

Electronic and Steric Effects of Methyl Substituent in Samarium (III) Phenolates on Their Initiation Activities in Polymerization of ϵ -Caprolactone

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ABSTRACT: Seven phenols with methyls substituting ortho or para hydrogens are firstly reported as ligands for Samarium (III) complexes. The resultant Samarium (III) phenolates were used as single component initiators for ring-opening polymerization (ROP) of ϵ -caprolactone (CL). The results were in good order and met well with structural changes in phenol ligands. To explain the ordered correlation between ROP results and ligand structures of these phenolates, quantum chemical (QC) method was applied to optimize the most stable conformations for substituted phenols. QC data indicated that changes in charge distribution and geometric parameters of phenol ligands also followed certain order, which could be attributed to electronic and steric effects caused by methyl substituents. It was found that: methyl in phenol, especially single ortho one, would induce more space around metal center and

easier nucleophilic attack from phenol oxygen to CL monomer, which means positive electronic effect and could induce increased initiation activity of corresponding phenolate. Meanwhile, two ortho methyls will take up considerable space around the metal center and bring along un-ignorable negative steric effect, which surpasses positive electronic effect also introduced by these two ortho methyls and finally leads to decreased activity in phenolates. This study revealed that there is correlation between the initiation characteristics of phenolates and the structures of their phenol ligands; QC calculation is a convenient, cheap, and helpful method to aid study on it. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 1828–1835, 2007

Key words: ring opening polymerization; calculations; ϵ -caprolactone; samarium (III) phenolate

INTRODUCTION

Poly(ϵ -caprolactone) (PCL) and its copolymers with several monomers have prospective applications in synthetic biomaterials for their good biodegradability and biocompatibility.^{1,2} Various organometallic complexes have been utilized to initiate ring-opening polymerization (ROP) of ϵ -caprolactone (CL).³ Our group has developed some rare-earth complexes as efficient initiators for CL polymerization.^{4,5} Especially, we have found some easily available rare-earth phenolates to be excellent single component initiators for ROP of CL and cyclic carbonate. Those rare-earth phenolates can present high activities at mild temperature and achieve high yield within

short time.^{6–10} The initiation mechanism has been proved as “coordination-insertion” with acyl-oxygen bond cleavage in monomer.^{6–10}

Although some coordination complexes, including Sm (III) complexes, have been utilized in ROP of CL and its copolymerization with lactide (LA), some easily obtained and cheap phenols, such as 2-methylphenol, 4-methylphenol, 2-tertbutyl-4-methylphenol, etc., have never been used to prepare initiators of this kind.^{11–15} Besides, there has never been any systematic study published on Sm (III) phenolates, leaving alone studies concentrated on the correlation between phenols' structures and initiation activities of corresponding phenolates. Considering plenty of phenols' possible structures and their much divergent costs, this kind of study could contribute to more rational initiator design.

Aiming to find out the correlation between phenols' structures and the initiation activities of phenolates, seven specifically substituted phenols, which are un-substituted phenol (P), 2-methylphenol (2M), 4-methylphenol (4M), 2,4-dimethylphenol (24DM), 2,6-dimethylphenol (26DM), 2-tertbutylphenol (2B), and 2-tertbutyl-4-methylphenol (2B4M) (Scheme 1), were chosen as ligands for Samarium (III) phenolates. To find out initiation characteristics of every

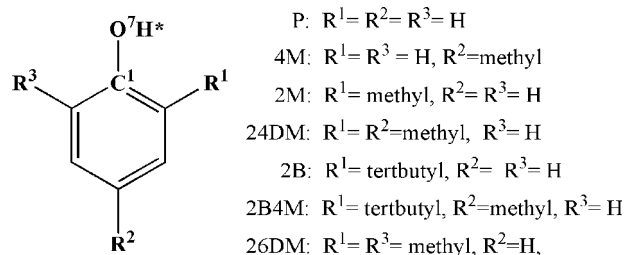
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Scheme 1 Structure for all the phenols used for Samarium (III) phenolates' synthesis.

phenolate, each of them was used as single component initiator for ROP of CL. Quantum chemical (QC) calculation was applied to obtain data describing charge distribution and bonding geometry in every phenol. Those QC calculational data could quantify structural differences among phenol ligands as well as possible electronic and steric effects induced by methyl substituents. To find out how different initiation characteristics were introduced by the electronic and steric effects of methyl substituents in phenol ligands, the experimental and calculational data were discussed in organized group in light of different sites and amounts of methyl substituents in the studied phenol ligands.

EXPERIMENTAL

Materials

CL (Acros) was dried over calcium hydride, distilled under reduced pressure, and stored in argon atmosphere at room temperature prior to use. Toluene was distilled over blue benzophenone-Na complex. Samarium oxide (Sm_2O_3) with purity of 99.99% was used as received. All the other chemicals were analytical grade and used as received.

Initiator preparation

Initiators were prepared with Schlenk tube and vacuum-line technique under purified argon. Anhydrous Samarium chloride was prepared by heating hydrated Samarium chloride and ammonium chloride mixture under reduced pressure.¹⁶ All the Sm (III) phenolates were synthesized according to the method described in the literature.¹⁷

Polymerization

ROP of CL was initiated by certain synthesized phenolate in toluene under argon atmosphere. One milliliter CL and certain volume of toluene were injected by syringe into glass ampoules (20 mL), which had been flamed and purged with argon for several times. The phenolate, which had been prepared as toluene

solution, was injected into the ampoule after monomer solution had been prewarmed in oil bath at set 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 resultant PCL was dried in vacuum at room temperature for 72 h.

Measurements

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

COMPUTATIONAL DETAILS

All the charge distribution and geometric parameters of studied phenols were optimized using the Restricted Hartree-Fock (RHF) method with Gaussian98 software package. This widely accepted and computationally cheap method predicts reliable geometries and quantum mechanic data for simple organic molecule with singlet.^{18–20} 6-31G (d, p) basis set was used, adding carbon and oxygen atom with *d* polarization functions while hydrogen with *p* polarization functions.^{19–24} All the presented calculation data were obtained after the optimization converged under extremely tight criteria. The stabilities of all the resultant Hartree-Fock wave functions and optimized molecular structures had been checked both with stable and frequency calculations respectively.²⁵

RESULTS AND DISCUSSION

Experimental results for ROP of CL initiated by Sm (III) phenolates

Characteristics for ROP initiated by seven Sm (III) phenolates were obtained at similar ROP conditions: temperature, $T = 40\text{--}70^\circ\text{C}$; initiator amount, the molar ratio of $[\text{CL}]/[\text{Sm}] = 800\text{--}1500$; monomer molar concentration, $[\text{CL}] = 0.5\text{--}2.5 \text{ mol/L}$; polymerization duration, time = 10–60 min. Compared with ROP initiated by our previously developed rare-earth phenolates and some reported samarium complexes at much higher temperature, ROP at chosen conditions were influenced by inter- and intramolecular transesterifications, which often present in ROP of CL and LA initiated by some coordination initiators.^{26–31} Instead of finding the most preferable ROP conditions for each phenolate, we chose the studied conditions to effectively space out the differences among initiation activities and ROP characteristics of

TABLE I
Effect of Temperature on ROP of CL Initiated by
Sm(P)₃, Sm(4M)₃, Sm(2M)₃, Sm(24DM)₃, Sm(2B)₃,
and Sm(2B4M)₃ Separately

Initiator	T/°C	Conv./%	$M_w \times 10^{-4}$	MWD
Sm(P) ₃	60	–	–	–
	70	–	–	–
	80	–	–	–
Sm(4M) ₃	40	4.0	–	–
	50	32.3	2.74	1.66
Sm(2M) ₃	40	13.5	1.35	1.57
	50	42.6	3.16	1.57
	70	92.0	3.77	2.30
Sm(24DM) ₃	40	28.9	3.26	1.44
	50	64.8	3.20	1.92
	70	98.8	2.57	2.41
Sm(2B) ₃	40	18.0	2.40	1.80
	60	82.4	3.01	3.01
Sm(2B4M) ₃	40	27.6	2.09	2.13
	60	79.7	4.51	2.34

Conditions: [CL]/[Sm] = 1000, [CL] = 2.0 mol/L, 60 min, toluene.

these phenolates. As turned out, it interested us most that, initiation and ROP characteristics of these Sm(III) phenolates varied in good order, which matched well with structural changes in their phenol ligands. Consequently, experiment results of these phenolates were discussed in organized groups in light of the sites and amounts of methyl substituents in their phenol ligands.

Effects of temperature (Table I), initiator amount, and monomer concentration (Fig. 1) on ROP of CL initiated by Sm(P)₃, Sm(4M)₃, Sm(2M)₃, and Sm(24DM)₃, respectively were compared together.

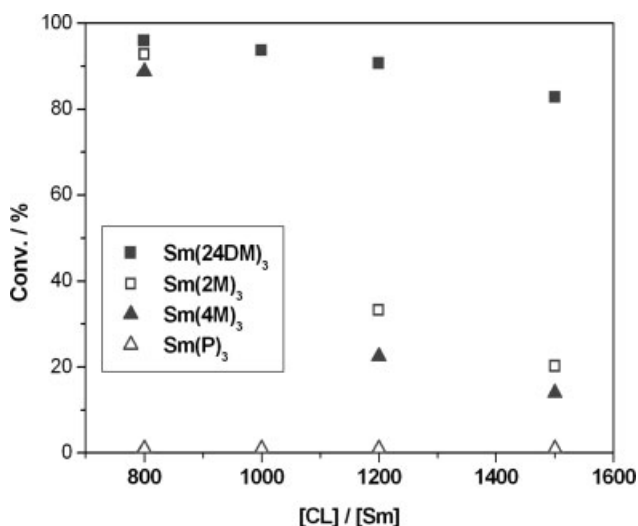


Figure 1 Effect of initiator amount (the molar ratio of [CL]/[Sm]) on ROP of CL initiated by Sm(P)₃, Sm(4M)₃, Sm(2M)₃, and Sm(24DM)₃, respectively. Conditions: [CL] = 2.0 mol/L, 60°C, 60 min, toluene.

Sm(P)₃, whose phenol ligand has no methyl substituent, could not initiate ROP of CL at all studied conditions. However, with [CL]/[Sm] = 800, the other three methyl-substituted phenolates could achieve monomer conversion $\geq 90\%$ after 60 min at 60°C (Fig. 1). In detail, despite changes in temperature and initiator amount, ROP initiated by Sm(2M)₃, whose phenol has a single ortho methyl, induced high monomer conversion than those initiated by Sm(4M)₃, whose phenol has only a para methyl. With methyls substituting both at one ortho and the para sites, Sm(24DM)₃ achieved highest monomer conversion in this group at all discussed conditions. Figure 2 demonstrated the effect of polymerization time on monomer conversion for Sm(2M)₃ and Sm(24DM)₃ at 70°C. Generally, the activity order for the four initiators at studied conditions was apparent: Sm(24DM)₃ > Sm(2M)₃ > Sm(4M)₃ \gg Sm(P)₃.

ROP Results of Sm(26DM)₃ were compared with those of Sm(2M)₃ and Sm(24DM)₃ in Table II. Although there are two ortho methyls in the ligand of Sm(26DM)₃, it could not initiate ROP as effectively as either Sm(2M)₃ or Sm(24DM)₃ at same conditions, which demonstrated the activity order for the three phenolates should be: Sm(26DM)₃ < Sm(2M)₃ < Sm(24DM)₃.

Sm(2B)₃ and Sm(2B4M)₃ were also included in this study for special purpose to be discussed later. Effects of temperature, initiator amount, and polymerization time on monomer conversion for ROP initiated by them separately were studied and their results were shown in Tables I, III and Figure 3. Obviously, they presented similar ROP characteristics at studied conditions despite structural differen-

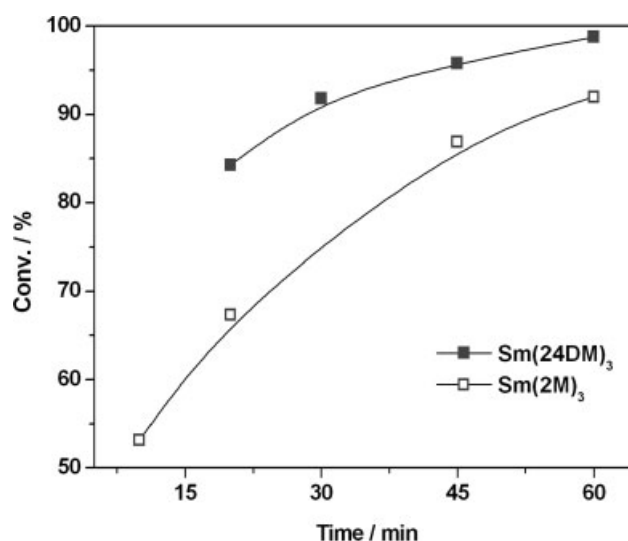


Figure 2 Effect of polymerization time on ROP of CL initiated by Sm(2M)₃ and Sm(24DM)₃ separately. Conditions: [CL]/[Sm] = 1000, [CL] = 2.0 mol/L, 70°C, toluene.

TABLE II
Effect of Initiator Amount and Polymerization Time on ROP of CL Initiated by Sm(26DM)₃, Sm(24DM)₃, and Sm(2M)₃ Separately

Initiator	[CL]/[Sm]	Time/min	Conv./%
Sm(26DM) ₃	1000	45	9.60
	800	60	22.3
Sm(2M) ₃	1000	45	55.1
	800	60	92.8
Sm(24DM) ₃	1000	45	93.6
	800	60	96.0

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

ces in their phenol ligands. In other words, Sm(2B)₃ and Sm(2B4M)₃ have similar initiation activities.

Electronic and steric effects of methyls on initiation activities of Sm (III) phenolates studied with QC calculation support

The above comparisons on characteristics of ROP initiated by phenolates with different structures gave us a contradiction: the clear order among initiation activities of these phenolates, Sm(2M)₃ > Sm(4M)₃ >> Sm(P)₃, seemed to indicate that, methyl substituent in phenol ligand, especially ortho one, tended to contribute to increased initiation activities of corresponding phenolates; however, the order of initiation activities, Sm(26DM)₃ < Sm(24DM)₃, rebutted it. The highest initiation activity of Sm(24DM)₃ seemed to support the prediction that phenol ligand with more methyl substituents would introduce higher initiation activity in the corresponding phenolate; nevertheless, the comparison in two groups of phenolates, Sm(26DM)₃ and Sm(2M)₃, Sm(2B)₃ and Sm(2B4M)₃, went against it. Therefore, although it is clearly demonstrated that there could be some correlation between initiation activities of phenolates and the sites and amounts of methyl substituents in their phenol ligands, experimental results alone were not sufficient to soundly clarify this correlation. Taking into account the initiation mechanism of ROP of CL

TABLE III
Effect of Polymerization Time on ROP of CL Separately Initiated by Sm(2B)₃ and Sm(2B4M)₃ at 50 and 60°C

T/°C	Time/min	Conv./%	
		Sm(2B) ₃	Sm(2B4M) ₃
50	30	36.4	29.5
	45	43.0	34.7
	60	54.4	44.5
	90	71.7	70.5
60	20	22.5	30.3
	45	71.7	67.5
	60	82.4	86.8

Conditions: [CL]/[Sm] = 1000, [CL] = 2.0 mol/L, toluene.

initiated by phenolates, we paid more attention to the electronic and steric effects introduced by ortho and para methyls in the phenol ligands.

According to the "coordination–insertion" initiation mechanism, CL coordinates to the metal center (Lnⁿ⁺, n = 2, 3) and inserts into Lnⁿ⁺–O bond with acyl-oxygen bond cleavage.^{6–10} In case of Sm (III) phenolates, Lnⁿ⁺ is Sm³⁺ and O is the oxygen from the hydroxyl group in phenol ligands, which could be demonstrated by Scheme 2.^{17,32} As illustrated in Scheme 3, at the right beginning of polymerization (Step 1), the first CL coordinates and inserts between Sm³⁺–O* bond in the phenolate, which is the initial active center (a). Then, the active sites around Sm³⁺ change from three Sm³⁺–O*Ar bonding sites into two plus a Sm³⁺–O*R one. In Step 2, the coming CL can coordinate and insert into any of the latter three bonding sites in the new active center (b). As a result, three kinds of propagation active centers (c–e) might be presented and active during the propagation stage. When the [monomer]/[initiator] ratio in the ROP system is high enough, (c) might be the major kind of active centers after the propagation process goes on for certain time. In this case, there will be no phenol ligand around the metal center and its structure would not influence the propagation stage. In other cases, (d) and (e), which have one or two initial ligands remained that can influence coordination and insertion of coming monomers, will play important roles at the propagation stage.

It can be proved as following that the second situation played the major role in this study. As reported, another coordination initiator, aluminum alkoxides, whose initiation and propagation reactions also follow "insertion–coordination" mecha-

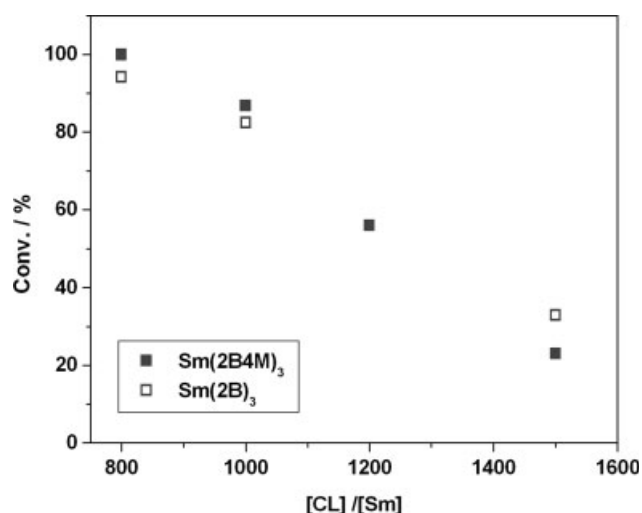
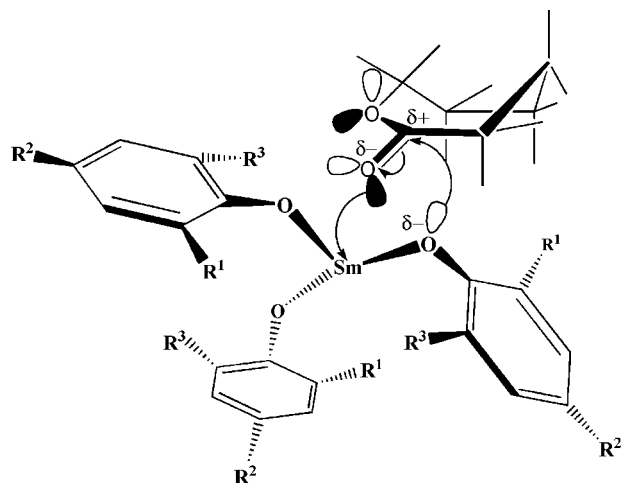


Figure 3 Effect of initiator amount on ROP of CL initiated by Sm(2B)₃ and Sm(2B4M)₃ separately. Conditions: 60°C, [CL] = 2.0 mol/L, 60 min, toluene.

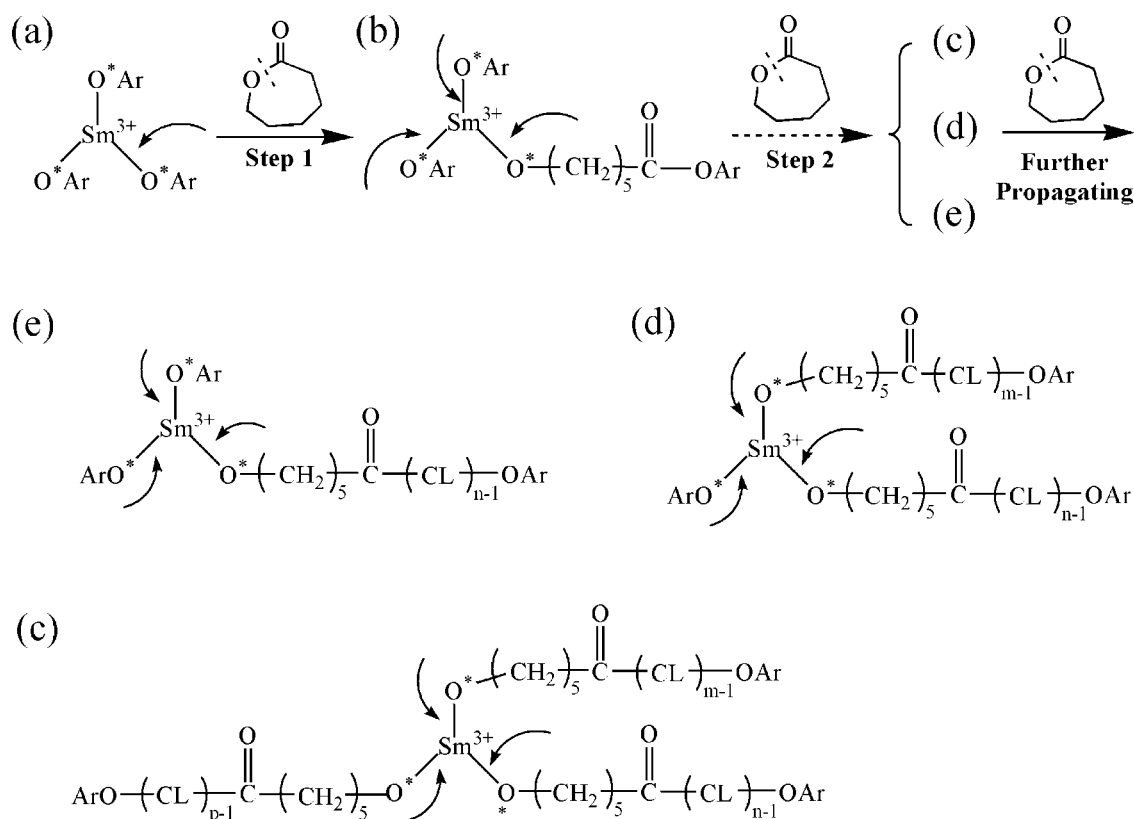


Scheme 2 The “coordination–insertion” initiation mechanism for ROP of CL initiated by Sm (III) phenolate.

nisms, induce intermolecular transesterifications in ROP of CL.^{26,27,30,31} Their transfer constant, $k_{tr-inter}$, is affected by the size of active center.²⁶ For example, $k_{tr-inter}$ for ...—O—Al(C₂H₅)₂ is almost two times higher than that for ...—OAl(OiBu)₂, which indicates that ligand structures of aluminum alkoxides affect the chain propagation stage and less crowded active center results in more intermolecular transesterifications.²⁶ It was reported in our previous study

that, Sm(26B4M)₃, which has 2,6-ditertbutyl-4-methylphenol as ligands and had been proved to be a less crowded active center than Sm(2B4M)₃, introduces more intermolecular transesterifications than the latter in ROP of CL at similar conditions studied in this article.³² In our current study, most of the ROP initiated by studied phenolates at chosen conditions suffered from intermolecular transesterifications and resulted in PCL with wide MWD. So, it indicated that: in ROP of CL initiated by Sm(III) phenolates at studied conditions, there are considerable (d) and (e) active centers, and many phenol ligands are still directly connected to Sm³⁺ during the propagation stage. The obtained conclusion could be even more directly supported if was available the accurate amount of phenol ligands transferred and not transferred to the end of living chains during the propagation stage. As a matter of fact, structures of those phenol ligands could influence new generation, propagation, and transesterification of living chains.

In other words, there are many phenol ligands directly connected to Sm³⁺ during the whole ROP process and playing important roles at studied conditions. Therefore, their influences could be reflected by outcomes like monomer conversion, which is obvious according to the obtained experiment results. It is not very accurate that all the influences brought along by ligand structures to phenolates are



Scheme 3 Coordination–insertion reactions of CL around Sm³⁺ and structures of active centers during the ROP process.

TABLE IV
Optimization of P, 4M, 2M, and 24DM by RHF/6-31G (d, p) Converged with Extremely Tight Criteria

Phenol	Distance/angstrom ^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
4M	+0.0016	0.0000	+0.0004	–0.0886	–0.0104	+0.0030	–0.0010
2M	+0.0046	–0.0003	+0.0008	–0.2779	–0.0189	+0.0088	+0.0002
24DM	+0.0061	–0.0003	+0.0011	–0.3756	–0.0292	+0.0116	–0.0008
26DM	+0.0061	–0.0014	+0.0012	+0.6315	+0.0006	+0.0146	+0.0072

^a The data presented in the lines for 4M, 2M, and 24DM were the outcome of subtracting the corresponding value of P from those for 4M, 2M, and 24DM, respectively.

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

discussed as the former's influences on the initiation activities of the latter. Nevertheless, it might be acceptable just like "initiator" is widely used to describe the roles of phenolates actually play in the whole ROP process.

It was indicated in Schemes 2 and 3 and discussion above that, if phenol ligands could bring in more space around Sm³⁺, the CL coordination and insertion would be easier; if the ligands had more negative charge on their phenol oxygen, the nucleophilic attack from the oxygen to the carbonyl carbon in CL could be easier and the acyl-oxygen bond in CL would also be easier to break. All these could contribute to increase initiation activities of corresponding phenolates. As all the phenolates studied in this article had the same rare-earth metal center Sm³⁺, discussion on its possible influence was absent from this study. Therefore, the correlation between structures of the phenol ligands and the initiation activities of the corresponding Sm (III) phenolates could be discussed in light of the space around Sm³⁺ and the amount of negative charge on phenol oxygen, which would be influenced by the electronic and steric effects of substituents in the phenol ligands in the following ways. First, electronic effect of substituents influences charge distribution and geometric parameters in the phenol, both of which would influence the bonding between phenol ligand and the metal center. Second, steric effect of substituents could bring changes to the space around Sm³⁺ in two opposite ways: for one thing, as any substituent will be larger than hydrogen atom, sub-

stituent would take up more space around Sm³⁺ and make it more crowded; for another, substituent with large size could cause repulsion among ligands, which pushes themselves apart from each other as well as away from the metal center, and increases the space around Sm³⁺. Undoubtedly, the space around Sm³⁺ must be influenced by the compromise of these two opposite steric influences.

To discuss the electronic and steric effects of methyl substituents separately, it was properly assumed in the following discussion that the possible difference in steric effect caused by para methyl (e.g. case in 4M, 24DM, and 2B4M) or a single ortho methyl substituent (e.g. case in 2M and 24DM) could be ignored. Because methyl is much smaller than phenyl, and at least half side of the phenol is unsubstituted in these cases.

On the basis of the same reason mentioned earlier to exclude possible influence from the metal center, data describing charge distribution and geometric parameters in studied phenols were obtained with simple but strict QC calculation on phenols rather than with very complicated and time consuming molecular modeling on Sm (III) phenolates. The QC data concerning hydroxyl hydrogen (H*), oxygen (O⁷), and the phenyl carbon (C¹) directly connected with O⁷ were picked out and discussed together with experiment results in certain groups for reasonable ignoring of steric differences among phenols in the same group.

QC Data for P, 4M, 2M, and 24DM were shown in Table IV. It was apparent that, in order of P-4M-2M-

TABLE V
Optimization of 2B4M and 2B by RHF/6-31G(d, p) Converged with Extremely Tight Criteria

Phenol	Distance ^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*
2B	1.3557	0.9422	1.8988	110.1401	0.3666	0.6620	0.3484
2B4M	0.0014	–0.0001	–0.0001	–0.1116	–0.0092	+0.0028	–0.0009

^a The data presented in the lines for 2B4M were the outcome of subtracting the corresponding value of 2B from those for 2B4M.

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

24DM, bonding distances, bonding angle, and charge distributions in the four phenols are in very good continuously increasing or decreasing orders, except for the order of positive charge on H*, which actually provide information to distinguish electronic effect introduced by ortho and para methyl substituents: para methyl induces decrease in positive charge on H* ($P > 4M$, $2M > 24DM$) while ortho methyl causes increase in it ($26DM > 2M > P$).

Meanwhile, as explained in our previous discussion, our major concern should be focused to parameters describing the bonding length between C¹ and H* and the negative charge on O⁷. Because the C¹—H* bonding length could indicate the distance between phenol phenyl and Sm³⁺ as well as the space around the latter. The negative charge on O⁷ would affect the nucleophilicity of the phenol ligand to the carbonyl carbon in CL monomer. According to Table IV, C¹—H* bonding length in four phenols changes in the order: $24DM > 2M > 4M > P$; in other words, methyl on phenols, especially ortho one, induces longer C¹—H* bonding length, which could indicate more vacant space around Sm³⁺ and contribute to easier CL coordination and insertion. As to the negative charge on O⁷, which changes in the same order: $24DM > 2M > 4M > P$, demonstrates that: methyl, especially ortho one, would induce more negative charge on O⁷, which could indicate easier nucleophilic attack from the ligand oxygen to the carbonyl carbon in CL monomer. These two factors are undoubtedly positive electronic effect to the initiation activities of corresponding phenolates and should be responsible for the activity order: $Sm(24DM)_3 > Sm(2M)_3 > Sm(4M)_3 \gg Sm(P)_3$.

To find out the steric effect caused by methyls as well as its interaction with the electronic effect brought along by those methyls, 26DM, which has two ortho methyls, was also chosen for experimental and calculational studies. Compared to those of P and 2M, most of the geometric parameters in 26DM meet very well with the proposed contribution from the substitution of ortho methyl; especially, the much increased positive charge on H*, the negative charge on O⁷, and the increased length of C¹—H* bonding. According to the discussion in the last paragraph, the latter two parameters demonstrated that two ortho methyls in 26DM have introduced considerable positive electronic effect. Therefore, supposing the two ortho methyls' steric effect in 26DM (either positive or negative) could be ignored, $Sm(26DM)_3$ should have been the most active one compared to $Sm(2M)_3$ and $Sm(24DM)_3$. However, ROP results in Table II proved that $Sm(26DM)_3$ is much less active than $Sm(2M)_3$, leaving alone $Sm(24DM)_3$, which demonstrated that two ortho methyls together bring in un-ignorable steric effect.

According to the model described earlier, only one side of benzyl ring is occupied in $Sm(2M)_3$ and $Sm(24DM)_3$; so, there is enough space around the metal center plus that the 2M and 24DM phenol ligands can easily rotate out of the way of an approaching CL. However, methyls at both sides of phenol ligands occupied lots of space around the metal center in $Sm(26DM)_3$, and the ligands cannot rotate that easily either; therefore, it is more difficult for CL monomer to coordinate and insert between Sm³⁺ and 26DM ligands. Moreover, the negative steric effect induced by two ortho methyls must have surpassed their positive electronic effect, and hence should be responsible for the order of initiation activity as: $Sm(26DM)_3 < Sm(2M)_3$, $Sm(26DM)_3 < Sm(24DM)_3$.

Generally, it could be concluded that: substituent inducing longer C¹—H* bonding length as well as more negative charge on O⁷ can bring along positive electronic effect and contribute to increased initiation activity in corresponding phenolates, when steric effect (either positive or negative) ignorable.

Here rises a question: what electronic effect (positive or negative) would be introduced, if the substituent induces shorter C¹—H* bonding length while more negative charge on O⁷? To answer this question, 2B and 2B4M were included in this study. Apparently, the difference between these two phenols could be attributed to the electronic effect introduced by the para methyl in 2B4M. According to Table V and the previous discussion on the electronic effect of methyl substituents, five within six groups of the calculational data met well with the contribution from para methyl found in P and 4M group; however, the C¹—H* bonding length in 2B4M is slightly shorter than that in 2B, opposite to the expected elongation. This slight disagreement might attribute to the introduction of tertbutyl at ortho site, which might have shielded or distributed part of the electronic effect from the para methyl. In general, there is slightly shorter C¹—H* bonding length while obviously more negative charge on O⁷ in 2B4M when compared with 2B. According to ROP results for $Sm(2B)_3$ and $Sm(2B4M)_3$ in Tables I, III and Figure 3, which presented that these two phenolates have similar initiation activities at studied conditions, it could be concluded that obviously increased negative charge on O⁷ versus slightly decreased C¹—H* bonding length will not bring in either positive or negative electronic effect.

CONCLUSIONS

Seven Sm (III) phenolates with specifically substituted phenol ligands demonstrated orderly changed initiation activities: $Sm(24DM)_3 > Sm(2M)_3$

T5

$> \text{Sm}(4\text{M})_3 \gg \text{Sm}(\text{P})_3, \text{Sm}(24\text{DM})_3 > \text{Sm}(2\text{M})_3 > \text{Sm}(26\text{DM})_3$, and $\text{Sm}(2\text{B})_3 \approx \text{Sm}(2\text{B}4\text{M})_3$, which met well with changes of the amounts and sites of methyl substituents in their phenol ligands. Taking into account, the initiation mechanism of phenolates in ROP of CL as well as QC calculational data describing differences of charge distribution and geometric characteristics among phenols, the correlation between the methyl-substituted structures of phenol ligands and the initiation activities of corresponding phenolates was found as follows: (1) Methyl, especially ortho one, tends to induce more negative charge on O^7 and longer $\text{C}^1\text{—H}^*$ distance; these two factors together induce positive electronic effect and contribute to higher activity of corresponding phenolates, when substituents' steric difference rationally ignored. (2) Two ortho methyls bring along negative steric effect, which surpass their positive electronic effect and induce decreased activity in corresponding phenolate. (3) When the substituent introduces more negative charge on O^7 but shorter $\text{C}^1\text{—H}^*$ distance (as the para methyl in 2B4M), these two opposite influences combined together would not bring in either positive or negative electronic effect.

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