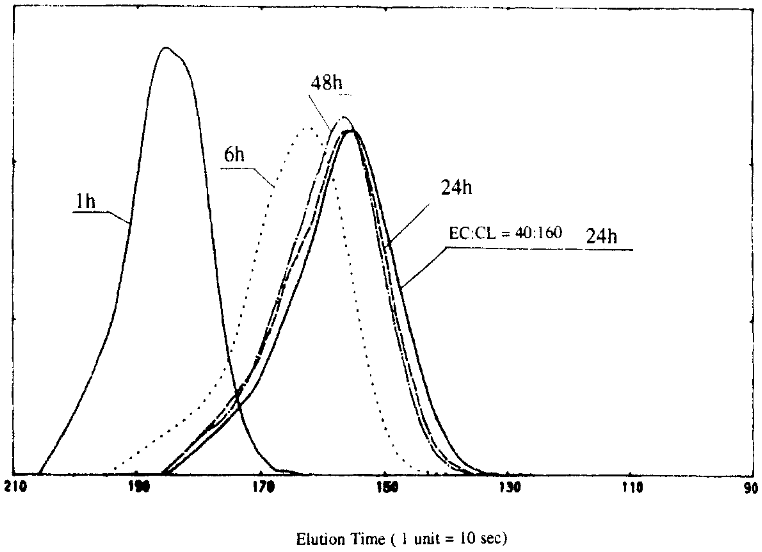

Figure 2. GPC data on the molecular weight distribution of ethylene carbonate (EC)/caprolactone (CL) copolymers made from $(C_5Me_5)_2Sm(THF)_2$ in toluene. Except as noted for the solid line on the right, all data are for reactions involving EC/CL ratios of 100/100.

ing to note that, in caprolactone polymerizations, reaction times as long as 6 h led to significant broadening and lowering of the molecular weight distribution, whereas, in the presence of ethylene carbonate, extending the reaction time from 6 to 48 h does not have this effect as shown by the GPC data in Figure 2.

Higher overall copolymer yields (up to 93%) could be achieved if the ethylene carbonate/caprolactone ratio was reduced to 1/4. If it is assumed that all of the caprolactone is consumed, the observed yields suggest that the maximum amount of ethylene carbonate present in the copolymer is about 22%. This estimate matches the ethylene carbonate content obtained by NMR spectroscopy (vide infra).

NMR analysis of the copolymers (Figure 1) shows that peaks assignable to ethylene carbonate components are present as well as the normal peaks for polycaprolactone. Comparison of the intensities of the carbonyl peaks indicated an ethylene carbonate content of around 20%. Each of the caprolactone peaks shows distinct doubling in the ethylene carbonate/caprolactone polymer which suggests that there are two types of caprolactone environments in the polymer, e.g., CL–*CL*–CL and EC–*CL*–CL. Although a few minor peaks have not been assigned, the ethylene carbonate peaks do not show a comparable doubling of closely spaced resonances which suggests that they exist in only one environment, e.g., CL–*EC*–CL. The three sequences just mentioned seem more probable than other possibilities (such as EC–CL–EC) given the low ethylene carbonate content in the copolymer. The absence of ^1H NMR resonances in the ether region around 3.75 ppm suggested that decarboxylation was not significant.

The NMR and yield data suggest that the amount of ethylene carbonate that can be incorporated into the copolymer is limited. An ethylene carbonate monomer can be incorporated into a growing caprolactone chain, but repeated incorporation of ethylene carbonate monomers apparently does not occur. Since this situation will lead to faster depletion of caprolactone and since the reaction will stop when all of the caprolactone is consumed, this explains why 1/1 ethylene carbonate/caprolactone reactions do not reach yields higher than 70%. Attempts to increase the ethylene carbonate content by stepwise addition of caprolactone were unsuccessful as shown in Table 2. These experiments show that the caprolactone polymerization systems continue to be active after all of the caprolactone is depleted in the presence of ethylene carbonate but that ethylene carbonate is not incorporated unless caprolactone is being incorporated also. This has interesting implications regarding the nature of the active site of catalysis.

Table 2. Ethylene Carbonate (EC)/ε-Caprolactone (CL) Copolymerization with Stepwise Caprolactone Addition Using $(C_5Me_5)_2Sm(THF)_x$ (0.005 M in Toluene at Ambient Temperature)

no. of steps	EC/CL/CL	time at each step (h)	yield (wt %)	EC content (mol %)
1	100/100/0	24 + 0	68	22
		48 + 0	70	22
2	100/50/50	6 + 18	66	24
		24 + 24	68	25

Copolymerization of ethylene carbonate and caprolactone using other Sm(II) reagents successful with caprolactone alone was also examined (Table 1). Although $(C_9H_7)_2Sm(THF)_{1.5}$, $(C_{13}H_9)_2Sm(THF)_2$, and $SmI_2(THF)_2$ all form polymers containing ethylene carbonate, the ethylene carbonate content is significantly smaller than that achieved with $(C_5Me_5)_2Sm(THF)_2$. The poor performance of $(C_9H_7)_2Sm(THF)_{1.5}$, which showed high reactivity in caprolactone polymerization, is probably due to limited solubility of the ethylene carbonate derivative of this indenyl complex in THF. $[(Me_3Si)_2N]_2Sm(THF)_2$, which is also a very active catalyst for caprolactone, forms copolymers with up to 23% ethylene carbonate content, but the molecular weight of these polymers is lower than that produced using $(C_5Me_5)_2Sm(THF)_2$. For this Sm(II) initiator, polymer degradation is important even in the presence of ethylene carbonate.

Conclusion

Ethylene carbonate can be incorporated into a caprolactone polymer using Sm(II) catalyst precursors to form rubbery polymers with up to 22% ethylene carbonate content. The incorporation of ethylene carbonate into the polymer requires the presence of caprolactone, and the presence of ethylene carbonate seems to inhibit polymer degradation in the $(C_5Me_5)_2Sm(THF)_2$ system.

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References and Notes

(1) Only some leading references are cited. Jérôme, R.; Teyssié, Ph. *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, Chapter 34, pp 501–510.

(2) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419–6424.

(3) Duda, A.; Penczek, S. *Macromolecules* **1990**, *23*, 1636–1639.

(4) Johns, D. B.; Lenz, R. W.; Luick, A. *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: London, Great Britain, 1984; Vol. 1, Chapter 7, pp 461–521.

(5) Yasuda, H.; Tanai, H. *Prog. Polym. Sci.* **1993**, *18*, 1097–1139.

(6) Kricheldorf, H. R.; Berl, M.; Schnarnagl, N. *Macromolecules* 1988, *21*, 286–293.

(7) Dubois, Ph.; Jacobs, C.; Jerome, R.; Teyssie, Ph. *Macromolecules* **1991**, *24*, 2266–2270.

(8) Song, C. X.; Feng, X. D. *Macromolecules* **1984**, *17*, 2764–2767.

(9) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991–994.

(10) Yui, N.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem.* **1990**, *191*, 481–488.

(11) Yamashita, M.; Takemoto, Y.; Yasuda, H. Rare Earths '92, Kyoto, Japan, June 1992; Paper PIK-05.

(12) McLain, S. J.; Drysdale, N. E. (E. I. du Pont de Nemours and Co.). U. S. Patent 5,028,667, 1991. McLain, S. J.; Ford, T. M.; Drysdale, N. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 463–464. McLain, S. J.; Drysdale, N. E. 203rd National Meeting of the American Chemical Society, San Francisco, CA, April 1992; Paper POLY-160. McLain, S. J.; Drysdale, N. E. 206th National Meeting of the American Chemical Society, Chicago, IL, August 1993; Paper INOR 427.

(13) Soga, K.; Hosada, S.; Tazuke, Y.; Ikeda, S. *J. Polym. Sci., Polym. Lett. Ed.* **1976**, *14*, 161–165. Vogdanis, L.; Heitz, W. *Makromol. Chem., Rapid Commun.* **1986**, 7, 543–547. Storey, R. F.; Hoffman, D. C. *Polym. Bull.* **1991**, *27*, 267.

(14) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330–2332.

(15) Kagan, H. B.; Namy, J. L. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Jr., Eyring, L., Eds.; Elsevier: Amsterdam, The Netherlands, **1984**; Vol. 6, Chapter 50.

(16) Evans, W. J.; Ulibarri, T. A. *Inorg. Synth.* **1990**, *27*, 155–157.

(17) Evans, W. J.; Drummond, D. K.; Zhang, H.; Atwood, J. L. *Inorg. Chem.* **1988**, *27*, 575–579.

(18) Evans, W. J.; Gummersheimer, T. S.; Boyle, T. J.; Ziller, J. W. *Organometallics* **1994**, *13*, 1281–1284.

(19) Evans, W. J.; Chamberlain, L. R.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 6423–6432.