

RING-OPENING POLYMERIZATION OF ϵ -CAPROLACTONE BY LANTHANOCENE CATALYSIS*

SUN Junquan (孙俊全)

(*Department of Chemical Engineering, Zhejiang University, Hangzhou 310027, China*)

PAN Zhida (潘智达) and YANG Shilin (杨士林)

(*Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, 310027, China*)

Laboratory of Rare-Earth Chemistry and Physics, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences

(*Changchun 130022, China*)

Abstract Ring-opening polymerization of ϵ -caprolactone (CL) catalyzed by lanthanocenes, $\text{O}(\text{C}_2\text{H}_4\text{C}_5\text{H}_3\text{CH}_3)_2\text{YCl}$ (Cat-YCl) and $\text{Me}_2\text{Si}[(\text{CH}_3)_3\text{SiC}_5\text{H}_3]_2\text{NdCl}$ (Cat-NdCl) has been carried out for the first time. It has been found that both yttrocene and neodymocene are very efficient to catalyze the polymerization of CL, giving high molecular weight poly(ϵ -caprolactone)(PCL). The effects of $[\text{cat}]/[\epsilon\text{-CL}]$ molar ratio, polymerization temperature and time, as well as solvents were investigated and polymerization temperature is found to be the most important factor affecting the polymerization. The bulk polymerization gives higher molecular weight PCL and higher conversion than that in solution polymerization. NaBPh_4 was found to promote the polymerization of ϵ -caprolactone, and thus to increase both the polymerization conversion and MW of poly(ϵ -caprolactone).

Keywords Ring-opening polymerization; ϵ -Caprolactone; Lanthanocene catalyst; Rare-earth catalysts; Biodegradable material

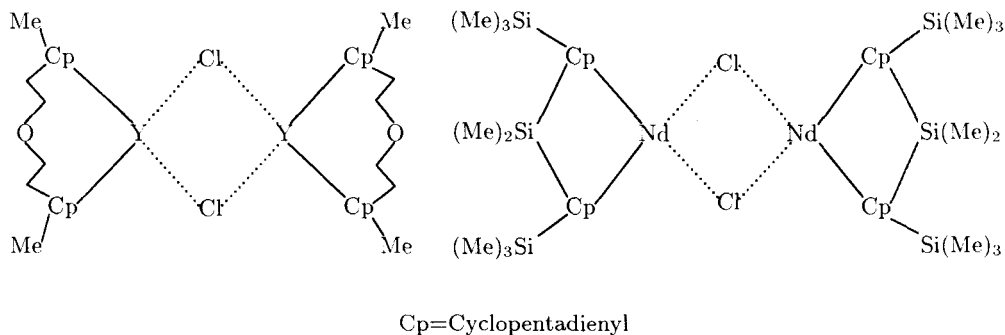
INTRODUCTION

Ring-opening polymerization of ϵ -caprolactone provides a convenient route to prepare biodegradable polyester, which can be used as a synthetic biomaterial or controlled drug release matrix. Various catalysts containing alkali metal^[1], aluminium^[2], zinc^[3], tin^[4] or early transition metal^[5] have been developed for the ring-opening

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polymerization of ϵ -caprolactone. Recently, rare earth catalysts which possess living polymerization characteristics^[6] and outstanding advantages in studying polymerization mechanism cause relatively active researches on polymerization of ϵ -caprolactone. Up to now, those rare earth catalysts mainly focus on halide-epoxide^[7] (LnX_3 , $\text{Ln}=\text{Y}$, La , Pr , Nd , Sm , Eu , Gd , Dy , Yb); alkoxides, such as $\text{Nd}(\text{O}-i\text{Pr})_3$ ^[8], tris(2,6-di-*tert*-butylphenoxy)yttrium ($\text{Y}(\text{OAr}')_3$)^[9] and metallocene hydride or alkylated complexes, $[(\text{C}_5\text{Me}_5)_2\text{SmH}]_2$ ^[6], $[(\text{C}_5\text{Me}_5)_2\text{LnMe}]$ ($\text{Ln}=\text{Sm}$, Y , Lu , Yb)^[10], $[(^t\text{BuCp})_2\text{NdCH}_3]$ ^[11], and divalent complexes, $(\text{C}_5\text{Me}_5)_2\text{Sm}$, $(\text{C}_5\text{Me}_5)_2\text{Sm}(\text{THF})_x$ ^[12]. But it has never been reported about rare earth metallocene halide for ϵ -caprolactone polymerization. We have found that $\text{O}(\text{C}_2\text{H}_4\text{C}_5\text{H}_3\text{CH}_3)_2\text{YCl}$ (Cat-YCl) and $\text{Me}_2\text{Si}[(\text{CH}_3)_3\text{SiC}_5\text{H}_3]_2\text{NdCl}$ (Cat-NdCl), the precursors of their corresponding alkyl metallocene with M-Cl bond, are also efficient for ring-opening polymerization of ϵ -caprolactone without any cocatalyst. But some Lewis bases, such as tetraphenyl boron sodium (NaBPh_4), can promote the polymerization. In the present paper, the preliminary results of the polymerization of ϵ -caprolactone catalyzed by $\text{O}(\text{C}_2\text{H}_4\text{C}_5\text{H}_3\text{CH}_3)_2\text{YCl}$ and $\text{Me}_2\text{Si}[(\text{CH}_3)_3\text{SiC}_5\text{H}_3]_2\text{NdCl}$ are reported.



EXPERIMENTAL

Materials

ϵ -caprolactone (Mitsubishi) was dried and distilled over CaH_2 under reduced pressure and stored in a refrigerator. Toluene and tetrahydrofuran (THF) were distilled over blue diphenyl ketone sodium complex. Other solvents were dried over molecular sieves. Catalysts were prepared according to the procedure of literature^[13].

Polymerization

All the polymerizations were carried out in a 25 mL ampoule, which was baked, evacuated and filled with pure argon for several cycles before use. Caprolactone, solvent and catalyst dissolved in toluene were introduced into ampoule sequentially.

Then the ampoule was placed in an oil bath to keep it at constant temperature. Afterwards, the polymer was precipitated in excess ethanol (containing 5% HCl) and washed with fresh ethanol for several times, and then dried at 50°C under vacuum.

Measurements

The intrinsic viscosity $[\eta]$ of PCL was determined in benzene at 30°C with an Ubbelohde viscometer. The viscosity-average molecular weight (M_η) was calculated by the following equation: $[\eta] = 9.94 \times 10^{-5} M_\eta^{0.82}$ ^[14]. IR spectra were measured on a Shimadzu IR-470 spectrophotometer. The GPC curves were recorded by gel permeation chromatograph (Waters-Associates M730) in THF at 25°C with polystyrene as the standard. ¹H-NMR spectra were taken on the JEOL 90Q in CDCl₃ at room temperature with TMS as the internal reference.

RESULTS AND DISCUSSION

Bulk polymerization of ϵ -caprolactone

Rare earth halides can catalyze the polymerization of CL at high temperature, but the activities of catalysts and the molecular weight of poly(ϵ -caprolactone) obtained are very low because of the stability of M—Cl bond. However, when two of the three halogen atoms of LnX₃ are substituted by cyclopentadienyl group, lanthanocene chlorides—Cat-YCl and Cat-NdCl, are very active for the polymerization of ϵ -caprolactone without cocatalyst, as shown in Table 1. For example, the polymerization of CL catalyzed by Cat-YCl and Cat-NdCl can proceed at 60°C and give 100% conversion in 3 or 10 h. The molecular weight of resultant PCL can be as high as 1.8×10^5 , while the polymerization of CL catalyzed by LnCl₃ can not proceed below 100°C and the molecular weight of PCL is lower than 4×10^4 ^[7]. This is obviously due to the different catalyst activities between rare earth halide and Cat-YCl, Cat-NdCl. The activity of lanthanocene depends on the polymerization temperature significantly. Table 1 illustrates the results of bulk polymerization of ϵ -caprolactone with Cat-YCl and Cat-NdCl. The conversion of CL and the molecular weight of PCL increase with increasing polymerization temperature. But when the temperature is higher than 60°C, the molecular weight of polymer obtained with catalyst Cat-YCl decreases slightly. This result is similar to that reported for solution polymerization of ϵ -CL catalyzed by Nd(O—i—Pr)₃^[15]. The fact may arise from polymer degradation at higher temperature. Below 60°C, the polymerization reaction with catalyst Cat-YCl proceeds rather slowly.

Table 1 The bulk polymerization of CL with rare earth catalyst

Catalyst	$\frac{[\text{CL}]}{[\text{Ln}]}$ Molar ratio	t (h)	T ($^{\circ}\text{C}$)	Conversion (%)	$M_n (\times 10^4)$
YCl_3^{a}	120	40	100	82.5	4.5
NdCl_3^{a}	120	40	100	85.0	4.7
$\text{Cat-YCl}^{\text{b}}$	200	10	40	73	13.8
$\text{Cat-YCl}^{\text{b}}$	200	10	60	100	20.5
$\text{Cat-YCl}^{\text{b}}$	200	10	80	100	18.6
$\text{Cat-NdCl}^{\text{b}}$	180	3	20	56	10.4
$\text{Cat-NdCl}^{\text{b}}$	180	3	50	100	12.9
$\text{Cat-NdCl}^{\text{b}}$	180	3	60	100	16.8
$\text{Cat-NdCl}^{\text{b}}$	180	3	70	100	19.7

a Data from Reference [7], b Monomer CL 1 mL

Fig.1 and 2 show the effect of $[\epsilon\text{-CL}]/[\text{Ln}]$ ($\text{Ln}=\text{Y}, \text{Nd}$) molar ratio on the polymerization. It can be found that at low $[\epsilon\text{-CL}]/[\text{Ln}]$ molar ratio, CL can completely convert into PCL, but the conversion of CL drops on further increase of $[\text{CL}]/[\text{Ln}]$ ratio. The molecular weight of PCL at first increases with rising of $[\epsilon\text{-CL}]/[\text{Ln}]$, and then it reaches a maximum at $[\text{CL}]/[\text{Ln}]$ ratio of about 300. From above two figures, it can be seen that either polymerization conversion of CL or MW of PCL decreases gradually on further rise of $[\text{CL}]/[\text{Ln}]$ molar ratio ($\text{Ln}=\text{Y}, \text{Nd}$), which might be caused by some side-reactions, such as coordinative competition between active polymer chain and monomer, transesterification^[9] or chain termination by other impurities.

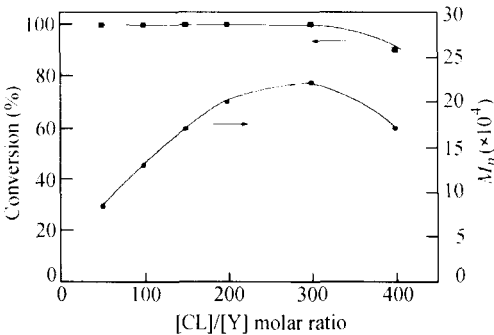


Fig.1 Effect of $[\text{CL}]/[\text{Y}]$ molar ratio on the polymerization of CL Condition: 60°C , 10 h, bulk, CL 1 mL, $(\text{OM})_2\text{YCl}$ as catalyst

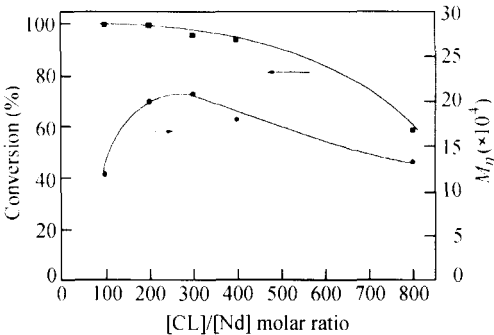


Fig.2 Effect of $[\text{CL}]/[\text{Nd}]$ molar ratio on the polymerization of CL Condition: 70°C , 3 h bulk, CL 1 mL, $(\text{MSiM})_2\text{NdCl}$ as catalyst

The relationships of the conversion of ϵ -CL and the molecular weight of PCL with polymerization time are illustrated in Fig.3 and 4, respectively. With the prolongation of polymerization time, both the conversion and molecular weight increase. It can be found that the polymerization with Cat-NdCl proceeds more rapidly than that with Cat-YCl, indicating that Cat-NdCl is more active than Cat-YCl.

From Fig.3 and Fig.4, it can also be found that Cat-YCl is less efficient than Cat-NdCl. The polymerization with Cat-YCl at 60°C for 6 h gave a conversion of about 81%, whereas the conversion reached 100% in 3 h when Cat-NdCl was used as catalyst.

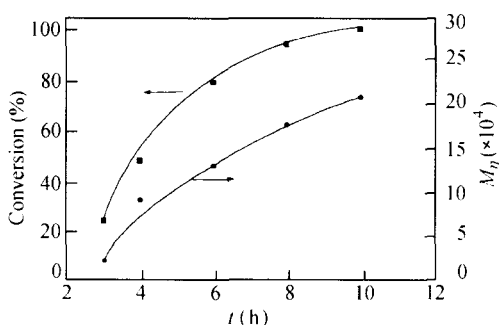


Fig.3 Effect of time on the polymerization of CL Condition: 60°C, $[\text{CL}]/[\text{Cat-YCl}]=200$, bulk, CL 1 mL

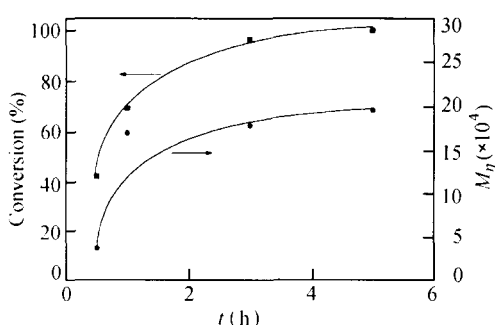


Fig.4 Effect of time on the polymerization of CL Condition: 70°C, $[\text{CL}]/[\text{Cat-NdCl}]=180$, bulk, CL 1 mL

The effect of NaBPh₄ on the polymerization

It is now well recognized that the metallocene catalysts for olefin polymerization can be promoted by some additives, such as tetraphenylborate (C_6H_5)₄B⁻, carborane ($\text{C}_2\text{B}_9\text{H}_{12}^-$) or fluorate borate (C_6F_5)₄B⁻ [16]. In the present study, tetraphenylboron sodium (NaBPh₄) (B) was selected to test the promoting effect on the polymerization of ϵ -caprolactone by Cat-YCl. The results are summarized in Table 2. It is obvious that Cat-YCl in the presence of NaBPh₄ has higher activity for the polymerization of ϵ -caprolactone. For example, within the same polymerization time of 4 h, in the presence of NaBPh₄, the conversion of CL is 64% and the molecular weight of PCL is 14.9×10^4 , while in the absence of NaBPh₄, the conversion is 47% and the molecular weight of PCL is 9.4×10^4 as shown in Fig.3. The mechanism of NaBPh₄ is being studied.

Solution Polymerization of CL

It is generally known, that polar solvent is favorable for ionic polymerization, which proceeds more rapidly in polar solvent than in nonpolar solvent. In order to

determine the effect of solvent medium on the polymerization of CL, several sorts of solvents with different dielectric constant (ϵ) were chosen in the polymerization. The results are shown in Table 3. The polymerization of CL which was carried out in THF gave PCL with high conversion. Here, in addition to the polarizability effect of THF, it is also an excellent solvent for both monomer and polymer, thus forming a homogeneous polymerization system. To compare with THF, the solvation ability of benzene is much poorer for both CL and PCL. It should be noted that the MW of PCL obtained from THF or ethyl acetate is lower than that from benzene. Especially, the polymerization conversion of CL in ethyl acetate is the lowest of the three, which may be related to the chain transfer reaction of ethyl acetate, nevertheless, the carbonyl group in ethyl acetate can also coordinate with rare earth ion, and thus inhibit the polymerization of CL.

Table 2 The bulk polymerization of CL in the presence of NaBPh₄

NaBPh ₄ /Y molar ratio	<i>t</i> (h)	Conversion (%)	<i>M_n</i> ($\times 10^4$)
0	4	47	9.4
0.5	4	64	14.9
0.5	7	93	20.8

Conditions: [CL]/[Cat-YCl]=200

molar ratio, 60°C, CL 1 mL

Table 3 Effect of solvent on the polymerization of CL

Solvent	ϵ	Conversion (%)	<i>M_n</i> ($\times 10^4$)
THF	7.85	93.6	5.09
Benzene	2.28	82.7	9.91
Ethyl- acetate	6.02	31.1	1.84

Conditions: [CL]/[Cat-YCl]=100

molar ratio, solvent/CL=1:1 (v/v),

CL 1mL 60°C

CONCLUSION

A single component lathanocene chloride, O(C₂H₄C₅H₃CH₃)₂YCl or Me₂Si-[(CH₃)₃-SiC₅H₃]₂NdCl is highly active for the polymerization of ϵ -caprolactone, giving high molecular weight polycaprolactone. The polymerization temperature, time, solvent and [CL]/[Ln] ratio greatly affect the polymerization. The addition of NaBPh₄ can promote the polymerization whose mechanism is now under study.

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