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Novel [$Sm_2I(NPPh_3)_5(DME)$] Initiator for the Living Ring-Opening Polymerization of ϵ-Caprolactone and δ-Valerolactone

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ABSTRACT: Ring-opening polymerization of ϵ-caprolactone (CL) and δ-valerolactone (VL) was carried out using the initiator system [$Sm_2I(NPPh_3)_5(DME)$] in the presence of toluene. Experimental molecular weights were in good agreement with the theoretical molecular weights for $[CL]_0/[\mathbf{1}]_0$ up to 350. Polydispersities are low at 0−20 °C but increase at higher temperatures. Addition of small amounts of coordinating solvents such as THF and DME decreased the rate of polymerization and thereby reduced the polydispersity. The active polymer chain ends have been shown by sequential copolymerization of CL and VL, resulting in block copolymers.

Introduction

Aliphatic polyesters such as PCL and PVL with high molecular weight and narrow molecular weight distribution are of great interest as biodegradable and biocompatible materials.[1−3] Initiators such as aluminum porphyrins,[4] alkylaluminum alkoxides,[5] tin(2-ethyl-hexanoate),[6] and transition metal[7] complexes have been developed for the ring-opening polymerization of lactones. Transesterification reactions either intermolecular with concomitant broadening of the polydispersity or intramolecular, leading to the formation of macrocycles or depolymerization, are inevitable with most of these initiators. Much work has recently focused on rare earth metal complexes for the ROP of lactones.[8−11] Structurally well-defined lanthanide complexes have attracted increasing attention as initiators for the living polymerization of lactones.[12−14]

In our earlier work, the new lanthanide initiators based on bis(trimethylsilyl)amido[15,16] and phosphorane iminato[17,18] ligands were synthesized and found to be very active for the ring-opening polymerization of CL. Polymerizations of CL initiated by the above-mentioned lanthanide initiators yielded always PCL of moderate polydispersities. This moderate polydispersities were mainly attributed to the faster rate of polymerization than initiation. The polymerizations of CL using these lanthanide initiators followed the scheme of a coordination−insertion mechanism. Further, the insolubility of triphenylphosphorane iminato ligand based initiators in toluene led to higher molecular weight than expected theoretically. Addition of coordinating solvents such as THF and DME increased the solubility of the initiators and decreased the rate of polymerization considerably. Taking into consideration the solubility of the initiators, new initiators based on the phosphorane iminato ligands were prepared in DME, to ensure the presence of DME inside the initiator system.[17]

This paper reports results of the initiation of the new samarium complex [$Sm_2I(NPPh_3)_5(DME)$] (**1**) for the controlled synthesis of PCL and PVL. The active chain ends of the living polymer were determined by block copolymerization of CL and VL.

Experimental Section

Materials. CL (99%, Aldrich) and VL (99%, Aldrich) were dried over CaH_2 for 5 days, distilled under reduced pressure, and degassed before use. Toluene and THF were dried over a benzophenone−potassium complex for 3 days, distilled, and degassed before use.

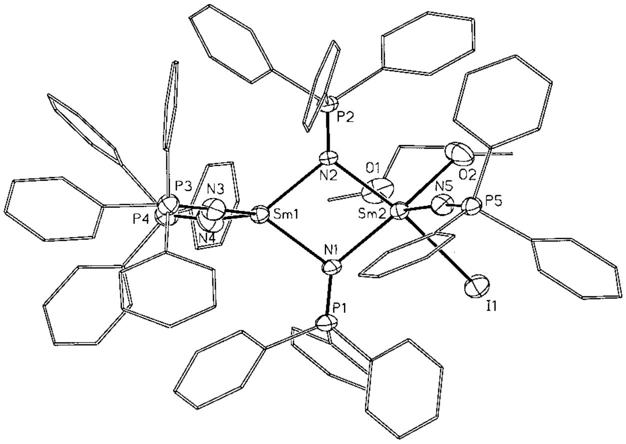

Figure 1. Crystal structure of **1**.[17]

Preparation of Initiator. 1 was prepared under argon using a Schlenk tube, a vacuum line, and glovebox techniques according to the reported procedure.[17] The crystal structure of the initiator is shown in Figure 1.

Polymerizations of CL. The polymerizations were carried out under an atmosphere of dry nitrogen using Schlenk type glassware, a vacuum line, and glovebox techniques. 0.0605 g (0.0315 mmol) of **1** was dissolved in 5 mL of toluene. CL (0.54 g, 4.7 mmol) was introduced into the toluene solution using a rubber septum and syringe with vigorous stirring. After completion of the polymerization the reaction mixture was precipitated in excess methanol containing a few drops of HCl. The polymers were purified by 2-fold reprecipitation from THF/methanol−HCl. Finally, the polymers were dried under high vacuum at room temperature for 24 h.

Other polymerizations of CL with varying amounts of **1** and temperature and polymerizations of VL were performed according to the procedure decribed before.

Yield, GPC data, and ^{13}C NMR spectroscopy are presented in the text.

Block Copolymerization of CL and VL. 0.131 g (0.6031 mmol) of **1** was dissolved in 10 mL of toluene. 1.078 g (9.4 mmol) of CL was added to the toluene solution by syringe with vigorous stirring. After 4 min, 1 mL of the mixture was taken out by syringe and precipitated in HCl/methanol. Then 1.056 g (10.55 mmol) of VL was added to the reaction mixture. The polymerization was quenched after 15 min by precipitation in HCl/methanol. Precipitates were isolated by filtration, washed

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Table 1. Effect of Initiator/Monomer Ratio on the Polymerization of CL and VL in the Presence of Toluene at Room Temperature

monomer	$[M]_0/[\mathbf{1}]_0$ (molar ratio)	time (min)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n	theor $M_n{}^a \times 10^{-4}$
CL	75	4	96	0.50	1.27	0.43
VL		10	90	0.32	1.23	0.34
CL	150	4	90	0.78	1.22	0.86
VL		10	92	0.78	1.29	0.69
CL	250	4	89	1.31	1.32	1.43
VL		10	90	1.02	1.39	1.13
CL	350	5	96	1.80	1.28	2.00
CL	500	5	96	2.37	1.17	2.85
CL	750	5	79	2.43	1.20	4.28

[a] Theoretical molecular weight calculated based on the monomeric form of the initiator.

by methanol, and dried in a vacuum. Yield, GPC data, and ^{13}C NMR spectroscopy are presented in the text.

Characterization. Gel permeation chromatography (GPC) was used to determine molecular weight and molecular weight distributions. A Knauer GPC apparatus equipped with two 10 μm (pore size) polymer mixed gel columns (600 × 8 mm, PSS) and a Knauer-differential refractometer/viscometer K200 were used. Molecular weights were analyzed by universal calibration (viscosity vs GPC elution time) using polystyrene standards. Polymers were dissolved in THF, and elution was performed at a flow rate of 0.63 mL/min (20 °C).

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AMX 500 MHz spectrometer in CD_2Cl_2 as solvent. C_6D_6 was used as solvent for end group analysis studies.

Results and Discussion

In our previous studies on the ROP of CL, initiators based on phosphorane iminato complexes such as $[La_2(\mu\text{-}NPPh_3)_2(\mu\text{-}THF)(NPPh_3)_4]$ and $[Yb(NPPh_3)_3]_2$ showed high activity for the ring-opening polymerization of CL to PCL with moderate polydispersity (≥1.4). The obtained molecular weight of the polymer was always higher than that of the calculated molecular weight. The faster rate of polymerization with respect to initiation and the poor solubility of the initiators accounted for the molecular weight distribution and the higher molecular weight of the polymer, respectively.

The new initiator system, $[Sm_2I(NPPh_3)_5(DME)]^{17}$ (**1**) (crystal structure in Figure 1), is very efficient in promoting the living polymerization of CL and VL in toluene. Use of $[CL]_0/[\mathbf{1}]_0 = 150$ produced PCL with a molecular weight of 0.7827×10^4 ($M_w/M_n = 1.22$). To elucidate the livingness of the polymerization, different $[M]_0/[\mathbf{1}]_0$ were polymerized in toluene at room temperature (Table 1). The molecular weight ($M_n = 0.4985 \times 10^4 - 2.368 \times 10^4$ for $[CL]_0/[\mathbf{1}]_0 = 75-500$) increased significantly with increasing $[CL]_0/[\mathbf{1}]_0$. The obtained molecular weights agree well with the theoretical molecular weights up to $[CL]_0/[\mathbf{1}] = 350$, assuming for the calculation of the theoretical molecular weight a coordination−insertion mechanism with two polymer chains per initiator molecule (for details see discussion below). Figure 2 shows the relationship between $[CL]_0/[\mathbf{1}]_0$ theoretical and experimental molecular weight and polydispersity. Deviation of experimental molecular weight from theoretical molecular weight is observed for $[CL]_0/[\mathbf{1}]_0 > 350$; however, polydispersity remained rather narrow for the whole range of $[CL]_0/[\mathbf{1}]_0$ tested. The deviation of experimental molecular weight from theoretical molecular weight for $[CL]_0/[\mathbf{1}]_0 > 350$ is most likely due to the high sensitivity of **1** toward traces of impurities (for example, traces of water). The effect of different $[CL]_0/[\mathbf{1}]_0$ on molecular weights suggests that two polymer molecules are formed from every molecule of initiator (the same applies for VL).

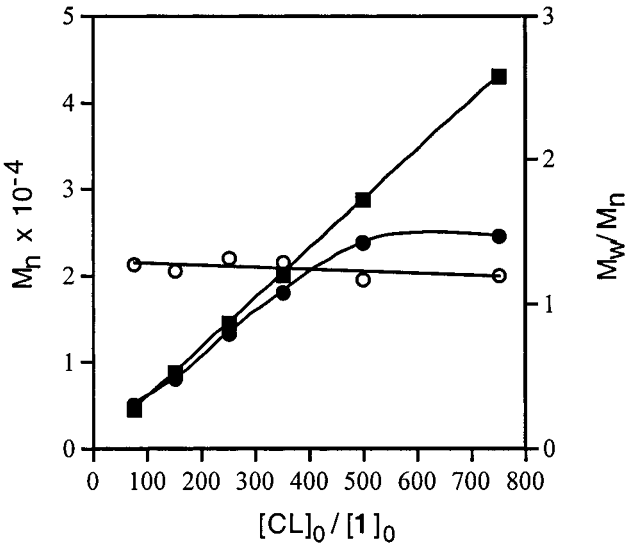

Figure 2. Polymerization of CL initiated with **1** in toluene at room temperature. Experimental M_n (●, determined by GPC), theoretical M_n (■), and M_w/M_n (○) as a function of $[M]_0/[\mathbf{1}]_0$ ($[CL]_0 = 4.7$ mM).

Table 2. Effect of Temperature on the Polymerization of CL in the Presence of Toluene

$[CL]_0/[\mathbf{1}]_0$ (molar ratio)	temp (°C)	time (min)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
150	0	6	92	0.77	1.16
150	20	4	90	0.78	1.22
150	40	3	91	0.87	1.39
150	75	3	90	1.15	1.35

Table 3. Effect of Coordinating Solvent on the Polymerization of CL in the Presence of Coordinating Solvents (THF and DME) at Room Temperature with $[CL]_0/[1]_0 = 150$

coord solvent	toluene:coord solvent^a	time (min)	yield (%)	$M_n \times 10^{-4}$	M_w/M_n
	100:0	4	90	0.78	1.22
THF	90:10	6	92	0.80	1.09
THF	80:20	6	92	0.83	1.12
DME	90:10	6	96	0.80	1.14

[a] Total amount of solvent 5 mL (concentration = 0.94 mmol/mL).

The molecular weight of poly(VL) ($M_n = 0.3218 \times 10^4 - 0.7781 \times 10^4$) also almost doubled when $[CL]_0/[\mathbf{1}]_0$ increases from 75 to 150. The molecular weight distribution was unchanged and remained between 1.23 and 1.29. The rather narrow molecular weight distribution of the polymer indicates that initiation is fast with respect to propagation compared to chain transfer or chain termination. The polymerization of CL was very fast and completed within 4 min. The polymerization of VL took 10 min to complete. Although the initiators are slightly soluble in toluene, their incomplete solubility might be responsible for the slight deviation in the molecular weight relative to the theoretical values (Table 1).

The molecular weight of PCL initiated by **1** in toluene at different temperatures is shown in Table 2. The polymerizations at higher temperature were faster than those at room temperature, and the molecular weights were higher. Upon increasing the polymerization tem-

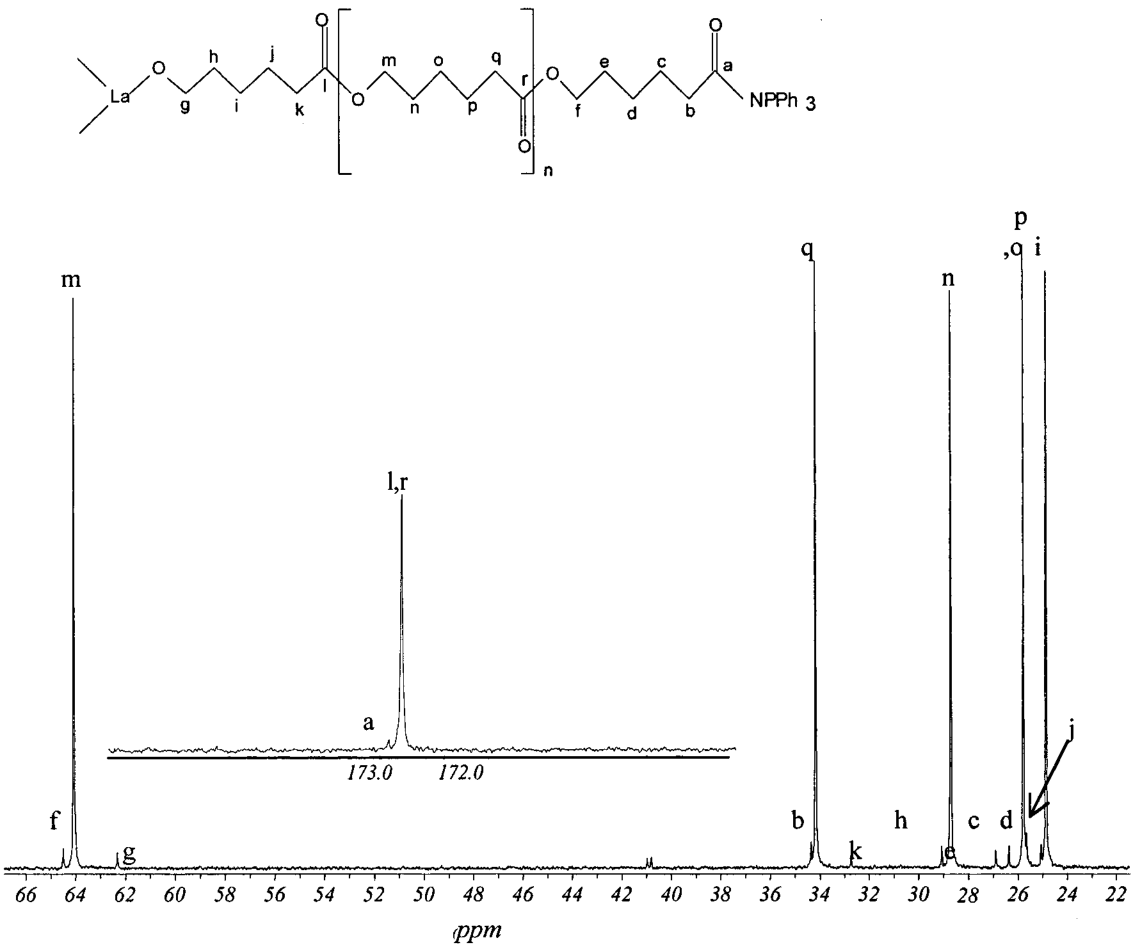

Figure 3. ^{13}C NMR spectrum of **1** with 30 equiv of CL in C_6D_6.

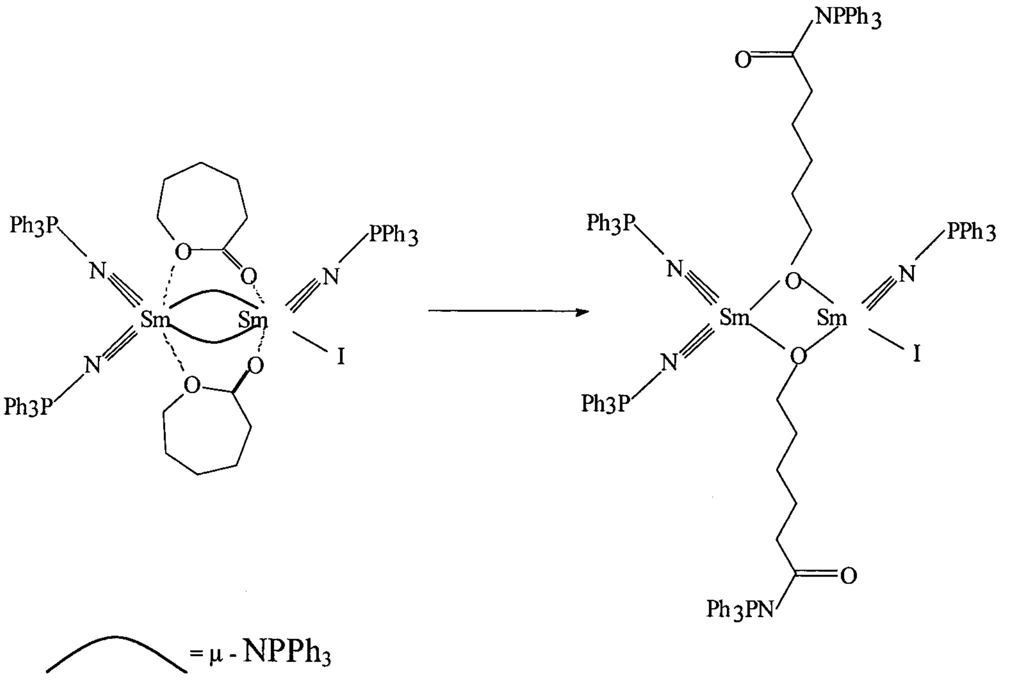

Figure 4. Proposed scheme for the initiation of the polymerization of CL by **1**.

perature, the efficiency of the initiator was reduced from 98.2% (for 20 °C) to 67.3% (for 75 °C). This increase in molecular weight may be accounted for the increase in the rate of polymerization at higher temperature. When decreasing the polymerization temperature below room temperature, i.e., at 0 °C, the rate of polymerization was lower. The polydispersity of the polymer also decreased with decreasing temperature. At low polymerization temperature (0 °C), the polydispersity of PCL was narrow ($M_w/M_n = 1.16$) and the molecular weight of the polymer remained unchanged ($M_n = 0.7741 \times 10^4$ at 0 °C).

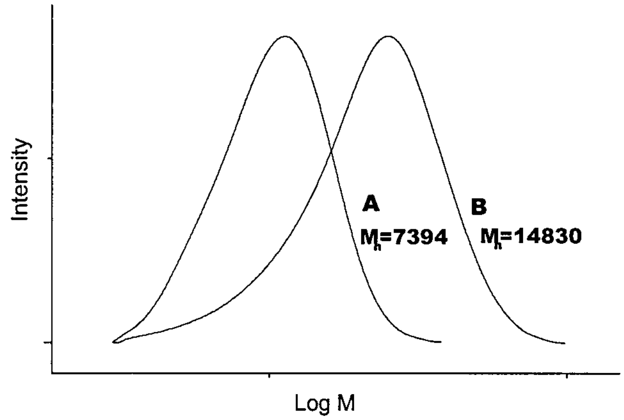

Figure 5. GPC traces for (A) PCL and (B) PCL-*block*-PVL.

Earlier work on $[Sm\{N(SiMe_3)_2\}_2(\mu\text{-}Br)]_2$ revealed that adding small amounts of coordinating solvents such as THF and DME to toluene decreased the rate of polymerization, thereby reducing the polydispersity considerably.[19] In this study, addition of THF and DME also increased the solubility of the initiator and reduced the rate of polymerization (Table 3). The slower rate of polymerization is probably due to the competition between monomer and solvent for coordination to the active metal center (Figure 1). Polymerization in the presence of both 10:90 and 20:80 (THF: toluene) did not effect the molecular weight of the polymer but reduced the polydispersity to 1.09 and 1.12, respectively, in comparison to the corresponding experiment without THF (here $M_w/M_n = 1.22$). DME (10:90, DME:toluene) also reduced the polydispersity to 1.14 without affecting the molecular weight. A possible explanation for the influence by coordinating solvents on the Sm complex is that the coordination sphere at the Sm atoms is changed by the number of ligands. Thus, it increases the rate of initiation by facilitating the coordination of the monomer to the metal centers. Addition of coordinating solvent reduces deleterious transesterification reactions, similar to that reported by Dubois et al.[20]

We attempted to study the initiation mechanism by NMR using $[CL]_0/[\mathbf{1}]_0 = 30$ in C_6D_6 solvent dry and inert conditions. The molecular weight of the resulting PCL was 4800 with a polydispersity of 1.3. In the ^{13}C NMR spectrum (Figure 3), peaks at 34.3 ppm ($-CH_2-CO-NPPh_3$) and at 64.5 ppm ($-Sm-O\text{-}CH_2-$) in addition to the main chain PCL peaks indicates that the acyl–oxygen bond is cleaved to amide end groups. The additional peak at 173.0 ppm also appeared due to $-CO-$ $NPPh_3$; the main chain carbonyl peak appears at 172.7 ppm. This also confirmed the acyl–oxygen scission and formation of amide end groups. Absence of $-CH_2I$ end group in the ^{13}C NMR spectrum suggests that only $NPPh_3$ groups take part in the initiation step. We therefore propose that initiation involves a coordination–insertion polymerization mechanism, in which the first step involves coordination of the two monomers to the metal center takes place simultaneously by coordination of the carbonyl oxygen atom of the monomer to the electron-deficient metal center. Subsequently, the bridging nitrogen atoms donate their lone pair of electrons to the carbonyl carbon atoms to selectively cleave the acyl–oxygen bond of the monomer. Finally, the ligand is transferred with the oxygen atoms as bridging atoms to stabilize the dimeric complex. This should happen in similar manner for VL. Oxygen bridges are well-known in dimeric organolanthanide complexes.[18] Similar acyl–oxygen cleavages by the coordination–insertion mechanism using rare-earth-based initiator were proposed previously by many authors.[10,11,21,22] The enhanced selectivity in terms of control on molecular weight and polydispersity with **1** as initiator for ROP of CL in comparison to previously used symmetrically substituted bimetallic rare earth metal complexes[10,18,21] might be hypothetically explained by the structure of the complexes and the monomer coordination. Coordination of CL with initiator complexes may be crucial and driven by different donor properties of oxygen atoms in CL as well as by different acceptor properties of the metal atoms in the complex. CL may coordinate with complex **1** as shown in Figure

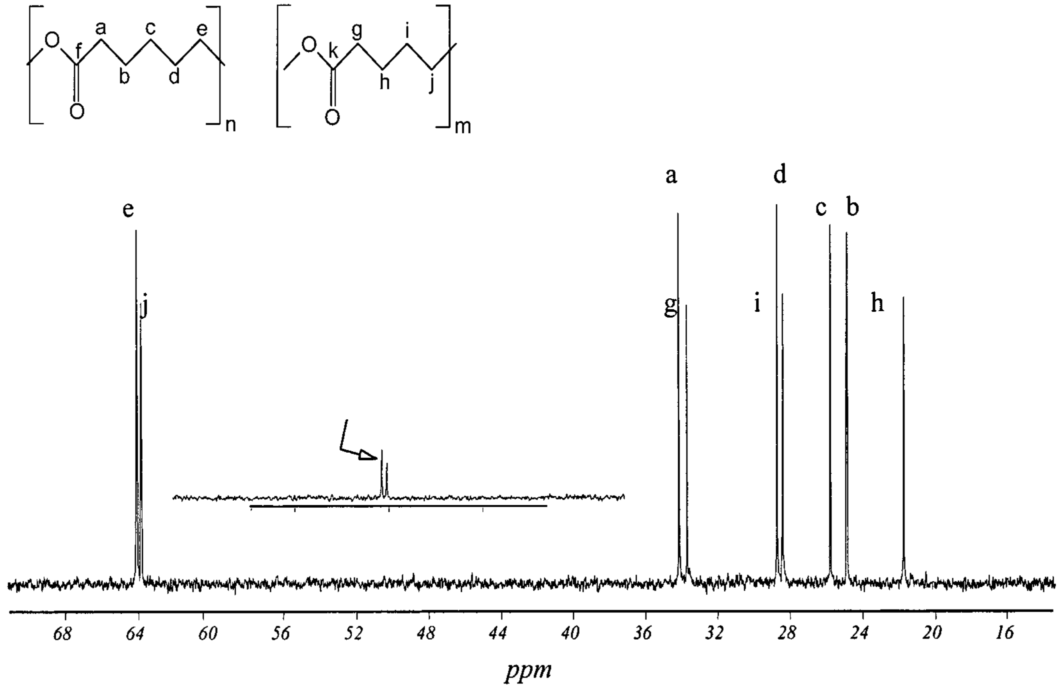

Figure 6. ^{13}C NMR spectrum of PCL-*block*-PVL.

4. This seems to be realistic since bridging by coordinating THF was observed in [{La(NPPh$_3$)$_3$}$_2$(THF)].[18] Furthermore, bridging donor properties were observed with nonhomopolymerizable butyrolactone in the structure of $K_3(O_3SCF_3)_3(C_4H_6O_2)_2$.[23] After the coordination of CL on the metal complex, selective ring opening and insertion must involve ligand transfer from the metal center. From the data presented here, two PCL chains most likely grow from one initiator molecule, which corresponds to one PCL chain per metal center. However, the coordination and substitution of Sm atoms in complex **1** are significantly different. Multichain growth for ROP of lactones is well-known for other initiator complexes.[24,25] If the proposed scheme shown in Figure 4 is realistic, Sm atoms will be strongly deactivated by coordination of iodine, which is known for other Sm−iodine complexes such as SmI_2. SmI_2 initiates ROP of CL only at elevated temperatures or at room temperature in the presence of Sm metal.[26,27]

The living character of the polymer chain ends was investigated by block copolymerization CL with VL using **1** (**1**/CL, 1:150). First, CL was polymerized using **1** as initiator. After complete polymerization of CL, the second monomer (VL) was introduced and the reaction was allowed to continue. The molecular weight of the polymer increased from 0. 7394 × 10^4 ($M_w/M_n = 1.29$) to 1.483 × 10^4 ($M_w/M_n = 1.26$) with high conversion (calculated from polymer yield = 84%). The unimodal GPC trace (Figure 5) of the copolymer shifted to higher molecular weight compared to the original PCL polymer. These results indicate that the polymer chain ends are still active even after complete consumption of the first monomer. Formation of block copolymers was also demonstrated by ^{13}C NMR spectroscopy. The peaks at 172.7 and 172.6 ppm correspond to the carbonyl carbons of CL and VL, respectively, and do not split in the spectrum of the PCL-*block*-PVL copolymer, indicating that the monomer moieties are not distributed in the copolymer (Figure 6).

Conclusion

The initiator based on [Sm$_2$I(NPPh$_3$)$_5$(DME)] initiates living ring-opening polymerization (ROP) of CL and VL with predictable molecular weight for $[CL]_0/[\mathbf{1}]_0$ up to 350 and rather narrow molecular weight distribution. Polymerization at lower temperature and addition of coordinating solvents further reduces the molecular weight distribution. Active polymer chain ends were demonstrated by block copolymerization of CL with VL. On the basis of molecular weight data and end-group analysis, two chains grow per initiator molecule with exclusive growth from each Sm atom in the unsymmetrical complex **1**. Complex **1** marks a remarkable progress for the controlled ROP of lactones initiated by rare earth metals since other bimetal initiators based on rare earth metals do not result in controlled ROP of lactones so far. Successful initiator design for bimetallic rare earth metal complexes might require an unsymmetrical ligand sphere.

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References and Notes

(1) Müller, H. M.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 477.
(2) Pierre, T. S.; Chiellini, E. *J. Bioact. Compat. Polym.* **1987**, *2*, 4.
(3) Vert, M.; Feijen, J.; Albertsson, A. C.; Scott, G.; Chiellini, E. In *Biodegradable Polymers and Plastics;* Royal Society: London, 1992.
(4) Isoda, M.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1997**, *30*, 57.
(5) Duda, A.; Penczek, S. *Macromol. Rapid Commun.* **1994**, *15*, 559.
(6) Kricheldorf, H. R.; Keiser-Saunders, I.; Boettcher, C. *Polymer* **1995**, *36*, 1253.
(7) Okuda, J.; Rushkin, I. L. *Macromolecules* **1993**, *26*, 5530.
(8) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 8296.
(9) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798.
(10) Agarwal, S.; Karl, M.; Dehnicke, K.; Seybert, G.; Massa, W.; Greiner, A. *J. Appl. Polym. Sci.* **1999**, *73*, 1669.
(11) Agarwal, S.; Mast, C.; Dehnicke, K.; Greiner, A. *Macromol. Rapid Commun.* **2000**, *21*, 195−212.
(12) Youqing, S.; Zhiquan, S.; Yifeng, Z.; Kemin, Y. *Macromolecules* **1996**, *29*, 8289.
(13) Yasuda, H.; Ihara, E. *Adv. Polym. Sci.* **1997**, *53*, 133.
(14) Stevels, W. M.; Dijkstra, P. J.; Feijen, J. *TRIP* **1997**, *5*, 300.
(15) Agarwal, S.; Karl, M.; Anfang, S.; Dehnicke, K.; Greiner, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem).* **1998**, *39* (2), 361.
(16) Agarwal, S.; Mast, C.; Anfang, S.; Karl, M.; Dehnicke, K.; Greiner, A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem).* **1998**, *39* (1), 414.
(17) Gröb, T.; Seybert, G.; Massa, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1897.
(18) Gröb, T.; Seybert, G.; Massa, W.; Weller, F.; Ravi, P. Greiner, A.; Dehnicke, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 4373.
(19) Ravi, P.; Dehnicke, K.; Greiner, A., manuscript under preparation.
(20) Dubois, Ph.; Jerome, R.; Teyssie, Ph. *Polym. Prepr.* **1994**, *35* (2), 536.
(21) Ravi, P.; Gröb, T.; Dehnicke, K.; Greiner, A. *Macromol. Chem. Phys.* **2001**, *202*, 2647.
(22) Yuan, M.; Li, X.; Xiong, C.; Deng, X. *E. Polym. J.* **1999**, *35*, 2131.
(23) Gröb, T.; Seybert, G.; Massa, W.; Greiner, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2001**, *627*, 1.
(24) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. K.; Feijen. J. *Polym. Prepr. (Polym. Div., Am. Chem. Soc.)* **1996**, *37* (2), 190.
(25) Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. K.; Feijen. J. *Macromolecules* **1996**, *29*, 3332.
(26) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330.
(27) Agarwal, S.; Brandukova-Szmikowski, N.; Greiner, A. *Macromol. Rapid Commun.* **1999**, *20*, 274.

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