

Rare Earth Complex Initiated Ring-Opening Polymerization of 2,2-Dimethyltrimethylene Carbonate

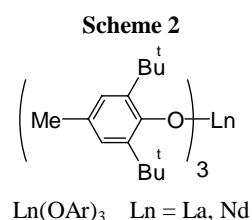
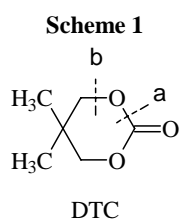
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Abstract: The ring opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) initiated by single component of tris(2,6-di-tert-butyl-4-methylphenoxy) lanthanide ($\text{Ln}(\text{OAr})_3$) is reported. The initiators are highly active to the polymerization and give high molecular weight polymers. ^1H NMR spectra and DSC measurement suggest the polymerization is free of decarboxylation. Mechanism study shows that the monomer insertion is *via* the break of acyl-oxygen bond of DTC.

Keywords: Tris(2,6-di-tert-butyl-4-methylphenoxy) lanthanide, 2,2-dimethyltrimethylene carbonate, ring-opening polymerization.

Aliphatic polycarbonate is a series of useful biodegradable materials attracting more interests recently. Poly(2,2-dimethyltrimethylene carbonate) (polyDTC) has been studied for a long time. Polymerization of DTC can be catalyzed by alkyl metals¹, trifluoromethanesulfonic acid and its esters², alcohol/methylaluminum diphenolate system³ and *etc.* Herein tris(2,6-di-tert-butyl-4-methylphenoxy) lanthanides ($\text{Ln}(\text{OAr})_3$, $\text{Ln}=\text{La}, \text{Nd}$) are firstly applied to initiate the polymerization of DTC. $\text{Ln}(\text{OAr})_3$ is prepared following Hitchcock's method⁴.



As shown in **Table 1**, both $\text{La}(\text{OAr})_3$ and $\text{Nd}(\text{OAr})_3$ exhibit high activity to initiate the polymerization of DTC yielding high molecular weight polymers compared with the data published.

The polymers are characterized to be free of decarboxylation by ^1H NMR operated at Bruker Avance DMX500 at 500MHz with CDCl_3 as solvent. Only two single peaks obtained on ^1H NMR at 3.967 and 1.001 with ratio of 1.0:1.5 for polyDTC (Run 3 in **Table 1**). PolyDTC's DSC measurements operated on Perkin-Elmer DSC-7 display two peaks at 97.3°C and 119.3°C in the first heating and only one peak at 120.4°C in the

second heating, which is corresponding to literatures¹.

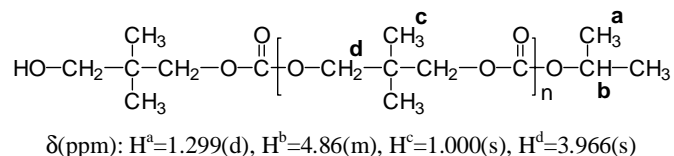
Table 1 Ring-opening polymerization of DTC initiated by Ln(OAr)₃^{a)}

Run	Initiator	[DTC] / [Ln(OAr) ₃]	Reaction Time	Yield (%)	M _w ^{b)} ×10 ⁻³	M _n ^{c)} ×10 ⁻³
1	La(OAr) ₃	1000	60 min	98	247	61.2
2	La(OAr) ₃	1700	5.5 hr	60	305	92.0
3	Nd(OAr) ₃	1000	5 min	99	280	85.9

a) Conditions: 15°C in toluene. b) Viscosity measurements¹. c) Measured by GPC.

For polymerization mechanism study, a polyDTC sample of low molecular weight terminated by isopropanol has been prepared and characterized by ¹HNMR. The end unit of isopropyl is found in ¹HNMR spectrum: the multiple peaks of H^a and the double peaks of H^b, which is shown in **Scheme 3**. It's clear that the isopropyl is introduced only at termination stage. Thus, the monomer is believed to insert into living chain *via* the break of acyl-oxygen bond (method a in **Scheme 1**), which differs from the break of alkyl-oxygen bond (method b) by some other catalyst systems. Based on the ratio of the intensities of H^c and H^a in ¹HNMR, the number average molecular weight of polyDTC is calculated as 1,480.

Scheme 3



Acknowledgment

This project is supported by The National Science and Technology Committee G1999064801.

References

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Received June 12, 2000