Articles

Ring-Opening Polymerization and Copolymerization of Lactones by Samarium(II) Aryloxide Complexes

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Received January 25, 1999; Revised Manuscript Received May 24, 1999

ABSTRACT: The samarium(II) aryloxide complexes $Sm(OAr)_2(THF)_3$ and $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4) showed an extremely high activity for the ring-opening polymerization of ϵ-caprolactone (CL) and δ-valerolactone (VL). By using $Sm(OAr)_2(THF)_3$ as an initiator, polyesters with very high molecular weight (M_n up to 6×10^5) and relatively narrow molecular weight distributions ($M_w/M_n < 1.65$) could be quantitatively obtained within a few minutes at room temperature. γ-Butyrolactone (BL) did not polymerize under the similar conditions. However, the copolymerization of BL with CL took place under the coexistence of both monomers, which gave CL−BL copolymers in which the BL units all exist in an isolated form, and the CL units all in blocks, as confirmed by the two-dimensional $^1H-^{13}C$ HMQC and HMBC NMR studies. Part of the previously reported ^{13}C NMR spectrum of poly(ϵ-caprolactone) was reassigned on the basis of the two-dimensional $^1H-^{13}C$ HMQC NMR study. In all these polymerization reactions, incorporation of the CH_3O group of quenching methanol into the end of polymer chains was observed.

Introduction

The ring-opening polymerization of lactones is a convenient method for the synthesis of biodegradable polyesters, which are of great potential for applications in various areas such as agriculture and medicine.[1] The polymerization reactions can be achieved by using a variety of metal catalysts,[1−6] among which lanthanide catalysts have received most current interest due to their high activity and the capability of producing narrow polydispersity polymers.[6] Divalent[6a,b] and trivalent[6c−g] lanthanide metallocene complexes and trivalent lanthanide alkoxides[6h−n] are typical examples of the lanthanide initiators for living polymerization of lactones.

As part of our recent studies on lanthanide(II) aryloxide complexes in polymerization reactions,[7,8] we have investigated their activity for the ring-opening polymerization of lactones. In this paper, we report the polymerization and copolymerization of ϵ-caprolactone (CL), δ-valerolactone (VL), and γ-butyrolactone (BL) by the samarium(II) aryloxide complexes $Sm(OAr)_2(THF)_3$[7a] and $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4).[7b] We have found that these easily available samarium(II) aryloxide complexes are extremely active for the polymerization of CL and VL. Compared to most of the previously reported initiators, they show a much higher activity and can produce polymers with very high molecular weights and relatively narrow molecular weight distributions. By using $Sm(OAr)_2(THF)_3$ as an initiator, copolymerization of CL with BL has been achieved, which gives a new type of CL−BL copolymers under the presence of both monomers. Careful examination of the resulting polymers by NMR spectroscopy has led to the discovery of incorporation of the alkoxy groups of quenching alcohols into the end of polymer chains and to reassignment of the previously reported ^{13}C NMR spectrum of poly(ϵ-caprolactone).

Results and Discussion

Polymerizations of ϵ-Caprolactone (CL) and δ-Valerolactone (VL). The polymerization reactions of CL and VL with $Sm(OAr)_2(THF)_3$ were carried out in toluene at room temperature. Upon addition of a monomer, an immediate color change from dark brown to pale yellow was observed, suggesting that the Sm(II) species was converted into a Sm(III) species.[6a] The resulting pale yellow solution became viscous very quickly, which thus seriously hampered the magnetic stirring. Addition of methanol precipitated the colorless polymers.

Representative results of the polymerization of CL and VL are shown in Table 1. The polymerization of 100 equiv of CL by $Sm(OAr)_2(THF)_3$ was completed in less than 2 min, yielding poly(ϵ-caprolactone) with $M_n = 3.4 \times 10^4$ and $M_w/M_n = 1.52$ (run 1, Table 1). When the monomer/initiator ratio was increased, the molecular weight of the resulting polymers also increased almost linearly, with little changes in the molecular weight distributions being observed (runs 1−4, Table 1; see also

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10.1021/ma9901011 CCC: $18.00
Published on Web 11/10/1999

Table 1. Polymerization of ϵ-Caprolactone (CL) and δ-Valerolactone (VL) by Samarium(II) Aryloxide Complexes[a]

run	initiator (mmol)	monomer	[monomer]/[Sm]	time (min)	yield (%)	M_n ($\times 10^{-4}$)[b]	M_w/M_n[b]	efficiency (%)
1	$Sm(OAr)_2(THF)_3$ (0.1)	CL	100	2	100	3.4	1.52	34
2	$Sm(OAr)_2(THF)_3$ (0.1)	CL	500	2	100	15.3	1.43	40
3	$Sm(OAr)_2(THF)_3$ (0.05)	CL	1000	5	100	26.5	1.41	46
4	$Sm(OAr)_2(THF)_3$ (0.02)	CL	2000	5	100	62.6	1.56	38
5	$Sm(OAr)_2(THF)_3$ (0.1)	VL	100	1	95	2.5	1.55	38
6	$Sm(OAr)_2(THF)_3$ (0.1)	VL	500	1	98	11.2	1.62	43
7	$Sm(OAr)_2(THF)_3$ (0.05)	VL	1000	2	95	15.8	1.65	63
8	$[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ (0.02)	CL	500	2	99	12.3	1.40	46

[a] All reactions were carried out at room temperature in toluene (ca. 1 mL per mmol of monomer). [b] Determined by gel permeation chromatography (GPC) against polystyrene standard.

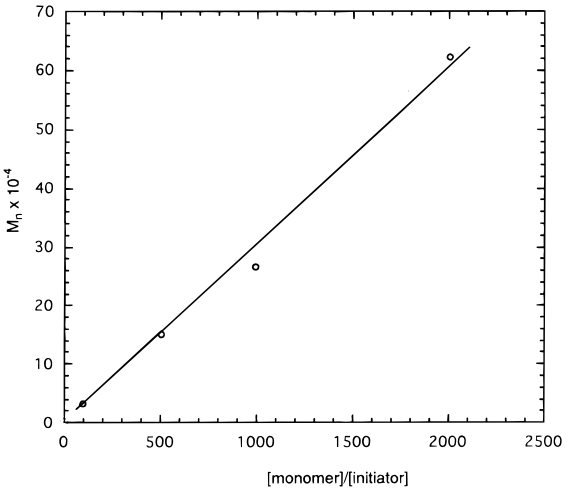


Figure 1. Molecular weight vs monomer-to-initiator ratio for the polymerization of ϵ-caprolactone with $Sm(OC_6H_2\text{-}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2(THF)_3$.

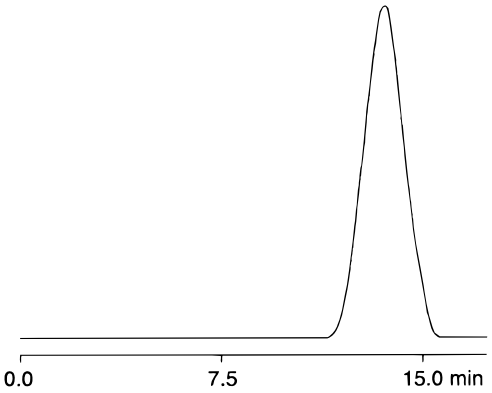
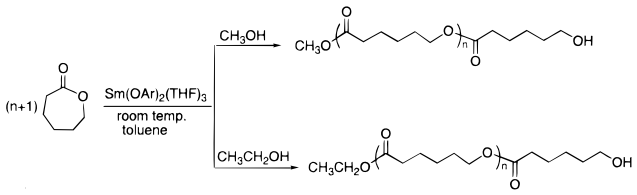


Figure 2. GPC profile of poly(ϵ-caprolactone) with $M_n = 62.6 \times 10^4$ and $M_w/M_n = 1.56$ (run 4, Table 1).

Figure 1). When 2000 equiv of CL was used, a polyester with M_n of as high as 62.6×10^4 and $M_w/M_n = 1.56$ was quantitatively obtained within 5 min (run 4, Table 1). It was also found that the present $Sm(OAr)_2(THF)$-based polymerization system was still active even after complete consumption of the substrate. For example, addition of 100 equiv of CL to a completed polymerization solution of CL (100 equiv) and $Sm(OAr)_2(THF)_3$ produced rapidly a polymer whose molecular weight ($M_n = 6.8 \times 10^4$) was as twice as that ($M_n = 3.4 \times 10^4$) obtained from the initial polymerization solution (cf. run 1, Table 1).

Under similar conditions VL could also be quantitatively polymerized by $Sm(OAr)_2(THF)_3$ within a few minutes. The molecular weight of the resulting poly(δ-valerolactone)s also increased as the monomer/initiator ratio was increased (runs 5−7, Table 1).

Scheme 1



These results clearly demonstrate that the samarium(II) bis(aryloxide) complex $Sm(OAr)_2(THF)_3$ is an extremely active initiator for the polymerization of CL and VL. It is much more active than the previously reported lanthanide metallocene complexes,[6a−g] probably due to the smaller steric hindrance of the ArO ligand compared to that of C_5Me_5.[6a,7c,8] It is also noteworthy that all polymer products obtained in the present reactions showed a unimodal molecular weight distribution (for an example, see Figure 2), which is in contrast with what was observed in the samarocene(II) $(C_5Me_5)_2Sm(THF)_x$-promoted reactions.[6a] The latter yielded polymers showing, to some extent, bimodal molecular weight distributions, due to the degradation of the initially formed polymers by the samarium species.[6a] The present reactions are also in contrast with those promoted by other non-metallocene Sm(II) initiators, such as $Sm(N(SiMe_3)_2)_2(THF)_2$ and $SmI_2(THF)_2$, which produced polymers with much broader polydispersities (around 3.0).[6a]

The C_5Me_5/OAr-ligated heteroleptic Sm(II) complex $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ is also active for the ring-opening polymerization of CL. When 500 equiv of CL was used, poly(ϵ-caprolactone) with $M_n = 12.3 \times 10^4$ and $M_w/M_n = 1.40$ was obtained almost quantitatively in 2 min (run 8, Table 1). Similar to those obtained in the case of $Sm(OAr)_2(THF)_3$, the polymer obtained in this reaction also showed a unimodal and moderately narrow molecular weight distribution, suggesting that ligand redistribution of $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ to give $Sm(OAr)_2$ and $(C_5Me_5)_2Sm$ did not occur during the polymerization.[7b,8]

As for the mechanistic aspects of the present polymerization reactions, it is apparent that the Sm(II) ion was oxidized at the early stage, and the polymerization was probably catalyzed by a Sm(III) species.[6a,9] However, details on the initial step of the polymerization reaction are not yet clear. A careful examination of the polymer products by ^1H NMR spectroscopy has revealed that these polymers all contained a methoxy end group, which appeared as a singlet at δ 3.67 in the ^1H NMR spectrum (Scheme 1 and Figure 3a). When the polymerization was quenched by ethanol instead of methanol, a polymer containing an ethoxy group was obtained, which showed a quartet at δ 4.13 for the CH_2 group and a triplet at δ 1.26 for the CH_3 group (Scheme 1 and Figure 4). Obviously, the methoxy and ethoxy groups

Table 2. Copolymerization of ϵ-Caprolactone (CL) with γ-Butyrolactone (BL) by $Sm(OAr)_2(THF)_3$[a]

run	BL (mmol)	CL (mmol)	time	content of BL (mol %)[b]	conversion of BL (%)	conversion of CL (%)	M_n ($\times 10^{-4}$)[c]	M_w/M_n[c]
1[d]	10	10	10 min	11	8	65	2.6	1.55
2	10	10	10 min	12	9	64	2.8	1.50
3	50	10	2 h	22	3	58	5.7	1.63
4[e]	20	20	10 min	11	8	64	12.9	1.42

[a] All reactions were carried out at room temperature by addition of a mixture of CL and BL to 0.1 mmol of $Sm(OAr)_2(THF)_3$ in toluene (ca. 1 mL of toluene per mmol of a monomer), unless otherwise noted. [b] The content of BL unit in copolymers, determined by ^1H NMR. [c] Determined by gel permeation chromatography (GPC) against polystyrene standard. [d] CL was added to a reaction mixture of $Sm(OAr)_2(THF)_3$ and BL. [e] 0.04 mmol of $Sm(OAr)_2(THF)_3$ was used.

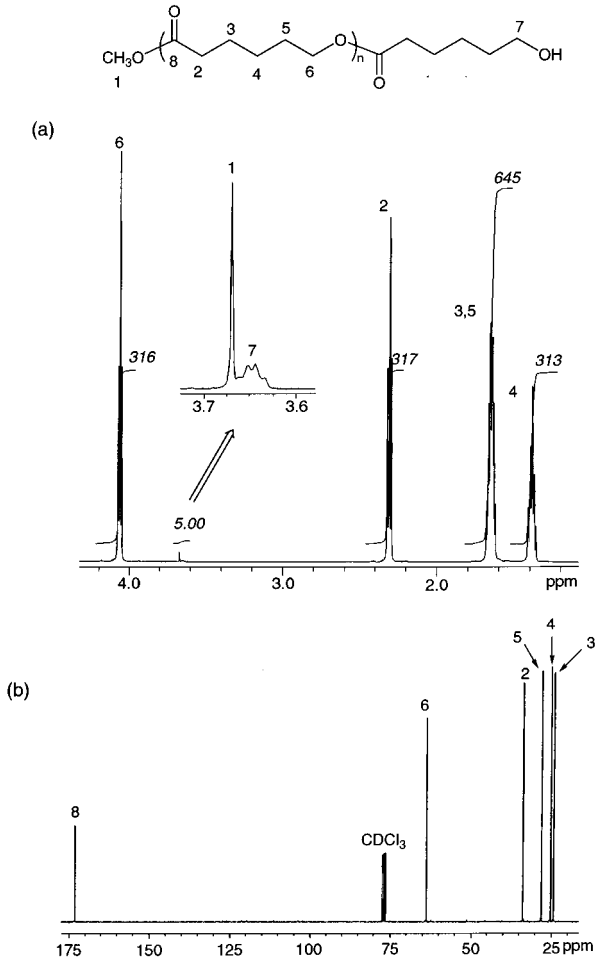


Figure 3. Full assignment of (a) ^1H NMR (600 MHz) and (b) ^{13}C NMR spectra of poly(ϵ-caprolactone) obtained by using $Sm(OC_6H_2$-$^tBu_2$-2,6-Me-4$)_2(THF)_3$ as an initiator and quenching with CH_3OH (cf. run 1, Table 1).

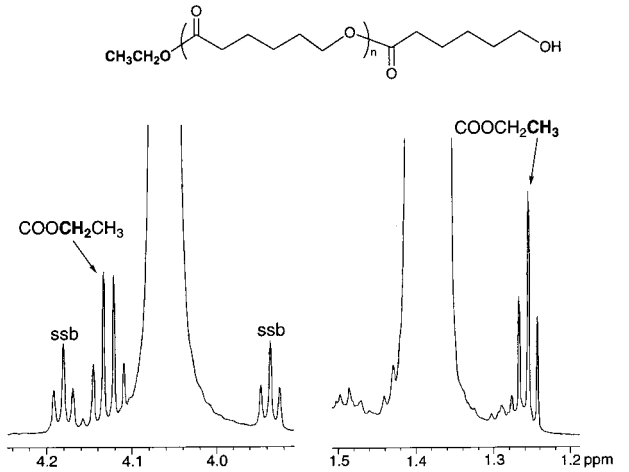


Figure 4. Part of the ^1H NMR spectrum (600 MHz) of poly(ϵ-caprolactone) obtained by using $Sm(OC_6H_2$-$^tBu_2$-2,6-Me-4$)_2(THF)_3$ as an initiator and quenching with CH_3CH_2OH.

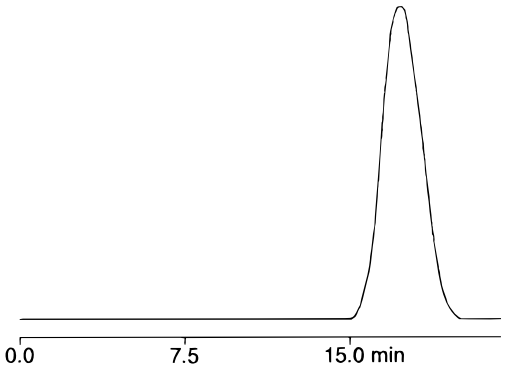


Figure 5. GPC profile of a CL−BL copolymer with $M_n = 2.8 \times 10^4$ ($M_w/M_n = 1.50$) and BL content of 12 mol % (cf. run 2, Table 2).

in these polymers were derived from the corresponding quenching alcohols. The present acylation of methanol and ethanol apparently requires the presence of an electrophilic acyl end group in the original polymer chains. This might suggest that an aryl ester end group (ArOOC) could probably be formed initially via an attack of the ArO group to a CL monomer.[10] However, attempts to gain structural information on the end group of a polymer or oligomer species prior to alcoholysis were not successful due to the influence of the paramagnetic samarium species.

Copolymerization of ϵ-Caprolactone (CL) with γ-Butyrolactone (BL). In contrast to CL (seven-membered ring) and VL (six-membered ring), the five-membered BL is thermodynamically stable and known as a nonpolymerizable monomer.[1a] For example, both CL and VL can be easily polymerized by $(C_5Me_5)_2YOMe$, whereas the reaction of BL with $(C_5Me_5)_2YOMe$ gives only a simple adduct, $(C_5Me_5)_2Y(OMe)(BL)$,[6d] which is stable and does not undergo ring-opening reaction. In an attempt to check the activity of $Sm(OAr)_2(THF)_3$ toward BL, the reaction of $Sm(OAr)_2(THF)_3$ with 100 equiv of BL was carried out in toluene at room temperature. Upon addition of BL an immediate color change from dark brown to pale yellow was observed as in the case of CL and VL. However, no polymer product was obtained. Interestingly, when 100 equiv of CL was added to this yellow reaction mixture, a CL−BL copolymer, which contained 11 mol % of BL unit, was obtained (run 1, Table 2). Addition of a mixture of 100 equiv of CL and 100 equiv of BL to a toluene solution of $Sm(OAr)_2(THF)_3$ also yielded a similar copolymer that contained 12 mol % of BL unit (run 2, Table 2; Scheme 2). When BL was increased from 100 to 500 equiv, the BL content in the copolymers increased from 12 to 22 mol % (run 3, Table 2). The increase of both CL and BL

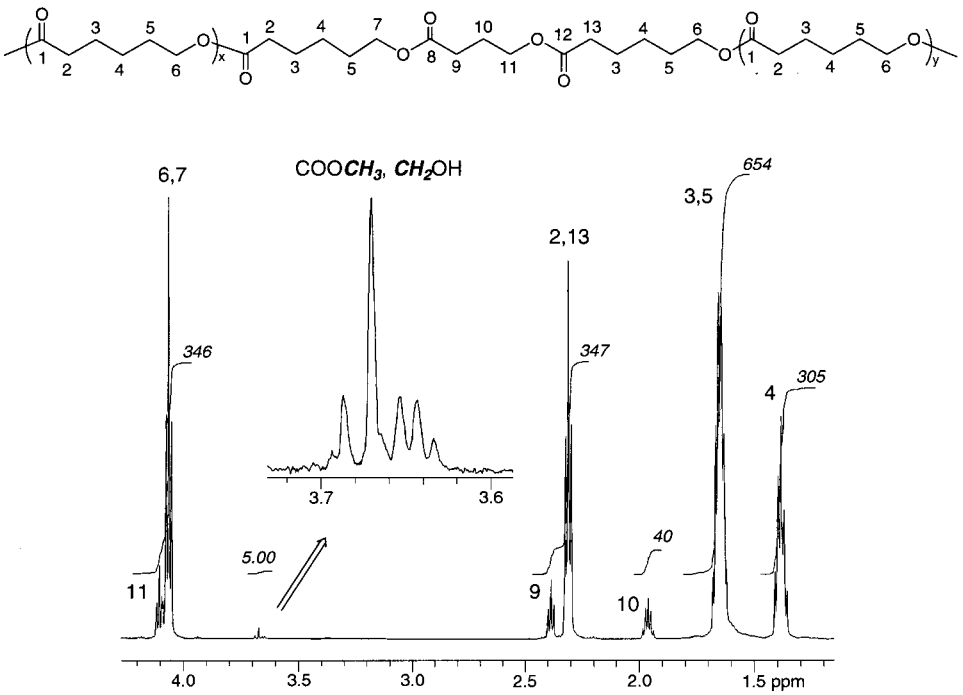


Figure 6. ^{1}H NMR spectrum (600 MHz) of a CL−BL copolymer with $M_n = 2.8 \times 10^4$ ($M_w/M_n = 1.50$) and BL content of 12 mol % (cf. run 2, Table 2).

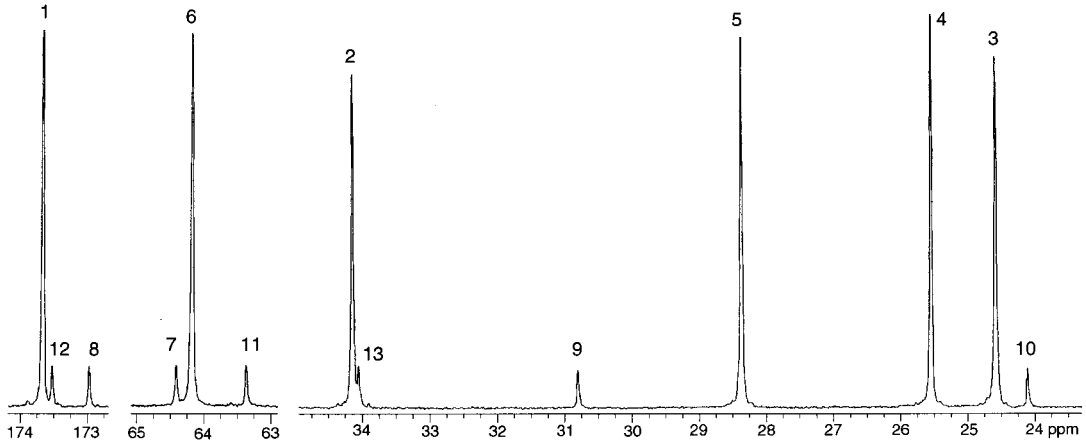
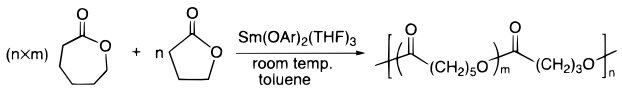


Figure 7. Full assignment of the ^{13}C NMR spectrum of a CL−BL copolymer with $M_n = 2.8 \times 10^4$ ($M_w/M_n = 1.50$) and BL content of 12 mol % (cf. run 2, Table 2).

Scheme 2



from 100 to 500 equiv led to the increase of the molecular weight (M_n) of the resulting copolymers from 3.1×10^4 to 12.9×10^4 (cf. runs 2 and 4, Table 2). The GPC profiles of the copolymer products all showed a unimodal narrow molecular distribution (M_w/M_n = 1.42−1.63). A typical example is shown in Figure 5.

The ^{1}H and ^{13}C NMR spectroscopic studies have shown that these CL−BL copolymers are different from any of the conventional alternating, block or random copolymers. The ^{1}H and ^{13}C NMR spectra of a CL−BL copolymer with BL content of 12 mol % are shown in Figures 6 and 7, respectively. The ^{1}H NMR spectrum showed two sets of signals, which have significantly different intensities (Figure 6). The one set of strong signals at δ 4.06, 2.31, 1.65, and 1.38 was identical with that of homo-poly(ϵ-caprolactone) (PCL) (cf. Figure 3a) and could therefore be assigned to the PCL units of the copolymer, while the other one set of weak signals at δ 4.10, 2.38, and 1.96 could be easily assigned to the BL unit (Figure 6). The significant difference in intensity between these two sets of signals clearly excludes the possibility that the copolymer is an alternating one. The ^{13}C NMR spectrum showed three signals (δ 173.22, 173.07, and 172.52) in the carbonyl carbon region (Figure 7). This suggests that the copolymer is neither block nor random, since a CL−BL block copolymer

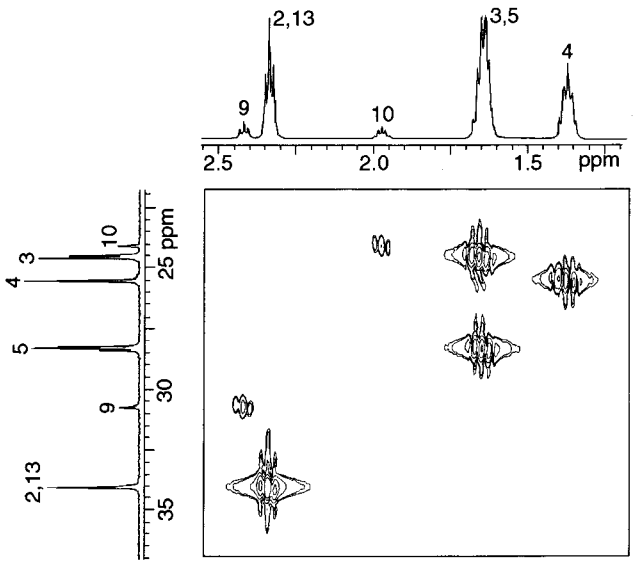


Figure 8. Part of the $^1H-^{13}C$ HMQC NMR spectrum of a CL−BL copolymer with $M_n = 2.8 \times 10^4$ ($M_w/M_n = 1.50$) and BL content of 12 mol % (cf. run 2, Table 2) (see also Figures 6 and 7).

should show four signals (two strong ones for the blocks and two very weak ones for the joint units) in the carbonyl carbon region, while a random CL−BL copolymer would give more complex signals.

Further studies by the two-dimensional $^1H-^{13}C$ HMQC (^1H-detected multiple quantum coherence) and HMBC (^1H-detected multiple-bond heteronuclear multiple quantum coherence) NMR experiments provided more detailed information on the structure of the copolymer. It was revealed that the BL units in the copolymer all exist in an isolated form and the CL units all in blocks; between each two CL blocks is inserted a single BL unit. The full assignment of the ^{13}C NMR spectrum for the CL−BL copolymer is given in Figure 7. The six strong signals at δ 173.22, 64.03, 34.07, 28.31, 25.50, and 24.54 were almost identical with those of homo-poly(ϵ-caprolactone) (PCL) and could therefore be assigned to the PCL units of the copolymer (Figure 7, see also Figure 3b). On the basis of the $^1H-^{13}C$ HMQC NMR spectrum shown in Figure 8, the signals at δ 30.73 and 24.05 could be easily assigned to the carbon atoms 9 and 10, respectively (Figure 7). The $^1H-^{13}C$ HMBC spectrum has shown that the ^{13}C NMR signals at δ 172.52 (Figure 9b) and δ 63.21 (Figure 9a) are both related to the protons on the carbon atoms 9 (δ 2.38) and 10 (δ 1.96). This suggests that the two carbon atoms appearing at δ 172.52 and δ 63.21 are not far from the carbon atoms 9 and 10 in the polymer skeleton and could therefore be assigned to the carbon atoms 8 (δ 172.52) and 11 (δ 63.21), respectively (Figure 7). By comparison with the ^{13}C NMR signals of the PCL units, it is now not difficult to assign the remaining signals at δ 173.07, 64.26, and 33.98 to the carbon atoms 12, 7, and 13, respectively (Figure 7). Furthermore, the HMBC NMR spectrum has shown that the ^{13}C NMR signal for the carbon atom 12 (δ 173.07), which belongs to a CL unit, is related to the protons on the carbon atom 11 (δ 4.10) of a BL unit (Figure 9b). This clearly shows that the CL unit and the BL unit are connected in the polymer.

It is also worthwhile to point out that the ^{13}C NMR signal of the carbon atom 4 (δ 25.50) in the PCL units is low field shifted compared to that of the carbon atom 3 (δ 24.54) (Figures 3b and 7), although the ^1H NMR signal of the protons on the carbon atom 4 (δ 1.38) is high field shifted compared to that on the carbon atom 3 (δ 1.65) (Figures 3a and 6), as confirmed by HMQC NMR spectroscopy (see Figure 8). In previous reports, the ^{13}C NMR signals for these two atoms were incorrectly assigned without confirmation by a two-dimensional $^1H-^{13}C$ NMR experiment.[4a,b,5c,6m]

It was also found that the copolymerization reactions of CL with BL took place only under the coexistence of both monomers. When 100 equiv of BL was added to a reaction mixture of CL (100 equiv) and $Sm(OAr)_2(THF)_3$, in which all the CL monomer had been completely polymerized, the incorporation of BL into the polymer was almost negligible (<1%), although the completed polymerization mixture was confirmed to be active for further polymerization of CL (vide supra). This result

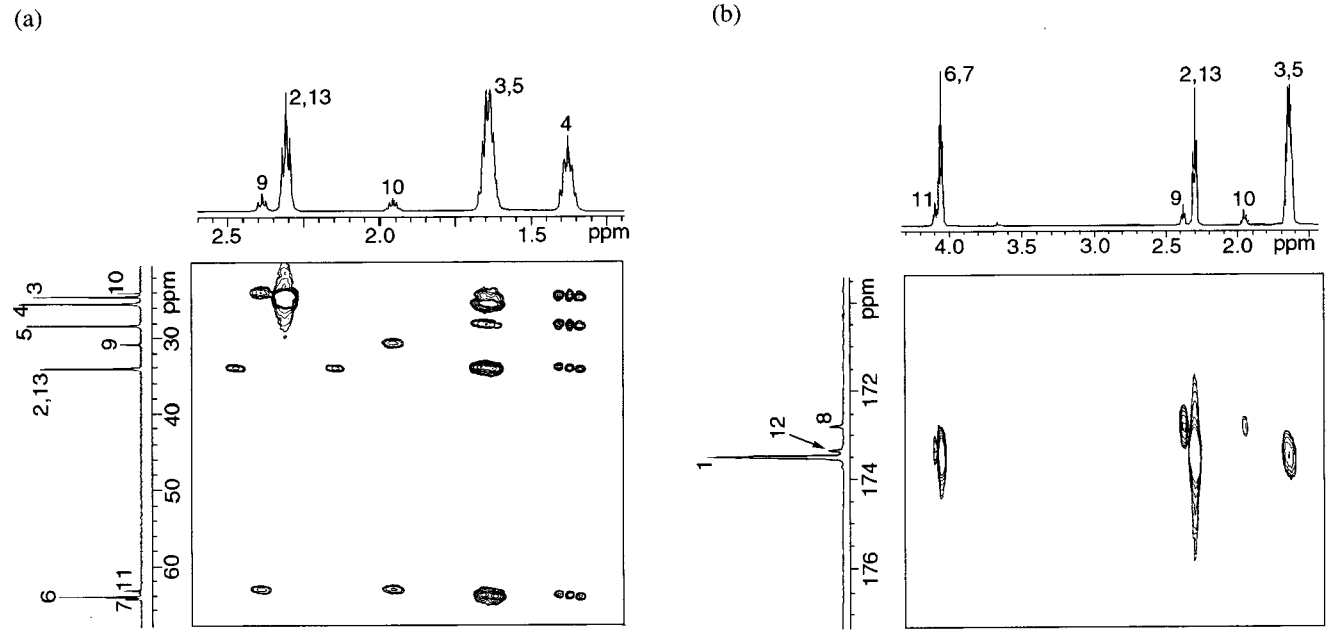


Figure 9. Part of the $^1H-^{13}C$ HMBC NMR spectrum of a CL−BL copolymer with $M_n = 2.8 \times 10^4$ ($M_w/M_n = 1.50$) and BL content of 12 mol % (cf. run 2, Table 2) (see also Figures 6 and 7).

well demonstrated that continuous insertion or polymerization of BL to form a BL block or BL homopolymer was difficult in the present system. This is consistent with the fact that no BL block was observed in the CL−BL copolymers, as well as with the well-known inertness of BL toward homopolymerization.[1a]

Although CL itself could be quantitatively polymerized by $Sm(OAr)_2(THF)_3$ within 5 min in the absence of BL (cf. Table 1), its conversion in the copolymerization reactions was only 65% or less under the similar conditions (see Table 2). Apparently, the polymerization speed of CL became much slower when BL was present. This is probably due to the coordination of the less polymerizable BL to the active Sm center, which interfered with the access of CL to the catalyst center.

As for the mechanistic aspects of the copolymerization, in view of the great difference in reactivity between CL and BL, the copolymerization reaction is probably initiated by polymerization of CL. Since BL is smaller than CL in size, it is easier for BL to access to the metal center than for CL. An attack of the PCL active site to a coordinated BL unit could result in the incorporation of the BL unit into the polymer.[9] Since continuous incorporation of BL does not occur as mentioned above, further propagation of the polymer chain should result from the subsequent insertion of CL units. Repetitions of these processes would give a CL−BL copolymer in which each two CL blocks are connected by a single BL unit.

Concluding Remarks

We have demonstrated that the easily available samarium(II) aryloxide complexes $Sm(OAr)_2(THF)_3$ and $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$ are excellent initiators for the ring-opening polymerization of CL and VL. By using $Sm(OAr)_2(THF)_3$ as an initiator, polyesters with very high molecular weight (M_n up to 6×10^5) and relatively narrow molecular weight distributions ($M_w/M_n < 1.65$) can be quantitatively obtained at room temperature within a few minutes. The copolymerization of CL with BL by $Sm(OAr)_2(THF)_3$ constitutes a rare example of solution copolymerization of the nonpolymerizable BL monomer.[11] The formation of CL−BL copolymers without BL blocks in the present reactions is unique, which is in sharp contrast with what was observed in the case of copolymerization of CL with VL[6d] and the bulk copolymerization of γ-BL with other lactones.[11a,g] The incorporation of the alkoxy groups of quenching alcohols into the polymer chains in the present system is also of interest, which, as far as we are aware, has not been reported previously, although the mechanistic aspects are yet to be clarified.

Experimental Section

All polymerization reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a Mbraun glovebox. The argon was purified by passing through a Dryclean column (4A molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). The nitrogen in the glovebox was constantly circulated through a copper/molecular sieves (4A) catalyst unit. The oxygen and moisture were constantly monitored by an O_2/H_2O Combi-Analyzer to ensure that both were always below 1 ppm. ^1H and ^{13}C NMR spectra were recorded on JNM-LA600 (600.0 MHz for ^1H) and JNM-GSX 270 (67.80 MHz for ^{13}C) spectrometers, respectively. Two-dimensional NMR measurements were carried out on a JNM-LA400 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Molecular weights and molecular weight distributions were determined against polystyrene standard by gel permeation chromatography (GPC) on a Shodex GPC System-11 apparatus with two KF 805L columns. THF was used as an eluent at 40 °C. Toluene for polymerizations was distilled from sodium benzophenone ketyl, degassed by the freeze−thaw method (three times), and dried over fresh Na chips in the glovebox. ϵ-Caprolactone (CL), δ-valerolactone (VL), and γ-butyrolactone (BL) were purchased from Tokyo Kasei Co., dried by stirring with CaH_2 for 24 h, distilled under reduced pressure, and degassed by the freeze−thaw method (three times). $Sm(OAr)_2(THF)_3$ (Ar = $C_6H_2{}^tBu_2$-2,6-Me-4)[7a] and $[(C_5Me_5)Sm(\mu\text{-}OAr)]_2$[7b] were prepared according to literature procedures.

A Typical Procedure for Polymerization Reactions. The procedures for the polymerizations of CL and VL are the same (cf. Table 1), and only a typical procedure for polymerization of CL is given below (run 2, Table 1). In the glovebox, $Sm(OAr)_2(THF)_3$ (80 mg, 0.1 mmol) was dissolved in 50 mL of toluene in a two-neck flask that was equipped with a magnetic stir bar and a dropping funnel containing 5.7 g of CL (50 mmol). The flask was taken outside and connected to a Schlenk line. CL was added through the funnel with vigorous stirring. The color of the mixture changed immediately from dark brown to pale yellow, and the resulting pale yellow solution quickly became viscous. The magnetic stirring was ceased within a minute due to the viscosity. Addition of methanol precipitated poly(δ-caprolactone), which after filtration was dried at 60 °C overnight and weighted (5.7 g, 100% yield). ^1H NMR (22 °C, $CDCl_3$) (see also Figure 3a): δ 4.06 (t, J = 6.8 Hz, 2 H), 2.31 (t, J = 7.5 Hz, 2 H), 1.65 (m, 4 H), 1.38 (m, 2 H). ^{13}C NMR (22 °C, $CDCl_3$) (cf. Figure 3b): δ 173.23, 64.04, 34.09, 28.33, 25.52, 24.57.

^1H NMR for poly(δ-valerolactone) (22 °C, $CDCl_3$): δ 4.08 (t, J = 5.9 Hz, 2 H), 2.34 (t, J = 6.9 Hz, 2 H), 1.68 (m, 4 H).

Quenching of the Polymerization Reaction of CL by Ethanol. The polymerization reaction was carried out in the same way as described above. Addition of ethanol precipitated a polymer whose ^1H NMR spectrum was identical with that of the PCL obtained above, except the part for the ester end group which was shown in Figure 4.

A Typical Procedure for Copolymerization of CL with BL (Run 2, Table 2). In the glovebox, $Sm(OAr)_2(THF)_3$ (80 mg, 0.1 mmol) was dissolved in 20 mL of toluene in a two-neck flask that was equipped with a magnetic stir bar and a dropping funnel containing a mixture of CL (1.14 g, 10 mmol) and BL (0.86 g, 10 mmol). The flask was taken outside and connected to a Schlenk line. The mixture of CL and BL was added through the funnel with vigorous stirring. The color of the mixture changed immediately from dark brown to pale yellow, and the resulting pale yellow solution became viscous. After 10 min, methanol was added to precipitate a colorless polymer, which after filtration was redissolved into $CHCl_3$ and precipitated again with methanol. After filtration and drying under vacuum, 0.80 g of a colorless polymer was obtained. The molar ratio of CL to BL in the polymer was 78:12 as confirmed by ^1H NMR. ^1H NMR (22 °C, $CDCl_3$) (see also Figure 6): δ 1.38 (m, PCL), 1.65 (m, PCL), 1.96 (quintet, J = 6.9 Hz, PBL), 2.31 (t, J = 7.5 Hz, PCL), 2.38 (t, J = 7.7 Hz, PBL), 3.63−3.71 (m, C$\boldsymbol{H_2}$OH), 3.67 (s, OCH_3), 4.06 (t, J = 6.8 Hz, PCL), 4.10 (t, J = 6.6 Hz, PBL). ^{13}C NMR (22 °C, $CDCl_3$) (see also Figure 7): δ 173.22, 173.07, 172.52, 64.26, 64.03, 63.21, 34.07, 33.98, 30.73, 28.31, 25.50, 24.54, 24.05.

Acknowledgment. This work was partly supported by the President's Special Research Grant of The Institute of Physical and Chemical Research (RIKEN) and a grant-in-aid from the Ministry of Education, Science, Sports, and Culture of Japan. T. K. is a Special Postdoctoral Researcher under the Basic Science Program of RIKEN. We are grateful to Katsuo Asakura of Chiba University for the measurements of and helpful discussion on the two-dimensional NMR and 600 MHz ^1H NMR spectra of the polymer products.

References and Notes

(1) For examples, see: (a) Johns, D. B.; Lenz, R. W.; Luick, A. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier Applied Science Publishers: London, Great Britain, 1984; Vol. 1, Chapter 7, p 461. (b) Duba, A.; Penczek, S. *Macromolecules* **1990**, *23*, 1636. (c) Dubois, Ph.; Jacobs, C.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1991**, *24*, 2266. (d) Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419. (e) Gref, R.; Minamitake, Y.; Peracchia, M. T.; Trubetskoy, V.; Torchilin, V.; Langer, R. *Science* **1994**, *263*, 1600. (f) Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* **1997**, *388*, 860. (g) Ni, Q.; Yu, L. *J. Am. Chem. Soc.* **1998**, *120*, 1645.

(2) Jérôme, R.; Teyssié, Ph. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: New York, 1989; Vol. 3, Chapter 34, p 501.

(3) (a) Nomura, R.; Ueno, A.; Endo, T. *Macromolecules* **1994**, *27*, 620. (b) Jedlinski, Z.; Kowalczuk, M.; Kurock, P. *Makromol. Chem. Macromol. Symp.* **1986**, *3*, 277. (c) Inoue, S.; Tomoi, Y.; Tsuruta, T.; Furukawa, J. *Makromol. Chem.* **1961**, *48*, 229.

(4) (a) Kylmä, J.; Seppälä, J. V. *Macromolecules* **1997**, *30*, 2876. (b) Kurcok, P.; Dubois, P.; Sikorska, W.; Jedliñski, Z.; Jérôme, R. *Macromolecules* **1997**, *30*, 5591. (c) Tian, D.; Dubois, Ph.; Jérôme, R. *Macromolecules* **1997**, *30*, 2575. (d) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 1320. (e) Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076. (f) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982. (g) Yasuda, T.; Aida, T.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 3931. (h) Teranishi, K.; Iida, M.; Araki, T.; Yamashita, S.; Tani, H. *Macromolecules* **1974**, *7*, 421. (i) Teranishi, K.; Araki, T.; Tani, H. *Macromolecules* **1972**, *5*, 660.

(5) (a) Vergara, J.; Figini, R. V. *Makromol. Chem.* **1977**, *178*, 267. (b) Trofimoff, L.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991. (c) Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286. (d) Kricheldorf, H. R.; Kreiser-Saunders, I. *Polymer* **1994**, *35*, 4175.

(6) (a) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 2330. (b) Evans, W. J.; Katsumata, H. *Macromolecules* **1994**, *27*, 4011. (c) Boffa, L. S.; Novak, B. M. *Macromolecules* **1994**, *27*, 6993. (d) Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. *Macromolecules* **1996**, *29*, 1798. (e) Yasuda, H.; Ihara, E. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1745. (f) Hultzsch, K. C.; Spaniol, T. P.; Okuda, J. *Organometallics* **1997**, *16*, 4845. (g) Boffa, L. S.; Novak, B. M. *Macromolecules* **1997**, *30*, 3494. (h) McLain, S. J.; Drysdale, N. E. U.S. Patent 5028667, 1991. (i) McLain, S. J.; Foed, T. M.; Drysdale, N. E. *Am. Chem. Soc., Div. Polym. Chem.* **1992**, *33*, 463. (j) Borgne, A. L.; Pluta, C.; Spassky, N. *Macromol. Rapid Commun.* **1994**, *15*, 955. (k) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromol. Chem. Phys.* **1995**, *196*, 1153. (l) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 3332. (m) Stevels, W. M.; Ankoné, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 8296. (n) Deng, X.; Zhu, Z.; Xiong, C.; Zhang, L. *J. Appl. Polym. Sci.* **1997**, *64*, 1295.

(7) (a) Hou, Z.; Fujita, A.; Yoshimura, T.; Jesorka, A.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Inorg. Chem.* **1996**, *35*, 7190. (b) Hou, Z.; Zhang, Y.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963. (c) Hou, Z.; Fujita, A.; Zhang, Y.; Miyano, T.; Yamazaki, H.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1998**, *120*, 754. (d) Yoshimura, T.; Hou, Z.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5382.

(8) (a) Hou, Z.; Tezuka, H.; Zhang, Y.; Yamazaki, H.; Wakatsuki, Y. *Macromolecules* **1998**, *31*, 8650. (b) Zhang, Y.; Hou, Z.; Wakatsuki, Y. *Macromolecules* **1999**, *32*, 939.

(9) For discussions on the mechanism of lanthanide(III) alkoxide-catalyzed ring-opening polymerization of lactones, see refs 6d and 6m.

(10) It was found that the ArO group in $CH_3(CH_2)_7COOAr$ (Ar = C_6H_2-^{t}Bu$_2$-2,6-Me-4) could be replaced by MeO upon reaction with an excess of MeOH.

(11) (a) Lee, C. W.; Urakawa, R.; Kimura, Y. *Macromol. Chem. Phys.* **1997**, *198*, 1109. (b) Kricheldorf, H. R.; Mang, T.; Jonte, J. M. *Makromol. Chem.* **1985**, *186*, 955. (c) Endo, T.; Okawara, M.; Yamazaki, N.; Bailey, W. J. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1283. (d) Bailey, W. J.; Iwama, H.; Tsushima, R. *J. Polym. Sci., Polym. Symp.* **1976**, *56*, 117. (e) Tada, K.; Numata, Y.; Saegusa, T.; Furukawa, J. *Makromol. Chem.* **1964**, *77*, 220. (f) Duda, A.; Penczek, S.; Dubois, P.; Mecerreyes, D.; Jérôme, R. *Macromol. Chem. Phys.* **1996**, *197*, 1273. (g) Nakayama, A.; Kawasaki, N.; Aiba, S.; Maeda, Y.; Arvanitoyannis, I.; Yamamoto, N. *Polymer* **1998**, *39*, 1213.

MA990101L