

Correlation between phenol structure and catalytic activity of samarium(III) phenolates in polymerization of ϵ -caprolactone

Part 2. Tertbutyl's electronic and steric effects

Fei Peng, Jun Ling, Zhiqian Shen*, Weiwei Zhu

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

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Abstract

Six Sm(III) phenolates were firstly synthesized with un-substituted phenol (P), 2-tertbutylphenol (2B), 4-tertbutylphenol (4B), 4-methylphenol (4M), 2-tertbutyl-4-methylphenol (2B4M) and 2,6-ditertbutyl-4-methylphenol (26B4M) separately. All the phenolates were used as single component catalyst for the ring-opening polymerization (ROP) of ϵ -caprolactone (CL). The experimental results showed that, with phenols substituted by single or double tertbutyls at different sites, Sm(III) phenolates resulted in ordered variations both in their catalytic activities and in ROP characteristics. In order to find the correlation between these ordered variations and tertbutyl substituents' electronic and steric effects, data describing phenols' geometric and charge distribution parameters were obtained with quantum chemical (QC) calculation and discussed with experimental results in organized groups. It was found that, single tertbutyl on phenol, especially ortho one, would induce mixed electronic effect but positive steric effect, latter of which induce easier ROP under mild conditions, increased catalytic activity while more inter- and intramolecular transesterifications, resulting in PCL with wider molecular weight distribution (MWD). Two ortho tertbutyls induce not only positive steric effect but also positive electronic effect, which induce the highest catalytic activity of Sm(26B4M)₃, most transesterifications and the resultant widest MWD of PCL.

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Keywords: Caprolactone; Ring opening polymerization; Sm(III) phenolates; Phenol structure; Quantum chemical calculation

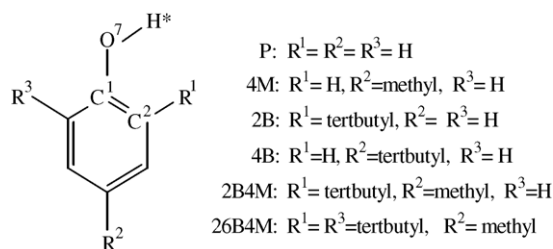
1. Introduction

Poly(ϵ -caprolactone) (PCL), which has good biodegradability and biocompatibility [1,2], is gaining interest for its numerous applications in the biomedical field. Our group has developed some rare earth phenolates as excellent single component catalysts for ROP of CL and cyclic carbonates [3–5]. The catalytic mechanism has been found as “coordination–insertion” with acyl-oxygen bond cleavage of monomer [3–5]. Therefore, clarifying the correlation between phenols' structure and phenolates' catalytic activities and ROP characteristics is quite necessary, considering its

promising contribution to an entry to tailor-made catalysts and the much divergent cost for variously structured phenols (Scheme 1).

In order to find out the correlation, nine phenols specifically substituted by methyls or/and tertbutyls were firstly utilized to synthesize nine novel Sm(III) phenolates, all of which were used as single component catalyst for ROP of CL. Quantum chemical (QC) calculation was utilized to obtain data describing geometric parameters and charge distribution in phenols. By discussing the experimental and calculational results together, the electronic and steric effects induced by methyls had been studied in our previous paper [6]; in this paper, those effects induced by tertbutyls and their influence on phenolates' catalytic activity and ROP characteristics of CL were studied with similar method and more evidences.

* Corresponding author. Tel.: +86 57187951059; fax: +86 57187951773.
E-mail address: zqshen@163.net (Z. Shen).



Scheme 1. Structure for all the phenols mentioned.

2. Experimental

2.1. Materials

CL (Acros) was dried over calcium hydride, distilled under reduced pressure and stored in argon atmosphere at room temperature prior to use. Solvents were dried and deoxygenated over blue benzophenone–Na complex and distilled. Samarium oxide (Sm_2O_3) with purity of 99.99% was used as received. All the other chemicals were analytical grade and used without further purification.

2.2. Catalyst preparation

Catalysts were prepared with Schlenk tube and vacuum-line technique under purified argon. Anhydrous samarium chloride was prepared by heating the mixture of hydrated samarium chloride and ammonium chloride under reduced pressure [7]. All the mentioned Sm(III) phenolates were synthesized according to the method described in the literature [8].

2.3. Polymerization

The ROP of CL with toluene as solvent was carried out under argon atmosphere in glass ampoules (20 mL), which had been flamed and purged with argon for several times before use. The catalyst was prepared as toluene solution and injected to each ampoule by syringe after 1 mL CL had been mixed with certain volume of toluene and the ampoule had been prewarmed in oil bath to certain temperature. After certain reaction time, the polymerization was terminated with 5 mL ethanol with 5% HCl. The obtained product was precipitated and kept in ethanol for 24 h, then filtrated and washed with ethanol several times. The purified PCL was dried in vacuum at room temperature for 72 h.

2.4. Measurements

The weight average molecular weight (M_w) and molecular weight distribution ($\text{MWD} = M_w/M_n$) were measured by gel permeation chromatograph (GPC) (Waters PL-GPC 220) at 40 °C, using THF as the eluent (1.00 mL/min) and polystyrene as the calibration standard.

3. Computational details

Charge distribution and geometric parameters of all mentioned phenols were optimized using the Restricted Hartree–Fork (RHF) method. This widely accepted and very computationally cheap method predicts reliable geometries and quantum chemical data for simple organic molecule with singlet [9–11]. A basis set of 6–31G(*d*, *p*) was used in the Gaussian 98 program [12], adding carbon and oxygen atom with *d* diffuse functions while hydrogen with *p* diffuse functions [10,11,13–16]. All the presented calculation data were obtained after the optimization converged under extremely tight criteria; the stability of all the resultant Hartree–Fork wavefunction and optimized molecular structure had been checked with stable and frequency calculations, respectively [17].

4. Results and discussion

4.1. Experimental results for ROP of CL catalyzed by Sm(III) phenolates

4.1.1. ROP of CL catalyzed by $\text{Sm}(\text{P})_3$, $\text{Sm}(\text{4B})_3$ and $\text{Sm}(\text{2B})_3$ separately

According to Table 1, $\text{Sm}(\text{P})_3$ could not catalyze ROP of CL under tested conditions. With one para tertbutyl on phenol, $\text{Sm}(\text{4B})_3$ could effectively catalyze ROP at 80 °C and obtain PCL with high monomer conversion (96.7%). With one ortho tertbutyl on phenol, $\text{Sm}(\text{2B})_3$ could catalyze ROP at 40 °C and obtain good conversion at 60 °C (94.2%) with less catalyst amount ($[\text{CL}]/[\text{Sm}] = 1000$); even with $[\text{CL}]/[\text{Sm}] = 1500$, $\text{Sm}(\text{2B})_3$ could also catalyze ROP at 60 °C. Clearly, compared with either $\text{Sm}(\text{P})_3$ or $\text{Sm}(\text{4B})_3$, $\text{Sm}(\text{2B})_3$ could effectively catalyze ROP of CL at lower temperature (60–70 °C) and with less catalyst amount ($[\text{CL}]/[\text{Sm}] = 1000$ –1500); the order for the three catalysts' activity should be: $\text{Sm}(\text{2B})_3 > \text{Sm}(\text{4B})_3 \gg \text{Sm}(\text{P})_3$. Besides, PCL obtained with $\text{Sm}(\text{2B})_3$ has wider MWD and it increases obviously with temperature.

Table 1
Effect of temperature and catalyst amount on ROP of CL catalyzed by $\text{Sm}(\text{P})_3$, $\text{Sm}(\text{4B})_3$ and $\text{Sm}(\text{2B})_3$ separately

Catalyst	<i>T</i> (°C)	$[\text{CL}]/[\text{Sm}]$	Conversion (%)	$M_w \times 10^{-4}$	MWD
$\text{Sm}(\text{P})_3$	60	800	–	–	–
	80	800	–	–	–
$\text{Sm}(\text{4B})_3$	60	800	–	–	–
	80	800	96.7	5.19	1.91
$\text{Sm}(\text{2B})_3$	40	1000	18.0	2.40	1.80
	50	1000	54.4	3.89	2.38
	60	800	94.2	10.1	2.27
	60	1000	80.0	3.01	2.97
	60	1500	33.0	2.81	2.21

Conditions: $[\text{CL}] = 2.0 \text{ mol/L}$, 60 min, toluene.

Table 2
Effect of temperature, catalyst amount and polymerization time on ROP of CL catalyzed by Sm(26B4M)₃

No.	<i>T</i> (°C)	[CL]/[Sm]	Time (min)	Conversion (%)	<i>M_n</i> × 10 ⁻⁴	<i>M_w</i> × 10 ⁻⁴	MWD
1	20	1000	10	49.3	5.30	8.33	1.57
2	20	1000	60	98.9	3.71	8.51	2.30
3	40	1000	20	100	2.93	7.14	2.44
4	40	1000	60	100	1.93	6.51	3.38
5	60	800	10	98.2	3.20	7.78	2.43
6	60	800	30	99.7	2.46	9.19	3.74
7	60	800	60	98.9	1.43	5.75	4.02
8	60	1000	20	100	2.88	7.08	2.46
9	60	1000	45	98.7	2.29	8.02	3.50
10	60	1000	60	99.1	1.56	5.93	3.81
11	60	1200	10	100	1.18	2.52	2.14
12	60	1200	60	97.8	0.80	2.54	3.18
13	60	1500	10	59.3	2.17	4.01	1.85
14	60	1500	60	99.0	1.34	4.35	3.24

Conditions: [CL] = 2.0 mol/L, toluene.

4.1.2. ROP of CL catalyzed by Sm(26B4M)₃, Sm(2B4M)₃ and Sm(4M)₃

The effects of polymerization temperature, duration and catalyst amount on ROP of CL catalyzed by Sm(26B4M)₃ were shown in Table 2; monomer concentration's effects were summarized in Fig. 1 and Table 3. Sm(26B4M)₃ kept good activity at 20 °C (conversion = 98.9% after 60 min polymerization); under monomer concentration [CL] ≥ 1.0 mol/L, monomer conversions could achieve nearly 100% at 60 °C. Especially, PCL with high *M_w* (7.14 × 10⁴) and conversion (100%) were obtained for 20 min polymerization at 40 °C, [CL]/[Sm] = 1000.

Tables 3 and 4 and Fig. 1 demonstrated ROP characteristics of CL catalyzed by Sm(2B4M)₃ and Sm(4M)₃. Although both of them could obtain good monomer conversions at 60 °C with [CL]/[Sm] = 800, they could not catalyze ROP of CL at 20 °C. With one more ortho tertbutyl in phenol than Sm(4M)₃, Sm(2B4M)₃ could catalyze ROP at 40 °C

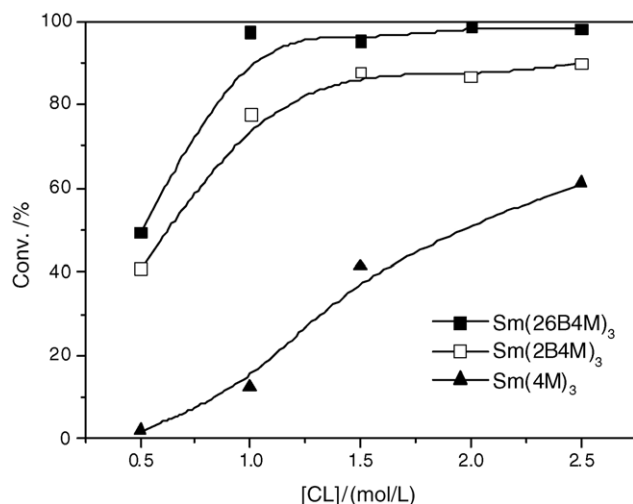


Fig. 1. Effect of monomer concentration on conversion of ROP of CL catalyzed by Sm(4M)₃, Sm(2B4M)₃ and Sm(26B4M)₃ separately, conditions: 60 °C, [CL]/[Sm] = 1000, 45 min for Sm(26B4M)₃, 60 min for Sm(2B4M)₃ and Sm(4M)₃, toluene.

Table 3
Effect of monomer concentration on ROP of CL catalyzed by Sm(26B4M)₃ and Sm(2B4M)₃ separately

Catalyst	[CL] (mol/L)	<i>M_w</i> × 10 ⁻⁴	MWD
Sm(26B4M) ₃	0.5	6.90	2.26
	1.5	8.02	3.15
	2.0	8.02	3.50
Sm(2B4M) ₃	0.5	2.63	2.03
	2.0	4.51	2.34
	2.5	4.92	2.54
Sm(4M) ₃	0.5	–	–
	1.5	2.57	1.39
	2.5	3.18	1.85

Conditions: 60 °C, [CL]/[Sm] = 1000, 45 min for Sm(26B4M)₃ and 60 min for Sm(2B4M)₃, toluene.

and always obtain higher monomer conversion under same conditions.

Clearly, with another two ortho tertbutyl, in the three phenolates Sm(26B4M)₃ could effectively catalyze the polymerization at the lowest temperature (20 °C) and achieve nearly full monomer conversions under the least catalyst amount ([CL]/[Sm] = 1500), lowest monomer concentration ([CL] = 1.0 mol/L) or after short-

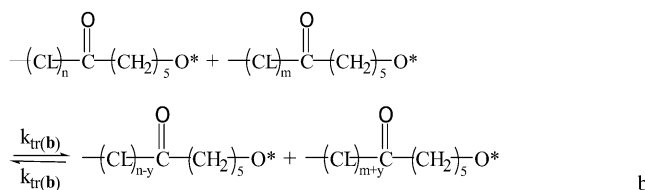
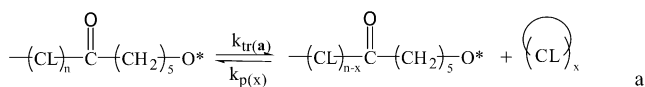
Table 4
Effect of temperature and catalyst amount on ROP of CL catalyzed by Sm(4M)₃ and Sm(2B4M)₃ separately

Catalyst	<i>T</i> (°C)	[CL]/[Sm]	Conversion (%)	<i>M_w</i> × 10 ⁻⁴	MWD
Sm(4M) ₃	20	1000	0	–	–
	40	1000	4.0	–	–
	60	800	88.8	2.80	1.84
	60	1200	22.5	1.61	1.83
	60	1500	14.0	1.39	1.85
Sm(2B4M) ₃	20	1000	0	–	–
	40	1000	27.6	2.09	2.13
	60	800	99.9	3.81	2.47
	60	1000	86.8	4.51	2.34
	60	1200	55.9	2.07	2.58
	60	1500	23.0	2.60	1.81

Conditions: [CL] = 2.0 mol/L, 60 min, toluene.

est duration (10 min), which indicated the activity order: $\text{Sm}(\text{26B4M})_3 > \text{Sm}(\text{2B4M})_3 > \text{Sm}(\text{4M})_3$.

Nevertheless, the MWD of PCL obtained by three phenolates, especially $\text{Sm}(\text{26B4M})_3$ and $\text{Sm}(\text{2B4M})_3$, was wider and increased with polymerization duration, temperature (Table 2), and monomer concentration (Table 3), which could be explained by intra- and intermolecular transesterifications (a and b) in ROP of CL catalyzed by coordination catalysts as follows



Intramolecular transesterification (a) lead to cyclics with low molecular weight [18–21], which are reported being present in ROP of CL or/and LA catalyzed by aluminum isopropoxide with “insertion–coordination” mechanisms. It was also mentioned, such transesterification reaction (a) increased with polymerization temperature and time [21]; cyclic PLA proved to be insoluble in methanol by ^1H NMR and GPC measurement, which was responsible for the broadening of MWD and the decrease in M_n [21]. Penczek et al. [18,19,22] also reported that aluminum alkoxides induce intermolecular transesterifications in ROP of CL (b), which result in two new active chains, one longer and the other one shorter, hence cause broadened MWD and decreased M_n accompanied with increased M_w .

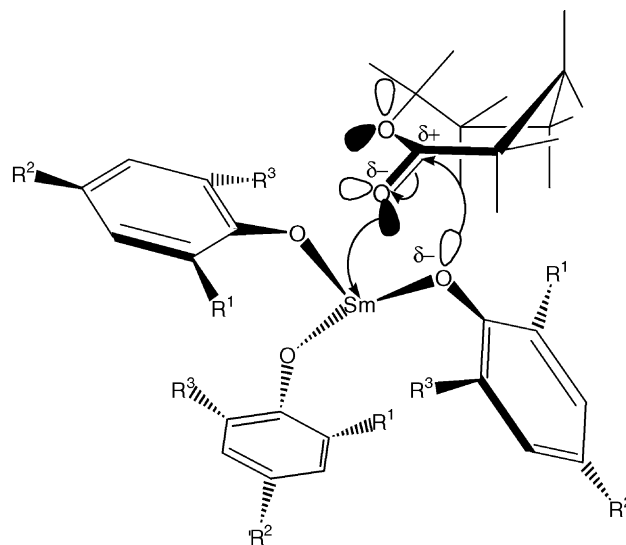
In our system, Sm(III) phenolates are coordination catalysts and catalyze ROP of CL with coordination–insertion mechanisms [3–5]; as ethanol was used for precipitation, most of GPC reports for PCL with wider MWD showed considerable oligomers with M_w ranging from 1000 to 500 presented, which caused wider MWD and distinctness between M_n and M_w . Undoubtedly, (a) must be involved and responsible for low M_n and wider MWD of PCL, the latter of which increased with polymerization temperatures (Tables 1, 2 and 4) and time (Table 2). Besides, as shown in Table 2, when polymerization time increased from 10 to 60 min, monomer conversion leveled off around 98–100% but M_n continued to decrease with increasing MWD; meanwhile, nos. 5–7 and 8–10 showed M_w increased at first and decreased later. This phenomenon could be well explained by the presence of reactions (a) and (b), both of which result in wider MWD in the whole polymerization process, but the former increase with time while the later induce higher M_w ; at early stage after high conversion, (b) might be dominate, contributing to wider MWD while increase in M_w ; later on, (a) increase with time and becomes dominate, inducing not only wider MWD and lower M_n but also decreased M_w .

Moreover, M_w and MWD of PCL increased with the number of ortho tertbutyl substituents: $\text{Sm}(\text{4M})_3 < \text{Sm}(\text{2B4M})_3 < \text{Sm}(\text{26B4M})_3$, despite changes in temperature, catalyst amount (Tables 2 and 4) and monomer concentration (Table 3), which will be well explained later, in light of tertbutyls’ electronic and steric effects on space around active center, and reported influence of active center’s size on $k_{\text{tr}(\text{b})}$ [18,19,23].

4.2. Influence of electronic and steric effects introduced by tertbutyl substituents on phenolates’ catalytic activity and ROP characteristics

The above experimental results indicated that, both phenolates’ catalytic activities and ROP characteristics changed regularly, keeping in good concordance with variations in tertbutyl substituents’ site ($\text{Sm}(\text{2B})_3$ – $\text{Sm}(\text{4B})_3$ – $\text{Sm}(\text{P})_3$ group) and number ($\text{Sm}(\text{4M})_3$ – $\text{Sm}(\text{2B4M})_3$ – $\text{Sm}(\text{26B4M})_3$ group) on phenols. In light of the “coordination–insertion” mechanism (Scheme 2) in ROP of cyclic esters catalyzed by rare earth phenolates [3–5], which indicates that both the charge distribution on the hydroxyl oxygen of phenol and the space around the metal center of phenolates would affect monomer coordination and insertion, it was proposed that the above concordance could be explained by substituents’ electronic and steric effects, when influence from Sm(III) cation left out from this paper.

As to substituents’ electronic effect, study in the previous paper [6], which discussed methyl’s electronic and steric effects on phenolates’ catalytic behaviors, has found that: (1) If substituents on phenol induce longer distance between phenyl and hydroxyl hydrogen (C^1 – H^* distance) together with increased negative charge on phenol oxygen (O^7), they might indicate more space around metal center and easier nucleophilic attack from O^7 in phenolates to acyl carbon in



Scheme 2. “Coordination–insertion” catalytic mechanism for ROP of CL catalyzed by samarium(III) phenolate.

monomer, which will induce easier monomer coordination on metal center and insertion into the metal-O⁷ bond. These indicate substituents' positive electronic effect; corresponding phenolate will catalyze easier ROP of CL under mild conditions or obtain higher monomer conversion under same conditions. (2) If substituents induce shorter C¹-H* distance and more negative charge on O⁷, they would not induce either absolutely positive or absolutely negative electronic effect, hence orders for phenolates' activities and ROP characteristics will be different from case to case.

As to the steric effect, especially those induced by ortho substituents, they will affect monomers' coordination and insertion by two reciprocal effects: for one thing, substituents would take up the space around the metal center and bring in negative effect to the monomers' coordination and insertion; for another, big substituents, especially ortho ones, would induce repulsion among ligands, which in turn would enlarge the space among ligands hence cause positive effect. The latter positive effect might even result in longer distance between the phenyl and the metal center, which would also contribute to easier coordination and insertion of monomer. Therefore, the final steric effect of substituents to phenolates' catalytic activity must be the compromise of the two.

Aiming to clarify tertbutyl' electronic and steric effects on phenolates' catalytic activities and ROP characteristics, data describing geometric parameters and charge distribution in specifically substituted phenols were obtained with QC calculation method. These concerning hydroxyl hydrogen (H*), O⁷ and the phenyl carbon (C¹) directly connected with O⁷ were picked out and discussed in certain groups, in light of ordered varieties in experimental results and substituents' site and number.

4.2.1. Electronic and steric effects introduced by single tertbutyl substituent

QC calculational data for P, 4B and 2B were compared in Table 5. As the geometric parameters showed, the C¹-O⁷ distance increased slightly from P to 4B but obviously to 2B; the O⁷-H* distances in the three phenols keep similar, however, the angle A(C¹-O⁷-H*) decreased a little from P to 4B but much to 2B. Therefore, the C¹-H* distance decreases slightly from P to 4B but obviously to 2B. Clearly, compared with para tertbutyl, ortho tertbutyl has more influence on those geometric parameters. As the charge distribution data showed, both the positive charge on H* and the negative charge on O⁷ increased in the order: P < 4B < 2B, while the positive charge on C¹ decreased in the same order: P > 4B > 2B.

Similarly, as shown in Table 6, comparison between 4M and 2B4M met well the above orders concerning single ortho tertbutyl's contribution: 2B4M has shorter C¹-H* distance but more negative charge on O⁷.

In general, single tertbutyl on phenol, especially ortho one, would induce shorter C¹-H* distance while more negative charge on O⁷. In light of the conclusion proved in the previous paper [6] and described above, tertbutyl induce mixed

electronic effect and could not be responsible to definite catalytic activity order or regularly changed ROP characteristics.

Therefore, the ordered variation in phenolates' activities and ROP characteristics should be explained by single tertbutyls' steric effect. Taking into account substituents' two possible reciprocal steric effects, it could be concluded that tertbutyls, especially ortho ones, bring positive steric effect predominant to the negative ones. So, steric effect positively induces more space among ligands and around the metal center, which results in easier monomer coordination and insertion. That's why phenolates with one more tertbutyls (Sm(4B)₃ versus Sm(P)₃), especially ortho ones (Sm(2B)₃ versus Sm(4B)₃; Sm(2B4M)₃ versus Sm(4M)₃), could catalyze ROP at lower temperature (Tables 1 and 4), with less catalyst amount (Table 1) or lower monomer concentration (Fig. 1), hence demonstrate higher catalytic activity (Sm(P)₃ < Sm(4B)₃ < Sm(2B)₃; Sm(4M)₃ < Sm(2B4M)₃).

Besides, tertbutyl' steric effect should also be responsible to higher M_w and wider MWD for PCL increasing in the order: Sm(4M)₃ < Sm(2B4M)₃. For one thing, it was proved that k_{tr(b)} depends on k_p and size of the active center species [18,19,23]. For example, -O-Al(C₂H₅)₂ and -OAl(OiBu)₂ active centers propagate CL with identical k_p, but k_{tr(b)}/k_p is for the former higher almost two times than for the latter [18], which indicate that less crowded active center results in more intermolecular transesterifications. Similarly, with one more ortho tertbutyl's positive steric effect increasing space among ligands and around the Sm(III) cation, Sm(2B4M)₃ induces not only higher catalytic activity but also higher k_{tr(b)}, the latter of which indicate more intermolecular transesterification and should be responsible for higher M_w and wider MWD (Tables 3 and 4).

4.2.2. Electronic and steric effects introduced by two ortho tertbutyl substituents

For the first view, ROP characteristics concerning Sm(26B4M)₃ and its outstanding activity (Sm(2B4M)₃ < Sm(26B4M)₃) could be explained by positive steric effect induced by two ortho tertbutyls; however, in light of the QC calculation data of 26B4M in Table 6, the above explanation was still beyond the whole answer: compared with 4M and 2B4M, two ortho tertbutyls in 26B4M not only result in more negative charge on O⁷ but also longer C¹-H* distance, the former of which met the previously found contribution of single ortho tertbutyl well, while the latter just went against it. As a result, the different polymerization characteristics, much higher catalytic activity of Sm(26B4M)₃, widest MWD and highest M_w obtained should not be solely attributed to the two ortho tertbutyls' positive steric effect but also to their irregular positive electronic effect.

In order to further study the irregularity in two ortho tertbutyls' electronic effect, more attention was paid to the optimized structure of 26B4M. As demonstrated in Scheme 3, no matter how H* was orientated in the initial structure, the same optimized stable structure for 26B4M was finally

Table 5
Optimization of P, 4B and 2B by RHF/6–31G(*d, p*) converged with extremely tight criteria

Phenol	Distance (Å) ^a			Angle ^a C ¹ –O ⁷ –H [*]	Total atom charge ^a		
	C ¹ –O ⁷	O ⁷ –H [*]	C ¹ –H [*]		C ¹	O ⁷ ^b	H [*]
P	1.3515	0.9426	1.9039	110.9223	0.3910	0.6557	0.3480
4B	+0.0009	–0.0000	–0.0004	–0.1097	–0.0056	+0.0037	+0.0012
2B	+0.0042	–0.0004	–0.0051	–0.7822	–0.0244	+0.0063	+0.0004

^a The data presented in the lines for 4B and 2B were the outcome of subtracting the corresponding value of P from those for 4B and 2B, respectively.

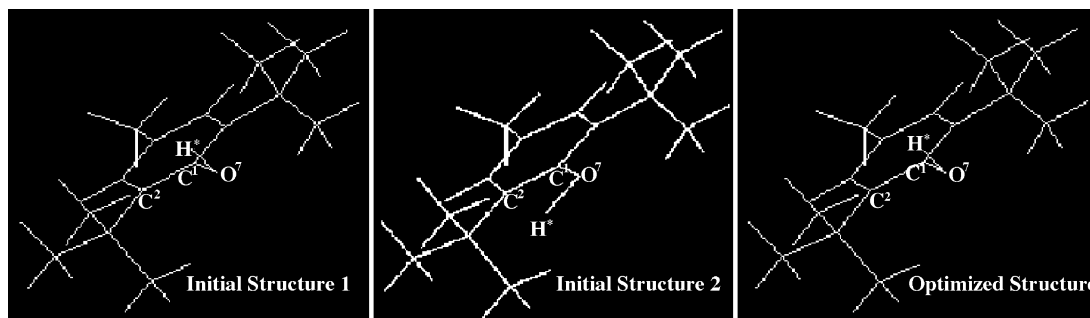
^b The absolute value of the negative charge on O⁷.

Table 6
Optimization of 4M, 2B4M and 26B4M by RHF/6–31G(*d, p*) converged with extremely tight criteria

Phenol	Distance (Å) ^a			Angle ^a C ¹ –O ⁷ –H [*]	Total atom charge ^a		
	C ¹ –O ⁷	O ⁷ –H [*]	C ¹ –H [*]		C ¹	O ⁷ ^b	H [*]
4M	1.3531	0.9426	1.9043	110.8337	0.3806	0.6587	0.3470
2B4M	+0.0040	–0.0005	–0.0056	–0.8052	–0.0232	+0.0061	+0.0005
26B4M	+0.0250	–0.0000	+0.0110	–1.0148	–0.0767	+0.0308	+0.0057

^a The data presented in the lines for 2B4M and 26B4M were the outcome of subtracting the corresponding value of 4M from those for 2B4M and 26B4M, respectively.

^b The absolute value of the negative charge on O⁷.



Scheme 3. Different initial structure (1 and 2) and the same final structure for 26B4M optimized with RHF/6–31G(*d, p*) method and extremely tight convergence criteria.

obtained, in which H^{*} is not coplanar with O⁷-phenyl plane, just opposite to those of all the other phenols. Several phenols' |D(C²–C¹–O⁷–H^{*})|, the absolute value of the dihedral angles between H^{*}–O⁷–C¹ plane and O⁷-phenyl plane, were compared in Table 7, in which 24DM stood for 2,4-dimethylphenol, 26IP for 2,6-diisopropylphenol and 26DM for 2,6-dimethylphenol. In comparison among 4M, 24DM and 2B4M, single ortho substituent, no matter big or small, does not apparently affect |D(C²–C¹–O⁷–H^{*})| and H^{*} almost stay in the O⁷-phenyl plane; however, comparison among 26DM, 26IP and 26B4M showed, when two ortho substituents present, the bigger they are, the more faraway

the H^{*}–O⁷ bond is from the O⁷-phenyl plane, which means the O⁷ is the more sp³ hybridized.

Therefore, it was proved that, due to the two ortho tert-butyls' site and big size, the H^{*}–O⁷ bond in 26B4M was forced to stay in the plane almost perpendicular to O⁷-phenyl plane for stable structure, hence induces more sp³ hybridized O⁷ and its less conjugation with phenyl ring. These two factors caused much more increased C¹–O⁷ distance and finally, irregularly longer C¹–H^{*} distance in 26B4M. It together with orderly increased negative charge on O⁷ induce positive electronic effect on Sm(26B4M)₃'s catalytic activity and the ROP characteristics.

Table 7
Absolute value of dihedral angles, |D(C²–C¹–O⁷–H^{*})|, for 4M, 24DM, 2B4M, 26B4M, 26IP and 26DM obtained from optimization with RHF/6–31G(*d, p*) method converged with extremely tight criteria

Angle	4M	24DM ^a	2B4M	26B4M	26IP ^b	26DM ^c
A(C ¹ –O ⁷ –H [*])	110.83	110.55	110.03	109.82	111.71	111.55
D(C ² –C ¹ –O ⁷ –H [*])	0.05	0.01	0.11	91.19	3.28	0.00

^a 24DM stood for 2,4-dimethylphenol.

^b 26IP stood for 2,6-diisopropylphenol.

^c 26DM stood for 2,6-dimethylphenol.

In addition, with contributions both from two ortho tert-butyls' positive steric effects and positive electronic effects, the space among ligands and around metal centers in $\text{Sm}(\text{26B4M})_3$ might be considerably enlarged and cause higher $k_{\text{tr}(\text{b})}$ [18,19,23], which results in highest M_w (Tables 2 and 4) as well as widest MWD increased with polymerization duration and temperature (Table 2).

5. Conclusion

The mentioned six Sm(III) phenolates demonstrated different catalytic activities in ROP of CL in concordance with tertbutyl substituents' site and number: $\text{Sm}(\text{2B})_3 > \text{Sm}(\text{4B})_3 \gg \text{Sm}(\text{P})_3$; $\text{Sm}(\text{26B4M})_3 > \text{Sm}(\text{2B4M})_3 > \text{Sm}(\text{4M})_3$. Together with M_w and MWD data, it was concluded that, with more tertbutyls on phenol, especially at ortho sites, corresponding Sm(III) phenolate could catalyze ROP of CL more easily under mild conditions and obtain higher monomer conversions under same conditions, obtaining higher M_w but wider MWD.

According to phenols' QC data on geometric parameters and charge distributions, it was found that, single tertbutyl, especially ortho one, induce mixed electronic effects but positive steric effect, the latter of which might result in more space around metal center and contribute to corresponding phenolates' higher catalyst activity and more intermolecular transesterifications in ROP of CL. Two ortho tertbutyls, however, induce not only positive steric effect but also irregular positive electronic effect; they both result in much more space around metal center and contribute to highest catalyst activity of $\text{Sm}(\text{26B4M})_3$ and most intermolecular transesterifications involved in ROP of CL catalyzed by it.

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