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Highly active rare earth catalysts for the solution polymerization of ε-caprolactone

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Summary

By using γ-butyrolactone (γ-BL) as the reaction media, highly active catalysts -- light rare earth chloride-epoxide-γ-BL-- for the solution polymerization of ε-caprolactone, have been obtained for the first time. With these catalyst, PCL with molecular weight as high as 40×10^4(Mv) can be prepared at 60°C for 1.5 hr. The amount of epoxide in catalyst solution, catalyst aging temperature and time affect the catalyst activity significantly. The mechanism study shows that in γ-BL, the weakening of Ln-Cl bonds by the donation of coordinated γ-BL with Ln^{3+} and the homogenous effect promote the reaction between light rare earth chloride and epoxide. The produced rare earth alkoxide initiates CL polymerization via a 'coordination-insertion' mechanism with acyl-oxygen bond cleavage.

Introduction

Among the polyesters, poly(ε-caprolactone)(PCL) possesses a special position because of its biocompatibility, biodegradability(1) and good miscibility with a variety of polymers(2). Therefore many kinds of catalysts have been developed for the polymerization of ε-caprolactone(CL)(3-7). Recently rare earth catalysts began to be used to CL polymerization, e.g., rare earth alkoxide(8) and $(C_5Me_5)_2LuCH_3$(9) were found to initiate CL living polymerization. We found that rare earth coordination catalysts are easily preparative catalysts for the polymerization(10). Further study showed that in the presence of epoxide, rare earth halides-- the very stable raw materials of organolanthanides, are highly effective for CL bulk polymerization with high molecular weight PCL formed even at room temperature(11). Heavy rare earth chloride-epoxide systems can also catalyze CL solution polymerization(11), while light rare earth chlorides($LaCl_3$, $PrCl_3$ $NdCl_3$)-epoxide can not because they difficutly react to give catalyst solution. However, in γ-BL these light rare earth chlorides react rapidly with epoxide and yield homogenous catalyst solutions which are highly effective for CL solution polymerization. The present paper reports the results of the solution polymerization of ε-caprolactone catalyzed by light rare earth chloride-epoxide-γ-BL systems.

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Experimental

Materials: ε-Caprolactone(Mitsubishi) and γ-butyrolactone were dried and distilled over CaH_2 twice under reduced pressure. Propylene oxide(PO), ethylene oxide(EO), epichlorohydrin (ECH) and allyl glycidyl ether(AGE) were dried over CaH_2. Toluene was distilled over the blue benzeophenone-Na complex. Other solvents were treated as usual methods. Rare earth oxides(Ln_2O_3) with purity of 99.99% were purchased from Shanghai Yaolong factory.

Catalyst Preparation: Anhydrous rare earth chlorides were prepared by heating the mixture of hydrated rare earth chlorides and ammonium chlorides under reduced pressure, respectively(11). Catalyst solutions for ε-caprolactone solution polymerization were obtained by the reaction of rare earth chloride with epoxide in γ-butyrolactone. The concentrations of rare earth ion and chlorine in the catalyst solution were titrated by EDTA and $HgNO_3$ respectively, and the value of Cl/Ln was thus calculated.

Separation of PO oligomer from catalyst solution: To a $NdCl_3$-γ-BL solution, stoichometric amount PO was added and stirred. After 2 hours, γ-BL was distilled out under reduced pressure. The residue was dissolved in 1M HCl, then abstracted by CH_2Cl_2. After distilled out CH_2Cl_2, the mixture of PO oligomer and γ-BL was obtained.

Polymerization (General Procedure): All the polymerization reactions were carried out under dry nitrogen. Afterward, the mixture was dissolved in toluene, the polymer was precipitated in excess methanol(containing 5% HCl), and washed by methanol for several times, then dried in vacuum.

Measurements: The intrinsic viscosity of PCL was determined in THF at 30°C with Ubbelohde viscosimeter and viscosity average molecular weight (Mv) was calculated by the equation: $[\eta]=1.09\times10^{-3}\ Mv^{0.60}$ (12). NMR spectra were recorded on a JEOL-90Q and a Bruker AR 500 NMR spectrometer in $CDCl_3$ at room temperature with TMS as the internal reference. The GPC curves were recorded by gel permeation chromatography (Waters 150) in THF at 25° C with polystyrene as the standard.

Results and Discussion

It was found that rare earth chlorides reacts with epoxide differently: heavy rare earth chlorides, such as $DyCl_3$, $ErCl_3$, $YbCl_3$, can react vigorously with ethylene oxide(EO), propylene oxide(PO), epichlorohydrin(ECH) and allyl glycidyl ether(AGE), giving homogeneous catalyst solutions. $EuCl_3$, $SmCl_3$ and $GdCl_3$ react with the epoxide smoothly and also give the homogeneous catalyst solution at last, while there are no parent reactions between ponder light rare earth chlorides($LaCl_3$, $PrCl_3$, $NdCl_3$) and these epoxide.

However, these light rare earth chlorides dissolved in γ-BL can react with epoxide rapidly(see mechanism discussion) and give highly active catalyst solutions for the polymerization of CL, as shown in Table I. It can be found all the catalyst systems formed by different rare earth chlorides and epoxide in γ-BL show high activities for the CL polymerization. Under the given conditions, the polymerization can be completed in 1.5 hours and PCLs with molecular weight as high as 42×10^4 are formed. The amount of γ-BL present in the polymerization media has little influence on the polymerization. It is about 20 to 50 times as much as that of the catalyst, which varies with the concentration of the prepared catalyst.

Table I. Solution Polymerization of CL with different catalyst systems

$LnCl_3$	Epoxide	Conv.(%)	$Mv\times10^{-4}$
La	PO	89	34.5
Pr	PO	99	39.7
Nd	PO	100	42.5
Sm	PO	100	42.5
Gd	PO	100	38.8
Nd	EO	100	36.7
Nd	ECH	96	39.1
Nd	AGE	92	36.2

Catalyst: $LnCl_3$-epoxide-γ-BL, $[LnCl_3] = 0.10mol/l$, Epoxide/Ln=5, 25°C, 5hr
Polym. conditions: $[Ln]=8.6\times10^{-4}mol/l$, $[CL]=4.7mol/l$, 60°C, 1.5hr, toluene .

The amount of added epoxide in $LnCl_3$-epoxide-γ-BL solution affects the catalyst activity significantly(Figure 1). The more PO presents in the catalyst solution, the shorter the time that the catalyst solution reaches its highest catalyst activity(t_h) is. For example, the t_h is less than 1 hour for PO/Nd=20 system, while about 4 hour for PO/Nd=5 systems. On the other hand, the higher PO amount in the catalyst solution causes the catalyst activity to decrease more rapidly. The $NdCl_3$-5PO-γ-BL system can keep its activity up to 30 hours, but the catalytic activity of $NdCl_3$-20PO-γ-BL system begins to decrease after 10 hours. At high catalyst aging temperature, the decreasing of the catalytic activity proceeds more rapidly. This may be due to the transfer reaction of the active species to PO molecules, which will be reported elsewhere. The molecular weight of PCL formed reaches a maximum, then decreases because the active species are produced gradually by the reaction of rare earth chloride with PO.

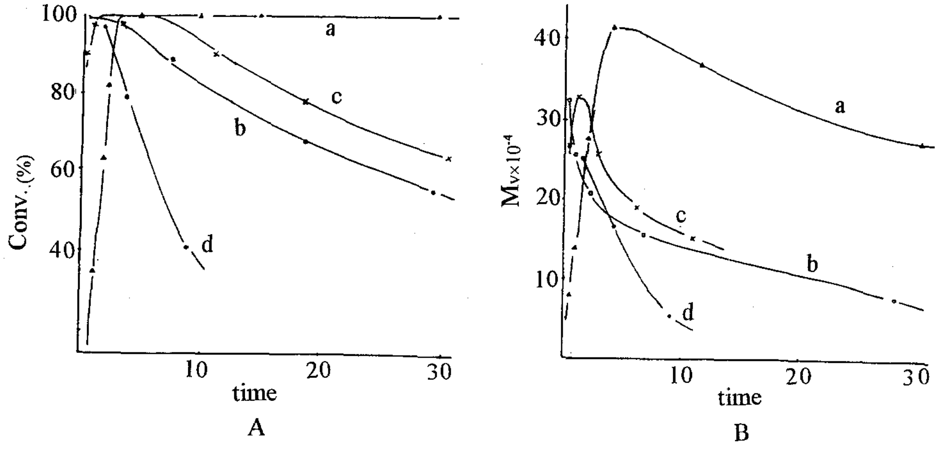


Figure 1. The effects of PO amount, catalyst aging temperature and time on the catalyst activity (A) and molecular weight of PCL(B) in CL polymerization catalyzed by $NdCl_3$-γ-BL-PO
Catalyst: PO/Nd=5, aging temperature: 20°C (a), 60°C (b)
PO/Nd=20, aging temperature: 20°C (c), 60°C (d)

Polym. conditions: [Nd]=8.6×10^{-4}mol/l. [CL]=4.7mol/l, 60°C, 1.5hr, toluene

The preparative conditions of high molecular weight PCL by $NdCl_3$-5PO-γ-BL system were investigated. Table II illustrates the effects of solvents on the polymerization. It can be found that nonpolar solvents, CCl_4 and toluene, are the best for the polymerization. In polar solvents, such as $CHCl_3$ CH_2Cl_2, the polymerization can not proceed under the given conditions. This trend is very similar to the results of CL polymerization catalyzed by rare earth alkoxides(13). Although 1,4-dioxane is nonpolar solvent, its coordination of oxygen with rare earth ion may also hinder the polymerization. Table III shows the CL polymerization at different polymerization time and temperature. At low temperature, the polymerization proceeds very slowly. High polymerization temperature leads to increase the polymerization rate, but lower the molecular weight of PCL formed.

Table II. Solvent effect on the CL polymerization

Solvent	Dielectric constant	Conv.(%)	$Mv\times10^{-4}$
Carbon tetrachloride	2.20	100	45.5
Toluene	2.33	100	42.3
Chloroform	4.78	oil	-
Dichloromethane	10.45	0	-
1,4-dioxane	2.25	0	-

Catalyst: $NdCl_3$-5PO-γ-BL. Polymerization conditions are the same as in Figure 1

Table III. CL solution polymerization catalyzed by $NdCl_3$-5PO-γ-BL system

Temp.(°C)	Polym Time(hr)	Conv.(%)	$Mv\times10^{-4}$
20	1.5	0	-
40	1.5	62.2	29.7
50	1.5	87.7	39.1
60	1.5	100	43.1
80	1.5	100	39.7
60	0.25	31.2	13.2
60	0.5	70	29.1
60	1.0	90	37.5
60	1.5	100	42.5
60	2.0	100	39.8

Other polymerization conditions are the same in Figure 1

Figure 2 shows the typical GPC curve of PCL obtained by the catalysts. It can be found that the molecular weight distribution is narrow, about 1.6. This means that initiation reaction of the polymerization is rapid. Other characterizations show that PCL obtained with the catalyst is similar to those prepared with other catalysts

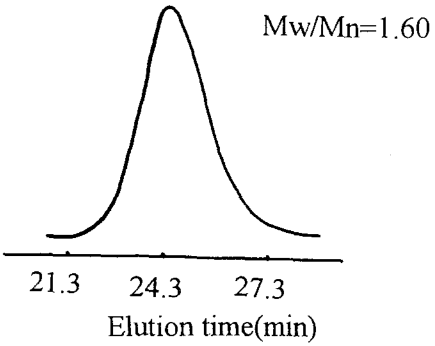
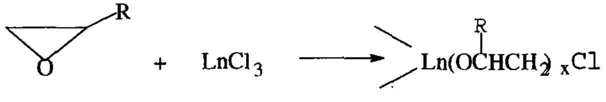


Figure 2. Typical GPC curve of PCL obtained with $NdCl_3$-5PO-γ-BL system

Mechanism Study

It has been shown that heavy rare earth chlorides react with epoxide and give rare earth alkoxides(eq.1)(11). Light rare earth chlorides are difficult to react with epoxide, but the reaction can proceed in γ-BL. Figure 3 shows the change of chlorine ion to neodymium ion ratio(Cl/Nd) in the catalyst solution after adding PO or ECH to the $NdCl_3$-γ-BL solution. It can be found the chlorine number of per neodymium ion decreases rapidly in the presence of epoxide. After hydrolyzed, a viscous liquid can be abstracted from the reaction solution(see experiment). The ^{1}H-NMR spectrum of the liquid shows that the liquid contains oligomer of PO (Figure 4).



(1)

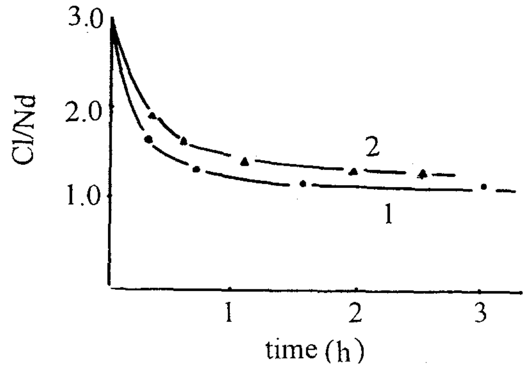


Figure 3. Change of Cl/Nd ratios in the $NdCl_3$-epoxide-γ-BL solution
$[NdCl_3]$=0.163mol/l, epoxide/Nd=5
1-PO, 2-ECH

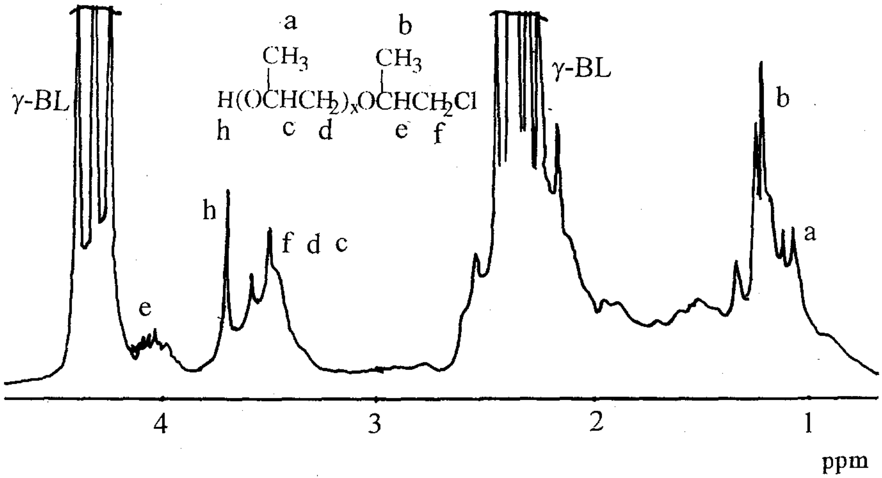


Figure 4. ^{1}H-NMR spectrum of organic compound separated from the hydrolyzed $NdCl_3$-PO-γ-BL solution

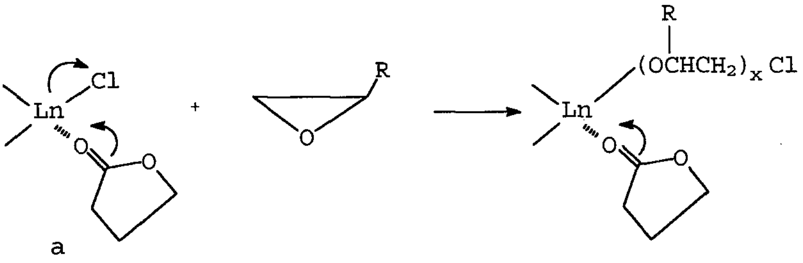
Table IV. The formation enthalpy(ΔH^F) of $LnCl_3$ and the basicity of Ln^{3+} (ϕ) (14)

$LnCl_3$	La	Nd	Sm	Dy	Yb
ΔH^F(kj/mol)	>730	719.1	696.6	677.4	638.9
Basicity(ϕ)	2.83	3.02	3.11	3.30	3.50

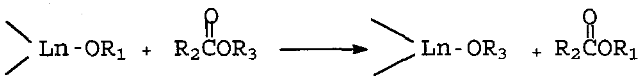
Therefore, it can be concluded that in γ-BL, light rare earth chlorides also react with epoxide to give the rare earth alkoxides by the oligomerization of PO, similar to the reaction between heavy rare earth chloride with epoxide(eq.1).

The different reactivates of rare earth chlorides in their reaction with epoxides may be ascribed to the discrepancy in stability and Lewis acidity of Ln^{3+}. Table IV shows the formation enthalpies and the relative Lewis basicities of rare earth ions. As can be seen from the data that light rare earth chlorides are much more stable than heavy rare earth chlorides, and the acidities of light rare earth ions are lower than those of heavy rare earth ions. Accordingly, during the reaction in equation 1, the high bond energy of Ln-Cl makes it difficult to break the bonds. At the same time, the low acidity of light rare earth ions(Ln^{3+}) weakens the coordination of Ln^{3+} with epoxide, then increases the difficulty of the reaction. Thus, light rare earth chlorides are difficult to react with epoxide.

Rare earth chlorides can easily dissolve in γ-BL. It has been demonstrated that in the presence of rare earth catalysts, lactone molecules coordinate with Ln^{3+} by their carbonyl oxygen(13) (eq.2 a). Accordingly when $LnCl_3$ is dissolved in r-BL, some γ-BL molecules coordinate with Ln^{3+} firmly. The strong donation effect of coordinate γ-BL weakens the Ln-Cl bond greatly, then makes the reaction easier(eq. 2). Simultaneously, the homogeneous reaction in γ-BL can also increase the reaction rate. Acyclic esters also have the promotive effects for the reaction between $LnCl_3$ and epoxides, but they can react with resultant rare earth alkoxides by exchanging their OR groups(transesterification reactions) (eq.3)(15).



(2)



$$>Ln-OR_1 + R_2\overset{O}{\overset{\|}{C}}OR_3 \longrightarrow >Ln-OR_3 + R_2\overset{O}{\overset{\|}{C}}OR_1$$

(3)

Figure 5 shows that PCL obtained by $NdCl_3$-5PO-γ-BL system has the CH_2OH and capronic ester end groups, suggesting that the produced rare earth alkoxides initiate the polymerization of CL with acyl-oxygen bond cleavages, which is so-called 'coordination-insertion' mechanism(eq. 3).

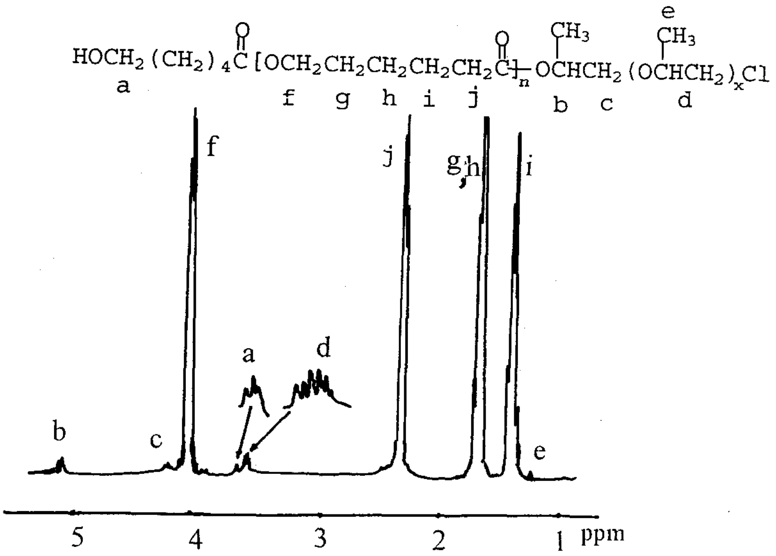
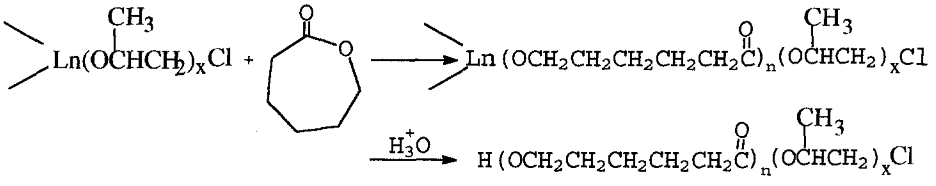


Figure 5. ^{1}H-NMR spectrum of PCL obtained by $NdCl_3$-5PO-γ-BL system



(3)

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