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Novel Rare Earth Catalysts for the Living Polymerization and Block Copolymerization of ϵ-Caprolactone

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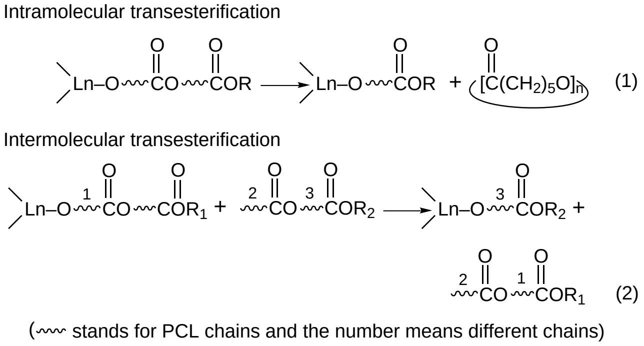
ABSTRACT: The steric effect of bulky groups of the catalyst can kinetically suppress the transesterification reactions by screening linear polymer chains from the active center during the polymerization of ϵ-caprolactone (CL) with rare earth alkoxide. Therefore, isopropoxy rare earth diethyl acetoacetate ($(EA)_2LnOiPr$ Ln = Nd, Y) and $Nd(OiPr)_3$-donor adducts (1,10-phenanthroline, 2,2′-bipyridyl, 18-crown-6 ether) are excellent catalysts for the living polymerization of ϵ-caprolactone, giving poly(ϵ-caprolactone) (PCL) with a narrow molecular weight distribution. Block copolymerizations of ϵ-caprolactone with trimethylene carbonate (TMC) and D,L-lactide (LA) have been attained successfully using $(EA)_2LnOiPr$ as catalyst. The characterizations by GPC, NMR, DSC, and polarizing microscope showed that the block copolymers, P(CL-*b*-TMC) and P(CL-*b*-D,L-lactide), have well-controlled sequences without random placement.

Introduction

Living polymerization is one of the most important achievements in polymer science. Ring-opening polymerization of ϵ-caprolactone (CL) had been carried out with various catalysts,[1] but only a few of them, e.g. aluminum alkoxide,[2] bimetallic μ-alkoxides,[3] porphynatoaluminum,[4] mono(cyclopentadienyl)titanium complexes,[5] and $(C_5Me_5)_2LnMe$ (donor) complexes,[6,7] initiate a living polymerization of ϵ-caprolactone. Mclain's[8] and our study[9,10] showed that the polymerization of ϵ-caprolactone catalyzed by rare earth alkoxide has some living characters, but the molecular weight distribution of poly(ϵ-caprolactone) (PCL) rapidly gets broader after the monomer is completely consumed, which suggests that there occur transfer reactions of active site to the polyester chain, namely transesterifications (eqs. 1 and 2). Both of the side reactions cause production of linear and cyclic oligomers and broadening of the molecular weight distribution of PCL and make it difficult to synthesize block copolymers of CL with other monomers, especially when the polymerization of the comonomer needs to be carried out at higher polymerization temperature.



(〰 stands for PCL chains and the number means different chains)

The transesterifications are rather common during the polymerization of CL by metal alkoxides. The ability of metal alkoxide catalyzing the transesterification relates to both the nature of the metal ion and groups surrounding the ion. Alkali metal alkoxides, known as typical anionic catalysts for the polymerization of ϵ-caprolactone, cause rapid backbiting degradation of PCL chains, resulting in a living ring−chain equilibrium system.[11,12] Transesterifictions by transition metal alkoxides are much slower than that with alkali metal alkoxides,[13] and aluminum alkoxide rarely causes the side reactions.[13,14] Groups attached to the ion of the catalyst also greatly influence the transesterification. For example, potassium dendritic alcoholate greatly suppress the reactions in comparison with the very rapid backbiting degradation by KO^tBu.[15] The transesterifications of PCL by titanium alkoxide ($Ti(OR)_4$) are fast,[13] but $Ti(\mu_5\text{-}C_5H_5)Cl_2OCH_3$ initiates the living polymerization of CL.[5] Another example is metallic porphyrin alkoxide, an excellent catalyst for the living polymerization of CL.[4] The large porphyrin ring might play an important role during the living polymerization.

Scheme 1. A Descriptive Diagram of the Effect of Catalyst Groups on the Transesterification

Taking into consideration that the volume of the polymer chain is much larger than that of the monomer, we suppose that bulky groups surrounding the active center of catalyst might hinder the polymer chain from access to the active center so that transesterifications are reduced (Scheme 1). Thus, we have prepared two kinds of rare earth catalysts with bulky coordinate groups, isopropoxy rare earth diethyl acetoacetate ($(EA)_2LnOiPr$) and neodymium isopropoxide-donor adducts, and have found that they are good catalysts for the living polymerization of ϵ-caprolactone. This paper reports the characteristics of the living polymerization and block copolymerization of ϵ-caprolactone with the two new catalysts.

Experimental Section

Materials. ϵ-Caprolactone (Mitsubishi) and γ-butyrolactone (γ-BL) were dried by refluxing over CaH_2 and distilled under reduced pressure, respectively. THF and benzene were

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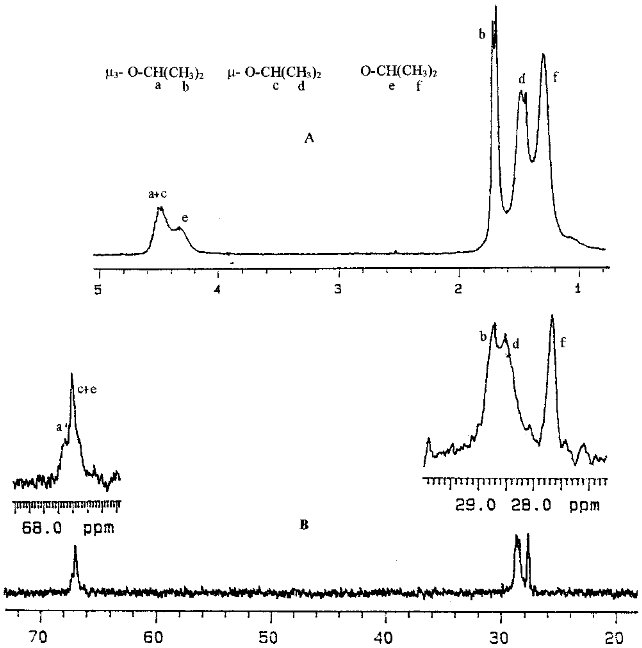

Figure 1. (A) ^{1}H- and (B) ^{13}C-NMR spectra of yttrium isopropoxide (Solvent: CCl_4). (Signals are assigned according to ref 21.)

distilled over the blue benzophenone−Na complex before use. Ethyl acetoacetate (Etacac) and 2-propanol were dried by adding a small piece of sodium and distilled, respectively. 1,10-Phenanthroline (phen) and 2,2′-bipyridyl (bip) were purified by sublimation. 18-Crown-6 ether (crown) was dried in vacuum. Rare earth oxides (99.99%) were purchased from Shanghai Yaolong factory.

Monomer Syntheses. D,L-Lactide was synthesized from lactic acid according to a known method.[16] It was recrystallized three times from ethyl acetate and dried under reduced pressure. After purification, the melting point of D,L-lactide was within 126−128 °C. Trimethylene carbonate (TMC) was prepared by the exchange reaction between 1,3-propanediol and diethyl carbonate,[17] purified by recrystallization from ethyl ether, and dried in vacuum. D,L-Lactide and TMC were further dried with CaH_2 as per following procedure: D,L-LA or TMC was dissolved in THF. The solution was carefully refluxed over CaH_2 about 4 h, filtered under nitrogen atmosphere, then concentrated and cooled to 0 °C. The strictly dried monomer was separated out under nitrogen atmosphere and the solvent was dried away in vacuum.

Catalyst Preparation. All catalyst preparations were performed using Schlenk tubes and vacuum-line techniques under purified nitrogen. Anhydrous rare earth chlorides were prepared by heating the mixture of hydrated rare earth chloride and ammonium chloride under reduced pressure.[18]

Rare earth isopropoxides were synthesized by the reaction of anhydrous rare earth chloride and sodium isopropoxide:[19] Anhydrous rare earth chloride (0.10 mol) was dissolved in refluxing 2-propanol. A solution of sodium isopropoxide (0.30 mol), prepared by dissolving metallic sodium in a mixture of 2-propanol and benzene (1/1 in volume), was added to the $LnCl_3$ solution and refuxed for 3 h. After being cooled to room temperature, sodium chloride was separated out and the solution was concentrated. On cooling, a crystalline of rare earth isopropoxide separated out from the solution and was isolated. The final rare earth isopropoxides were dried in high vacuum to dry away solvent and 2-propanol. (Elemental analysis: $Nd(OiPr)_3$: Nd, 45.07; C, 32.22; H, 6.40. $Y(OiPr)_3$: Y, 33.87; C, 39.21; H, 7.75. ^{1}H- and ^{13}C-NMR spectra of $Y(OiPr)_3$ are shown in Figure 1.) The elemental analysis of neodymium isopropoxide is consistent with the literature data,[20] which indicated that neodymium isopropoxide prepared by this method actually is a cluster, $Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OiPr)_2(\mu\text{-}OiPr)_9(OiPr)_6$. There is no report about the structure of yttrium isopropoxide prepared by the reaction between YCl_3 and NaOiPr, but Figure 1 shows that the obtained yttrium isopropoxide is also a cluster, similar to that isolated from the reaction of yttrium metal in 2-propanol.[21] In this paper, we use $Ln(OiPr)_3$ to stand for the rare earth isopropoxides prepared by the above method in spite of their structures.

Isopropoxy rare earth diethyl acetoacetate was prepared by the exchange reaction of rare earth isopropoxide with ethyl acetoacetate:[22] Into a benzene solution of $Ln(OiPr)_3$ (0.025 mol) was dropped a benzene solution containing 0.05 mol of ethyl acetoacetate with stirring. The reaction mixture was refluxed for 4 h, during which the binary azeotrope of benzene−isopropanol was fractionated out at 72 °C. The solution was concentrated and cooled. The solid compound was isolated and dried in high vacuum at room temperature. ^{1}H-NMR of $(CH_3)_2CHOY[CH_3C(O)CHC(O)OCH_2CH_3]_2$: 5.1 ppm (1H), $OCH(CH_3)_2$; 4.90 ppm (2H), $C(O)CHC(O)$; 2.05 ppm (6H), $CH_3C(O)$; 4.37 ppm (4H), OCH_2; 1.2−1.6 ppm, (12H), OCH_2CH_3 and $OCH(CH_3)_2$. Elemental analysis: $Y(OC_3H_7)(O_3C_6H_9)_2$: Y, 21.86; C, 44.42; H, 6.11. $Nd(OC_3H_7)(O_3C_6H_9)_2$: Nd, 31.33; C, 39.03; H, 5.41. The ^{1}H-NMR spectrum and elemental analyses show that the prepared isoproxy rare earth (Nd and Y) diethyl acetoacetate are consistent with their chemical formulas.[22]

Preparation of donor adducts of neodymium isopropoxide. Adducts of $Nd(OiPr)_3$ with 18-crown-6 ether and 2,2′-bipyridyl were prepared in THF: A THF solution containing a stoichiometric amount of the donor was added to the $Nd(OiPr)_3$−THF solution and refluxed. Afterward, a small amounts of γ-BL was added and aged for 24 h. The above complexes are soluble in THF. $Nd(OiPr)_3$−1,10-phenanthroline complex was prepared by a similar method, but γ-butyrolactone was used as solvent instead of THF because the complex is insoluble in THF.

Polymerization. Polymerization was carried out in a previously flamed and nitrogen-purged glass reactor. Monomer, solvent, and catalyst solution were introduced into the reactor with stirring under a dried nitrogen atmosphere. After a determined time, methanol containing 5% aqueous HCl was quickly added to the reactor to terminate the reaction, then the mixture was poured into a large excess of methanol. The polymer was isolated, washed with methanol, and dried at 30 °C in vacuum.

Block copolymerization. The block copolymerization was carried out in a small Schlenk tube. The prepolymer with a narrow molecular weight distribution was prepared as above by the homopolymerization of the first monomer (A) initiated by $(EA)_2LnOiPr$, then the second monomer (B) was introduced to the prepolymer by Schlenk methods with rapid stirring and polymerized at 50 or 70 °C. After a proper time, the polymerization was terminated with methanol containing 5% HCl, then the following copolymer treatments were similar to that of the homopolymer. The copolymers P(CL-*b*-TMC) and P(CL-*b*-D,L-LA) were extracted by CCl_4 or acetone to free the homopolymers, respectively.

Measurements. ^{1}H- and ^{13}C-NMR spectra were recorded in CCl_4 or $CDCl_3$ on a Unity 200 spectrometer using TMS as internal standard. The number-average molecular weight and molecular weight distribution of the polymer were determined with gel permeation chromatography (Waters 150, column size 10^2, 5×10^2, 10^3, 10^4 Å) in THF at 25 °C using polystyrene as standard. Molecular weights of PCL were corrected by universal calibration method. Thermal properties of the copolymer were measured on a Perkin-Elmer DSC-7. The sample was quenched to −100 °C and maintained at this temperature for 3 min and then heated at a rate of 20 °C per min. The microphotograph of P(CL-*b*-LA) was take on a Olympus BH-2 polarizing microscope at ambient temperature.

Results and Discussion

Polymerization of ϵ-caprolactone with the $(EA)_2LnOiPr$ (Ln = Nd, Y) System. Figure 2 shows the time−conversion curves of CL polymerization with $(EA)_2NdOiPr$ and $(EA)_2YOiPr$. Both polymerizations proceed rapidly up to 100% conversion at room temperature. CL polymerization with $(EA)_2YOiPr$ is a little slower than that with $(EA)_2NdOiPr$, which might be due to the smaller ionic radius of the yttrium ion.[10] Figure 3 shows that number-average molecular weights of PCL

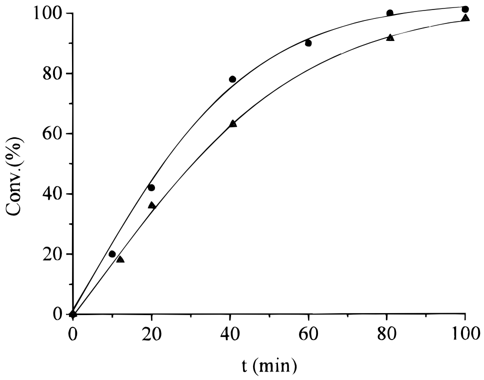

Figure 2. Time−conversion curves of ϵ-caprolactone polymerization catalyzed by $(EA)_2LnOiPr$. $[(EA)_2LnOiPr] = 2.45 \times 10^{-3}$ mol/L, [CL] = 1.47 mol/L, 25 °C, THF; ●, $(EA)_2NdOiPr$; ▲, $(EA)_2YOiPr$.

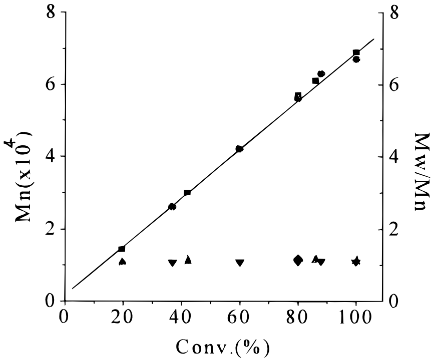

Figure 3. Relationship between molecular weight and molecular weight distribution of PCL and the conversion of ϵ-caprolactone in CL polymerization catalyzed by $((EA)_2$ LnOiPr. Conditions are the same as in Figure 2. ■, ▲, $(EA)_2NdOiPr$; ●, ▼, $(EA)_2YOiPr$.

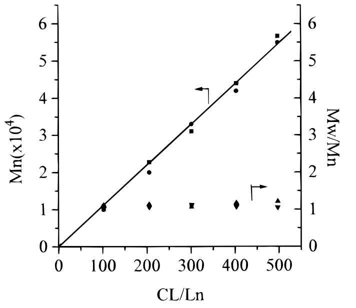

Figure 4. The dependence of molecular weights of PCL on CL/Ln ratios. $[(EA)_2LnOiPr] = 2.45 \times 10^{-3}$ mol/L, [CL] = 1.47 mol/L, 25 °C, THF; ■, ▲, $(EA)_2NdOiPr$; ●, ▼ $(EA)_2YOiPr$.

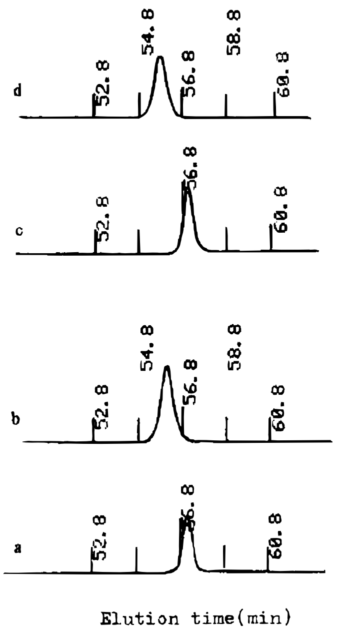

Figure 5. GPC curves of PCL obtained by sequential polymerization of ϵ-caprolactone: (a) first stage, PCL at 100% conversion, CL/Nd = 100, 60 min, $M_n = 10\,470$, $M_w/M_n = 1.07$, (b) second stage, PCL at 100% conversion, CL/Nd = 100, 60 min, $M_n = 22\,140$, $M_w/M_n = 1.11$, (c) first stage, PCL at 100% conversion, CL/Nd =100, 60 min, $M_n = 11\,700$, $M_w/M_n = 1.05$, (d) second stage, PCL at 100% conversion, CL/Nd = 100, 60 min, $M_n = 23\,340$, $M_w/M_n = 1.10$. Catalyst: a, b, $[(EA)_2NdOiPr]$; c, d, $[(EA)_2YOiPr]$. Conditions: 25 °C, THF, $[(EA)_2LnOiPr] = 4.45 \times 10^{-3}$ mol/L.

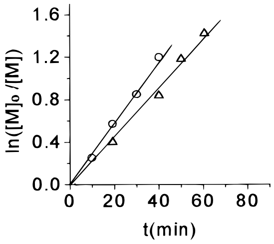

Figure 6. $\ln([M]_0/[M])$ as a function of time in ϵ-caprolactone polymerization. Conditions are the same as in Figure 2. ○, $(EA)_2NdOiPr$; △, $(EA)_2YOiPr$.

increase linearly with the conversion of CL. Molecular weight distributions of polymers stay very narrow (smaller than 1.10) throughout the polymerization.

The dependence of molecular weights of PCL on monomer/catalyst ratios (CL/Nd or CL/Y) is shown in Figure 4. Polymerization degrees (DP) of PCL measured by GPC are consistent with CL/Ln ratios. Moreover, PCL samples obtained at various CL/Ln ratios all have the same narrow molecular weight distributions ($M_w/M_n < 1.10$).

After consumption of a CL feed by the catalysis of $(EA)_2NdOiPr$ or $(EA)_2YOiPr$, another portion of CLwas introduced. The fresh monomer was also rapidly polymerized up to 100% conversion in 1 h at room temperature. The GPC elution curves (Figure 5) show that molecular weights of PCL obtained at every polymerization stage are consistent with the corresponding CL/Ln, maintaining a narrow molecular weight distribution. No oligomers were detected in the polymerization mixture, as shown by the absence of any peak in the lower molecular weight region of the GPC chromatography.

The kinetics of ϵ-caprolactone polymerization with $(EA)_2LnOiPr$ in THF at room temperature was also investigated. The linear plots of $\ln([M]_0/[M])$ versus t indicate that the polymerization is first-order in monomer (Figure 6). The first order in catalyst is also obtained from the slopes of the plots in Figure 7. Therefore, the polymerization of ϵ-caprolactone catalyzed by $(EA)_2LnOiPr$ proceeds according to a simple overall kinetic law as described by eq 3.

$$Rp = d[CL]/dt = k[CL][(EA)_2LnOiPr] \qquad (3)$$

Generally, the polymerization of CL shows fractional or high (close to 2) order in catalyst if the catalyst aggregates in the polymerization solution.[23,24] Therefore the kinetic equation (3) shows that, under the polymerization conditions, $(EA)_2LnOiPr$ is monomeric, rather than aggregated in the polymerization media. This disassociated structure is very important for the sequential block copolymerization because, during the

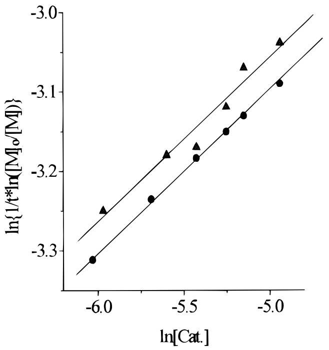

Figure 7. $\ln\{1/t \ln([M]_0/[M])\}$ as a function of ln[cat.] in CL polymerization. [CL] = 1.47 mol/L, 20 °C, THF. ▲, $(EA)_2NdOiPr$; ●, $(EA)_2YOiPr$.

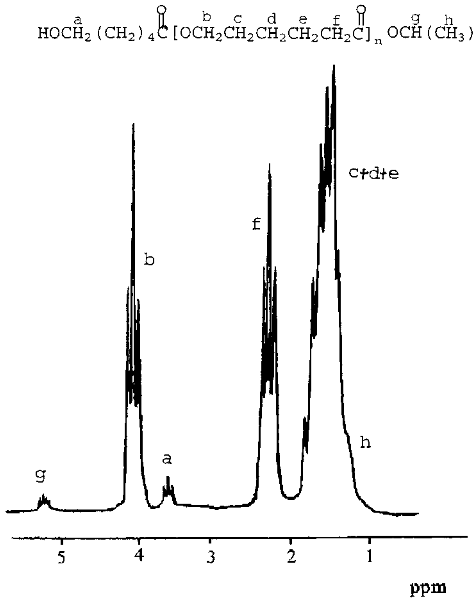

Figure 8. ^{1}H-NMR of PCL obtained by $(EA)_2YOiPr$.

block copolymerization, the association of the catalyst will lead to formation of homopolymer.[25]

Figures 3 and 4 demonstrate that one $(EA)_2LnOiPr$ molecule initiates one PCL chain. The ^{1}H-NMR spectrum of PCL obtained with $(EA)_2YOiPr$ shows that only isopropoxy ester ($COOCH(CH_3)_2$, 5.02 ppm) and hydroxylmethylene (CH_2OH, 3.6 ppm) end groups are present (Figure 8), suggesting that only the isopropoxy group in $(EA)_2LnOiPr$ initiates the polymerization of CL, while ethyl acetoacetate groups do not because of their stable coordination with Ln^{3+}. In fact, yttrium or lanthanum triethyl acetoacetate ($Ln(EA)_3$) cannot initiate the polymerization of CL under the same conditions. So the monomeric structure of $(EA)_2LnOiPr$ and the process of CL polymerization by this compound can be depicted as in Scheme 2.

Block Copolymerizations of ε-Caprolactone with Trimethylene Carbonate (TMC) and D,L-Lactide (D,L-LA). Taking advantage of the living polymerization, block copolymers of CL with oxirane,[4] lactide,[25] and 5,5-dimethyl trimethylene carbonate[26] have been synthesized. By one-step polymerization, Endo et al. obtained the block copolymer of TMC with oxetane.[27] Although some papers reported random copolymerizations of CL with TMC,[28] ethylene carbonate,[29] and 5,5-dimethyl trimethylene carbonate,[30] to our knowledge, there is no report about the block copolymerization of CL with TMC. Using the living nature of CL polymerization by $(EA)_2LnOiPr$, the block copolymers of CL with TMC and D,L-lactide has been successfully synthesized, as shown in Table 1.

Figure 9 clearly shows that GPC elution curves of the copolymers obtained after the completion of the second polymerization stage shift to a higher molecular weight region. The narrow molecular weight distribution and the symmetric GPC curves of the copolymers corroborate the absence of homopolymers in the products. In fact, extraction experiments did not show any homopolymers in either P(CL-*b*-TMC) or P(CL-*b*-D,L-LA).

Figure 10 is the ^{1}H-NMR spectra of P(CL-*b*-TMC) and P(CL-*b*-D,L-lactide) copolymers and signal assignments.[25,28] The compositions of copolymers can be directly calculated by the integration ratios of signals at 2.3 ppm (PCL) to 2.05 ppm (PTMC) in P(CL-*b*-TMC) and 4.0 ppm (PCL) to 5.2 ppm (PLA) in P(CL-*b*-D,L-lactide). The figure shows that the sequential block copolymerization of ε-caprolactone with trimethylene carbonate and D,L-lactide catalyzed by $(EA)_2LnOiPr$ can be perfectly controlled.

For comparison, the ^{13}C-NMR spectra of block and random copolymers of CL with TMC and CL with D,L-LA are shown in Figures 11 and 12, respectively. In the spectrum of P(CL-*b*-TMC), carbonyl signals of PCL (173.4 ppm) and PTMC (154.9 ppm) blocks do not split, and no signals appear at 64.58 and 60.6 ppm, while the splitting of carbonyl signals and signals at 64.58 and 60.6 ppm are the characteristics of random copolymer of CL-TMC (Figure 11B).[28,31] Similarly, no signals due to the random sequences of CL with D,L-LA appear between 173.4 and 169.7 ppm[32] (carbonyl group in PLA block) in the spectrum of P(CL-*b*-D,L-lactide) spectrum. These observations demonstrate that the two kinds of block copolymer are free of any random sequence.

The DSC curves of the copolymers are given in Figure 13. P(CL-*b*-TMC) copolymer shows two glass transition temperatures at −63 and −28 °C, corresponding to the amorphous phases of PCL block and PTMC block,[28] respectively. The melting endotherm (T_m = 62 °C) is derived from the fusion of spherocrystals of PCL block in P(CL-*b*-TMC), which can be clearly seen by the polarizing microphotograph (Figure 14). Besides the T_g and T_m transitions of PCL block, P(CL-*b*-D,L-LA) has the glass transition (ca. 50 °C) of the PLA block, but overlapped by the melting transition of the PCL block. PCL spherocrystals of PCL block in P(CL-*b*-LA) seen by SEM is similar to that in the ref.[31] These thermal behaviors of the block copolymers are very different from that of corresponding random copolymers, the T_g values of which fall between those of PCL and PTMC or PLA, and no melting endotherm appears when the compositions of the random copolymers are 50 to 50 (Figure 13, lines C and D).

Therefore, the results of ^{13}C-NMR spectra and DSC clearly indicate that the block copolymers P(CL-*b*-TMC) and P(CL-*b*-D,L-LA) prepared by $(EA)_2LnOiPr$ are pure block copolymers. The success of sequential block copolymerizations of ε-caprolactone with trimethylene carbonate and D,L-lactide confirms the living character of ε-caprolactone polymerization with $(EA)_2LnOiPr$.

Table 1 also shows that the polymerization order of comonomers does not affect the block copolymerization of CL with TMC. The block copolymers of P(CL-*b*-TMC) could be formed by either CL or TMC being firstly polymerized. However, the copolymerization order is of critical importance in CL-LA block copolymerization: Active species obtained by CL being firstly polymerized ($PCL\text{-}OLn(EA)_2$)) initiated the polymerization of D,L-LA, giving block copolymer of well-controlled chain lengths. In contrast, active species resulting from

Scheme 2. The Descriptive Structure of $(EA)_2LnOiPr$ (a) and the Process of CL Polymerization with This Compound

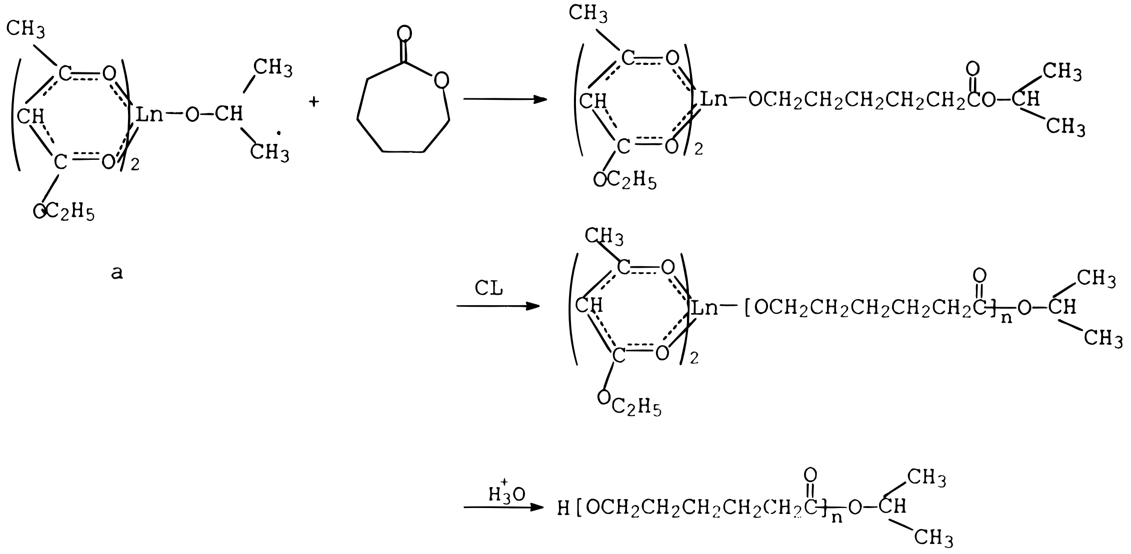

Table 1. Block Copolymerization of ϵ-Caprolactone with TMC and D,L-Lactide Catalyzed by $(EA)_2LnOiPr^a$

	comonomer		first-stage polymerization					second-stage polymerization				
catalyst	A	B	temp (°C)	time (h)	conv (%)	M_n (×10^4)	M_w/M_n	temp (°C)	time (h)	conv (%)	M_n (×10^4)	M_w/M_n
$(EA)_2YOiPr$	CL	TMC	20	0.5	100	2.2	1.08	50	12	95	4.5	1.25
	TMC	CL	50	12	95	2.1	1.25	50	5	100	4.5	1.35
	CL	LA	20	0.5	100	2.1	1.07	70	12	91	5.2	1.31
	LA	CL	70	12	94	2.7	1.28	70	12	0		
$(EA)_2NdOiPr$	CL	TMC	20	0.5	100	2.1	1.09	50	8	90	4.4	1.45
	TMC	CL	50	10	92	2.0	1.49	50	2	100	4.3	1.45
	CL	LA	20	0.5	100	2.2	1.08	70	12	90	5.1	1.38
	LA	CL	70	12	97	2.8	1.38	70	12	0		

[a] Copolymerization conditions: $[(EA)_2LnOiPr] = 5.0 \times 10^{-3}$ mol/L, A/Ln = 200, B/Ln = 200.

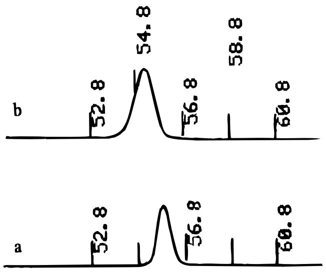

Figure 9. GPC curves of the block copolymerizations of CL with $(EA)_2LnOiPr$. Sample, Table 1, no. 1; others (Table 1, nos. 2, 3, 5, 6, and 7) are similar to this curve: (a) prepolymer and (b) copolymer.

D,L-LA (PLA-OLn$(EA)_2$)) failed to initiate the polymerization of CL. This result is similar to those of Teyssie, who used $Al(OiPr)_3$ as catalyst,[25] and that of Yasuda about the block copolymerization of MMA with lactones.[7] The polymerization order of comonomers in the sequential block copolymerization is related to the relative reactivities of comonomers. It has been demonstrated that the reactivity of ϵ-caprolactone is similar to that of trimethylene carbonate,[31] but largely smaller than that of D,L-lactide[32] in their copolymerization with rare earth catalysts.

Living Polymerization of ϵ-Caprolactone with $Nd(OiPr)_3$-Donor Adducts. The above results indicate that the coordinate groups on rare earth ions, ethyl acetoacetate, can reduce the transesterification so that living polymerization of CL is achieved. Another convenient route to introduce bulky groups to Ln^{3+} is by the coordination reaction of donor with rare earth isopropoxide. However, Poncelet et al.[21] has pointed that the cluster of yttrium isopropoxide ($Y_5(\mu_5\text{-}O)(\mu_3\text{-}OiPr)_4(\mu_2\text{-}OiPr)_4(OiPr)_5$) does not react with the weak donor reagents, such as THF, $MeOCH_2CH_2OMe$, and pyridine, due to shielding by a layer of isopropyl groups. So stronger donor is needed for the complexation.

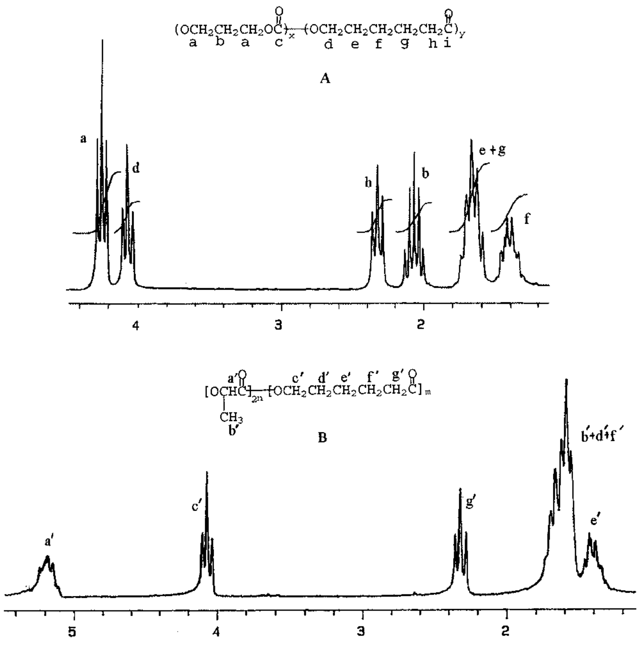

Figure 10. ^1H-NMR spectra of P(CL-*b*-TMC) (A) and P(CL-*b*-D,L-lactide) (B). Samples: A, Table 1, no. 1.; B, Table 1, no. 3.

Figure 15 is the ^1H-NMR spectrum of $Y(OiPr)_3$-2,2′-bipyridyl. In comparison with the NMR spectra of pure $Y(OiPr)_3$ (Figure 1), it can be seen that the presence of 2, 2′-bipyridyl decreases intensities of signals of μ_3-OiPr

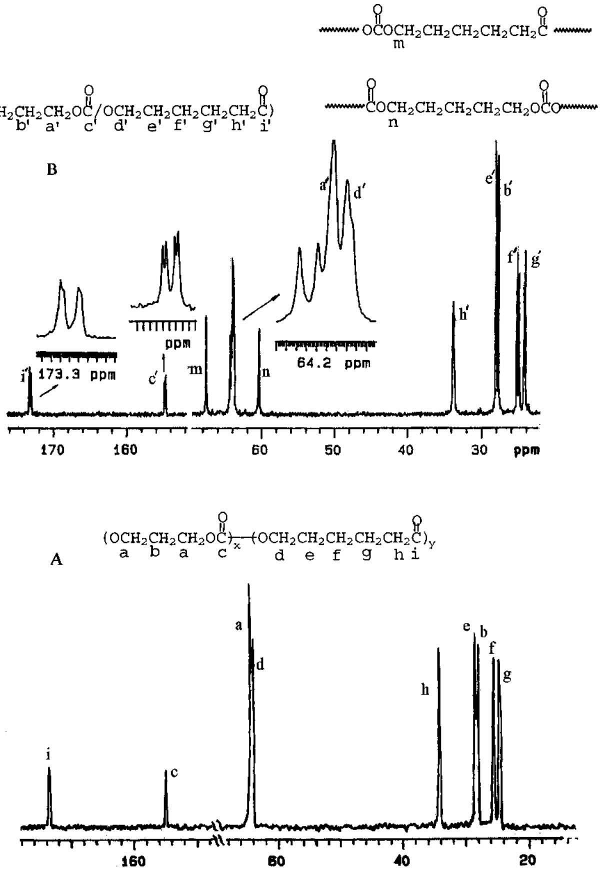

Figure 11. ^{13}C-NMR spectra of block (A) and random (B) copolymers of CL with TMC. Samples: A, P(CL-*b*-TMC), Table 1, no. 1; B, P(CL-*co*-TMC).[31] (Signals assigned according to refs 28 and 31.)

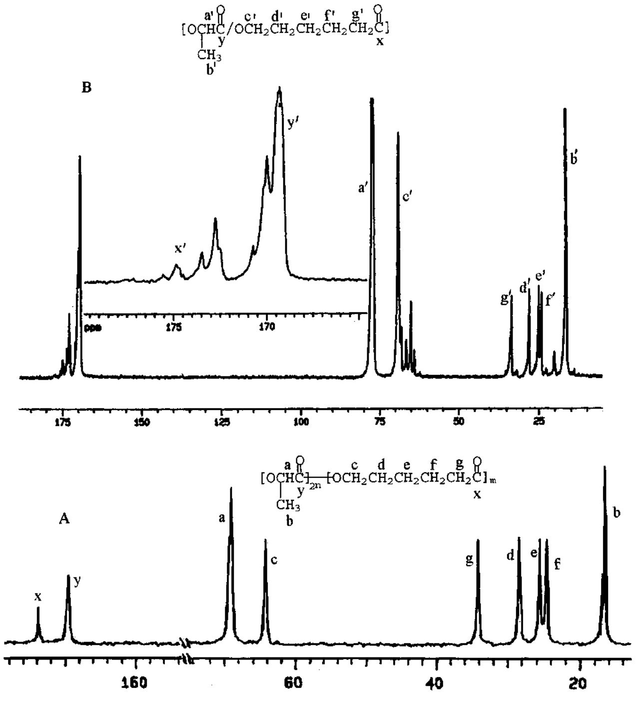

Figure 12. ^{13}C-NMR spectra of block (A) and random (B) copolymers of CL-D,L-LA. Samples: A, P(CL-*b*-D,L-LA), Table 1, no. 3.; B, P(CL-*co*-D,L-LA).[32] (Signals are assigned according to refs 32 and 33.)

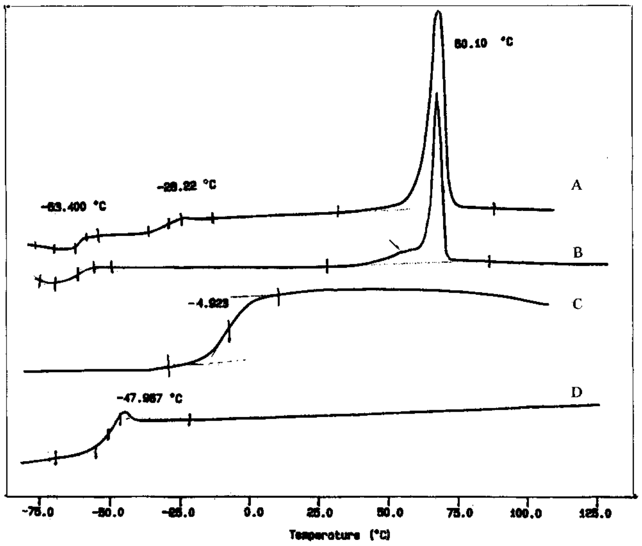

Figure 13. DSC curves of copolymers of CL with TMC and D,L-LA. Samples: A, P(CL-*b*-TMC), Table 1, no. 1; B, P(CL-*b*-D,L-LA), Table 1, no. 3; C, P(CL-*co*-D,L-LA), CL/LA = 50/50; D, P(CL-*co*-TMC), (CL/TMC = 50/50). (The random copolymers of CL- TMC and CL-D,L-LA were prepared by bulk copolymerization of the corresponding monomers.[31,32])

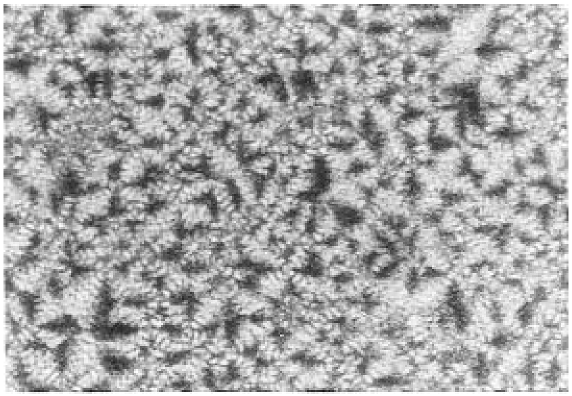

Figure 14. Polarizing microphotograph of poly(CL-*b*-TMC). Sample: Table 1, no. 1.

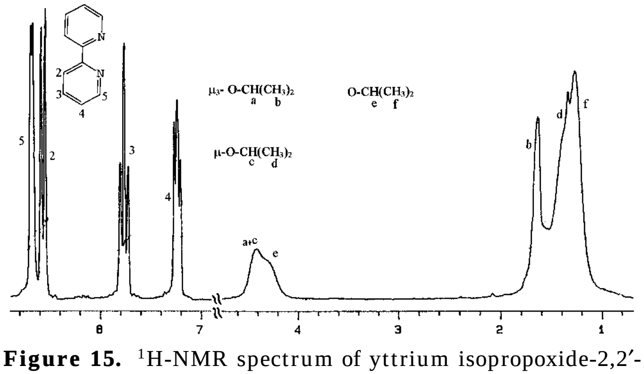

Figure 15. ^{1}H-NMR spectrum of yttrium isopropoxide-2,2′-bipyridyl. Solvent: CCl$_4$.

(4.5 ppm for C*H* and 1.7 ppm for C*H*$_3$) and μ-OiPr (1.47 ppm for C*H*$_3$)[21] and increases that of the free OiPr of yttrium isopropoxide, indicating that 2,2′-bipyridyl reacts with yttrium isopropoxide and causes yttrium isopropoxide to somewhat disassociate. Upon addition of γ-butyrolactone (nonpolymerizable γ-butyrolactone with similar molecular structure of CL was used as a model compound of CL to imitate the polymerization condition), signals of μ_3-OiPr disappear completely. The similar spectra were also obtained by adding 18-crown-6 or 1,10-phenanthroline to Y(OiPr)$_3$ solution (Figure 16). Therefore, above results demonstrate that these donors can coordinate with Y^{3+} in the Y(OiPr)$_3$ cluster, different from the no reaction between yttrium isopropoxide and weaker donors.[21] The NMR analyses of La(OiPr)$_3$-donor systems reached the same conclusion. The reaction between neodymium isopropoxide and donors is difficult

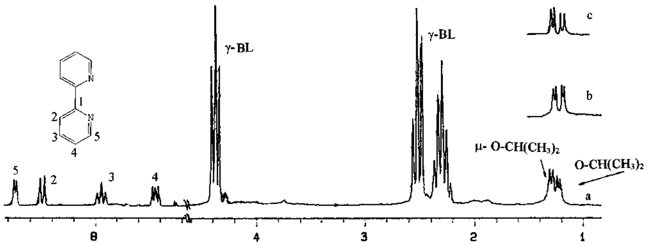

Figure 16. ^{1}H-NMR spectrum of Y(OiPr)$_3$-donor adducts in the presence of γ-butyrolactone: (a) Y(OiPr)$_3$-2bip, (b) Y(OiPr)$_3$−phen, and (c) Y(OiPr)$_3$−crown. [Y(OiPr)$_3$] = 0.35 mol/L; CCl$_4$ as solvent (CCl$_4$/γ-BL = 1/1 in volume). (Only the methyl signals of Y(OiPr)$_3$−phen and Y(OiPr)$_3$−crown adducts are shown in b and c, respectively.)

Table 2. Living Polymerization of ϵ-Caprolactone Catalyzed by Adducts of Nd(OiPr)$_3$

donor	donor/Nd	CL/Nd	temp (°C)	time (h)	conv (%)	$M_n \times 10^{-4}$ theor.	$M_n \times 10^{-4}$ GPC	M_w/M_n
crown^a	1:1	300	25	0.5	60	0.68	0.70	1.02
		300	25	1.0	99	1.12	1.15	1.05
		300	25	3.0	100	1.12	1.14	1.10
		210	25	1.0	100	0.80	0.80	1.05
phen^a	1:1	300	25	0.5	100	1.12	1.17	1.10
		300	25	1.0	100	1.12	1.11	1.05
		456	25	1.0	100	1.73	1.77	1.04
bip^a	2:1	680	25	0.5	70	1.81	1.80	1.08
		680	25	1	100	2.58	2.58	1.10

^{a,b} Conditions: a = [Nd(OiPr)$_3$] = 3.71 × 10^{-3} mol/L; b = [Nd(OiPr)$_3$] = 1.0 × 10^{-2} mol/L.

to investigate by NMR spectrum because Nd^{3+} is a paramagnetic ion and the NMR signals of catalysts containing Nd^{3+} are too broad to reflect the details of the molecular structure, but from the reactions between La(OiPr)$_3$ or Y(OiPr)$_3$ with donors, it can be postulated that Nd(OiPr)$_3$ can also react with these stronger donors. The complexation reaction between Nd(OiPr)$_3$ and 1,10-phenanthroline can be obviously seen by the fact that when THF solutions of Phen and Nd(OiPr)$_3$ are mixed, a precipitate immediately separates out from the solution, and elemental analysis showed that the precipitate is an adduct of Nd(OiP)$_3$ with 1,10-phenanthroline. The exact structures of these complexes of rare earth isopropoxide and donors are under investigated.

Table 2 shows the results of ϵ-caprolactone polymerization by using Nd(OiPr)$_3$-donor adducts. Similar to those of CL polymerization with (EA)$_2$LnOiPr, molecular weight distributions of PCL samples obtained with the complexes are all very narrow (M_w/M_n < 1.10). By comparison with the polymerization of CL with Nd(OiPr)$_3$,[10] it has been found that in the presence of donor ligands, the molecular weight distribution of PCL is narrower, and it broadens very slowly even after 100% conversion of CL. This proves that the presence of donor suppresses the transesterification.

Conclusions

A high steric hindrance of groups attached to a rare earth ion can prevent PCL chains from coordinating on the ion, and therefore minimize the transesterification reactions and achieve a real living polymerization by isopropoxy rare earth diethyl acetoacetate ((EA)$_2$LnOiPr, Ln = Nd, Y) and neodymium isopropoxide-donor adducts. Block copolymers P(CL-*b*-TMC) and P(CL-*b*-D,L-LA) could be synthesized by (EA)$_2$LnOiPr. The block copolymers have well-controlled chain lengths, a narrow molecular weight distribution, and pure block structures.

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