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Novel Single Rare Earth Aryloxide Initiators for Ring-Opening Polymerization of 2,2-Dimethyltrimethylene Carbonate

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ABSTRACT: The ring-opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) initiated with highly active single rare earth tris(2,6-di-*tert*-butyl-4-methylphenolate) ($Ln(OAr)_3$, Ln = La, Nd, Dy, Y) is reported for the first time. The catalytic activities of various $Ln(OAr)_3$ systems are decreasing in the following sequence: La > Nd > Dy ∼ Y. PolyDTC ($M_w = 17.1 \times 10^4$, MWD = 2.79) initiated by $La(OAr)_3$ at [DTC]/[initiator] = 1000 was obtained with a conversion of 97.9% within 1 h in toluene at 15 °C. ^1H NMR, GPC, and DSC are used to characterize the polymer's structure and to investigate the polymerization mechanism. PolyDTC obtained has no ether unit developed from CO_2 elimination. The polymerization of DTC occurs according to a coordination anionic mechanism, and the ring is opened via acyl−oxygen cleavage leading to an Ln−O active center.

Introduction

Aliphatic polycarbonates are good biomaterials because of their biodegradability, biocompatibility, and low toxicity.[1] Therefore, the development of simple, convenient, and efficient initiators for the ring-opening polymerization of cyclic carbonate is important from both practical and fundamental viewpoints. Ring-opening polymerization of 2,2-dimethyltrimethylene carbonate (DTC) has attracted much attention in recent years.[2] Besides cationic polymerization and anionic polymerization systems, metal alkoxide-based systems including alcohol/methylaluminum diphenolate[3] and rare earth alkoxides[4] have been reported for initiating coordination polymerization of DTC. To the best of our knowledge, no article has yet been published using single metal aryloxides as initiators for DTC polymerization.

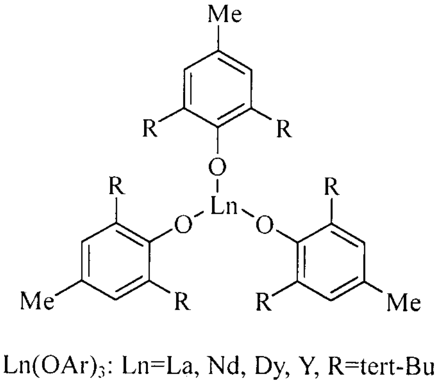
We have found that rare earth tris(2,6-di-*tert*-butyl-4-methylphenolate)s ($Ln(OAr)_3$, Ln = La, Nd, Dy, Y; Scheme 1) are highly active in coordination ring-opening polymerization of DTC. Both the polymerization features and mechanisms are described herein.

Experimental Section

All experiments including initiators' syntheses and polymerizations were carried out under argon atmosphere free of moisture and oxygen. DTC (mp 108.5−109.5 °C) and $Ln(OAr)_3$ were synthesized according to the literature.[5,6] ϵ-CL was distilled under reduced pressure before use. All polymerizations were performed in 15 mL ampules. Initiator dissolved in toluene was introduced into monomer solution by a syringe. Methanol with 5% HCl was used as terminator and precipitator except for some mechanismic studies.

^1H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer using $CDCl_3$ with tetramethylsilane (TMS) as internal standard. Differential scanning calorimeter (DSC) curves were taken on Perkin-Elmer Pyris 1 in the temperature range −30 to +150 °C with a heating rate of 10 °C/min. Gel permeation chromatography (GPC) analyses were carried out at 25 °C on a Waters 150 °C apparatus with tetrahydrofuran (THF) as eluent (1.0 mL/min). Polystyrene standards were used for calibration. Viscosity measurements were carried out with an Ubbelohde viscometer at 23.0 ± 0.1 °C using THF as a solvent. The average molecular weight of polyDTC from light scattering experiments was related to the intrinsic viscosity using the following equation:[7] $[\eta] = 8.32 \times 10^{-3}\overline{M}_{LS}^{0.79}$.

Scheme 1. Structure of $Ln(OAr)_3$



Results and Discussion

Polymerization Features. Rare earth tris(2,6-di-*tert*-butyl-4-methylphenolate)s are easy to prepare from cheap and available reagents, easy to purify, thermally stable, and structurally well characterized compounds. $Ln(OAr)_3$ without respect to light or heavy rare earth metals is an effective initiator for ring-opening polymerization of DTC. Table 1 shows the results of polymerizations of DTC with these systems. The data show that all initiators induce the polymerization with a high rate at 15 °C, giving conversions over 90% within 15 min. Lanthanum tris(2,6-di-*tert*-butyl-4-methylphenolate) exhibited the highest activity, having an efficiency of 492 kg PDTC mol^{-1} Ln h^{-1} (run 1) and produced a rather high molecular weight polyDTC (12−25 × 10^4) with MWD of 2.4−2.8. The reason for different catalytic activities and molecular weights with various light (La) and heavy (Dy, Y) rare earth systems may be due to the differences between their electronic structures and coordination abilities. A more detailed interpretation would require further investigation. Both the conversion and molecular weight of polyDTC show very small changes within the polymerization temperature from 0 to 45 °C with $La(OAr)_3$ as initiator as shown in Table 2. Figure 1 illustrates the time dependence of DTC conversion and molecular weight of polyDTC initiated by $La(OAr)_3$ and $Dy(OAr)_3$ systems. With $La(OAr)_3$

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Table 1. Polymerization of DTC with $Ln(OAr)_3$ Systems[a]

run	Ln	[DTC]/[Ln(OAr)$_3$]	time (min)	conv (%)	M_{LS}[b] × 10^{-4}	M_w[c] × 10^{-4}	MWD[c]
1	La	1000	15	94.6	12.3	11.6	2.71
2	Nd	150	5	97.0	11.4	11.6	2.28
3	Dy	50	15	90.2	4.3		
4	Y	50	10	94.6	5.8		
5	La	1000	60	97.9	24.7	17.1	2.79
6	Nd	150	60	91.3	12.4	12.4	2.68
7	Dy	50	60	89.3	3.9		
8	Y	50	60	93.4	5.1		

[a] [DTC] = 0.50 mol/L, 15 °C in toluene. [b] Viscosity measurements. [c] Measured by GPC.

Table 2. Temperature Dependence of DTC Polymerization with $La(OAr)_3$[a]

run	temp (°C)	time (min)	conv (%)	M_{LS}[b] × 10^{-4}
9	0	15	92.0	11.6[c]
10	15	15	94.5	15.6
11	25	15	92.1	14.5
12	45	15	90.8	15.7

[a] [DTC] = 0.50 mol/L, [DTC]/[La(OAr)$_3$] = 1000, toluene as solvent. [b] Viscosity measurements. [c] GPC: $M_w = 11.4 \times 10^4$, MWD = 2.39.

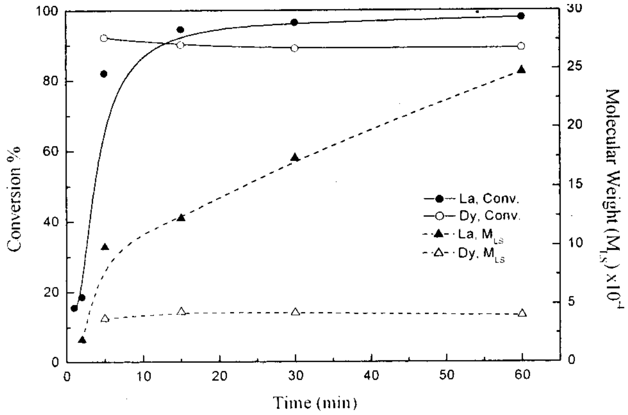


Figure 1. Time–conversion and time–M_{LS} relationships of ring-opening polymerization of DTC. (A) $La(OAr)_3$:[DTC] = 0.50 mol/L in toluene at 15 °C, [DTC]/[La(OAr)$_3$] = 1000. (B) $Dy(OAr)_3$:[DTC] = 0.50 mol/L in toluene at 15 °C, [DTC]/[Dy(OAr)$_3$] = 50.

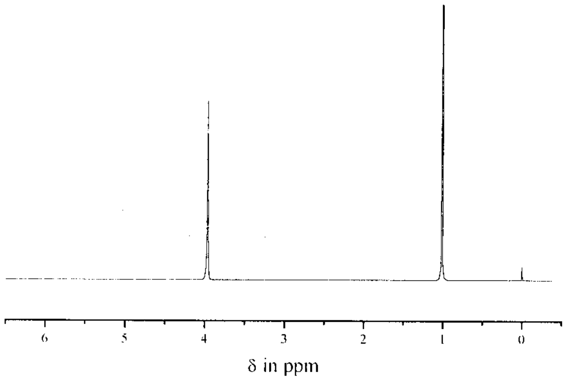


Figure 2. ^{1}H NMR spectrum of polyDTC.

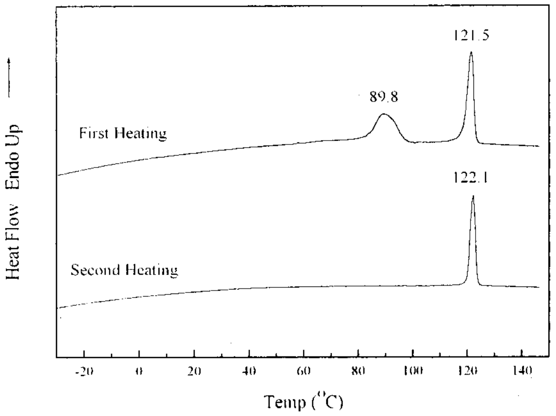


Figure 3. DSC curve of polyDTC.

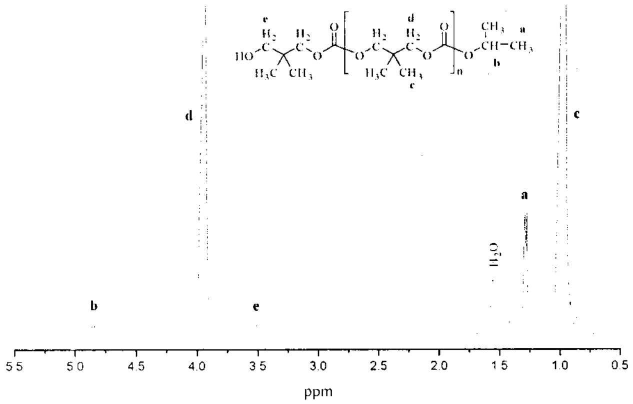
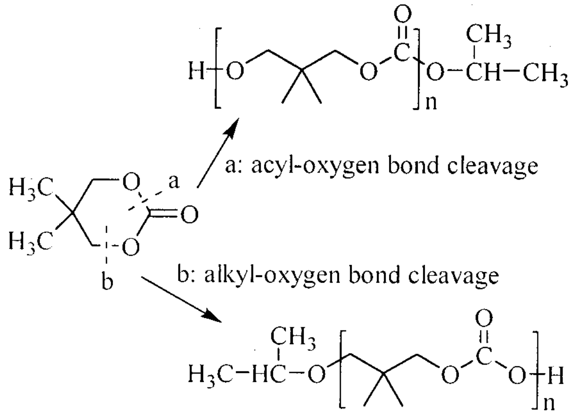


Figure 4. ^{1}H NMR spectrum of polyDTC with 2-propanol as terminator, initiated by $La(OAr)_3$.

Scheme 2. Ring-Opening Modes of DTC



conversion and molecular weight increase dramatically with increasing polymerization time.

The polyDTCs prepared have been characterized by ^{1}H NMR and DSC. Only two single peaks at 3.967 and 1.001 ppm with the intensity ratio of 1.0:1.5 were observed with ^{1}H NMR (Figure 2). The absence of peaks at δ between 3.1 and 3.3 ppm indicates that the polyDTCs obtained are free of ether units developed from CO_2 elimination which always occurs in cationic polymerization. DSC curves of polyDTC with two heating cycles are shown in Figure 3. Two peaks appear at the first heating cycle at 89.8 °C ($\Delta H \approx 16.9$ J/g) and 121.5 °C ($\Delta H \approx 20.3$ J/g), and only one peak is detected at 122.1 °C ($\Delta H \approx 22.9$ J/g) at the second heating cycle, which coincides with other results,[8] indicating that there are three crystalline modifications of polyDTC.

Mechanistic Aspects. From the data mentioned above, it becomes clear that DTC polymerization with $Ln(OAr)_3$ takes place according a "coordination insertion" mechanism consistent with other metal alkoxide systems.[4,9] To clarify whether the ring opening of DTC occurs via acyl–oxygen cleavage (Scheme 2, mode a) or alkyl–oxygen cleavage (Scheme 2, mode b), a sample of low molecular weight polyDTC terminated by 2-propanol has been prepared, and its ^{1}H NMR spectrum is

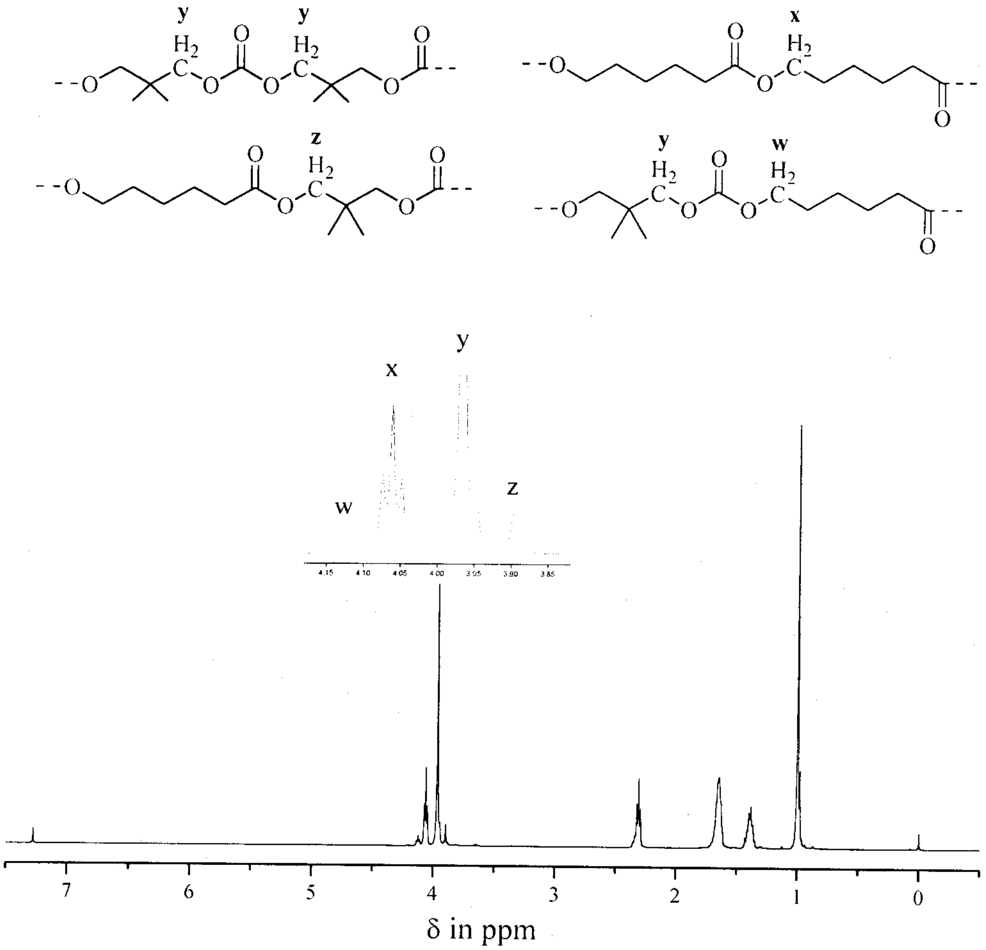
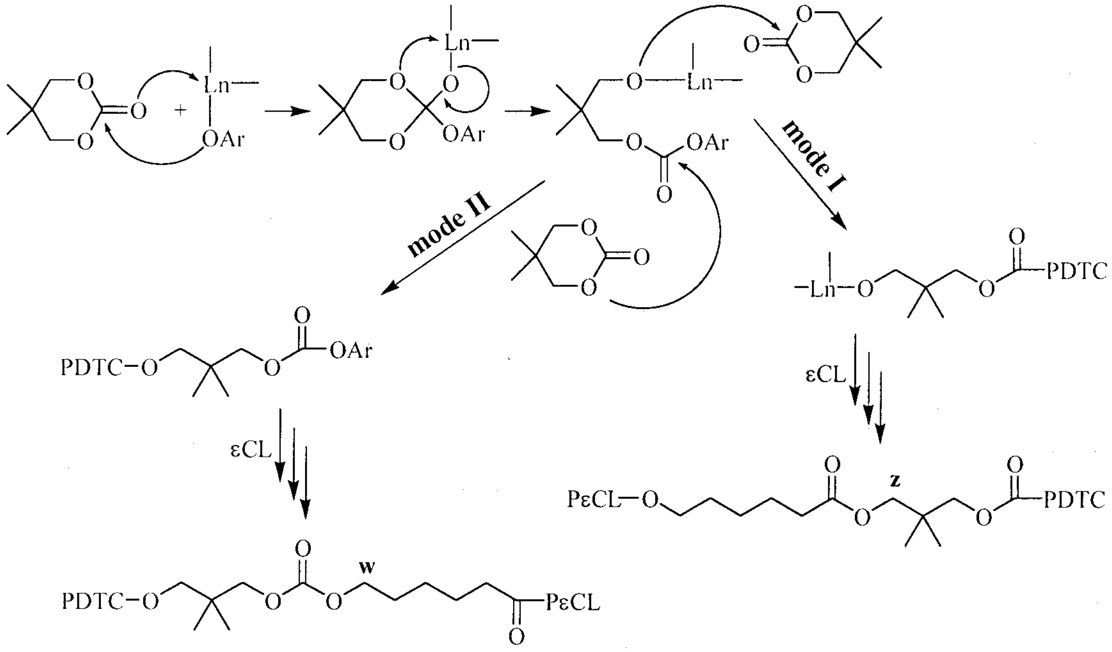


Figure 5. ^{1}H NMR spectrum of polyDTC-*b*-εCL.

Scheme 3. Comparison of Two Mechanisms of Monomer Insertions



shown in Figure 4. The chemical shifts (δ) of the hydrogen atom of the CH group next to the OCOO group (mode a) are about 4.8 ppm and about 3.2 ppm next to the $OCH_2C(CH_3)_2$ group (mode b). Furthermore, the ^{1}H NMR signals of the CH_3 group in isopropyloxyl are a double peak at about 1.3 ppm by mode a and about 1.1 ppm by mode b. From Figure 4, a double peak of H^a at 1.299 ppm, a multiple peak of H^b at 4.86 ppm, and no signals at 3.1–3.3 ppm were observed. Therefore, it can be concluded that the monomer inserts into the growing chain via cleavage of the acyl–oxygen bond (mode a in Scheme 2).

According to Scheme 3, there are two possibilities for monomer insertion, namely monomer insertion into the

Table 3. ^{1}H NMR Contribution of PolyDTC-*b*-ϵCL Initiated by Nd(OAr)$_3$

			DTC (%) in polymer	intensity in ^{1}H NMR[a]				ratio (%)[b]
run	M$_1$	M$_2$		H^w	H^x	H^y	H^z	
13	DTC	ϵ-CL	49.9	0.1427	0.9605	1.9986	0.1995	39.8
14	ϵ-CL	DTC	42.1	0.1283	1.3190	2.0000	0.1051	22.1

[a] δ(H^w) = 4.111−4.137 (triple), δ(H^x) = 4.048−4.075 (triple), δ(H^y) = 3.967 (single), δ(H^z) = 3.898 (single). [b] Difference between H^{w}and H^z.

Ln−O end (mode I) or into the OCO−OAr end (mode II). If the monomer inserts into the Ln−O bond, the ring-opening polymerization proceeds via a “coordination anionic mechanism”. Otherwise, it is an “insertion cationic mechanism”. Since ϵ-caprolactone (ϵ-CL) can be copolymerized with DTC initiated by Ln(OAr)$_3$ via the same acyl−oxygen bond cleavage, two experiments were designed to obtain low molecular weight polyDTC-*b*-ϵCL as listed in Table 3. With large amount of initiator, the first monomer (M$_1$, being DTC in run 13 and ϵ-CL in run14) was polymerized for 2 min, and then the second monomer (M$_2$) was introduced and the polymerization was allowed to continue for an additional 2 min. The copolymers were terminated by methanol with 5% HCl, dried for 24 h in vacuo, and subjected to ^{1}H NMR analysis. The two copolymers gave similar ^{1}H NMR spectra shown in Figure 5. The four peaks at δ from 3.89 to 4.14 ppm originate from CH$_2$ groups next to OCO: H^w, H^x, H^y, and H^z of DTC and ϵ-CL units. From the intensity ratio of these H peaks, it is possible to determine the direction of the monomer insertion into the active chain because of the orientation of the monomers' units. After ϵ-CL (the second monomer) has inserted into the active chain of polyDTC (run 13), a CH$_2$ containing H^z group of DTC is formed under mode I in Scheme 3, while a CH$_2$ containing H^w group of ϵ-CL is formed under mode II. In the case of run 14, the CH$_2$ signal becomes H^w linking to mode I or H^z to mode II because ϵ-CL is the first monomer. The intensity data of the peaks of H^w, H^x, H^y, and H^z in ^{1}H NMR spectra are summarized in Table 3. In the case of run 13, the H^z intensity is 39.8% higher than H^w, which conforms to the mode I insertion. In contrast, the H^w intensity is 22.1% higher than H^z in the case of DTC inserting to the polyϵCL active chain (run 14), which confirms also the mode I insertion.

Data in Table 3 show that some degree of H^w in CH$_2$ existed in mode I. This may be caused by DTC remaining after the 2 min first stage polymerization. Thus, a statistical sequence of random blocks (denoted as X block) is formed at the beginning period in the second polymerization stage. In the X block, two CH$_2$ groups of H^w and H^z are formed when DTC inserts into an ϵ-CL active end then followed by ϵ-CL. Therefore, the block copolymer of polyDTC-*b*-ϵCL has the structure A−X−B, where A and B blocks are homopolymers. The results above show that the ring-opening polymerization of DTC proceeds via an anionic coordination mechanism (mode I in Scheme 3).

The initiation and propagation courses of DTC with Ln(OAr)$_3$ initiator can be described as a “coordination addition, acyl−oxygen cleavage” mechanism. First, the acyl group in DTC coordinates to rare earth metal with the occurrence of the addition reaction. Then a growing chain is developed after the rare earth metal shifts to the oxygen atom of OCH$_2$C(CH$_3$)$_2$, and the acyl−oxygen bond breaks. The following DTCs are inserted into the growing chain at the Ln−O bond.

In conclusion, a novel highly active initiator−rare earth aryloxide−was developed for the ring-opening polymerization of cyclic carbonates and lactones. PolyDTC with molecular weight of 17.1 × 10^4 and MWD of 2.79 can be prepared after 1 h polymerization in conversion of 97.9% with La(OAr)$_3$ at [DTC]/[initiator] = 1000 in toluene at 15 °C. As shown by ^{1}H NMR, the polymers obtained are free of ether units formed by possible CO$_2$ elimination.

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