

Note

Ring-opening Polymerization of ϵ -Caprolactone by Lanthanide Tris(2,6-dimethylphenolate)s

ZHANG, Li-Fang^a (张丽芳) SHEN, Zhi-Quan^{*} (沈之荃) YU, Cui-Ping^a (于翠萍)

^a Institute of Polymer Science, Zhejiang University, Hangzhou, Zhejiang 310027, China

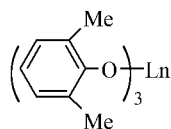
^b Department of Chemistry, Shanxi Normal University, Linfen, Shanxi 041004, China

Lanthanide tris(2,6-dimethylphenolate)s [Ln(ODMP)₃] were used as initiators for ring-opening polymerization of ϵ -caprolactone (CL) for the first time. The influence of different rare earth elements and solvents was investigated. ¹H NMR spectral data of polycaprolactone (PCL) obtained showed that the polymerization mechanism is in agreement with the coordination-insertion mechanism and the selective cleavage of the acyl-oxygen bond of CL.

Keywords ring-opening polymerization, ϵ -caprolactone, lanthanide tris(2,6-dimethylphenolate)

Ring-opening polymerization of CL is a main route of preparing biodegradable and biocompatible PCL, for which there has been growing interest in the development of efficient initiators for the ring-opening polymerization of CL. Recently, rare earth compounds as initiators have been attracting increasing attention because of their low toxicity and high efficiency. Our group reported a series of rare earth catalysts for the ring-opening polymerization and copolymerization of CL.¹⁻⁵ This paper deals with the ring-opening polymerization of CL initiated with Ln(ODMP)₃ (Scheme 1) for the first time, discussing the effect of rare earth element as well as solvent.

Scheme 1



Ln(ODMP)₃; Ln = La, Nd, Sm, Gd, Er, Y

Ln(ODMP)₃ was synthesized according to literature.⁶ Table 1 gives the results of the ring-opening polymerization of CL with six kinds of rare earth compounds. The data indicate that the initiation efficiency of light rare earth compounds is higher than that of heavy rare earth compounds. The sequence of polymerization activity is: La > Nd ≈

Sm ≈ Gd > Er ≈ Y. La(ODMP)₃ has the highest activity and can prepare PCL with viscosity average molecular weight (M_η) about 6.5×10^4 and the molecular weight distribution of 1.66. The effect of different organic solvents on the ring-opening polymerization of CL with La(ODMP)₃ is summarized in Table 2. By comparison with the yield of PCL in four solvents, it is found that

Table 1 Influence of different rare earth elements on the polymerization of CL^a

Ln(ODMP) ₃	[CL]/[Ln]	Conversion (%)	$M_\eta \times 10^{-4}$
La	1000	100	6.46
	800	100	5.60
Nd	1000	50.5	5.25
	800	94.8	3.54
Sm	1000	50.7	4.56
	800	94.8	2.75
Gd	1000	48.7	3.57
	800	92.2	2.55
Er	1000	7.44	1.87
	800	14.1	1.23
Y	1000	—	—
	800	14.4	2.13

^a Reaction conditions: [CL] = 2.5 mol/L, 1 h, 60 °C in toluene.

Table 2 Effect of solvents on the polymerization of CL^a

Solvent	[CL]/[La]	Conversion (%)	$M_\eta \times 10^{-4}$
Toluene	1000	100	6.46
	800	100	5.60
CCl ₄	1000	100	3.03
	800	100	2.95
CH ₂ Cl ₂	1000	17.3	2.39
	800	47.9	0.93
THF	1000	16.8	0.73
	800	15.3	0.66

^a Reaction conditions: [CL] = 2.5 mol/L, 1 h, 60 °C.

* E-mail: zqshen@163.net

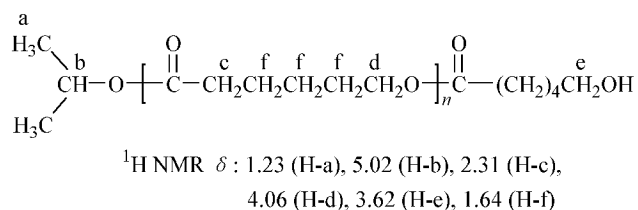
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toluene is preferable for the ring-opening polymerization of CL.

DSC measurement of PCL obtained shows a single peak at 70.2 °C. To determine the polymerization mechanism, a PCL of low molecular weight terminated by isopropanol was prepared. ¹H NMR spectrum shows a double peak and the multiple peak at δ 1.23 and 5.02, which are assigned to methyl (H-a) and methenyl (H-b) proton of isopropyl, respectively (Scheme 2). This indicates that isopropyl is introduced only at termination stage.

Scheme 2



Therefore, the ring-opening polymerization of CL proceeds via a coordination insertion mechanism with the cleavage of acyl-oxygen bond of CL.

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