Ring-opening Polymerization of ε-Caprolactone Initiated by Rare Earth Complex Catalysts

XIANMO DENG, ZHIXUE ZHU, CHENGDONG XIONG, LIANLAI ZHANG

Chengdu Institute of Organic Chemistry, Academia Sinica, P.O. Box 415, Chengdu 610041, People's Republic of China

ABSTRACT: The polymerization of caprolactone (ε-CL) was initiated by yttrium triisopropoxide $\{Y(OP_r^i)_3\}$, bimetallic isopropoxide of yttrium and aluminum $\{Y[Al(OP_r^i)_4]_3\}$, yttrium and tin(II) $\{Y[Sn(OP_r^i)_3]_3\}$, and tin(II) and yttrium $\{Sn[Y(OP_r^i)_4]_2\}$, respectively. The polymerization was carried out through coordinative insertion of a monomer into the free metal–oxygen bond. The molecular weight and yield of poly(ε-caprolactone) (PCL) were affected drastically by the mol % of the initiator to the monomer (C_0/M_0). The results showed that $Y(OP_r^i)_3$ and $Sn[Y(OP_r^i)_4]_2$ were more effective than were $\{Y[Al(OP_r^i)_4]_3\}$ and $\{Y[Sn(OP_r^i)_3]_3\}$ for the polymerization of ε-CL. When polymerization was conducted at 5°C using $Y(OP_r^i)_3$ as the initiator or at 10°C using $Sn[Y(OP_r^i)_4]_4$ as the initiator, polymers with a molecular weight of 45.9×10^3 or 54.0×10^3 and high yield resulted in 30 or 5 min, respectively. The polymer was characterized by FTIR, H-NMR, and GPC. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1295–1299, 1997

Key words: ring-opening polymerization; ε-caprolactone; bimetal alkoxide; rare earth catalysts

INTRODUCTION

Poly(ε-caprolactone) (PCL) is a very attractive biomaterial with nontoxicity, biodegradability, biocompatibility, permeability, and the capacity of blending with various polymers. It has found various uses, especially in surgery and sustained drug-release systems.[1,2]

In the past two decades, many initiators (metal halides, oxides carbonates, carboxylates, alkoxides, etc.) were investigated for ring-opening polymerization of ε-caprolactone (ε-CL). Teyssie et al. studied the living polymerization of ε-CL initiated by aluminum functional alkoxides $\{(C_2H_5)_{3-p}Al(OCH_2—X)_p$, $p = 1$–3; X = —CH$_2$Br, —(CH$_2$)$_2$CH=CH$_2$; —(CH$_2$)$_2$NEt$_2\}$,[3–8] and bimetallic

(Al, Zn) μ-oxo alkoxides $\{(RO)_2Al—O—Zn—O—Al(OR)_2\}$,[9–13] with a coordination–insertion mechanism. With a PHB—O—AlEt$_2$ macroinitiator, Gross et al. prepared PHB–PCL and PHB–PLA diblock copolymers.[14] Penczek et al. investigated the polymerization of ε-CL initiated by Et$_2$AlOCH$_3$, Et$_2$AlOCH$_2$CH=CH$_2$, and $[(CH_3)_2CHCH_2]_2AlOCH_3$ through an anionic and pseudionic pathway.[15] Kricheldorf et al. investigated systematically the polymerization of several lactones initiated by various metal alkoxides,[16] such as Mg(OEt)$_2$, Al(OP$_r^i$)$_3$, Zn(OBu)$_2$, Ti(OBu)$_4$, Zr(OP$_r^i$)$_4$, Bu$_2$Sn(OMe)$_2$, and Bu$_3$SnOMe. Inoue et al. discovered that aluminum porphyrins, such as (porphinato)aluminum alkoxides and porphyrin–diethylaluminum chloride (TPP–Et$_2$AlCl), were effective initiators for the polymerization of ε-CL with characteristics of living polymerization.[17–20]

Rare earth metal compounds were effective initiators for alkene, alkyne, and epoxide; however, little attention has been paid to the polymerization of ε-

---

CL. The first example for it is the rare earth metal alkoxides investigated by McLain and Drysdale.[21,22] In the present article, we focused on the study of polymerization of ε-CL by $Y(OP_r^i)_3$ and some new yttrium compounds such as $Y[Al(OP_r^i)_4]_3$, $Y[Sn(OP_r^i)_3]_3$, and $Sn[Y(OP_r^i)_4]_2$.

EXPERIMENTAL

Materials

Anhydrous yttrium chloride was prepared by heating mixtures of yttrium chloride hydrate with ammonium chloride in a current of dry chlorine and hydrogen chloride gases. Isopropanol was initially distilled over sodium isopropoxide and stored under a 4 Å molecular sieve. Toluene was distilled under nitrogen after being dried by refluxing over calcium hydride. ε-CL (Aldrich) was dried over calcium hydride for 48 h at room temperature and then distilled under reduced pressure.

Preparation of Initiators

Yttrium triisopropoxide $Y(OP_r^i)_3$ (Ref. 23): To a rapidly stirred solution of potassium isopropoxide in isopropanol, the solution of yttrium trichloride in isopropanol was added. Instantaneous precipitation of potassium chloride occurred with the evolution of heat. The mixture was reacted at 80°C for 4 h; then, the isopropanol was distilled off under reduced pressure. The solid remains were dissolved in toluene and then filtered.

   Double metal isopropoxides $\{Y[Al(OP_r^i)_4]_3$, $Y[Sn(OP_r^i)_3]_3$, and $Sn[Y(OP_r^i)_4]_2\}$ (Refs. 24 and 25): To a solution of anhydrous yttrium chloride in isopropanol, stannous(II) chloride (or aluminum chloride) and potassium in isopropanol was added. A significantly exothermic reaction occurred along with instantaneous precipitation of potassium chloride. The mixture was reacted at 80°C for 6 h. Then, the isopropanol was distilled off under reduced pressure. The solid remains were dissolved in toluene and filtered.

Polymerization Procedure

The polymerization was carried out in a toluene solution of ε-CL under stirring in a dry flask, purged with nitrogen. The initiator solution was successively added through a rubber septum with a syringe. The reaction was terminated by adding

Table I   Polymerization of ε-CL Initiated by $Y(OP_r^i)_3$[a]

Sample	C_0/M_0[b] (‰)	Yield (%)	$\bar{M}_n$ ($\times 10^{-3}$)
A1	1.0	42	16.0
A2	1.5	77	19.5
A3	2.0	93	20.6
A4	2.0	97	45.9
A5	2.5	87	17.4
A6	3.0	69	18.4

[a] Reaction temperature 10 or 5°C (for A4); time 30 min.
[b] $M_0 = 3.77$ mol/L in toluene solution.

an excess of $2N$ HCl solution. The polymer solution was washed with water up to neutral pH. The polymer was precipitated in excess heptane. After being filtered, the product was dried under a vacuum to a constant weight.

Characterization

FTIR spectra were recorded on a Nicolet MX-1 IR spectrometer. The sample was prepared by casting film from an acetone solution onto a KBr plate. ^{1}H-NMR spectra were obtained by a Varian FT-80A apparatus at room temperature with CDCl$_3$ as the solvent. TMS was used as an internal standard. Molecular weights and molecular weight distribution were determined by GPC with a Water Associates Model ALC/GPC 244 apparatus at room temperature, using THF as the solvent, and calibrated with polystyrene standards.

RESULTS AND DISCUSSION

Polymerization of ε-CL Initiated by $Y(OP_r^i)_3$

In the first part of this work, yttrium triisopropxide $Y(OP_r^i)_3$ was synthesized and used as an initiator for the polymerization of ε-CL. The results are shown in Table I. The polymerization reaction was affected drastically by the mol % of the initiator to the monomer (C_0/M_0) and the reaction temperature. The molecular weight and yield of PCL gradually increased with increase of C_0/M_0 ranging from 1.0 to 2.0‰. On the contrary, they decreased gradually with increase of C_0/M_0 ranging from 2.0 to 3.0‰. Interestingly, at a relatively lower temperature, higher yield and higher molecular weight resulted, as shown in Table I (A4). When polymerization was initiated in 2.0‰ of

Table II   Polymerization of ε-CL Initiated by $Y[Al(OP_r^i)_4]_3$[a]

Sample	C_0/M_0[b] (‰)	Yield (%)	$\bar{M}_n$ ($\times 10^{-3}$)
B1	0.5	40	4.98
B2	0.8	97	13.3
B3	1.0	96	6.88
B4	2.0	95	4.40

[a] Reaction temperature 10°C; time 50 min.
[b] $M_0 = 3.77$ mol/L in toluene solution.

Table IV   Polymerization of ε-CL Initiated by $Sn[Y(OP_r^i)_4]_2$[a]

Sample	C_0/M_0[b] (‰)	Yield (%)	$\bar{M}_n$ ($\times 10^{-3}$)
D1	0.8	67	43.5
D2	1.0	97	54.0
D3	1.5	93	3.12
D4	2.0	81	2.77

[a] Reaction temperature 10°C; time 5 min.
[b] $M_0 = 3.77$ mol/L in toluene solution.

C_0/M_0 at 10 or 5°C for 30 min, polymers with a molecular weight of 20.6×10^3 or 45.9×10^3 were obtained, respectively.

Polymerization of ε-CL Initiated by $Y[Al(OP_r^i)_4]_3$ and $Y[Sn(OP_r^i)_3]_3$

$Y(OP_r^i)_3$ and $Al(OP_r^i)_3$ have been found to be effective initiators for the polymerization of ε-CL. Bimetallic ispropoxide of a yttrium and aluminum $\{Y[Al(OP_r^i)_4]_3\}$ complex catalyst was also an effective initiator for the polymerization of ε-CL. From Table II, it was found that a high molecular weight and high yield of PCL resulted from 0.8‰ of C_0/M_0. Compared with the polymerization of ε-CL initiated by $Al(OP_r^i)_3$,[16] the polymerization of ε-CL can be carried out at a lower temperature and with a fast reaction rate by using $Y[Al(OP_r^i)_4]_3$ as the initiator.

The initiator of bimetallic isopropoxide of yttrium and tin(II) $\{Y[Sn(OP_r^i)_3]_3\}$ was also synthesized for the polymerization of ε-CL. The results are summarized in Table III. The molecular weight and yield of PCL were also influenced by C_0/M_0. At a mol % of 1.0‰, the monomer was converted into the polymer with relatively high molecular weight and high yield. The polymeriza-

tion reaction initiated by $Y[Sn(OP_r^i)_3]_3$ went to completion in 5 min at 40°C, while the polymerization of ε-CL by $Bu_2Sn(OMe)_2$ required several hours at 100°C.[16]

Polymerization of ε-CL Initiated by $Sn[Y(OP_r^i)_4]_2$

The synthesis and structure of $Pb[Sb(OR)_4]_2$ were studied by Mehrotra et al.[26] Similar to $Pb[Sb(OR)_4]_2$, bimetallic isopropoxide of tin(II) and yttrium $Sn[Y(OP_r^i)_4]_2$ was synthesized. It proved to be very effective for the polymerization of ε-CL (see Table IV). The polymerization reaction showed a fast rate at low temperature and ε-CL can be polymerized into PCL with a higher molecular weight and a higher yield than those initiated by the other three rare earth metal complex catalysts. For instance, D2, PCL with a molecular weight of 54.0×10^3 and yield of 97, was obtained at 10°C and 5 min. The molecular weight and yield of PCL were also affected by a C_0/M_0 similar to the polymerization of ε-CL initiated by $Y(OP_r^i)_3$.

Characterization of PCL

The FTIR spectrum of PCL showed the absorption band at 3453 cm^{-1} assigned to terminal hydroxy groups of PCL. The bands at 2946 and 1173 cm^{-1} were due to the C—H stretch of —CH$_2$— and the —C—O stretch. The strong absorption at 1756 cm^{-1} was assigned to the —C=O stretch. The ^{1}H-NMR spectrum of PCL displayed peaks at 1.50, 2.25, and 4.0 ppm, which are assigned to —(CH$_2$)$_4$—, —CO—CH$_2$—, and —OCH$_2$— methylene protons, respectively.

The results of GPC are shown in Figure 1. It was found that the molecular weight distribution of PCL was relatively broad, caused mainly by a transesterification reaction during the polymer-

Table III   Polymerization of ε-CL Initiated by $Y[Sn(OP_r^i)_3]_3$[a]

Sample	C_0/M_0[b] (‰)	Yield (%)	$\bar{M}_n$ ($\times 10^{-3}$)
C1	0.5	50	8.82
C2	1.0	97	12.6
C3	2.0	86	10.8
C4	2.5	88	4.97

[a] Reaction temperature 40°C; time 5 min.
[b] $M_0 = 3.77$ mol/L in toluene solution.

ization of ε-CL by $Y(OP_r^i)_3$, $Y[Al(OP_r^i)_4]_3$, $Y[Sn(OP_r^i)_3]_3$, and $Sn[Y(OP_r^i)_4]_2$. As shown in McLain and Drysdale's work, the molecular weight distribution became broad as the yttrium complex catalyzed the transesterification at a longer reaction time.[21]

The polymerization of ε-CL initiated by $Y(OP_r^i)_3$ and $Al(OP_r^i)_3$ was carried out through coordinative insertion of the monomer into the Y—O bond and the Al—O bond, respectively.[21] Similarly, metal–oxygen bonds exist in the compounds of $Y[Al(OP_r^i)_3]_3$, $Y[Sn(OP_r^i)_3]_3$, and $Sn[Y(OP_r^i)_4]_2$. Therefore, the mechanism of polymerization of ε-CL initiated by these bimetallic catalysts should also be a coordination–insertion pathway with a monomer coordinative insertion into the Al—O bond, Sn—O bond, or Y—O bond, as shown in Scheme I.

From Tables I–IV, it can be seen that $Y(OP_r^i)_3$ and $Sn[Y(OP_r^i)_4]_2$ were more effective initiators than were $Y[Al(OP_r^i)_4]_3$ and $Y[Sn(OP_r^i)_3]_3$. This can be explained by the above mechanism because different metal–oxygen bonds show different catalyst activity: The Y—O bond is more active than is the Al—O bond and the Sn—O bond.
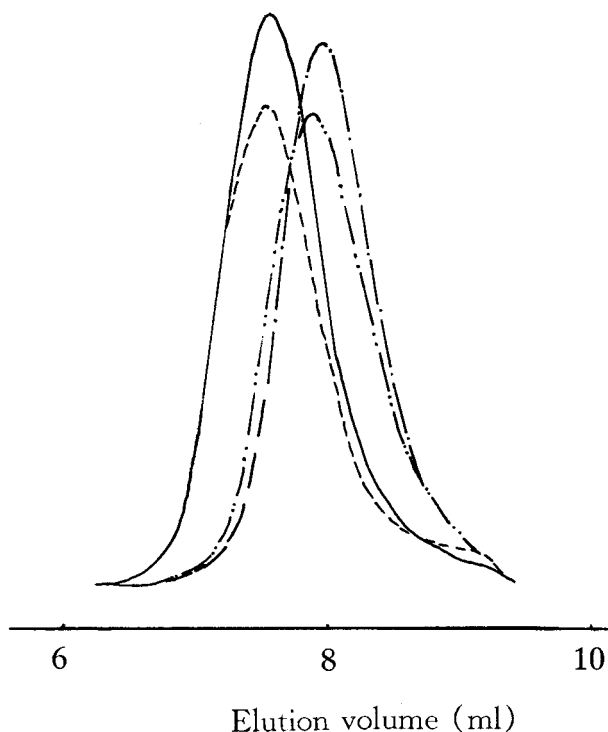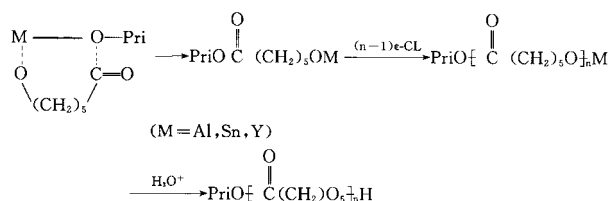
Scheme I Mechanism of polymerization of ε-CL initiated by rare earth complex catalysts.

CONCLUSION

The polymerization of $\varepsilon - CL$ was initiated by a rare earth metal catalyst through coordinative insertion of a monomer into a metal–oxygen bond. $Y(OP_r^i)_3$ and $Sn[Y(OP_r^i)_4]_2$ were found more effective for the polymerization of ε—CL than were $Y[Al(OP_r^i)_4]_3$ and $Y[Sn(OP_r^i)_3]_3$, due to greater activity of the Y—O bonds. PCL with a molecular weight of 45.9×10^3 and 54.0×10^3 were synthesized in a high yield at 5°C for 30 min using $Y(OP_r^i)_3$ as the initiator or at 10°C for 5 min using $Sn[Y(OP_r^i)_4]_2$ as the initiator.

Figure 1 GPC traces of PCL initiated by $Y(OP_r^i)_3$, $Y[Al(OP_r^i)_4]_3$, $Y[Sn(OP_r^i)_3]_3$, and $Sn[Y(OP_r^i)_4]_2$: (——) A4; (– · · –) B2; (– · –) C2; (----) D2.

REFERENCES

1. J. M. Vion, R. Jerome, Ph. Teyssie, M. Aubin, and R. E. Prudhomme, *Macromolecules,* **19,** 1828 (1986).
2. S. J. Ory, C. B. Hammond, S. G. Yancy, R. W. Hendren, and C. G. Pitt, *Am. J. Obstet. Gynecol.,* **145,** 600 (1983).
3. Ph. Dubois, R. Jerome, and Ph. Teyssie, *Polym. Bull.,* **22,** 475 (1989).
4. Ph. Dubois, R. Jerome, and Ph. Teyssie, *Polym. Prepr.,* **31,** 7 (1990).
5. Ph. Dubois, R. Jerome, and Ph. Teyssie, *Macromolecules,* **24,** 977 (1991).
6. P. Vanhoorne, Ph. Dubois, R. Jerome, and Ph. Teyssie, *Macromolecules,* **25,** 37 (1992).
7. P. Vanhoorne, Ph. Dubois, and R. Jerome, *Makromol. Chem. Makromol. Symp.,* **42/43,** 103 (1991).
8. P. Vanhoorne, Ph. Dubois, and R. Jerome, *Macromolecules,* **24,** 6542 (1991).
9. A. Hamitou, T. Ouhadi, R. Jerome, and Ph. Teyssie, *J. Polym. Sci. Polym. Chem. Ed.,* **15,** 865 (1977).
10. T. Ouhadi, A. Hamitou, R. Jerome, and Ph. Teyssie, *Macromolecules,* **9,** 927 (1976).
11. J. Hauschen, R. Jerome, A. J. Hubert, and Ph. Teyssie, *Macromolecules,* **6,** 651 (1973).

12. J. Hauschen, R. Jerome, and Ph. Teyssie, *Macromolecules,* **14,** 242 (1981).
13. A. Haimitou, R. Jerome, and Ph. Teyssie, *J. Polym. Sci. Polym. Chem. Ed.,* **15,** 1035 (1977).
14. R. S. Michael, S. P. McCarthy, and R. A. Gross, *Macromolecules,* **26,** 888 (1993).
15. A. Duda, Z. Florjanczyk, A. Hoffman, S. Slomkowski, and S. Penczek, *Macromolecules,* **23,** 1640 (1990).
16. H. R. Kricheldorf, M. Berl, and N. Scharnagl, *Macromolecules,* **21,** 286 (1988).
17. T. Yasuda, T. Aida, and S. Inoue, *Bull. Chem. Soc. Jpn.,* **59,** 3931 (198).
18. M. Endo, T. Aida, and S. Inoue, *Macromolecules,* **20,** 2982 (1987).
19. S. Inoue, *J. Macromol. Sci.-Chem. A,* **25**(5–7), 571 (1988).
20. W. X. Cao, G. F. Lin, X. Y. Li, and X. D. Feng, *Polym. Bull.,* **20,** 117 (1988).
21. S. J. McLain and N. E. Drysdale, *Polym. Prepr.,* **33,** 174 (1992).
22. S. J. McLain and N. E. Drysdale, U.S. Pat. 5,028,667 (1991).
23. K. S. Mazdiyasni, C. T. Lynch, and J. S. Smith, *Inorg. Chem.,* **5,** 342 (1966).
24. R. C. Mehrotra, M. M. Agrawal, and A. Mehrotra, *Syn. React. Inorg. Met.-Org. Chem.,* **3,** 407 (1973).
25. D. C. Bradley, R. C. Mehrotra, and D. P. Gaur, *Metal Alkoxides,* Academic Press, New York.
26. T. Athar, R. Bohra, and R. C. Mehrotra, *Syn. React. Inorg. Met.-Org. Chem.,* **19,** 195 (1989).