

Ring-opening Polymerization of ϵ -Caprolactone Using Lanthanide Tris(4-*tert*-butylphenolate)s as a Single-component Initiator

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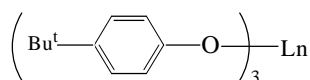
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Abstract: The ring-opening polymerization of ϵ -caprolactone (CL) initiated by novel single lanthanide tris(4-*tert*-butylphenolate)s [Ln(OTBP)₃] is reported. Single-component La(OTBP)₃ can effectively prepare polycaprolactone (PCL) with over 90% yield and viscosity average molecular weight about 60×10^3 under quite mild conditions: molar ratio of CL to initiator is 1000, 60 °C, 2 h in toluene. Mechanism study indicates that the monomer inserts into the growing chain *via* the break of acyl-oxygen bond of CL.

Keywords: Lanthanide tris(4-*tert*-butylphenolate)s, ϵ -caprolactone, ring-opening polymerization.

It is well known that polycaprolactone is a good biodegradable and biocompatible aliphatic polyester receiving much attention for its medical, pharmaceutical and environmental applications. There are various initiators/catalysts based on tin, aluminum, transition metal or rare earth metal developed for the ring-opening polymerization and copolymerization of ϵ -caprolactone¹⁻⁴. In recent years, Shen *et al.* in our group have successfully developed several new rare earth catalysts for the ring-opening polymerization and copolymerization of ϵ -caprolactone, such as rare earth halide, rare earth alkoxide, rare earth acetylacetonate and rare earth aryloxide⁵⁻⁸. This paper reports the ring-opening polymerization of ϵ -caprolactone using lanthanide tris(4-*tert*-butylphenolate)s [Ln(OTBP)₃] as a new single-component initiator.

Scheme 1



Ln(OTBP)₃, as shown in **Scheme 1**, was prepared from anhydrous LnCl₃ and 4-*tert*-butylphenol according to the method of literature⁹. **Table 1** lists the influence of different lanthanide compounds on the polymerization. The data show that their catalytic activities are in following sequence: La > Gd > Nd > Y > Er. La(OTBP)₃ has the higher activity and can prepare polycaprolactone with over 90% yield and viscosity average molecular weight about 60×10^3 under following quite mild conditions: molar

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ratio of $[CL] / [La] = 1000$, 60°C , 2 h in toluene. The effect of different sorts of solvents of $La(OTBP)_3$ system is shown in **Table 2**.

Table 1 Influence of different lanthanide compounds on the polymerization

$Ln(OTBP)_3$	$[CL] / [Ln]$	Conv. (%)	$\overline{M}_v \times 10^{-3}$
La^{3+}	1000	99.1	60.9
	500	95.4	37.5
Nd^{3+}	1000	-----	-----
	500	82.8	31.1
Gd^{3+}	1000	1.1	-----
	500	97.8	48.0
Er^{3+}	1000	-----	-----
	500	4.7	7.3
Y^{3+}	1000	-----	-----
	500	30.6	21.6

Conditions: $[CL] = 2.70 \text{ mol / L}$, 60°C , 2 h, toluene

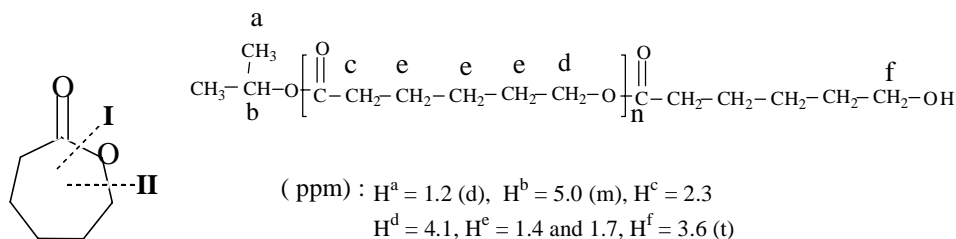
Table 2 Effect of different solvents on the polymerization of CL

Solvent	Conv. (%)	$\overline{M}_v \times 10^{-3}$
Toluene	99.4	64.1
Hexane	92.5	44.1
THF	74.6	31.9
CH_2Cl_2	49.2	23.7

Conditions: $[CL] = 2.70 \text{ mol / L}$, $[CL] / [La] = 1000$, 60°C , 2 h

The PCL obtained has a melting temperature of 70°C and 65% crystallinity. The $^1\text{HNMR}$ data were similar to that of other PCL (CH_2 1.4 and 1.7 ppm, $CH_2C=O$ 2.3 ppm, CH_2-O 4.1 ppm). In order to study the polymerization mechanism, a PCL sample with low molecular weight terminated by isopropanol has been prepared and characterized by $^1\text{HNMR}$. The $^1\text{HNMR}$ spectrum indicated that isopropyl group is at the end of the chain. The signal of H^a is a double peak and the multiple peak corresponded to H^b (**Scheme 2**). It is clear that the isopropyl is introduced into the living chain only at the termination stage. The results of $^1\text{HNMR}$ indicated that monomer inserted into the growing chains with the acyl-oxygen bond scission (**I**) rather than the break of alkyl-oxygen bond (**II**).

Scheme 2



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