

RING-OPENING POLYMERIZATION OF 2,2-DIMETHYLTRIMETHYLENE CARBONATE INITIATED BY *IN SITU* GENERATED, TETRAHYDROSALEN STABILIZED YTTRIUM BOROHYDRIDE COMPLEX AND RANDOM COPOLYMERIZATION WITH ϵ -CAPROLACTONE*

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Abstract The poly(2,2-dimethyltrimethylene carbonate) (PDTC) with one hydroxyl and one formate terminal functions was synthesized by *in situ* generated, tetrahydro salen stabilized yttrium borohydride complex. The influences of monomer/initiator molar ratio, temperature and reaction time on polymerization of DTC were investigated. Under the condition: [DTC]/[I] = 500, 55°C, toluene: 0.5 mL, DTC: 0.6 g, PDTC with $M_n = 15600$ and PDI = 2.15 was obtained. Through $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ analyses, the structure of PDTC was characterized and a coordination-insertion mechanism was proposed. In addition, the random copolymerization of DTC and caprolactone (CL) initiated by rare-earth borohydride compound was studied. The microstructure of PDTC-*co*-PCL includes four diads: DTC-CL, CL-CL, DTC-DTC and CL-DTC, which were determined by the specific signals in $^1\text{H-NMR}$ spectra. Based on the typical signals of the formate ($\delta = 8.08$) and hydroxyl ($\delta = 3.34$) end groups of PDTC-*co*-PCL, a mechanism involving DTC monomer inserts before CL during the initiation process was presumed. Furthermore, the thermal properties of amorphous copolymer were characterized by differential scanning calorimetry (DSC). The results support the random structure of PDTC-*co*-PCL.

Keywords: Ring-opening polymerization; 2,2-Dimethyltrimethylene carbonate; ϵ -Caprolactone; Rare-earth borohydride complex.

INTRODUCTION

Aliphatic polyesters and polycarbonates, such as poly(ϵ -caprolactone) (PCL), polylactide (PLA), poly(trimethylene carbonate) (PTMC), poly(2,2-dimethyltrimethylene carbonate) (PDTC), *etc.* and their derivative copolymers or polymer blends attract growing attention in recent years for their favorable biocompatibility and biodegradability^[1–8]. Among the biodegradable polymers, aliphatic polyesters were warmly welcomed because their hydrolytic products can be metabolized into nontoxic and non-allergic substances. Application of such polymers prepared by ring-opening polymerization of lactones have already been developed worldwide, including bioresorbable devices in surgery (sutures, stents, bone internal fixation devices, scaffolding matrices for tissue regeneration) and in pharmacology (drug delivery vehicles)^[9, 10]. Compared with the conventional polyesters such as poly(lactide acid) and poly(adipic anhydride), aliphatic polycarbonates' degradable products are less acidic and easier for modification^[11, 12]. In order to prepare these biomedical and environmentally benign polymers, Shen *et al.* and Guillaume *et al.*^[13–16] have made a lot of efforts by using rare-

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earth catalysts. As previous report, the Salen ligand stabilized, *in situ* generated rare-earth borohydride compounds are proved to be an efficient initiators for the ring-opening polymerization (ROP) of ϵ -caprolactone^[17, 18] and the resulting dihydroxytelechelic polymers allows further modification or functionalization.

In the present study, we report the polymerization of DTC initiated by *in situ* generated, tetrahydrosalen-stabilized yttrium borohydride complex. Comparisons of the related polymerization of CL with the same initiator were also drawn. Furthermore, we investigate the random copolymerization of DTC with CL in the aspects of the polymerization condition, the mechanistic insights and the influence of copolymer composites on the thermodynamics and crystallinity of the product PDTC-*co*-PCL.

EXPERIMENTAL

Materials

All experiments concerning air-sensitive compounds were carried out under argon atmosphere, using standard Schlenk technique. ϵ -CL (Alpha product, 99%) was dried over CaH_2 and freshly distilled under reduced pressure prior to use. 2,2-Dimethyltrimethylene carbonate (DTC) was synthesized according to the literature^[19], recrystallized three times in the *co*-solvent (THF:diethyl ether = 1:4) and then dried under vacuum at 40°C before use. Dimethoxyethane (DME) is freshly distilled from potassium using benzophenone ketyl as indicator. *In situ* generated, tetrahydrosalen-stabilized yttrium borohydride compound, used as an initiator in the study, was prepared according to the previous report^[20].

Polymerization

All the polymerizations including the homopolymerization of DTC and its copolymerization with ϵ -CL were performed in previously flamed and argon-purged glass ampules. For example, the initiator solution was added into 0.6 g of DTC and 0.5 mL of CL in toluene in the ampule by syringe. The polymerization was quenched by 5% HCl ethanol and the copolymer was washed several times and dried in vacuum. The copolymers with different DTC/CL unit molar ratios were obtained by varying the comonomer molar ratio in feed.

Measurements

^1H -NMR and ^{13}C -NMR spectra were performed on a Bruker Avance DMX500 spectrometer using tetramethylsilane (TMS) as internal standard and CDCl_3 as a solvent. Molecular weight and molecular weight distribution was determined by a Waters 1525/2414 GPC (gel permeation chromatography) system with THF as the eluent. Polystyrene standards were used to generate a calibration curve. Differential scanning calorimetry (DSC) measurements were carried out with a Perkin Elmer Pyris 1 apparatus. Samples were heated from -60°C to 150°C (first heating scan) with a heating rate of $10\text{ K}\cdot\text{min}^{-1}$, immediately cooled to -60°C and heated again to 150°C (second heating scan).

RESULTS AND DISCUSSION

Homopolymerization of DTC Initiated by Yttrium Borohydride Complex

According to a reported *in situ* generation method^[20], the rare-earth borohydride complex can be easily prepared by the salt metathesis of tetrahydrosalen-stabilized rare-earth chloride compound and borohydride sodium. A high reactivity of the similar initiator has been proved during the polymerization of TMC^[21]. In the present study, the yttrium borohydride compound is found to be an efficient initiator for the ring-opening polymerization of DTC. Table 1 shows the influence of different reaction conditions on the ROP of DTC. As summarized, the molar weight (M_n) of PDTC increases with monomer/initiator ratio ($[\text{M}]/[\text{I}]$) from 6500 to 20300 while the molar weight distribution (PDI) of PDTC ranges from 1.72 to 2.32. Distinguished from the previous report^[21, 22], the linear relationship between the yield and M_n of PDTC with the $[\text{M}]/[\text{I}]$ or reaction time was not observed within the tested range. With higher temperature or prolonged reaction time, the PDI of the polymer product becomes larger. The molecular weight of PDTC increases with temperature (from 40°C to 55°C , M_n increases from 1.02×10^4 to 1.56×10^4) at first but strongly decreases at higher temperature ($T =$

85°C, $M_n = 0.87 \times 10^4$). The reason may be that higher temperature causes the occurrence of ester exchange reaction during the propagation which led to the lower M_n and larger PDI. The trend of the effect of reaction time on the yield and M_n is the same as that of temperature.

Table 1. Polymerization of DTC in different [M]/[I] ratio, temperature and time

Entry	[M]/[I]	T (°C)	Time (min)	Conversion (%) ^a	$M_n \times 10^{-4}$ ^b	PDI
1	200	55	60	86	0.65	1.76
2	300	55	60	90	0.87	1.75
3	400	55	60	94	1.35	2.32
4	500	55	60	91	1.56	2.15
5	600	55	60	90	1.91	2.12
6	1000	55	60	88	2.01	1.86
7	1200	55	60	84	2.03	1.72
8	500	40	60	90	1.02	1.92
9	500	70	60	90	1.21	2.23
10	500	85	60	88	0.87	2.36
11	500	55	30	78	0.93	1.75
12	500	55	90	91	1.54	2.16
13	500	55	120	90	1.31	2.25
14	500	55	180	89	1.28	2.28

General polymerization conditions: toluene = 0.5 mL, DTC = 0.6 g, the initiator concentration $[Y] = 5.38 \times 10^{-5}$ mol/mL;

^a The conversion was calculated as weight of the polymer obtained/weight of the monomer used;

^b Measured by GPC referenced to polystyrene standards

To elucidate the mechanism of polymerization of DTC, a PDTC sample with low molecular weight terminated by 5% HCl ethanol solvent was characterized by $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Fig. 1 and Fig. 2). The analyses of the PDTC product reveal two distinct end groups: a formate and a hydroxyl, which can be identified by the typical signals [$-\text{OC}(\text{O})\text{H}$ at $\delta_{\text{H}} = 8.09$ and $\delta_{\text{C}} = 161.06$ (singlet), HOCH_2- at $\delta_{\text{H}} = 3.35$ and $\delta_{\text{C}} = 68.21$ (triplet)]. Moreover, the absence of peaks at $\delta_{\text{H}} = 3.3-3.1$ and $\delta_{\text{C}} = 66.5-67.7$ demonstrates that the PDTC is free of ether units which are formed by the decarboxylation of the carbonate during the polymerization^[23-25].

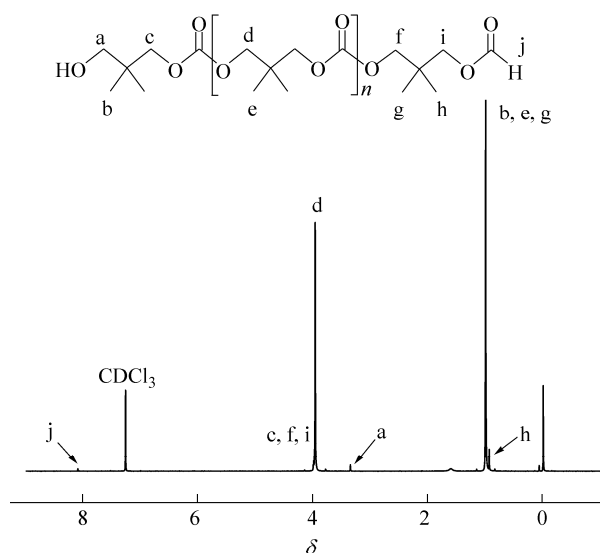


Fig. 1 $^1\text{H-NMR}$ spectra of PDTC in CDCl_3

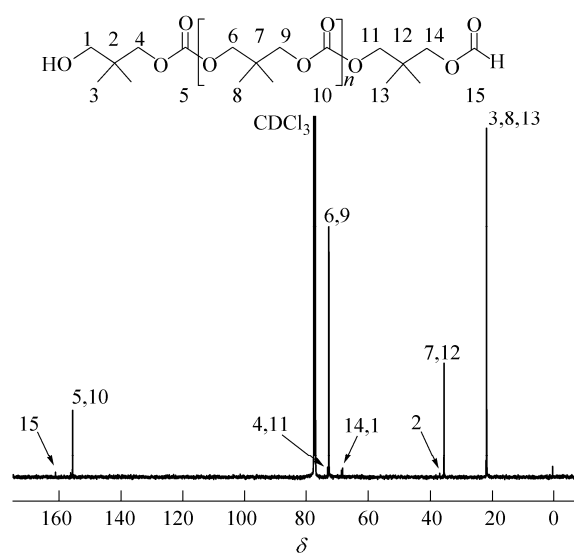
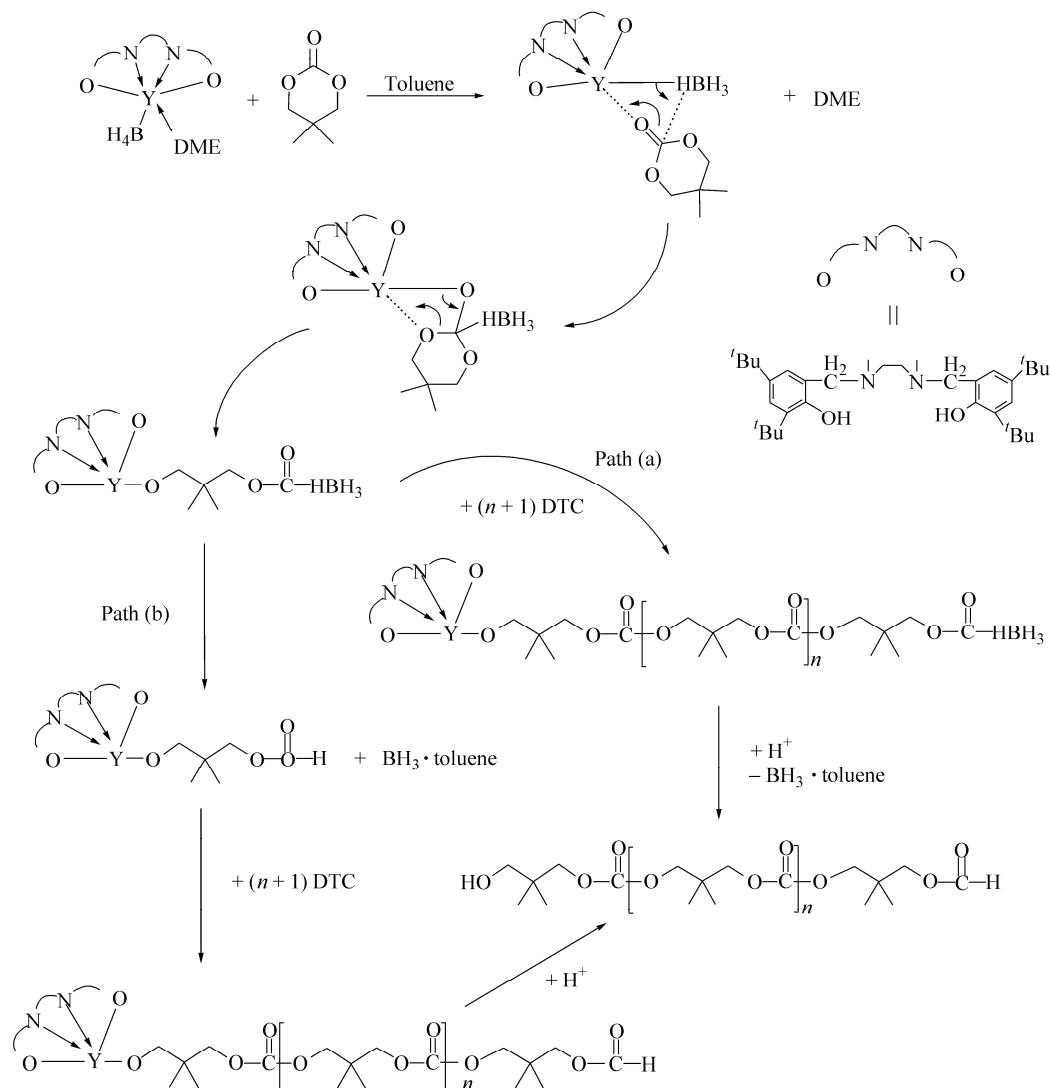


Fig. 2 $^{13}\text{C-NMR}$ spectra of PDTC in CDCl_3

Compared to the dihydroxyl end-capped PCL^[17, 18] prepared by employing the same initiator, the PDTC product exhibits two distinguished functional end groups — one formate and one hydroxyl. Thus, a different

mechanism for the polymerization of DTC can be proposed (Scheme 1). First, the monomer DTC molecule substitutes the DME to coordinate to the metal nuclei. Then, the carbon atom of DTC carbonyl is attacked by $Y[ONN'O](BH_4)(DTC)$ with either an oxygen-acyl or oxygen-alkyl bond cleavage. However, there are no specific ^1H -NMR or ^{13}C -NMR signals of $-CH_3$ end group given by oxygen-alkyl bond cleavage; the results support the most likely oxygen-acyl bond scission to generate the yttrium alkoxide species. Secondly, unlike the initiation process of ϵ -caprolactone by yttrium borohydride compound, the reduction of $-C(O)-HBH_3$ end group (the terminal carbonyl function is reduced by the α -hydrogen of $-HBH_3$ group and formed a $-CH_2OBH_2$ group) does not occur according to the absence of the signal of terminal $-CH_2OH$ function which can be developed by the reduction and final hydrolysis. Thirdly, two paths involve the whole polymerization process were presumed. According to path (a), the incoming monomer inserts into the $Y-O$ alkoxide species to propagate the polymer chain and finally the polymerization is quenched by the acidic hydrolysis of $Y-O$ bond and $-O-HBH_3$ to induce $-CH_2OH$ and $-OC(O)H$ end groups, respectively. Path (b) involves the initial $BH_3 \cdot$ toluene elimination, then propagation of the chain with the insertion of DTC monomer and consequently the hydrolysis process that leads to the hydroxyl and formate telechelic PDTC.



Scheme 1 Presumed mechanism for the polymerization of DTC initiated by yttrium borohydride compound

Copolymerization of DTC and CL Initiated by Yttrium Borohydride Complex

The influence of different conditions on the copolymerization of DTC and CL was investigated. As shown in Table 2, the molecular weight and the yield of PDTC increase with the temperature and time. Better than the homopolymerization of DTC exhibiting broaden molecular weight distributions (PDI: 1.72–2.32), the copolymer displays narrower molecular weight distributions (PDI: 1.59–1.88) which indicate the copolymerization is more controllable. The indicative signals in $^1\text{H-NMR}$ spectra at $\delta = 3.8$ –4.2 represent four chain segments of DTC-CL (d), CL-CL (g), DTC-DTC (h) and CL-DTC (i), which are in good agreement with previous report^[26]. Moreover, the specific signals of the formate ($\delta = 8.08$) and hydroxyl ($\delta = 3.34$) terminal functions of PDTC-*co*-PCL were observed (Fig. 3), suggesting that the DTC monomer inserts into the Y–O bond first rather than CL during the initiation process. Otherwise, the dihydroxyl telechelic copolymer could be formed.

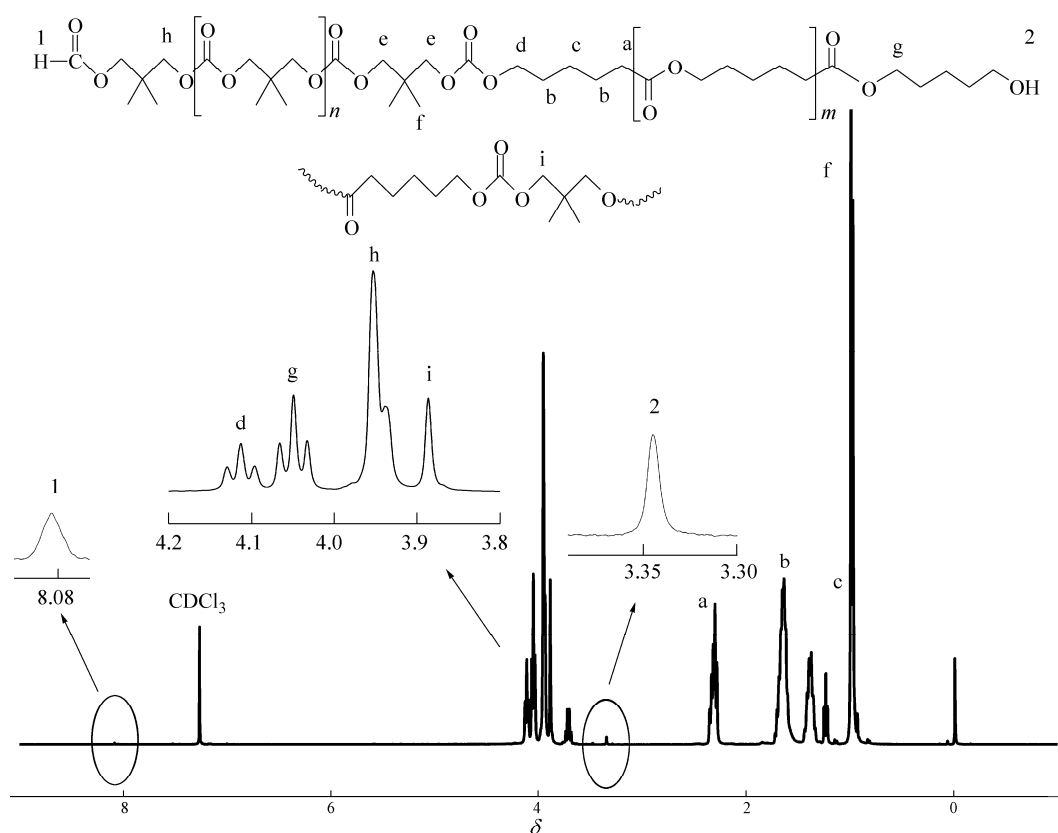


Fig. 3 $^1\text{H-NMR}$ spectra of PDTC-*co*-PCL in CDCl_3

DSC analysis of the PDTC-*co*-PCL reveals the thermal properties of the copolymer are varying with different CL/DTC compositions, as summarized in Table 3. The thermal properties of PDTC and PCL were also listed for comparison. Beyond our expectation, DSC investigation of PDTC exhibits an endotherm at 106.0°C ($\Delta H_m = 59.7$), which is not consistent with the conventional two endotherms at approximately 90 – 100°C and 120°C by the previous report^[22, 27, 28]. It probably suggests that one crystalline phase exists in the PDTC. On the other hand, the copolymers we obtained are semicrystalline or amorphous copolymers, which is corresponding to most reports employing rare-earth borohydride compound as an initiator. Figure 4 shows that T_m of the PDTC-*co*-PCL becomes lower with the content of DTC in copolymer increasing. Meanwhile, the lower T_m with higher CL unit content in copolymer indicates the lower crystallinity of copolymer. Therefore, this thermal property implies the CL component may have plasticizing effect on the copolymer and enhance its tenacity.

Table 2. Random copolymerization of DTC&CL with different [M]/[I] ratio, temperature and time

Entry	[CL+DTC]/[I]	<i>T</i> (°C)	Time (min)	Conversion (%) ^a	<i>M_n</i> × 10 ^{-4b}	PDI
1	800	55	60	88	2.50	1.79
2	1000	55	60	91	2.93	1.73
3	1200	55	60	95	3.22	1.63
4	1400	55	60	98	2.88	1.66
5	1600	55	60	84	1.61	1.60
6	1600	40	60	65	1.39	1.59
7	1600	70	60	97	2.51	1.82
8	1600	85	60	98	2.91	1.83
9	1600	55	30	62	1.42	1.48
10	1600	55	120	96	2.09	1.88

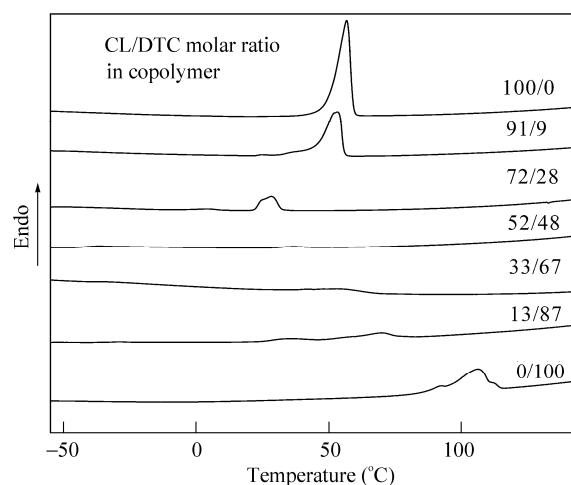
General conditions: toluene = 0.5 mL, DTC = 0.6 g, CL = 0.5 mL, the initiator concentration [Y] = 5.38 × 10⁻⁵ mol/mL;

^a The conversion was calculated as weight of the polymer obtained/ weight the monomer used;

^b Measured by GPC referenced to polystyrene standards

Table 3. DSC data of PDTC-*co*-PCL

Entry	CL/DTC (molar ratio in feed)	CL/DTC (molar ratio in copolymer)	<i>T_{m1}</i> (°C)	ΔH_{m1} (J·g ⁻¹)	<i>T_{m2}</i> (°C)	ΔH_{m2} (J·g ⁻¹)
1	100:0	100:0	—	—	56.7	113.3
2	90:10	91:9	—	—	53.2	70.5
3	70:30	72:28	4.9	2.0	28.3	18.9
4	50:50	52:48	—	—	36.3	1.9
5	30:70	33:67	—	—	54.9	9.9
6	10:90	13:87	28.0	0.36	84.1	38.3
7	0:100	0:100	—	—	106.0	59.7

**Fig. 4** DSC of PDTC-*co*-PCL with various CL/DTC molar ratio in copolymer

CONCLUSIONS

In summary, the rare-earth borohydride compound Y[ONN'O](BH₄)(DME) was proved to be an efficient initiator for the ring-opening polymerization of DTC and its random copolymerization with CL. From NMR characterizations, the structures of both PDTC and PDTC-*co*-PCL possessing formate and hydroxyl end-functions were confirmed. The results from NMR spectra support the coordinate-insertion mechanism with oxygen-alkyl bond cleavage and DTC monomer first insertion. The yttrium borohydride species of initiator have influences on the polymerization process and finally lead to the formation of formated end-group, which may have great potentials for further modification.

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