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# Aryloxy and benzyloxy compounds of hafnium: Synthesis, structural characterization and studies on solvent-free ring-opening polymerization of ϵ-caprolactone and δ-valerolactone

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ABSTRACT

A large variety of aryloxy compounds and benzyloxy derivatives of Hf(IV) were synthesized from Hf(O-*t*Bu)$_4$ using the alcoholysis route. These compounds were completely characterized using various spectroscopic and analytical methods along with single crystal X-ray diffraction studies. Multinuclear NMR studies prove high degree of fluxional behavior of these compounds in solution. They adopt a dimeric structure in the solid-state as seen from X-ray diffraction studies on a few of them. These compounds are powerful catalysts for the ring-opening polymerization of ϵ-caprolactone (CL) and δ-valerolactone (VL) resulting in high number average molecular weight ($M_n$) polymers and controlled molecular weight distributions (MWDs). Significant control in the polymerization was achieved with these compounds as initiators in comparison to their titanium and zirconium analogues. Kinetic studies reveal that the rates of such polymerizations are in general slower than the corresponding titanium and zirconium derivatives. $^1$H NMR and MALDI-TOF studies of low molecular weight oligomers suggest that these polymerizations proceed by the activated monomer mechanism.



## 1. Introduction

The increasing need to search for alternative polymeric materials as substitute to commodity polymers based on non-renewable resources together with the desire to produce environmentally benign biodegradable plastics has provided a thrust towards the polymerization of cyclic esters and lactide [1–5]. The polymers are regarded as alternative materials to the conventional oil-based materials that have been derived from completely renewable resources such as corn and sugar beet [6–10]. The applications of these green polymers have been popular in the biomedical and pharmaceuticals sector including drug delivery, fabrication of implants and scaffolds for tissue engineering [11]. These polymers are used in the film and fiber industry [12]. Such versatile potential results from their permeability, biodegradability and biocompatibility [13–15].

A methodology employed in the synthesis of these polymers is the metal mediated ring-opening polymerization of cyclic lactone monomers and lactide [11,16,17]. The coordination-insertion polymerization derived from metal initiators is the most commonly practiced for such polymer synthesis because of its capability of producing high $M_n$ polymers with narrow MWDs [1,16,18–29]. The existing method of catalyst construction commonly employs a rigid, polydentate ancillary ligand around the metal center with one or more pendant initiating groups. The ligand has a profound influence on the catalyst nuclearity and shows an impact on the coordination-insertion growth mechanism. Initiators with Group 4 metals have been popular as they exhibit reasonable control on the polymerization process. Initiators with a ligating backbone containing chiral phenoxyimine [30], tris(phenoxy)amine [31], bis(β-ketoamidate) [32], bis(iminophenoxy) [21,33], *N*-heterocyclic carbine [34], bis(phenoxy)amine [35–37], pyrrolylamine [38], tris(alkoxy) [39,40], tris(alkoxy)amine [41–43], bis(amido) [44], chalcogen-bridged bis(aryloxy) [45] and methylene-bridged bis(phenoxy) [46] derivatives have been reported. In addition, there are reports employing titanium *n*-butoxide and zirconium *n*-propoxide [47] and titanium phenoxide [48] as initiators. A titanium alkoxide based metal organic framework was recently reported to possess activity for such processes [49]. The use of metallocene ester enolates for the polymerization of lactide is reported [50]. The polymerization of lactide using titanium and zirconium complexes of phenylenediamine bis(phenolate) ligand [51] and sulphonamide supported backbone have been reported

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recently [52]. Titanium complex of isoquinolinyl-naptholate [53] and zirconium complex of trans-substituted diamido/diamine cyclam are reported to be active for CL polymerization [54]. The polymerizations described from such initiators have exclusively relied upon the coordination-insertion mechanism [1]. The initiation of polymerization is rapid and there is minimal chance of unwanted trans-esterification reactions. In case of polymerization of cyclic esters, there is no systematic correlation between the structural features of the ancillary ligand and polymerization characteristics. The ease with which the acyl oxygen bond of the cyclic ester monomer cleaves depends on the electron environment provided by the initiating group (most often as an alkoxy fragment) contained in the initiator [1]. The precise need of the ancillary ligand is not very justified for the polymerization of cyclic esters which propagate in a non-stereospecific manner. Logically, such polymerizations should proceed in the desired manner by controlling the electronic environment around the metal alkoxy fragment. An alternative approach to the polymerization of cyclic esters is the activated monomer mechanism [55–59] whose practical utility has not been substantially investigated as compared to the coordination-insertion mechanism. None of the initiators derived from the above ligand backbone have been investigated in this regard. A reason that may be attributed to this observation is the use of intolerable protic initiators along with these organometallic compounds as catalysts. Hence, there are possibilities of loss of catalyst identity during the polymerization process.

Our recent results indicate that iron and ruthenium chloride catalysts in the presence of protic initiators like alcohols produce comparable or better results for CL and VL, using the activated monomer mechanism [60], as compared to the ones reported for alkoxide initiators containing bulky ligands where the polymerization proceeds by the coordination-insertion mechanism [25]. Using such a methodology, much shorter polymerization time, far higher $M_n$ and low MWDs were observed. This proved our initial contentions that elaborate ligands may not be an absolute necessary requirement in the development of such a technology involving the polymerization of cyclic ester monomers [60]. This had prompted us to investigate extensively the role of aryloxy and benzyloxy compounds of group 4 metals in the polymerization of CL and VL [61]. The work described here is a detailed account of our polymerization results with new aryloxy and benzyloxy compounds of hafnium. The feasibility and utility of such compounds as catalysts in the presence of a coordinated protic initiator (like alcohol) was additionally an important goal. It is pertinent to mention here that VL polymerization using hafnium containing initiators have not been reported.

## 2. Experimental section

### 2.1. General procedures

All reactions were performed under dry argon atmosphere using standard Schlenk techniques or in a glove box with rigorous exclusion of moisture and air. Toluene was dried by heating under reflux over sodium and benzophenone and distilled fresh prior to use. $CDCl_3$ used for NMR spectral measurements was dried over calcium hydride, distilled and stored in a glove box. $^1H$ and $^{13}C$ NMR spectra were recorded with a Bruker Avance 400 instrument. Chemical shifts for $^1H$ and $^{13}C$ NMR spectra were referenced to residual solvent resonances and are reported as parts per million relative to $SiMe_4$. ESI-MS spectra of the samples were obtained from Waters Q-Tof micro mass spectrometer. MALDI-TOF measurements were performed on a Bruker Daltonics instrument in dihydroxy benzoic acid matrix. Elemental analyses were done with a Perkin Elmer Series 11 analyzer.

Molecular weights and the polydispersity indices of the polymers were determined by GPC instrument with Waters 510 pump and Waters 410 Differential Refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 × 300 mm) were connected in series. Measurements were done in THF at 27 °C. Number average molecular weights ($M_n$) and polydispersity ($M_w/M_n$) of polymers were measured relative to polystyrene standards. For CL, molecular weights ($M_n$) were corrected according to Mark-Houwink corrections [62]. All phenols and benzyl alcohol derivatives used in this study along with Hf(O-*t*Bu)$_4$ were purchased from Aldrich and used without subsequent purification. CL and VL were purchased from Aldrich, dried over $CaH_2$ overnight and distilled fresh prior to use. $CDCl_3$ used for NMR spectral measurements was purchased from Aldrich.

### 2.2. Synthesis of [Hf(O-2-FC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**1**)

Under an argon atmosphere, to a stirred solution of 2-$FC_6H_4OH$ (0.10 g, 0.84 mmol) in 2.5 mL toluene at −25 °C, was added a solution of Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) in 2.5 mL toluene. The reaction mixture was allowed to attain ambient temperature and stirred for 24 h. The solvent was removed under reduced pressure to yield a white solid which was purified by crystallization from toluene at −25 °C. The crystallized solid was recovered by filtration and dried in vacuum. Yield (0.25 g, 86%). M. Pt. 181 °C. $^1H$ NMR (400 MHz, $CDCl_3$, 55 °C): δ 7.01–5.98 (16H, *ortho*, *meta*, *para*), 1.31 (br, 9H, C*Me*$_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, 55 °C): δ 152.53 (Ar-F), 150.16 (Ar-O), 124.96 (Ar-C), 121.67 (Ar-C), 117.52 (Ar-C), 115.74 (Ar-C), 69.63 (*C*Me$_3$), 31.31 (C*Me*$_3$). ESI-MS: *m*/*z* 1306 {(Hf(O-2-FC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ − (O-2-FC$_6$H$_4$) + Na}$^+$. Anal. Calcd for $C_{28}H_{26}F_4O_5Hf$: C, 48.25; H, 3.76. Found: C, 48.37; H, 3.85.

### 2.3. Synthesis of [Hf(O-2-ClC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**2**)

2-$ClC_6H_4OH$ (0.11 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.29 g, 91%). M. Pt. 188 °C. $^1H$ NMR (400 MHz, $CDCl_3$, 55 °C): δ 7.30–6.87 (16H, *ortho*, *meta*, *para*), 5.50 (br, 1H, O*H*), 1.25 (br, 9H, C*Me*$_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, 55 °C): δ 151.37 (Ar-O), 128.99 (Ar-C), 128.43 (Ar-C), 121.37 (Ar-Cl), 119.88 (Ar-C), 116.26 (Ar-C), 78.13 (*C*Me$_3$), 31.23 (C*Me*$_3$). ESI-MS: *m*/*z* 1421 {(Hf(O-2-ClC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ − (O-2-ClC$_6$H$_4$) + Na}$^+$. Anal. Calcd for $C_{28}H_{26}Cl_4O_5Hf$: C, 44.09; H, 3.44. Found: C, 44.13; H, 3.61.

### 2.4. Synthesis of [Hf(O-2-BrC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**3**)

2-$BrC_6H_4OH$ (0.15 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.36 g, 90%). M. Pt. 191 °C. $^1H$ NMR (400 MHz, $CDCl_3$, 55 °C): δ 7.52–6.79 (16H, *ortho*, *meta*, *para*), 5.48 (br, 1H, O*H*), 1.27 (br, 9H, C*Me*$_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, 55 °C): δ 157.56 (Ar-O), 132.17 (Ar-C), 129.31 (Ar-C), 121.93 (Ar-C), 116.38 (Ar-C), 113.85 (Ar-Br), 78.12 (*C*Me$_3$), 31.19 (C*Me*$_3$). ESI-MS: *m*/*z* 1732 {(Hf(O-2-BrC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ − (O-2-BrC$_6$H$_4$) + Na}$^+$. Anal. Calcd for $C_{28}H_{26}Br_4O_5Hf$: C, 35.75; H, 2.79. Found: C, 35.81; H, 2.83.

### 2.5. Synthesis of [Hf(O-3-FC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**4**)

3-$FC_6H_4OH$ (0.10 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.26 g, 90%). M. Pt. 186 °C. $^1H$ NMR (400 MHz, $CDCl_3$, 55 °C): δ 7.34–6.48 (16H, *ortho*, *meta*, *para*), 5.22 (br, 1H, O*H*), 1.25 (br, 9H, C*Me*$_3$). $^{13}C$ NMR (100 MHz, $CDCl_3$, 55 °C): δ 164.89 (Ar-F), 161.95 (Ar-O), 129.65 (Ar-C), 115.35 (Ar-C), 108.00 (Ar-C), 106.94 (Ar-C), 81.10 (*C*Me$_3$), 30.44 (C*Me*$_3$). ESI-MS: *mz* 1306 {(Hf(O-3-FC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ − (O-3-FC$_6$H$_4$) + Na}$^+$. Anal. Calcd for $C_{28}H_{26}F_4O_5Hf$: C, 48.25; H, 3.76. Found: C, 48.35; H, 3.83.

### 2.6. Synthesis of [Hf(O-4-tBuC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**5**)

4-*t*BuC$_6$H$_4$OH (0.13 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.34 g, 94%). M. Pt. 192 °C. $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 7.25 (8H, br, *meta*), 6.78 (8H, br, *ortho*), 1.30 (br, 9H, C*Me*$_3$), 1.28 (br, 36H, Ar-C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 159.43 (Ar-O), 141.81 (Ar-*t*-Bu), 125.23 (Ar-C), 119.11 (Ar-C), 79.02 (*C*Me$_3$), 34.01(Ar-*C*Me$_3$), 31.98 (C*Me*$_3$), 30.45 (Ar-C*Me*$_3$). ESI-MS: *m*/*z* 1572 {(Hf(O-4-*t*BuC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ –( O-4-*t*BuC$_6$H$_4$) + Na}$^+$. Anal. Calcd for C$_{44}$H$_{62}$O$_5$Hf: C, 62.21; H, 7.36. Found: C, 62.38; H, 7.41.

### 2.7. Synthesis of [Hf(O-4-FC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**6**)

4-FC$_6$H$_4$OH (0.10 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of **(1)** was employed. Yield (0.27 g, 93%). M. Pt. 198 °C. $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 6.94–6.77 (16H, *ortho*, *meta*), 4.99 (br, 1H, O*H*), 1.27 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 157.09 (Ar-F), 155.96 (Ar-O), 119.83 (Ar-C), 116.54 (Ar-C), 80.04 (*C*Me$_3$), 30.36 (C*Me*$_3$). ESI-MS: *m*/*z* 1306 {(Hf(O-4-FC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ – (O-4-FC$_6$H$_4$) + Na}$^+$. Anal. Calcd for C$_{28}$H$_{26}$F$_4$O$_5$Hf: C, 48.25; H, 3.76. Found: C, 48.45; H, 3.82.

### 2.8. Synthesis of [Hf(O-4-IC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**7**)

4-IC$_6$H$_4$OH (0.18 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.43 g, 91%). M. Pt. 209 °C. $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 7.52–7.50 (8H, *meta*), 7.32–7.25 (m, C$_7$H$_8$), 6.63–6.61 (8H, *ortho*), 4.94 (br, 1H, O*H*), 2.36 (s, C$_7$H$_8$), 1.28 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 160.47 (Ar-O), 138.60 (Ar-C), 138.16 (C$_7$H$_8$), 129.20 (C$_7$H$_8$), 128.38 (C$_7$H$_8$), 125.46 (C$_7$H$_8$), 121.81 (Ar-C), 85.93 (Ar-I), 80.79 (*C*Me$_3$), 31.37 (C*Me*$_3$), 21.92 (C$_7$H$_8$). ESI-MS: *m*/*z* 2061 {(Hf(O-4-IC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ – (O-4-IC$_6$H$_4$) + Na}$^+$. Anal. Calcd for C$_{28}$H$_{26}$I$_4$O$_5$Hf: C, 29.80; H, 2.32. Found: C, 29.98; H, 2.44.

### 2.9. Synthesis of [Hf(OC$_6$F$_5$)$_4$(HO-tBu)]$_2$ (**8**)

C$_6$F$_5$OH (0.15 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Yield (0.38 g, 93%). M. Pt. 198 °C. $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 1.25 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 141.16 (Ar-F), 139.05 (Ar-F), 136.73 (Ar-F), 134.26 (Ar-O), 78.48 (*C*Me$_3$), 30.37 (C*Me*$_3$). ESI-MS: *m*/*z* 1809 {(Hf(O-C$_6$F$_5$)$_4$(HO-*t*Bu))$_2$ – (O-C$_6$F$_5$) + Na}$^+$. Anal. Calcd for C$_{28}$H$_{10}$F$_{20}$O$_5$Hf: C, 34.15; H, 1.02. Found: C, 34.28; H, 1.24.

### 2.10. Synthesis of [Hf(2, 4, 6-F$_3$C$_6$H$_2$)$_4$(HO-tBu)]$_2$ (**9**)

2, 4, 6-F$_3$C$_6$H$_2$OH (0.12 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and a procedure identical to that used for the synthesis of (**1**) was followed. Yield (0.32 g, 91%). M. Pt. 179 °C. $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 6.55 (8H, *meta*), 1.30 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 155.42 (Ar-F), 152.91 (Ar-F), 135.38 (Ar-O), 99.87 (Ar-C), 80.19 (*C*Me$_3$), 29.26 (C*Me*$_3$). ESI-MS: *m*/*z* 1557 {(Hf(2,4,6-F$_3$C$_6$H$_2$)$_4$(HO-*t*Bu))$_2$ – (O-2,4,6-F$_3$C$_6$H$_2$) + Na}$^+$. Anal. Calcd for C$_{28}$H$_{18}$F$_{12}$O$_5$Hf: C, 39.99; H, 2.16. Found: C, 40.17; H, 2.23.

### 2.11. Synthesis of [Hf(O-CH$_2$-4-OMeC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**10**)

4-MeOC$_6$H$_4$CH$_2$OH (0.12 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of **(1)** was employed. Colorless viscous oil was obtained. Yield (0.30 g, 88%). $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 7.29 (br, 8H, *ortho*), 6.90 (br, 8H, *meta*), 4.62 (br, 8H, –OC*H*$_2$Ar), 3.81 (br, 12H, ArOC*H*$_3$), 1.27 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 159.32 (Ar-OCH$_3$), 134.26 (-OCH$_2$Ar), 128.74 (Ar-C), 114.05 (Ar-C), 76.18 (*C*Me$_3$), 74.12 (-OC*H*$_2$Ar), 55.38 (Ar-OC*H*$_3$), 33.32 (C*Me*$_3$). ESI-MS: *m*/*z* 1488 {(Hf(O-CH$_2$-4-OMeC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ – (O-CH$_2$-4-OMeC$_6$H$_4$) + Na}$^+$. Anal. Calcd for C$_{36}$H$_{46}$O$_9$Hf: C, 53.96; H, 5.79. Found: C, 54.15; H, 5.88.

### 2.12. Synthesis of [Hf(O-CH$_2$-4-MeC$_6$H$_4$)$_4$(HO-tBu)]$_2$ (**11**)

4-MeC$_6$H$_4$CH$_2$OH (0.10 g, 0.84 mmol) and Hf(O-*t*Bu)$_4$ (0.10 g, 0.21 mmol) were reacted and an identical procedure used for the synthesis of (**1**) was employed. Colorless viscous oil was obtained. Yield (0.28 g, 90%). $^1$H NMR (400 MHz, CDCl$_3$, 55 °C): $\delta$ 7.21 (br, 8H, *ortho*), 7.02 (br, 8H, *meta*), 4.87 (br, 8H, –OC*H*$_2$Ar), 2.37 (br, 12H, ArC*H*$_3$), 1.20 (br, 9H, C*Me*$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, 55 °C): $\delta$ 140.51 (-OCH$_2$Ar), 135.71 (Ar-CH$_3$), 128.69 (Ar-C), 127.21 (Ar-C), 72.86 (*C*Me$_3$), 71.76 (-OCH$_2$Ar), 31.37 (C*Me*$_3$), 21.27 (Ar-*C*H$_3$). ESI-MS: *m*/*z* 1376 {(Hf(O-CH$_2$-4-MeC$_6$H$_4$)$_4$(HO-*t*Bu))$_2$ – (O-CH$_2$-4-MeC$_6$H$_4$) + Na}$^+$. Anal. Calcd for C$_{36}$H$_{46}$O$_5$Hf: C, 58.65; H, 6.29. Found: C, 58.76; H, 6.39.

### 2.13. General procedure for the bulk polymerization of CL and VL

For CL polymerization, 23.6 μmol of the aryloxy compound or benzyloxy derivative of hafnium were taken in a flask under an argon atmosphere. The contents were stirred at 80 °C and 0.50 mL CL (0.54 g, 4.71 mmol) was added neat. The mixture was rapidly stirred at the given temperature. A rise in viscosity was observed and finally the stirring ceased. For VL polymerization, 26.9 μmol was used for 0.50 mL (0.54 g, 5.38 mmol) of monomer and a similar procedure was followed. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [60,61]. The polymerizations were quenched by pouring the contents into cold heptane. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

### 2.14. General procedure for the polymerization of CL and VL in toluene

For CL polymerization, 23.6 μmol of the aryloxy compound or benzyloxy derivative of hafnium and 2 mL of dry toluene were taken in a flask under a nitrogen atmosphere. The contents were stirred at 80 °C and 0.5 mL CL (0.54 g, 4.71 mmol) was added neat. The mixture was rapidly stirred. For VL polymerization, 26.9 μmol was used for 0.50 mL (0.54 g, 5.38 mmol) of monomer and a similar procedure was followed. The progress of the polymerization was followed by monitoring the disappearance of the monomer using TLC technique [60,61]. The polymerizations were quenched by pouring the contents into cold heptane. The polymer was isolated by subsequent filtration and dried till a constant weight was attained.

### 2.15. X-ray structure determination of compounds **1** and **5**

Single crystals suitable for structural studies were obtained by crystallization from toluene at –25 °C. X-ray data collection was performed with Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromated Mo ($K_\alpha$) ($\lambda$ = 0.7107 Å) radiation source. The data were collected with 100% completeness

**Table 1**
Crystal data for the structures **1**and **5**.

| Compound | **1** | **5** |
|---|---|---|
| Empirical formula | $C_{56}H_{52}F_8O_{10}Hf_2$ | $C_{88}H_{124}O_{10}Hf_2$ |
| Formula weight | 1393.97 | 1698.90 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2(1)/n$ | $P1$ |
| Temp/K | 173 | 173 |
| Wavelength/Å | 0.71073 | 0.71073 |
| $a$/Å | 13.5740(3) | 10.925(2) |
| $b$/Å | 19.8799(5) | 14.781(3) |
| $c$/Å | 21.1234(6) | 15.230(3) |
| $\alpha$/deg | 90.0000(0) | 97.63(3) |
| $\beta$/deg | 107.5720(10) | 107.12(3) |
| $\gamma$/deg | 90.0000(0) | 103.00(3) |
| $V$/Å$^3$ | 5434.2(2) | 2237.2(8) |
| $Z$ | 4 | 2 |
| $D_{calc}$/g cm$^{-3}$ | 1.699 | 1.261 |
| Reflns collected | 36576 | 28916 |
| No. of indep reflns | 11867 | 10226 |
| GOF | 0.939 | 1.177 |
| Final $R$ indices/$I > 2\sigma(I)$ | $R_1 = 0.0317$ | $R_1 = 0.0347$ |
| | $wR_2 = 0.0990$ | $wR_2 = 0.0833$ |
| $R$ indices/all data | $R_1 = 0.0470$ | $R_1 = 0.0559$ |
| | $wR_2 = 0.1215$ | $wR_2 = 0.1015$ |

$R_1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR_2 = [\sum(F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$.

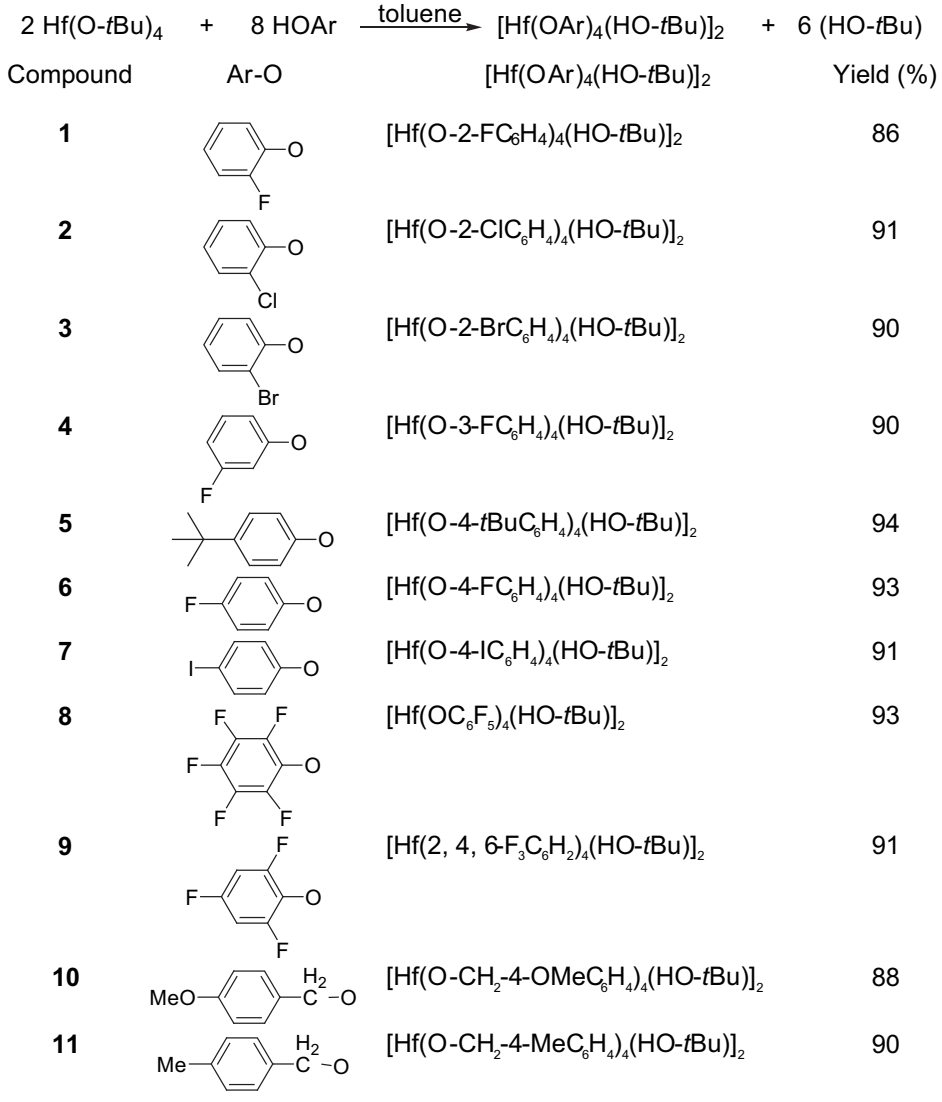
for $\theta$ up to 25°. $\omega$ and $\varphi$ scans was employed to collect the data. The frame width for $\omega$ was set to 0.5° for data collection. The frames were integrated and data were reduced for Lorentz and polarization corrections using SAINT-NT. The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 and refined using SHELXL-97 [63]. The crystal data are summarized in Table 1. The non-hydrogen atoms were refined with anisotropic displacement parameter. All the hydrogen atoms could be located in the difference Fourier map. The hydrogen atoms bonded to carbon atoms were fixed at chemically meaningful positions and were allowed to ride with the parent atom during refinement.

## 3. Results and discussion

### 3.1. Synthesis and characterization of compounds

A variety of different Hf aryloxy compounds **1**–**9** were synthesized from Hf(O-*t*Bu)$_4$ and phenols having different substituents on the phenyl ring, using the alcoholysis route [64,65] as depicted in Scheme 1.

These compounds were prepared by the reaction of Hf(O-*t*Bu)$_4$ with the appropriate phenol in 1:4 stoichiometric ratio in toluene under ambient conditions. Removal of the solvent under reduced




**Scheme 1.** Synthesis of aryloxy and benzyloxy derivatives of Hf.

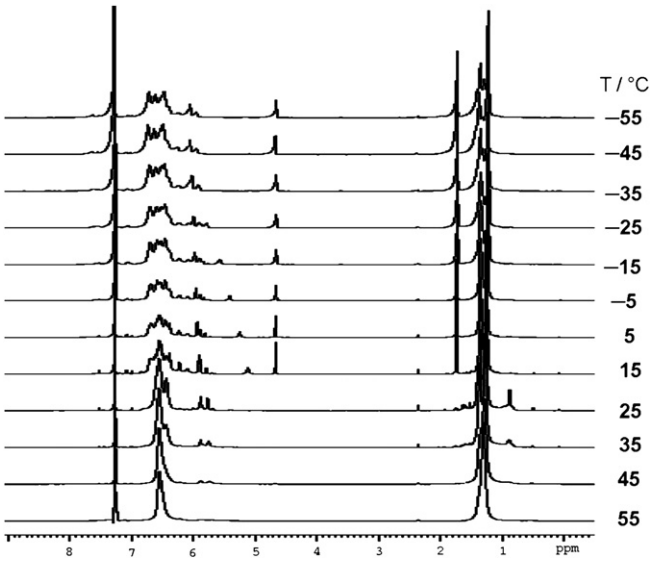



**Fig. 1.** Variable temperature $^1$H NMR of **9** in $CDCl_3$.

pressure afforded the crude product which was further purified by crystallization from toluene at −25 °C. These compounds were isolated as colorless solids in appreciably high yields and purity as HO-*t*Bu adducts. They possess high melting points (179–209 °C).

The benzyloxy derivatives namely Hf(O-$CH_2$-4-$OMeC_6H_4$)$_4$(HO-*t*Bu) (**10**) and Hf(O-$CH_2$-4-$MeC_6H_4$)$_4$(HO-*t*Bu) (**11**) were synthesized by reacting Hf(O-*t*Bu)$_4$ with the corresponding substituted BnOH, using a procedure identical to those of the aryloxy compounds. The yield of these colorless viscous oils were high.

These compounds (**1**–**11**) have been characterized thoroughly by $^1$H and $^{13}$C NMR spectroscopy, electrospray ionization mass spectrometry (ESI-MS) and their purity has been assured by correct elemental analysis values.

The $^1$H NMR of these compounds at 25 °C contains several different signals in addition to the expected ones. However, at 55 °C the spectral characteristics were reasonable in accord with the expectations. At 55 °C, the $^1$H NMR of these compounds possesses the expected signals in the correct ratio of integration. Compound **7** has residual lattice toluene which could not be removed completely even by drying under high vacuum ($10^{-6}$ Torr) for several hours. These compounds readily decompose when heated under such conditions. The $^1$H NMR signals for all the compounds appear broad, suggesting a high degree of fluxional behavior of such molecules. The expected multiplicities of the respective signals disappear completely. The relative degree of signal broadening is higher than the corresponding titanium and zirconium compounds, implying a highest tendency of fluxional behavior in these compounds [61]. The −OH proton of the coordinated HO-*t*Bu remains silent in compounds **1**, **5**, **8**, **9**, **10** and **11** respectively. For the others, the −OH signal is broad and appears at *ca.* 5 ppm. Such observations of fluxionality and oligomer formation are in agreement with the literature precedents pertaining to metal alkoxides [66–68]. The presence of coordinatively unsaturated hafnium centers provides a relatively easy associative route for either ligand scrambling or external ligand exchange. For the benzyloxy derivatives **10** and **11** the signals appear broad and the −OH peak of HO-*t*Bu were silent. Variable temperature $^1$H NMR studies were performed on **1** and **9**. Fig. 1 depicts our results from **9** respectively (For **1**, see Supplementary data).

A common feature is that there are additional signals for each moiety in these compounds under ambient temperature whose number diminishes with the rise in temperature. At 55 °C, the spectral pattern is simplified considerably and matches with the expected pattern. Such observations indicate fluxionality and suggested complicated solution dynamics [66–68].

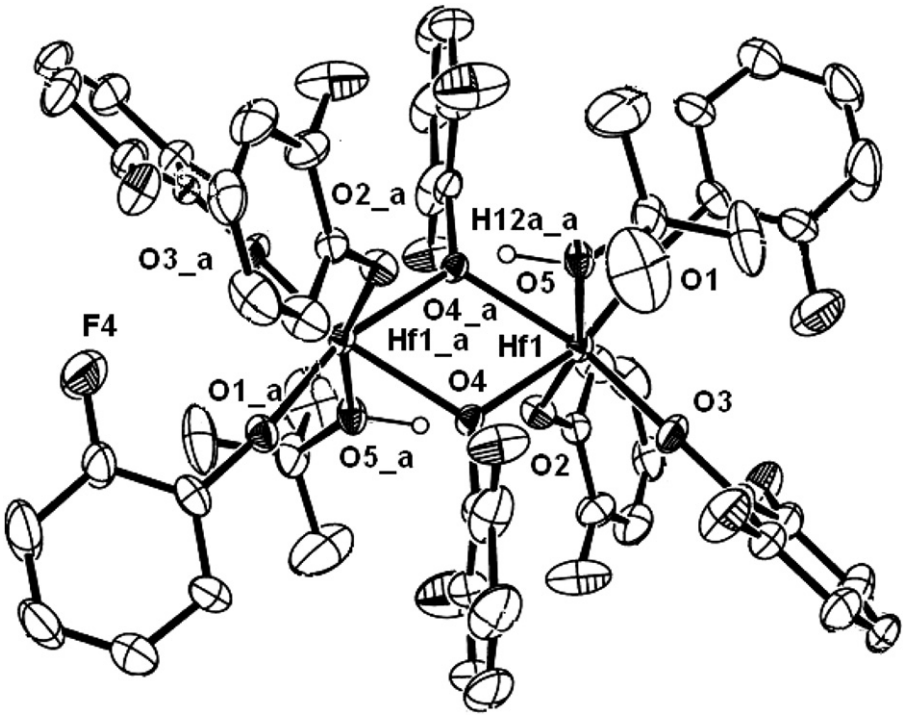



**Fig. 2.** Molecular structure of **1**; thermal ellipsoids were drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Hf(1)–O(4), 2.162(3); Hf(1)–O(4_a), 2.177(3); Hf(1)–Hf(1_a), 3.525(3); Hf(1)–O(2), 2.018(3); Hf(1)–O(1), 1.919(4); Hf(1)–O(5), 2.243(3); Hf(1)–O(3), 1.923(3); Hf(1)–O(4_a)–Hf(1_a), 108.69(13); O(4)–Hf(1)–O(4_a), 71.31(13); O(1)–Hf(1)–O(5), 92.65(14); O(1)–Hf(1)–O(3), 102.00(15); O(2)–Hf(1)–O(3), 98.61(16); O(2)–Hf(1)–O(4), 86.00(13); O(1)–Hf(1)–O(4_a), 93.95(13); O(3)–Hf(1)–O(4_a), 162.53(14).

At 25 °C, the $^{13}C$ NMR spectra of these compounds show additional peaks for the various moieties present in these molecules. The observed spectra at 55 °C were simplified and the information was found to be in accord with the conclusions drawn from $^{1}H$ NMR spectra. In all the aryloxy compounds **1**–**9**, the *ipso* carbon of the phenyl ring is deshielded with respect to the corresponding phenol and the changes in position of the signals contributed by the other carbon atoms of the phenyl ring are not appreciable. The $CMe_3$ signal corresponding to the coordinated HO-*t*Bu is deshielded considerably ($\delta = 69.63–80.79$ ppm) as compared to the free alcohol ($\delta = 68.80$ ppm) as a result of coordination with the hafnium center. For the benzyloxy derivatives **10** and **11** the signals appear as expected.

ESI-MS studies reveal the presence of $\{M_2\text{-}(OAr) + Na\}^+$ [M = Hf $(OAr)_4$(HO-*t*Bu) (**1**–**9**)] peak and $\{M_2\text{-}(OCH_2Ar) + Na\}^+$ [M = Hf $(OCH_2Ar)_4$(HO-*t*Bu) (**10** and **11**)] peak as the sodium adduct in prominent intensity. These observations indicate that such molecules exist predominantly in the dimeric state.

### 3.2. Single crystal X-ray diffraction studies

Amongst the various aryloxy compounds synthesized, suitable single crystals for X-ray diffraction studies were obtained from **1** and **5**. Single crystals were grown in a glove box from dilute toluene solutions of the respective compounds at −25 °C over a period of three weeks. The molecular structure of **1** and **5** has been depicted in Figs. 2 and 3 respectively.

These compounds possess centrosymmetric dimeric structure in the solid-state having edge shared distorted octahedral hafnium centers coordinated to a molecule of HO-*t*Bu. The two hafnium centers are separated by *ca.* 3.5 Å which is larger than the titanium and comparable to zirconium analogues [61]. This explains the greater degree of fluxionality possessed by these compounds as concluded from the NMR studies. The terminal Hf–O bonds of the phenoxy moieties are shorter than those contributing towards the formation of the bridged bonds. The four Hf–O bonds constituting the core are almost indistinguishable suggesting nearly equal covalent and dative contributions, leading to a stable dimeric core. The coordinated HO-*t*Bu can be easily recognized by the bond distance Hf(1)–O(5), being longer than the other Hf–O distances. The distorted octahedral environment around the hafnium centers is apparent from the bond angles. All the parameters described agree well with the literature precedents [38]. The crystal data for **1** and **5** are represented in Table 1.

### 3.3. Polymerization activity and characteristics

Our recent work in this area indicate that metal initiators with elaborate ligands constituting the backbone are not an essential requirement towards the polymerization of at least lactones [60,61]. Utilizing the activated monomer mechanism, it is possible to produce high $M_n$ polymers with controlled MWDs. A variation of electronic environments of the phenyl ring constituting the –OAr moiety is anticipated to produce consequences in such polymerizations. Our observations using the titanium and zirconium compounds supported the contention and it prompted us to understand the effect of hafnium [61]. To the best of our belief, polymerizations in the presence of such compounds have not been reported so far using hafnium derivatives. It was considered appropriate to compare the results using different aryloxy compounds (**1**–**9**) to those using the benzyloxy derivatives **10** and **11** respectively. These polymerizations were performed under bulk conditions at 80 °C using **1**–**11**. In addition, there is no report of bulk polymerization of lactones using organometallic hafnium derivatives [31,36,38]. Polymerization under ambient temperatures yielded oligomers of low molecular weight. The results are summarized in Tables 2 and 3 respectively.

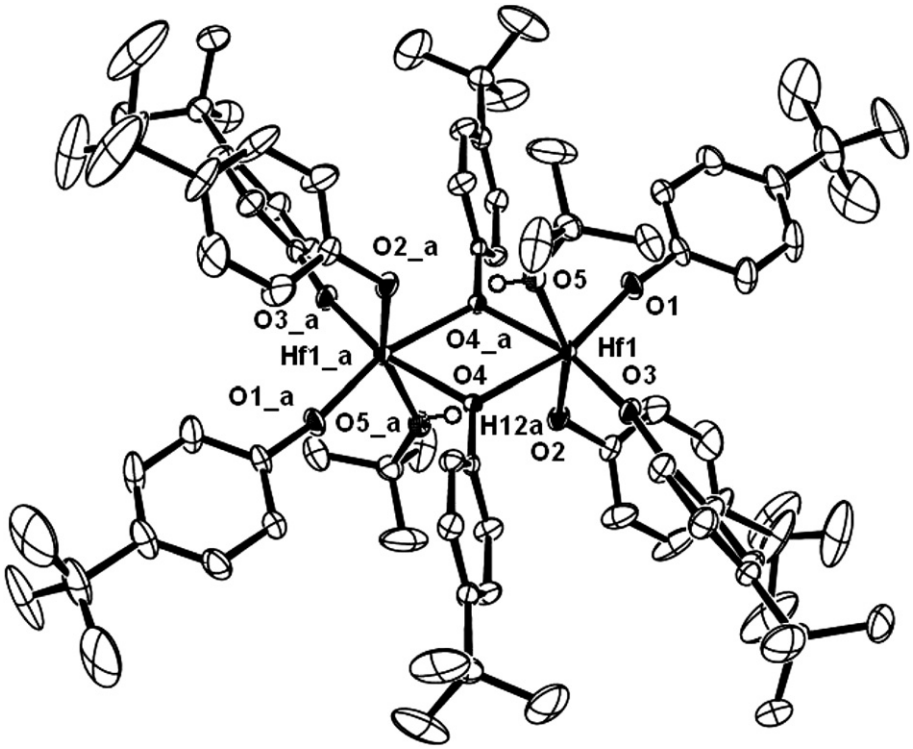



**Fig. 3.** Molecular structure of **5**; thermal ellipsoids were drawn at 30% probability level. Selected bond lengths (Å) and angles (deg): Hf(1)–O(4), 2.157(2); Hf(1)–O(4_a), 2.158(3); Hf(1)–Hf(1_a), 3.524(9); Hf(1)–O(2), 2.029(3); Hf(1)–O(1), 1.929(3); Hf(1)–O(5), 2.238(3); Hf(1)–O(3), 1.919(3); Hf(1)–O(4_a)–Hf(1_a), 109.50(11); O(4)–Hf(1)–O(4_a), 70.50(11); O(1)–Hf(1)–O(5), 93.49(12); O(1)–Hf(1)–O(3), 102.19(13); O(2)–Hf(1)–O(3), 97.72(13); O(2)–Hf(1)–O(4), 85.29(11); O(1)–Hf(1)–O(4_a), 94.17(12); O(3)–Hf(1)–O(4_a), 163.10(11).

**Table 2**
Results of CL polymerization using various hafnium aryloxy compounds and benzyloxy derivatives in 200:1 ratio at 80 °C.

| Initiator | $t^a$/min | $M_n{}^b$/(kg/mol) | $M_w/M_n$ |
|---|---|---|---|
| $[Hf(O\text{-}2\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**1**) | 32 | 15.83 | 1.18 |
| $[Hf(O\text{-}2\text{-}ClC_6H_4)_4(HO\text{-}tBu)]_2$ (**2**) | 43 | 33.61 | 1.19 |
| $[Hf(O\text{-}2\text{-}BrC_6H_4)_4(HO\text{-}tBu)]_2$ (**3**) | 74 | 35.56 | 1.17 |
| $[Hf(O\text{-}3\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**4**) | 88 | 22.11 | 1.19 |
| $[Hf(O\text{-}4\text{-}tBuC_6H_4)_4(HO\text{-}tBu)]_2$ (**5**) | 81 | 106.71 | 1.19 |
| $[Hf(O\text{-}4\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**6**) | 98 | 34.82 | 1.19 |
| $[Hf(O\text{-}4\text{-}IC_6H_4)_4(HO\text{-}tBu)]_2$ (**7**) | 25 | 45.85 | 1.19 |
| $[Hf(OC_6F_5)_4(HO\text{-}tBu)]_2$ (**8**) | 75 | 22.54 | 1.18 |
| $[Hf(2,4,6\text{-}F_3C_6H_2)_4(HO\text{-}tBu)]_2$ (**9**) | 35 | 85.21 | 1.18 |
| $[Hf(O\text{-}CH_2\text{-}4\text{-}OMeC_6H_4)_4(HO\text{-}tBu)]_2$ (**10**) | 85 | 18.57 | 1.19 |
| $[Hf(O\text{-}CH_2\text{-}4\text{-}MeC_6H_4)_4(HO\text{-}tBu)]_2$ (**11**) | 80 | 16.27 | 1.18 |

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed at 100% conversion.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for $M_n$.

Analysis of the results depicted in Tables 2 and 3 reveal that as we increase the size of electron-withdrawing group at 2-position of aromatic periphery of initiators (see Table 1 and Table 2, initiator **1**, **2** and **3**), rise in $M_n$ and decrease in polymerization activity with respect to polymerization time were observed. Further changing electron-withdrawing group from 2-position to 3-position and 2-position to 4-position, rise in $M_n$ and decrease in polymerization activity with respect to polymerization time were observed (see Tables 1 and 2, initiator **1**, **4** and **6**) and changing electron-withdrawing group by electron-donating group at 4-position of the aromatic periphery of initiator leads with rise in $M_n$ and increase in polymerization activity with respect to polymerization time (see Tables 1 and 2, initiator **5** and **6**). In case of pentasubstitution of electron-withdrawing groups on the aromatic periphery of initiator yielded $M_n$ close to the theoretical one and low polymerization activity with respect to polymerization time (see Table 1, initiator **8**), which shows a control in polymerization. We have obtained higher $M_n$ in case of **5** and **9** initiators, higher polymerization activity shown in case of initiator **9** with respect to time and $M_n$ for CL polymerization and highest polymerization activity was shown by initiator **7** with respect to polymerization time (see Table 1). Further we have obtained highest polymerization activity and highest $M_n$ in case of initiator **9** for VL polymerization (see Table 2). The benzyloxy derivatives **10** and **11** were inferior to the aryloxy compounds **1**–**9**. Good degree of control in the polymerization process was observed. Our polymerization results deserve special mention since we have been able to obtain high $M_n$ and controlled MWDs using our simple initiator system. These results are superior than the ones reported using hafnium initiators containing elaborate ligands [31,36,38].

**Table 3**
Results of VL polymerization using various hafnium aryloxy compounds and benzyloxy derivatives in 200:1 ratio at 80 °C.

| Initiator | $t^a$/min | $M_n{}^b$/(kg/mol) | $M_w/M_n$ |
|---|---|---|---|
| $[Hf(O\text{-}2\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**1**) | 41 | 13.39 | 1.16 |
| $[Hf(O\text{-}2\text{-}ClC_6H_4)_4(HO\text{-}tBu)]_2$ (**2**) | 56 | 77.49 | 1.18 |
| $[Hf(O\text{-}2\text{-}BrC_6H_4)_4(HO\text{-}tBu)]_2$ (**3**) | 88 | 112.95 | 1.16 |
| $[Hf(O\text{-}3\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**4**) | 101 | 104.40 | 1.18 |
| $[Hf(O\text{-}4\text{-}tBuC_6H_4)_4(HO\text{-}tBu)]_2$ (**5**) | 93 | 102.01 | 1.17 |
| $[Hf(O\text{-}4\text{-}FC_6H_4)_4(HO\text{-}tBu)]_2$ (**6**) | 113 | 98.07 | 1.17 |
| $[Hf(O\text{-}4\text{-}IC_6H_4)_4(HO\text{-}tBu)]_2$ (**7**) | 46 | 90.08 | 1.16 |
| $[Hf(OC_6F_5)_4(HO\text{-}tBu)]_2$ (**8**) | 86 | 29.61 | 1.15 |
| $[Hf(2,4,6\text{-}F_3C_6H_2)_4(HO\text{-}tBu)]_2$ (**9**) | 40 | 125.84 | 1.18 |
| $[Hf(O\text{-}CH_2\text{-}4\text{-}OMeC_6H_4)_4(HO\text{-}tBu)]_2$ (**10**) | 92 | 32.09 | 1.16 |
| $[Hf(O\text{-}CH_2\text{-}4\text{-}MeC_6H_4)_4(HO\text{-}tBu)]_2$ (**11**) | 86 | 29.82 | 1.15 |

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed at 100% conversion.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards.

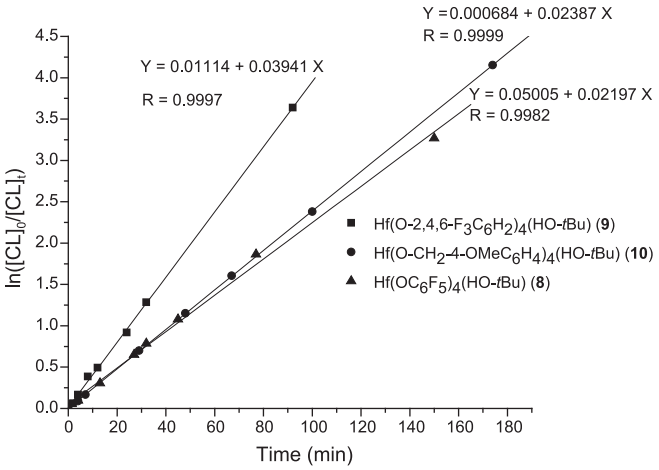



**Fig. 4.** Semilogarithmic plots of CL conversion in time initiated by **8**, **9** and **10**: $[CL]_o/[Hf]_o = 1000$ at 80 °C.

The variations of $M_n$ with $[CL]_o/[Hf]_o$ ratio using **8**, **9** and **10** for CL polymerizations were studied. The plots are linear indicating that there is a continual rise in $M_n$ with an increase in $[CL]_o/[Hf]_o$ ratio. The polymerization behavior of VL using these initiators was found to be similar (see Supplementary data).

### 3.4. Kinetics of polymerization

The kinetic studies for the polymerization of CL and VL using **8**, **9** and **10** were performed. The kinetic studies for the polymerization of CL in ratio $[CL]_o/[Hf]_o = 1000$ were done at 80 °C. There is a first-order dependence of the rate of polymerization on monomer concentration. No induction period was observed. Similar observations were noticed for VL (see Supplementary data). The $\ln[CL]_o/[CL]_t$ versus time plot (Fig. 4.) show linear variation. From the slope of the plots, the values of the apparent rate constant ($k_{app}$) for CL polymerizations initiated by **8**, **9** and **10** were found to be $2.19 \times 10^{-2}$ min$^{-1}$, $3.94 \times 10^{-2}$ min$^{-1}$ and $2.38 \times 10^{-2}$ min$^{-1}$. For VL, the results are similar and the apparent rate constant ($k_{app}$) for polymerizations initiated by **8**, **9** and **10** were found to be $2.06 \times 10^{-2}$ min$^{-1}$, $2.97 \times 10^{-2}$ min$^{-1}$ and $1.47 \times 10^{-2}$ min$^{-1}$ (Fig. 5). Polymerization studies on VL using hafnium compounds are not reported.

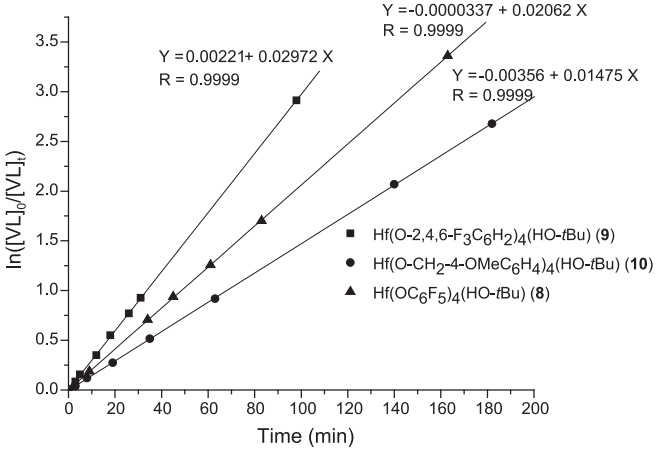



**Fig. 5.** Semilogarithmic plots of VL conversion in time initiated by **8, 9** and **10**: $[VL]_o/[Hf]_o = 1000$ at 80 °C.

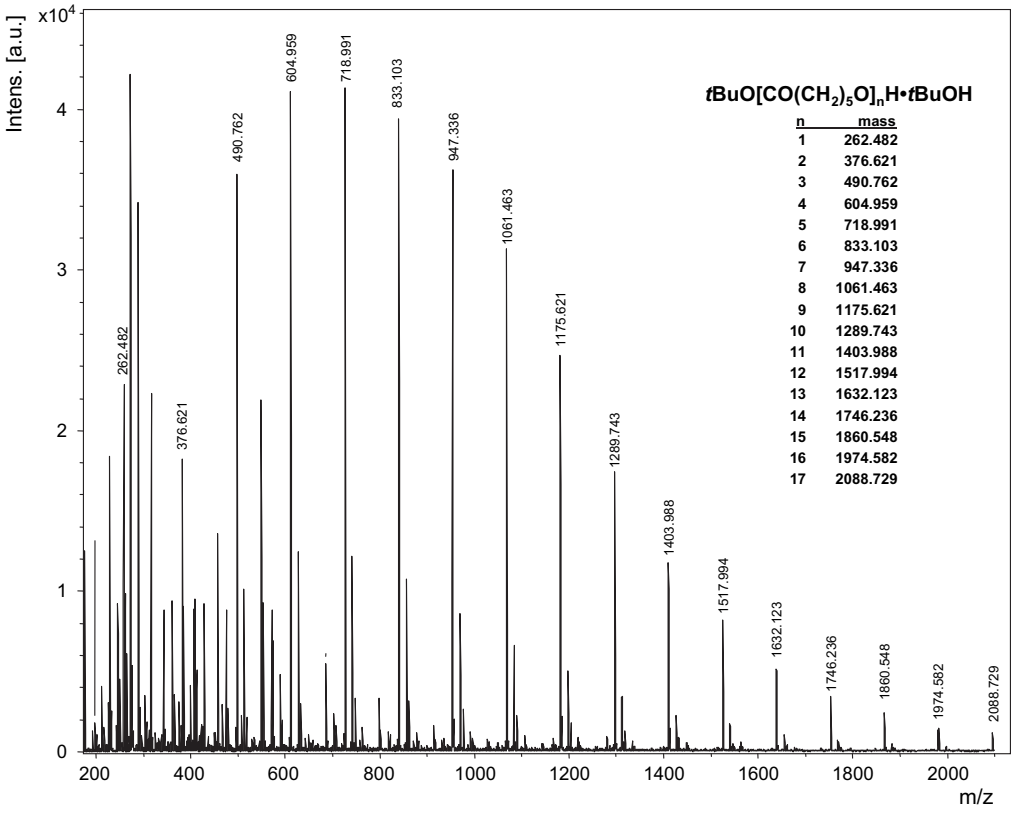



**Fig. 6.** MALDI-TOF (dihydroxy benzoic acid used as matrix) of the crude product obtained from a reaction between CL and **1** in 20:1 ratio.

### 3.5. Mechanism of polymerization

A convenient tool to gain insight into the polymerization mechanism using **1**–**11** is a thorough understanding of the polymer composition upon using these compounds as initiators through MALDI-TOF and $^1$H NMR spectroscopy. We selected **1** and **5** as prototype representatives. Low $M_n$ oligomer of PCL was synthesized by stirring CL with **1** or **5** in 20:1 M ratio under neat conditions at 80 °C. The product was washed with heptane. The residue after removal of heptane was analyzed thoroughly using MALDI-TOF and $^1$H NMR spectroscopy.

With **1**, the major product of the composition *t*BuO[CO$(CH_2)_5$O]$_n$H is formed as understood through the analysis of MALDI-TOF and $^1$H NMR spectra, depicted in Figs. 6 and 7 respectively.

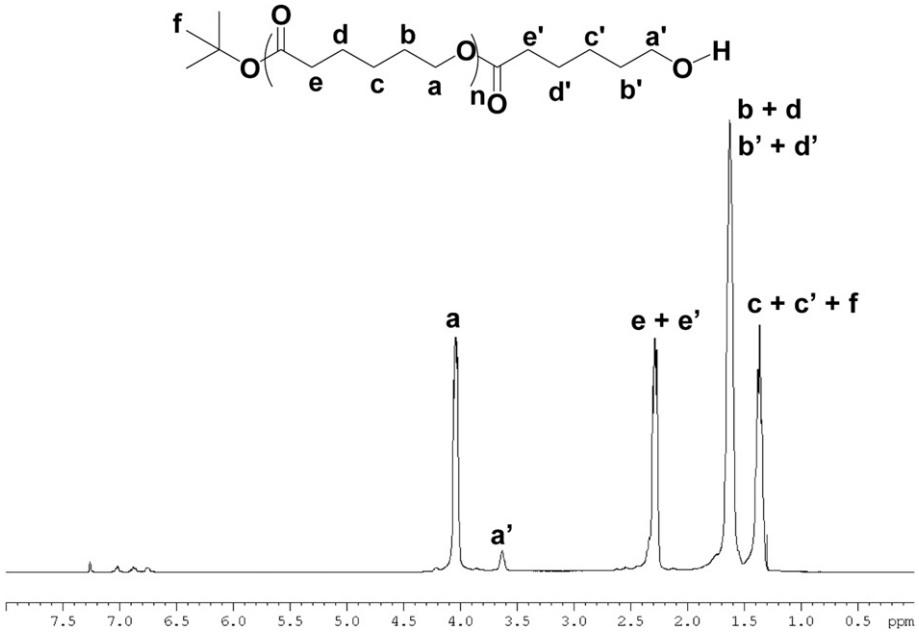
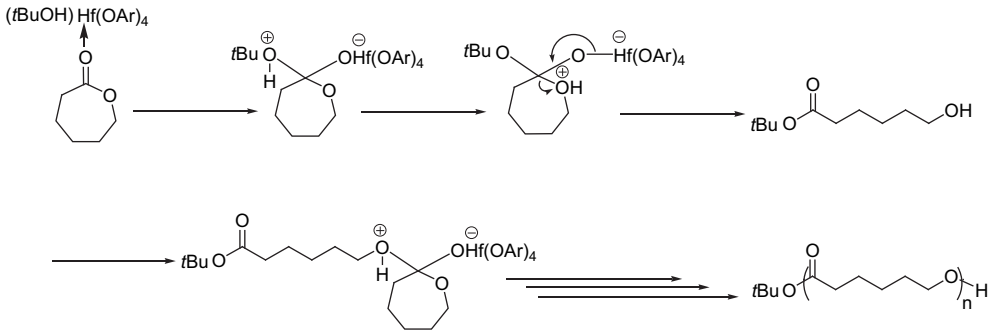



**Fig. 7.** $^1$H NMR spectrum of the crude product obtained from a reaction between CL and **1** in 20:1 ratio (the hydroxy proton peak corresponding to *t*BuO[CO$(CH_2)_5$O]$_n$H was silent [48]).



**Scheme 2.** Polymerization proceeds through the activated monomer mechanism with hafnium compounds.

Fig. 6 reveals the presence of $t$BuO[CO($CH_2$)$_5$O]$_n$H·$t$BuOH ($m/z$ = 376.6, 490.7, 604.9, 718.9, 833.1, 947.3,…) as major set of peaks in addition to this presence of $t$BuO[CO($CH_2$)$_5$O]$_n$H·Na with inclusion of one molecule of $t$BuOH (399.1, 513.3, 627.4, 741.5, 855.6, 969.7,…) as minor set of peaks indicating the required product as expected from end capped group analysis and peaks corresponding to transesterification reactions were not observed. This is an implication that coordinated HO-$t$Bu has an active role as an initiator and the polymerization proceeds through the activated monomer mechanism as depicted in Scheme 2 [55–61].

It may be clearly understood that the product 2-F$C_6H_4$O[CO($CH_2$)$_5$O]$_n$H which would have resulted from coordination-insertion mechanism, is completely absent. This was again evidenced by synthesized low $M_n$ oligomer of PCL with CL and **10** in 20:1 M ratio under neat conditions at 80 °C. The product was washed with heptane. The residue after removal of heptane was analyzed thoroughly using $^1$H NMR spectroscopy. The end capped group analysis suggests that the major product of the composition is found to be $t$BuO[CO($CH_2$)$_5$O]$_n$H depicted in Fig. 8, which is further supports the activated monomer mechanism. The obvious implication is given a choice; the system prefers to adopt the activated monomer pathway where coordinated HO-$t$Bu initiates the polymerization. Similar results were seen for **5** (see Supplementary data). The CL ring opens due to result of activation of the acyl oxygen bond. The product obtained from the first ring-opening initiates the second cycle. The polymerization propagates in a similar manner.

### 3.6. Comparison of polymerization results

For comparison of our results with those known for CL polymerization, we present here results for polymerizations conducted in the presence of toluene (Table 4).

In the presence of toluene, these polymerizations are better controlled resulting in low MWDs. Our results are superior or at least comparable to literature reports [38]. Such observations are also seen for the bulk polymerizations conducted in the absence of solvents. The polymerization in solution performed at much shorter time than the time mentioned in Table 4 results with lower monomer conversions.

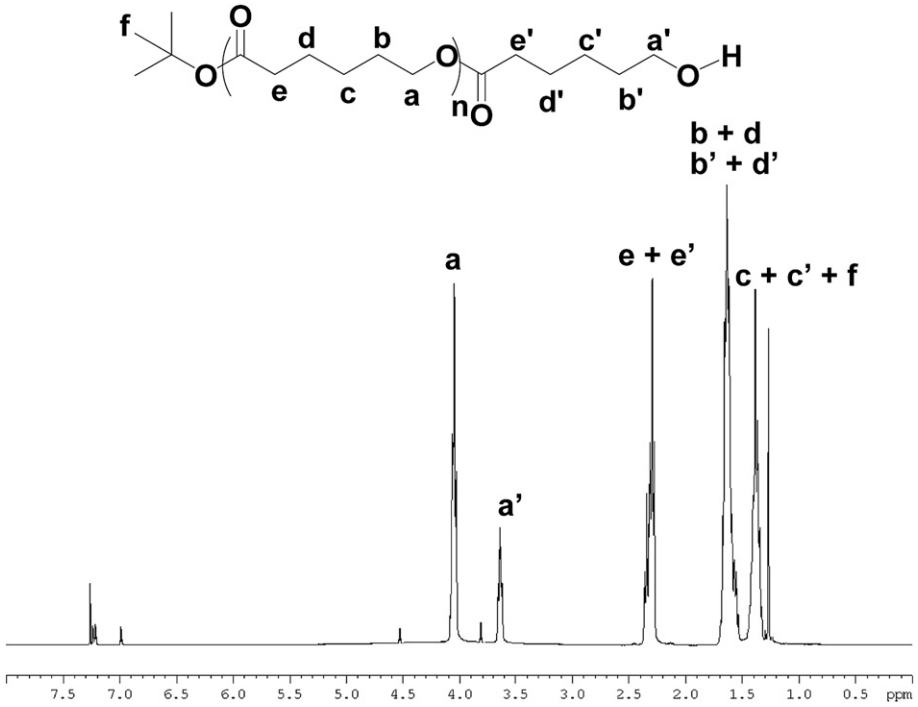



**Fig. 8.** $^1$H NMR spectrum of the crude product obtained from a reaction between CL and **10** in 20:1 ratio (the hydroxy proton peak corresponding to $t$BuO[CO($CH_2$)$_5$O]$_n$H was silent [48]).

**Table 4**
Results of CL polymerization using **5**, **8**, **9** and **10** in 200:1 ratio at 80 °C in toluene.

| Initiator | $t$[a]/min | $M_n$[b]/(kg/mol) | $M_w/M_n$ |
|---|---|---|---|
| [Hf(O-4-$t$BuC$_6$H$_4$)$_4$(HO-$t$Bu)]$_2$ (**5**) | 155 | 28.22 | 1.15 |
| [Hf(OC$_6$F$_5$)$_4$(HO-$t$Bu)]$_2$ (**8**) | 142 | 18.44 | 1.16 |
| [Hf(2,4,6-F$_3$C$_6$H$_2$)$_4$(HO-$t$Bu)]$_2$ (**9**) | 78 | 30.70 | 1.14 |
| [Hf(O-CH$_2$-4-OMeC$_6$H$_4$)$_4$(HO-$t$Bu)]$_2$ (**10**) | 185 | 12.18 | 1.14 |

[a] Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed at 100% conversion.
[b] Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for $M_n$.

## 4. Conclusions

In summary, we have used the alcoholysis route for synthesizing several new aryloxy compounds and benzyloxy derivatives of hafnium. These compounds have high degree of fluxionality and possess an inherent tendency for oligomerization in solution. They are powerful activators for the polymerization of CL and VL. There is greater control in the polymerization when titanium and zirconium are replaced by hafnium. The polymerization rates are slower as compared to the titanium and zirconium analogues. These results are based upon a simplified approach to the polymerization of cyclic esters using mild Lewis acids as catalysts and coordinated alcohol as initiator, using the activated monomer mechanism. The methodology employed and the concepts reported may be considered crucial for bulk scale procedures. The achievement of obtaining high $M_n$ and controlled MWDs without having to resort to elaborate ligands is a noted feature for our system.

## Acknowledgements

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## Appendix. Supplementary data

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2010.08.031.

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