Polymerization of Lactides and Lactones. IV. Ring-Opening Polymerization of ε -Caprolactone by Rare Earth Phenyl Compounds

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ABSTRACT: Ring-opening polymerization of ε -caprolactone (CL) has been initiated with rare earth phenyl compounds in both bulk and solution. These rare earth phenyl initiators can give polycaprolactone (PCL) with high yield and high molecular weight. The polymerization mechanism is through a coordination-deprotonation-insertion process, by which the monomer inserts on the Ln—O bond of rare earth enolate. The efficiency of rare earth phenyl compounds for CL is high. The effects of reaction conditions, such as reaction time, reaction temperature, and monomer/initiator molar ratio, on the polymerization are discussed. The polymer was characterized by FTIR, ¹H-NMR. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1401–1408, 1999

Key words: ε -caprolactone; rare earth phenyl compound initiators; ring-opening polymerization

INTRODUCTION

Poly- ε -caprolactone (PCL) with high molecular weight is of interest as a biodegradable and biocompatable material.^{1–3} Ring-opening polymerization of lactones provides a convenient and efficient approach to preparing polyesters. Usually the polymerization of lactides and lactones is carried out in the presence of tin salts, such as Sn(2-ethyl-hexanoate),^{4–6} which has been proven effective for polymerization of ε -caprolactone (CL) in bulk. In other systems, many nontin catalysts containing alkali metals,⁷ aluminum,⁸ and early transition metals⁹ have been developed for the ring-opening polymerization of CL. These catalysts have several advantages in synthesizing high-molecular weight polylactone.

Recently, rare earth metal compounds have been used for the ring-opening polymerization of lactides and lactones. Shen¹⁰ and McLain et al.^{11,12} reported the polymerization of lactide and lactones with lathanide alkoxides. Shen et al.¹³ also reported that rare earth halides showed high activity for the polymerization of lactones in the presence of epoxide. Yasuda,¹⁴ Evans,¹⁵ and Feijen¹⁶ studied the living-opening polymerization of lactones with orgnolanthanide complexes; these complexes were extremely active regarding these monomers. In recent years, we have focused on the study of ring-opening polymerization of lactones and lactides with rare earth compounds, and several new catalysts were patented^{17,18} and reported.¹⁹ In this article we report on the polymerization of CL initiated by rare earth phenyl compounds, discussing the process as well as the conditions of reaction.

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No.	M/I	Time (min)	Temperature (°C)	Yield (%)	$M_n \ (imes 10^4)$
1	100	30	60	86	6.5
2	250	30	60	81	8.8
3	1000	30	60	60	9.3
4	250	30	100	91	8.9
5	250	30	40	53	7.6
6	250	60	60	78	8.3

Table I Bulk Polymerization of CL with (C₆H₅)₃Y

EXPERIMENTAL

Materials

CL (Aldrich Co., Milwaukee, WI, USA) was dried over calcium hydride for 48 h at room temperature and then distilled under reduced pressure. Toluene, benzene, tetrahydrofuran (THF), 1,4-dioxane, and ethyl ether (Et₂O) were dried and distilled from sodium just before use. Anhydrous rare earth halide was prepared by reaction of rare earth oxide with HCl, then dehydrated by thionyl chloride.²⁵ Bromobenzene was distilled and stored over 4-Å molecular sieves.

Preparation of Initiator

Phenyl lithium was prepared from metal lithium with bromobenzene in Et_2O solution while stirring at room temperature. After the reaction was completed, Et_2O was distilled under reduced pressure, and THF was added to the reaction mixture. The phenyl lithium in THF solution was filtered and sealed for later use.

Rare earth phenyl compounds were prepared by modified literature procedures.^{26,27} Anhydrous rare earth halide and THF were added into a dried glass reactor previously flamed and nitrogen purged several times. The mixture was stirred for 24 h at room temperature, then cooled to approximately -10 to -20°C. Phenyl lithium THF solution was added dropwise, and the reaction was kept at -10°C for 8 h. The mixture was stirred for an additional 24 h at room temperature and then filtered. The filtrate was concentrated under vacuum and precipitated from hexane. The complex was filtered, washed with hexane, and recrystallized three times from THF/ hexane solution to give a crystalline powder.

Polymerization Procedure

In Bulk

Monomer was added into a dried glass reactor previously flamed and nitrogen purged several times. The initiator was injected with a syringe in the form of THF solution. The reaction was carried out at constant temperature for a suitable period. The polymerization was terminated by cooling in water. The reaction product was then dissolved in CHCl₃ and recovered by precipitation in an excess of diethyl ether. The purified product was dried under vacuum at 40°C for 48 h.

In Solution

Monomer was added into a glass reactor and dried as before. Solvent was added, and the initi-

No.	M/I	Time (min)	Temperature (°C)	Yield (%)	M_n $(imes 10^4)$
1	500	30	60	92	13.4
2	1500	30	60	20	13.1
3	500	30	80	96	14.6
4	500	30	25	80	7.9
5	500	10	60	71	11
6	500	60	60	97	9.5
7	500	90	60	96	9.4

Table II Bulk Polymerization of CL with (C₆H₅)₃Nd

No.	M/I	Time (min)	Temperature (°C)	Yield (%)	$M_n \ (imes 10^4)$
1	500	5	170	94	16.9
2	250	5	170	96	14.3
3	1000	5	170	87	17.8
4	500	30	170	90	12.5
5	500	60	170	92	11.3
6	500	5	80	78	10.4
7	500	5	120	89	13.2

Table III Bulk Polymerization of CL with (C₆H₅)₃Sm

ator was injected by means of a syringe in the form of THF solution. The polymerization was carried out, and the crude product was purified as for bulk polymerization. pounds are effective for the ring-opening polymerization of CL. The polymerization can be conducted either in bulk or in solution.

Measurements

¹H-NMR spectra of polymer were recorded in CDCl_3 with a Bruker AC-P 300 MHz apparatus at 25°C. IR spectra were recorded on a NICOLET MX-1 IR apparatus. Intrinsic viscosity of PCL was measured with an Ubbelohde viscometer in benzene at 30°C, and the viscosity average molecular weight (M_n) was calculated from the following equation²⁸:

$$[n] = 9.94 \times 10^{-5} M_n^{0.82}$$

RESULTS AND DISCUSSION

The results of polymerization of CL initiated by rare earth phenyl compounds are shown in Tables I–V. These results indicate that rare earth phenyl com-

Bulk Polymerization of CL with $(C_6H_5)_3Y$

Table I gives the results of bulk polymerization of CL with $(C_6H_5)_3$ Y. It can be seen that the yield of 91% and high-molecular weight PCL is obtained normally within 30 min. Rising reaction temperature causes a higher polymer yield. The reaction conditions (e.g., M/I, temperature, time) have a greater influence on the yield than on the molecular weight of PCL, possibly suggesting that the propagation step is much faster than the initiation step. The yield of PCL increases with the decrease in the monomer/initiator ratio. This is due to the higher concentration of initiator that increases the number of active species, leading to high conversion of monomer. Figure 1 shows reaction time is critical to the PCL yield in the primary stage of 30 min in the M/I ratio 250. The increase in reaction time leads to an increase in PCL yield, until it reaches a maxi-

Table IV Solution Polymerization of CL with (C₆H₅)₃Sm^a

			Time	Temperature		M_n
No.	M/I	Solvent	(h)	(°C)	Yield (%)	(×10 ⁴)
1	50	Toluene	2	70	80	5.6
2	125	Toluene	2	70	65	6.8
3	250	Toluene	2	70	61	5.8
4	500	Toluene	2	70	42	6.1
5	125	Toluene	2	100	85	5.5
6	125	THF	2	70	Oligomer	
7	125	Benzene	2	70	70	5.3
8	125	Dioxane	2	70	Oligomer	

^a Monomer/solvent = 20% (w/v).

No.	M/I	Time (min)	Temperature (°C)	Yield (%)	M_n $(imes 10^4)$
1	50	120	170	90	5.2
2	150	120	170	82	7.2
3	200	120	170	62	7.4
4	300	120	170	49	7.8
5	100	120	170	88	7.1
6	100	80	170	61	6.4
7	100	30	170	43	5.8
8	100	150	170	86	7.5
9	100	200	170	83	7.2
10	100	300	170	79	6.7
11	100	120	180	89	7.7
12	100	120	150	83	7.2
13	100	120	120	77	6.5
14	100	120	80	58	4.4

Table V Polymerization of CL with C₆H₅Li

mum after 30 min. Beyond that time, the PCL yield begins to decrease, and the molecular weight decreases slightly over time. It could be said from the results that $(C_6H_5)_3$ Y catalyzes not only the polymerization of PCL, but also the decomposition of the polymer. A similar process has been observed and discussed by other authors.²⁰ The mechanism for this decrease is said to be intramolecular transesterification in the later stage of polymerization.

Bulk Polymerization of CL with (C₆H₅)₃Nd

The results of bulk polymerization of CL are given in Table II and shown in Figure 2. It can be seen that even at low concentration of initiator (*M*/*I* = 1500), polymerization of CL can still proceed quickly, and high molecular weight PCL is also obtained. Similar to the (C_6H_5)₃Y system, *M*/*I* ratio, reaction time, and reaction temperature are impor-

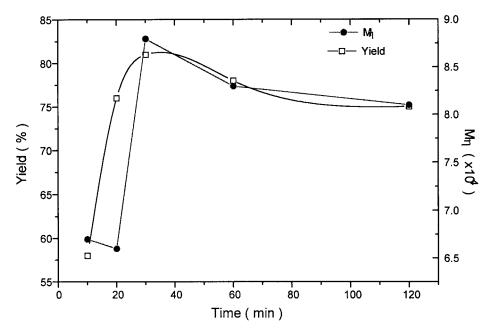


Figure 1 Effect of reaction time on the yield of PCL with $(C_6H_5)_3Y$. Reaction conditions: 60°C; M/I = 250.

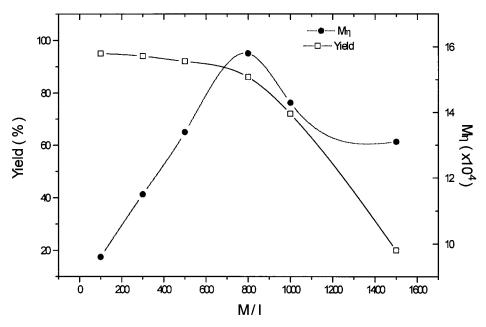


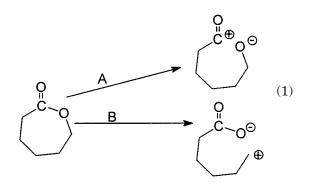
Figure 2 Effect of M/I on the molecular weight and yield of PCL with $(C_6H_5)_3$ Nd. Reaction conditions: 60°C; 30 min.

tant in controlling the yield and the M_n of polymer. It can be seen from Figure 2 that with an increase in *M/I* molar ratio, the molecular weight of PCL drops. There is an optimum M/I value to get the highest possible molecular weight; but a low *M/I* ratio is the option to get a high PCL yield. Increasing M/I molar ratio to 100-800 has little influence on the yield of PCL (see Fig. 2), but when *M/I* exceeds 800, the PCL yield decreases significantly. Higher reaction temperature is beneficial to increase the yield of PCL in the investigated temperature range. As reaction time increased after 30 min, the yield and molecular weight of PCL began to decrease. This might be due to the fact that (C₆H₅)₃Nd could catalyze the decomposition of the polymer as well. In general, (C₆H₃)₃Nd is a more efficient catalyst than $(C_6H_5)_3Y$ for the polymerization of CL in terms of Table 2, considering the M_n and yield of the product.

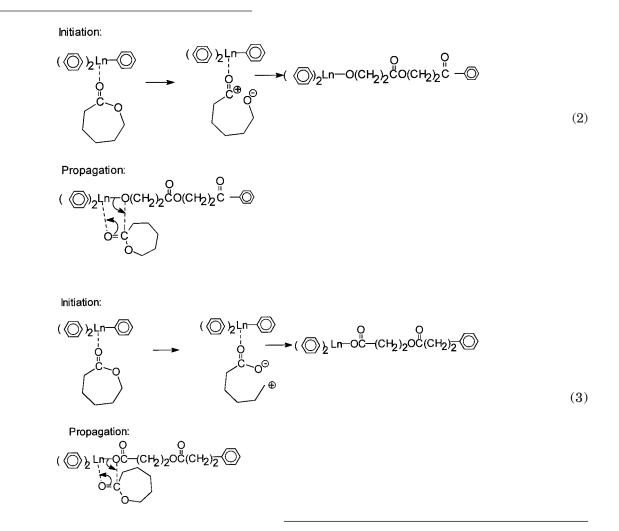
We also studied the possibility of using other rare earth compounds such as $(C_6H_5)_3Sm$, as catalysts for the polymerization of CL. The polymerization was carried out both in bulk and in solution. The results are shown in Tables III and IV. Although polymerization could be conducted in both cases, high M_n and high-yield products were obtained in the bulk polymerization. A series of $(C_6H_5)_3Sm$ -initiated polymerizations of CL were conducted in four solvents of different polarity: toluene, benzene, THF, and 1,4-dioxane. Table IV shows not much difference between polar solvents and nonpolar solvents, such as toluene and benzene. However, only oligomers were obtained when polymerization was carried out in polar THF and dioxane. The differences between polymerizations in polar and nonpolar solvents are in accordance with those reported by other authors.^{14–16}

Mechanism of Polymerization

In the case of the polymerization of CL, based on the conclusions of other initiated systems,²⁰⁻²² two mechanisms for cleavage might occur: the cleavage of acyl-oxygen bond (A) and the cleavage of alkyl-oxygen bond (B) of monomer, as shown in eq. (1).



From Kriecheldorf's point of view^{23,24} on the polymerization of lactone and lactide with metal alkoxide and cyclic Bu₂Sn derived initiators, we deduced that the polymerization of CL with the present initiators might proceed two different ways [eqs. (2) and (3)].

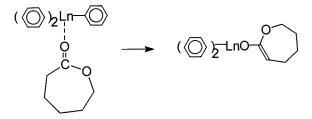


It is difficult to differentiate by kinetic methods the way in which the propagation of the macromolecule goes, via acyl-oxygen cleavage [eq. (2)] or via alkyl-oxygen cleavage [eq. (3)]. Instead, IR and H-NMR spectroscopy were used to analyze qualitatively and even quantitatively the end groups of various kinds in our studies. The IR spectrum shows an absorption at 3500 cm^{-1} . which is characteristic of the hydroxyl group. The bands at 2946 and 1173 cm^{-1} belong to the C—H stretch of —CH₂— and the —C—O stretch, respectively. The strong absorption at 1756 cm^{-1} is assigned to the -C=O stretch. The ¹H-NMR spectrum of PCL initiated by the present initiators shows peaks at 1.50, 2.25, and 4.00 ppm that are assigned to methylene protons of $-(CH_2)_4$ -,

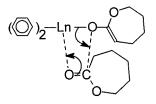
-CO-CH₂-, and -OCH₂-, respectively. But no absorption of protons from the initiators was observed, even though the figures were magnified. This indicates that there is no end group of the initiator in the PCL. The analysis may indicate that it is impossible for the polymerization of CL to be carried out according to eqs. (2) or (3) by which routes we would be able to see -C₆H₅ protons at 7–8 ppm from H-NMR. The result suggests that the initial step of polymerization of CL with rare earth initiators proceeds neither through the cleavage of the acyl-oxygen bond nor through the cleavage of the alkyl-oxygen bond. According to other authors, ^{14–16} the Ln—C σ or Ln—H σ bonds are reactive and effective for the polymerization of lactones. The mechanism for polymerization of lactones has been demonstrated to be coordination-insertion. Usually, high molecular weight PCL can be prepared by coordination catalysts,⁸ whereas anionic catalysts lead to a living-chain equilibrium and produce cyclic oligomers.⁷ The initiators discussed in this article also possess an Ln—C σ bond and strong coordination ability due to the characteristics of rare earth metals. They might perform through a route similar to that of other rare earth complexes reported by other authors. For comparison, polymerization of CL with C₆H₅Li was conducted; the results are recorded in Table V. The experiment showed that C₆H₅Li is an effective initiator for the bulk polymerization of CL, but it cannot initiate the polymerization of CL in either toluene or THF solution. Although the C₆H₅Li is effective for bulk polymerization of CL, there are obvious differences in the polymerization between C_6H_5Li and rare earth phenyl compounds as catalyst. The yield and molecular weight of PCL using C₆H₅Li are lower than those of rare earth phenyl compounds, showing that the catalyst efficiency of rare earth phenyl compounds is higher than that of C_6H_5Li . It is suggested that the polymerization of CL with rare earth phenyl compounds should operate via a coordination mechanism.

Based on the foregoing analysis, the mechanism of CL polymerization with rare earth phenyl compounds should be according to the following equation:

Initiation:



Propagation:



(4)

We suggest that the mechanism of CL polymerization is through a coordination-deprotonationinsertion process. Rare earth phenyl compounds can coordinate with CL, and the phenyl removes a proton from CL to form a rare earth enolate. The chain propagation of CL is achieved by monomer insertion into the Ln—O bond of the rare earth enolate.

CONCLUSIONS

This article has shown that polymerization of CL can be initiated efficiently by rare earth phenyl compounds through the mechanism of coordination–deprotonation–insertion by monomer insertion into the Ln—O bond of the rare earth enolate. These rare earth phenyl initiators can give high-yield and high molecular weight PCL products. When the polymerizations are done in bulk, the initiating efficiency of rare earth phenyl compounds is higher than that of C_6H_5Li .

REFERENCES

- 1. Dubois, Ph.; Jacobs, C.; Jerome, R.; Teyssie, Ph. Macromolecules 1991, 24, 2266.
- Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. Macromolecules 1992, 25, 6419.
- Duda, A.; Penczek, S. Macromolecules 1990, 23, 1636.
- Kricheldorf, H. R.; Meier-Haack, J. Macromol Chem 1993, 194, 715.
- Super, H.; Grijpma, D. W.; Penings, J. Polym Bull 1994, 32, 509.
- Ito, T.; Tokai, M.; Uno, K. (to Yoyo Boscki) Jpn Pat. 5-287056, 1993; Chem Abstr 1994, 120, 77984c.
- 7. Ito, K.; Yamashita, Y. Macromolecules 1978, 11, 68.
- Ouhadi, T.; Stevens, C.; Teyssie, Ph. Makromol Chem Macromol Suppl 1975, 1, 191.
- Endo, M.; Adia, T.; Inoue, S. Macromolecules 1987, 20, 2982.
- Shen, Z. Q.; Shen, Y. Q.; Zhang, Y. F. J Polym Sci Part A: Polym Chem 1994, 32, 597.
- Shen, Z. Q.; Shen, Y. Q.; Zhang, Y. F. Polym J 1995, 27, 59.
- McLain, S. J.; Drysdale, N. E. Polym Prepr 1992, 33, 174; 1992, 33, 463.
- Shen, Y. Q.; Shen, Z. Q.; Zhang, Y. F. Macromolecules 1996, 29, 3441.
- Yamashita, M.; Takemoto, Y.; Ihara, E.; Yasuda, H. Macromolecules 1996, 29, 1798.
- 15. Evans, W. J.; Katsumata, H. Macromolecules 1994, 27, 2330.
- Yui, N.; Di jkstra, P. J.; Fei jen, J. Makromol Chem 1990, 191, 481.

- 17. Deng, X. M.; Yuan, M. L. China Pat. 96117591, 5, 1996.
- Yuan, M. L.; Deng, X. M.; Xiong, C. D. China Pat. 96117690, 3, 1996.
- Deng, X. M.; Zhu, Z. X.; Xiong, C. D. J Appl Polym Sci 1997, 64, 1295.
- 20. Jacobs, C.; Jerome, R.; Teyssie, Ph. Macromolecules 1991, 24, 2266.
- 21. Jacobs, C.; Dubois, Ph.; Jerome, R.; Teyssie, Ph. Macromolecules 1991, 24, 3027.
- 22. Vanhoorne, P.; Dubois, Ph.; Teyssie, Ph. Macromolecules 1992, 25, 37.

- 23. Kricheldorf, H. R.; Lee, S.-R.; Bush, S. Macromolecules 1996, 29, 1375.
- Kricheldorf, H. R.; Lee, S.-R. Macromolecules 1995, 28, 6718.
- 25. Freeman, J. M.; Smith, M. L. J Inorg Nucl Chem 1958, 7, 224.
- 26. Hodgson, K. O.; Marse, F. J Am Chem Soc 1973, 95, 8650.
- 27. Hart, F. A.; Massey, A. G. J Organomet Chem 1970, 21, 174.
- Koleskeand, J. V.; Lundberg, R. D. J Polym Sci Polym Phys Ed 1969, 7, 897.