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Hepta-coordinated heteroleptic derivatives of zirconium(IV): Synthesis, structural characterization and ring opening polymerization of ϵ -caprolactone



Vuppalapati Giri Prasanth^a, Ravindranath S. Rathore^b, Madhvesh Pathak^{a,*}, Kulathu Iyer Sathiyanarayanan^{a,1}

^a School of Advanced Sciences, VIT University, Vellore 632014, Tamilnadu, India
^b BIF, School of Life Sciences, University of Hyderabad, Hyderabad 500046, Telangana, India

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ABSTRACT

A series of new hepta-coordinated heteroleptic derivatives of zirconium(IV) of the types $[(CH_3COCHCOCH_3)_2ZrL]$ (1, 3, 5 and 7) and $[(C_6H_5COCHCOC_6H_5)_2ZrL]$ (2, 4, 6 and 8) (L = a dianionic [ONO]-tridentate ancillary ligand) was synthesized quantitatively by reacting Zr(OPrⁱ)₄·PrⁱOH with the tridentate Schiff's base ligands H_2L^x ($H_2L^1 = C_{13}H_{11}NO_2$; $H_2L^2 = C_{13}H_{10}BrNO_2$; $H_2L^3 = C_{14}H_{13}NO_3$; $H_2L^4 = C_{17}H_{13}NO_2$ and β -diketones (acetylacetone/dibenzoylmethane) in a 1:1:2 stoichiometry using dry benzene and ethanol as solvents. All these newly synthesized solid derivatives were fairly soluble in common organic solvents. They were characterized by elemental analyses, FTIR and NMR (¹H and ¹³C) spectral studies. Single crystal XRD data of complexes **1**, **2**, **3** and **5** indicated the hepta-coordination and monomeric nature of these complexes. Furthermore, all these derivatives were tested for the ring opening polymerization of ε -caprolactone. The dibenzoylmethane derivatives were inactive in polymerizing ε -caprolactone unlike the acetylacetonate complexes. The molecular weight and polydispersity index values of polycaprolactone were obtained by GPC analysis. Kinetic studies for the rate of polymerization of ε -caprolactone by these catalytically active zirconium(IV) complexes authenticated the first order dependence of the polymerization rate on the monomer concentration. Among these, complex 3, with an electronegative bromine atom on the Schiff's base moiety, exhibited the best catalytic activity with a conversion of >95% in 2 h.

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1. Introduction

In chemical history, metallo-organic derivatives of zirconium (IV) have been documented emphatically as noteworthy precursors of nano-structured zirconia [1,2] giving substantial yields with high purity by the sol-gel synthetic route. Very recently, we have carried out a unique investigation on the wettability of a polyvinylidene fluoride-nano zirconia composite material from a newly synthesized metallo-organic complex of zirconium(IV) [3]. Apart from this application, these heteroleptic derivatives of zirconium(IV) have also been employed as initiators in the ring-opening polymerization of cyclic esters [4–13].

Polycaprolactone (PCL) is biodegradable, biocompatible and eco-friendly polyester [14,15]. It is extensively used in packaging materials, tissue engineering scaffolds, controlled drug delivery systems and in biocompatible implants [16–19]. PCL can be produced by the ring-opening polymerization of ε -caprolactone (ε -CL) using suitable metal complexes as initiators [20,21]. Instead of exploiting the rapidly depleting petrochemical resources to procure conventional polymers and in order to replenish our deteriorating ecosystem, the production of polymeric materials like PCL and polylactide could be carried out by utilizing their relevant monomers, which in turn could be outsourced from tremendous renewable natural capital [8,22].

Although there are numerous metal complexes reported as catalysts for the ring opening polymerization (ROP) of cyclic esters, the low toxicity and great activity of metallo-organic complexes of zirconium(IV) in producing high molecular weight polymers with good polydispersity index (PDI) values motivated us to enter this field [12]. Nowadays, zirconium complexes incorporated with



^{*} Corresponding author. Tel.: +91 416 2202553.

E-mail addresses: madhveshpathak@vit.ac.in (M. Pathak), sathiya_kuna@ hotmail.com (S. Kulathu lyer).

¹ Co-corresponding author. Tel.: +91 416 2202081.

ligands such as amine phenolates [7], bis(imino) phenoxides [10], phenols, benzyl alcohols [9], pyrrolyl N-donors [11], benzotriazole phenoxides [23] and salen [8] have been well documented for the polymerization of cyclic esters and the effect of substituents on the ligands in the polymerization activity has also been interpreted clearly. However, the unavoidable hydrolytic instability (high moisture sensitivity), which is a major problem of these complexes, cannot be ignored.

Substitution of easily hydrolysable alkoxy groups on metal alkoxides with non-hydrolysable chelating ligands, such as schiffs bases, β -diketonates and β -ketoesters will result in the production of complexes with increased stability against hydrolysis [3,24,25]. Thus, we were inspired to synthesize new zirconium(IV) derivatives associated with non-hydrolysable ligands and with good ROP activity; herein we report the synthesis of eight hepta-coordinated metallo-organic zirconium(IV) complexes by treating zirconium isopropoxide with Schiff's bases and β -diketonates in a stoichiometry of 1:1:2, followed by a detailed study of these derivatives on ϵ -CL polymerization activity.

2. Results and discussion

2.1. Synthesis and characterization

The complexes **1-8** were synthesized by the reaction of Zr $(OPr^{i})_{4}$ ·Pr^{*i*}OH with the corresponding Schiff's bases and β -diketonates in a 1:1:2 molar ratio in an anhydrous solvent mixture of benzene and ethanol (Scheme 1). The isopropanol liberated during the progress of these one pot alcohol elimination reactions was removed along with benzene and ethanol by continuous

fractionation. The yellow to brown colored solid products obtained were washed with n-hexane repeatedly and have been characterized by FTIR, elemental analysis, ¹H and ¹³C NMR spectra. While efforts to obtain crystals in suitable solvents, like a DCM-hexane mixture, were unsuccessful, diffraction quality crystals of **1**, **2**, **3** and **5** were finally grown in a benzene-hexane mixture, and they were structurally characterized by single crystal XRD.

2.1.1. FTIR spectra

The characteristic bands in the FTIR spectra of the complexes were assigned by comparing the spectra of the free ligands with the new derivatives. The absence of a strong broad peak around 3400 cm^{-1} in all the complexes indicated the deprotonation of the ligands. A strong peak observed at around 750 cm^{-1} in all the derivatives confirmed the formation of Zr–O bonds. The appearance of a strong band at around 540 cm^{-1} indicated the coordination of a nitrogen atom to zirconium [26]. Shifting of the C⁻–O stretching frequency of acetylacetone and dibenzoylmethane from 1740 to 1590 cm^{-1} and the appearance of a strong intense peak at around 1520 cm^{-1} due to C⁻–C revealed the quasi-aromatic nature and bidentate coordination pattern of these β -diketonate moieties. Ar-H and C–H stretching frequencies are observed at around 3050 and 2950 cm⁻¹, respectively.

2.1.2. ¹H NMR

In the ¹H NMR spectra of the complexes, the disappearance of the OH peaks corresponding to the Schiff's bases and β -diketonate (enolic OH) ligands confirm the deprotonation of the OH groups and Zr–O bond formation. Coordination of the nitrogen atom to the zirconium metal center was evidenced by the slight downfield



Scheme 1. Synthesis of the zirconium(IV) derivatives 1-8.

shift in the N=CH peaks of the Schiff's base ligands. Appearance of two individual singlets in the ¹H NMR spectrum (with high and low proton integration values) for the methyl and methine protons (respectively) of the acetylacetonate moiety in complex **1**, indicated the effect of the Schiff's base ligand on the chemical equivalence of these protons. Further, a similar type of pattern was observed in the ¹³C NMR spectrum of the same complex for the methyl, methine and carbonyl carbons of the acetylacetonate moiety. Almost, an identical trend of NMR (¹H and ¹³C) spectra were noticed in the remaining analogous complexes **3**, **5** and **7** to authenticate their plausible structures.

2.1.3. Structure of the zirconium(IV) complexes

The structures of the four zirconium(IV) complexes were established by collecting intensity data from their single crystal XRD. In the hepta-coordinated derivatives, six O atoms and one N atom are attached to the metal center Zr(IV) in a pentagonal bipyramidal geometry (10 faces, 15 edges), possessing D5h symmetry as shown in Fig. 1. The Zr-coordination spheres are formed by chelating bidentate β -diketonates [acetylacetonate (acac)/dibenzoylmethane (dbm)] along with the tridentate Schiff's bases in complexes **1**, **2**, **3** and **5**. In the acac and dbm residues, the O···O bite distances and the O–Zr–O bite angles varied in the ranges 2.620(5)–2.658(3) Å and 75.09(9)–75.49(12)°, while in H₂L¹ and its substituent residues, the O···N bite distances and O–Zr–N bite angles were in the 2.32(3)–2.991(4) Å and 65.2(9)–81.30(12)° ranges respectively. The coordination bond distances were observed to be as follows: Zr–O (acac/dbm) 2.121(3)–2.215(2) Å, Zr–O (H₂L¹/derivatives) 1.829(14)–2.216(15) Å and Zr–N 2.323(3)– 2.393(8) Å. The observed geometries are in good agreement with their average values [27]. In all the ligands, the six-membered chelate rings formed by the O, N atoms are slightly puckered. Among the metal complexes, slight puckering of the chelate rings in the flexible ligands arises due to packing forces and to accommodate weak hydrogen bonds, which is a common observation in coordination compounds [28,29].

Compounds **1** and **2**, having the H_2L^1 ligand, possess crystallographically-imposed two-fold symmetry with Z' = 0.5 and the Zr atom located at the two-fold axis. The Schiff's base H_2L^1 ligand does not possess any point-group symmetry. However, the molecules in the unit cell occupy (in a 0.5:0.5 ratio) two different orientations related by two-fold rotation, leading to C2 point group symmetry with the metal lying at the two-fold axis. In **1** and **2**, the asymmetric unit comprises of one acac/dbm ligand, and half of the H_2L^1 ligand with half the occupancy of the Schiff's base (-C=N-).

In the monoclinic crystals (**1**, **3**, **5**), four molecules are packed *via* weak $C-H\cdots O/\pi$ and van der Waals interactions and the



Fig. 1. A perspective view of the sevenfold coordination polyhedron, possessing a pentagonal bipyramid geometry in the metal complexes (i) **1**, (ii) **2**, (iii) **3** and (iv) **5**. Displacement ellipsoids are drawn at the 35% probability level. Color scheme: C-gray, H-white, Br-brown, N-blue, O-red, Zr-green. Solvent benzene and positional disorder in **1** and **2** are not shown for clarity. In complex **2**, the two different orientations of the H₂L¹ residues, related by a two-fold axis are distinguished by dashed bond connectivity at C7 and N1. (Colour online.)



Fig. 2. ¹H NMR of complex 1: (a) unexposed to air. (b) Exposed to air.

central hydrophobic channels running along *b*-axis are occupied by the benzene solvent. On the other hand, the packing mode in the orthorhombic crystal **2** is slightly different from this common pattern due to the presence of a bulky phenyl group in dbm. In this case, the hydrophobic channel is occupied by the benzene solvent along the *c*-axis. Packing diagrams are shown in the Supplementary Fig. S17 and weak intermolecular interactions are listed in the Supplementary Table S1.

2.2. Stability studies

The moisture stability of these complexes was studied by comparing the ¹H NMR spectra recorded for complex **1** in exposed as well as in unexposed conditions. Despite exposing complex **1** to air for 2 weeks, no new peaks appeared nor did any existing signals disappear in the ¹H NMR spectra (Fig. 2). Similar behavior of the same derivative (air exposed and unexposed) in DMSO was also observed in the UV–Vis investigations. No shift/decay in the characteristic imine absorption peak at 420 nm was noticed in the spectra. Further, the UV–Vis spectra of complex **1** were recorded periodically thrice (with a time interval of 24 h) using a solvent mixture of water and DMSO in a 1:9 ratio. There was no variation (shift/decay) at all in the position of the band at 420 nm. Thus, the ¹H NMR and UV–Vis spectral studies evidently reveal the appreciable air stability of derivative **1** as well as its analogous complexes.

2.3. Polymerization studies

All the derivatives were trialed for the ROP of ϵ -CL in the presence of external benzyl alcohol as the polymerization did not proceed without addition of benzyl alcohol. The polymerization

reactions were performed under a dry nitrogen environment in DCM at 50 °C. Dibenzoylmethane derivatives 2, 4, 6 and 8 were inactive in polymerizing ϵ -CL due to steric effects, whereas acetylacetonate derivatives 1, 3, 5 and 7 were guite active in polymerizing ε -CL. The temperature dependence of these polymerization reactions was studied while performing ε -CL polymerization using complex 1 at 25, 50 and 70 °C (Table 2, entries 1–3). The monomer conversion was found to be negligible at room temperature, but it was better at higher temperatures. Molecular weight and PDI values of the PCL produced were determined by gel permeation chromatography (GPC) and the PDI values were found to be in a narrow range from 1.17 to 1.31. This indicates that the ε -CL polymerization occurred in a controlled manner. Systematic ε-CL polymerization studies of 3 with increasing monomer to initiator concentrations [M]₀:[Zr]₀ resulted in polymers with increasing average molecular weights $M_{\rm n}$ and a narrow range of PDI values (1.17-1.29) revealed that the polymerizations proceeded in a controlled fashion. The linear relationship between M_n and $[M]_0$: $[Zr]_0$ (Fig. 3) showed by complex 3 (Table 2, entries 6-10) specified the "living" character of polymerization process. The experimental results revealed that complexes 1, 3, 5 and 7 are highly active in polymerizing ϵ -CL with >90% conversion in 2 h. However, the superior polymerization activity of complex **3** (monomer conversion >95%) could be due to the electron withdrawing bromine substituent on the benzene ring of the Schiff's base moiety. The ¹H NMR spectrum of PCL ([M]_o:[Al]_o = 100; Table 2, entry 3; where the end groups were found to be benzyloxy and hydroxyl groups) (Fig. 4) indicates that the polymerization takes place through a "coordination insertion" pathway. The integral ratio between H_g (CH₂ protons of PCL from the hydroxyl group end) at 3.58 ppm and H_b (CH₂ protons of PCL from t benzyloxy group end) at

Table 1						l	Table 1	1
Crystal data for all the four Zr-complexes.	ur Zr-coi	four	the	all	for	data	Crystal	(

Complex	1	2	3	5
Crystal data				
Chemical formula	$C_{23}H_{23}NO_6Zr$, (C_6H_6)	C ₄₃ H ₃₁ NO ₆ Zr, 2(C ₆ H ₆)	C ₂₃ H ₂₂ BrNO ₆ Zr, 1/2(C ₆ H ₆)	$C_{24}H_{25}NO_7Zr$, (C_6H_6)
Co-crystallizing solvent	benzene	benzene	benzene	benzene
Molecular weight	578.75	905.12	618.60	608.78
Crystal size (mm)	$0.38\times0.26\times0.19$	$0.35 \times 0.30 \times 0.30$	$0.38\times0.25\times0.22$	$0.25\times0.16\times0.10$
Morphology	prism, yellow	block, orange	rectangular, Yellow	square, yellow
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	P2/c	Pbcn	C2/c	C2/c
Unit cell parameters				
a (Å)	11.8514(3)	12.2550(3)	40.8686(12)	23.8636(7)
b (Å)	8.1243(2)	19.1718(6)	8.0987(2)	16.4613(5)
<i>c</i> (Å)	15.9914(4)	19.3124(6)	16.0193(4)	16.0004(4)
β(°)	117.738(2)		103.4146(11)	116.0474(12)
$V(Å^3)$	1362.78(6)	4537.5(2)	5157.4(2)	5647.0(3)
Z Z'	2/0.5	4/0.5	8/1	8/1
Cell measuring reflections	8293	9928	8597	7596
θ -range (°)	2.9-26.4	2.2-26.0	2.6-25.6	2.3-25.9
Absorption correction, μ (mm ⁻¹)	multi-scan, 0.446	multi-scan, 0.295	multi-scan, 2.016	multi-scan, 0.437
F (000)	596	1872	2488	2512
$D_{\rm x}$ (calculated) (g cm ⁻³)	1.410	1.325	1.593	1.432
Data collection				
Radiation (Å)	0.71073 (Mo Ka)	0.71073 (Mo Kα)	0.71073 (Mo Ka)	0.71073 (Mo Kα)
T (°K)	296	296	296	296
θ range (°)	2.5-25	2.1-25	2.0-25	1.8-25.0
Indices	$h = -14 \rightarrow 13$	$h = -14 \rightarrow 14$	$h = -43 \rightarrow 48$	$h = -28 \rightarrow 28$
	$k = -9 \rightarrow 9$	$k = -22 \rightarrow 22$	$k = -9 \rightarrow 9$	$k = -19 \rightarrow 19$
	$l = -15 \rightarrow 19$	$l = -22 \rightarrow 22$	$l = -19 \rightarrow 14$	$l = -15 \rightarrow 19$
Scan type	ϕ and ω scans	ϕ and ω scans	ϕ and ω scans	ϕ and ω scans
Independent reflections	2399	4004	4542	4980
Observed reflections $[l > 2\sigma(l)]$	2274	2523	3926	4061
Refinement				
Final indices (R_{obs}, wR_{all})	R = 0.0288, wR = 0.0809	R = 0.0552, wR = 0.1875	<i>R</i> = 0.0384, <i>wR</i> = 0.0877	R = 0.0426, wR = 0.1156
Goodness-of-fit (S)	1.644	1.167	1.128	1.070
Extinction coefficient	0.0013(9)	0.0009(4)	nil	nil
$(\Delta/\sigma)_{\rm max}$	0.000	0.002	0.001	0.002
$\Delta ho_{ m max}$ and $\Delta ho_{ m min}$ (e Å ⁻³)	0.705, -0.518	1.120, -0.650	0.626, -0.647	1.133, -0.331
Data/restraints/parameter	2399/5/181	4005/459/377	4542/0/321	4980/0/359
	·			

Weight $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where $P = (F_0^2 + 2F_c^2)/3$, parameters *a* and *b* are: 0.0367 and 0.5310 (1), 0.0779 and 8.0725 (2), 0.0332 and 14.8582 (3), 0.0445 and, 18.3655 (5), respectively.

Table 2

Polymerization of ϵ -CL catalyzed by complexes 1, 2, 3, 5 and 7.^a

Entry	Cat.	[M] _o :[Zr] _o :[ROH] _o	T (°C)	Time (h)	Conv. ^b (%)	$M_{\rm n}^{\rm c}$ (calcd)	M_n^d (obsd)	Yield ^e (%)	PDI ^d
1	1	200:1:2	25	24	12	-	-	-	-
2	1	200:1:2	50	2	94	10800	11500	93	1.31
3	1	200:1:2	70	2	94	10800	9700	94	1.24
4	2	200:1:2	50	24	-	-	-	-	-
5	2	100:1:2	50	24	-	-	-	-	-
6	3	100:1:2	50	2	98	5700	5400	91	1.25
7	3	200:1:2	50	2	98	11300	11000	95	1.17
8	3	300:1:2	50	2	96	16900	16200	95	1.27
9	3	400:1:2	50	2	98	22000	20000	91	1.25
10	3	500:1:2	50	2	96	27 500	24000	93	1.29
11	5	200:1:2	50	2	91	10500	13500	90	1.24
12	7	200:1:2	50	2	93	10700	11900	92	1.29

^a All polymerization reactions were carried out in 15 mL of DCM.

^b Measured from ¹H NMR analysis.

^c M_n (calcd) = [114.14 × [M]_o:[Zr]_o × conversion yield/([ROH]_{eq})] + M(ROH).

^e Isolated yield.

^d Obtained from GPC analysis.

5.00 ppm is close to 1, evidence that the polymerization is initiated by the insertion of a benzyloxy group into ε -CL, forming an zirconium alkoxide intermediate that consequently reacts with the excess lactones, giving polyesters [30–33].

A keen literature survey enabled to compare the reported as well as present work on ε -CL polymerization judiciously. The concerned activity of these new zirconium(IV) derivatives are almost at a par with the zirconium complexes associated with benzyloxy,

aryloxy [9], bis(imino) phenoxide [10,34] and bis(aminophenolate) [13] ligands. Although these newly synthesized zirconium(IV) complexes have better activity than zirconium complexes supported by pyrrolyl-linked N-donor [11], aminebisphenolate [7], diamine [35], pyrrole and phenolic [36] ligands, they show a bit lower activity than the previously existing zirconium derivatives incorporated with salen [8,12], salan type diamine bis(phenolate) [37], salicylaldiminato [38], N-alkyl substituted amine biphenolate



Fig. 3. Catalytic polymerization of ϵ -CL by 3 at 50 °C in DCM.

[39], imino phenoxide [40] and catecholate [41] ligands. Thus, the present investigations also appear to contribute in the field of ε -CL polymerization significantly.

2.4. Kinetic studies for the polymerization of ε -caprolactone

Kinetic studies [9,37] for the polymerization of ε -caprolactone using complexes **1**, **3**, **5** and **7** as catalysts were also carried out in the presence of benzyl alcohol in a [M]₀/[Zr]₀/[BnOH] ratio of 200:1:2 at 50 °C. The experimental results are displayed in Figs. S21 and 5. The graph plotted between the % conversion of ε -CL and time was sigmoidal. Four linear curves obtained by plotting ln ([ε -CL]₀/[ε -CL]_t) versus time clearly exhibited the well established pattern of first order kinetics for the polymerization of ε -CL. The rate constants for these ε -CL polymerization reactions catalyzed by complexes **1**, **3**, **5** and **7** have been determined as 2.12×10^{-2} , 3.19×10^{-2} , 1.99×10^{-2} and 2.07×10^{-2} min⁻¹, respectively. Thus the rate of polymerization by these complexes could be arranged in the order **3** > **1** > **7** > **5** by exploiting the computed values of the rate constants.

3. Experimental

3.1. General

All the complexes were synthesized in a moisture-free environment. Solvents and reagents were made anhydrous by conventional methods [42]. Zirconium(IV) isopropoxide, acetylacetone and dibenzoylmethane were purchased from Sigma Aldrich. The Schiff's base ligands were prepared according to the literature. The zirconium content was estimated gravimetrically as ZrO₂ [26]. Melting points were examined on an Elchem digital melting point apparatus. FTIR spectra [4000–400 cm⁻¹] were recorded on a SHIMADZU IR affinity 1 spectrometer with anhydrous KBr pellets. ¹H and ¹³C NMR spectra were obtained from a Bruker ADVANCE III 400 spectrometer in CDCl₃ solution at 400 and 100.65 MHz frequencies using TMS as an internal standard. Weight average molecular weight (M_w) , number average molecular weight (M_n) , and molecular weight distributions were determined against polystyrene as a standard by GPC using a PL gel 5 µm MLXED-C column on an Agilent 1100 series liquid chromatography system with THF as the eluent. Elemental analyses of complexes were carried out on an Elementar Vario EL III instrument.

3.2. Synthesis of the Schiff's bases H_2L^1 , H_2L^2 , H_2L^3 and H_2L^4

The Schiff's base ligands H_2L^1 , H_2L^2 , H_2L^3 and H_2L^4 were prepared by the reaction of 2-aminophenol with salicylaldehyde, 5-bromosalicylaldehyde, 3-methoxysalicylaldehyde and 2-hydroxy-1-napthaldehyde in a 1:1 molar ratio in refluxing methanol [43–48].

3.3. Synthesis of the complexes

3.3.1. Synthesis of the complex [(CH₃COCHCOCH₃)₂ZrL¹] **1**

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), the ethanolic Schiff's base H_2L^1 (2.13 g, 10 mmol) and acetylacetone (2.00 g, 20 mmol) were taken as reactants in a stoichiometry of 1:1:2 using



Fig. 4. The ¹H NMR spectrum of PCL catalyzed by complex 3 (entry 6, Table 2).



Fig. 5. Semi-logarithmic plots of ε-CL conversion in time initiated by 1, 3, 5 and 7: [M]_o/[Zr]_o/[BnOH] = 200:1:2 at 50 °C.

benzene as a solvent. The resulting reaction mixture was refluxed for 2 h and the liberated isopropanol was fractionated out, along with benzene and ethanol. A yellow colored product, obtained after the removal of excess solvent under vacuum, was washed twice with n-hexane. (Yield: 4.87 g, 97.4%. Mp: 218–220 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 1.83 (s, 9H, CH₃), 1.97 (s, 3H, CH₃), 5.43, 5.60 (s, 2H, CH), 6.59–6.66 (m, 3H, Ar-H), 6.71–6.74 (t, 1H, *J* = 8.0 Hz, Ar-H), 6.99–7.02 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.24–7.33 (m, 3H, Ar-H), 9.52 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 24.86, 26.61, 100.45, 104.05, 114.53, 117.4 6, 117.65, 117.95, 120.07, 122.84, 129.30, 133.70, 134.72, 138.64, 155.86, 162.34, 163.17, 190.56, 191.20. FTIR (solid KBr) v (cm⁻¹): 3059.10, 2960.73, 1581.63, 1525.69, 1024.20, 754.17, 655.8, 615.29, 518.85. *Anal.* Calc. for C₂₃H₂₃NO₆Zr: C, 55.18; H, 4.63; N, 2.80; Zr, 18.22. Found: C, 55.20; H, 4.67; N, 2.81; Zr, 18.25%.

As the patterns of these reactions are almost similar, the remaining seven complexes (**2-8**) were also synthesized by following the above-said procedure.

3.3.2. Synthesis of the complex $[(C_6H_5COCHCO C_6H_5)_2ZrL^1]$ 2

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^1 (2.13 g, 10 mmol) and dibenzoylmethane (4.48 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 7.35 g, 98.1%. Mp: 258–260 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 6.59–6.61 (d, 2H, J = 8.0 Hz, Ar-H), 6.66–6.70 (t, 1H, J = 8.0 Hz, Ar-H), 6.73–6.77 (t, 1H, J = 8.0 Hz, Ar-H), 7.00–7.04 (t, 1H, J = 8.0 Hz, Ar-H), 7.08 (s, 2H, C-H), 7.22-7.26 (t, 8H, J = 8.0 Hz, Ar-H), 7.28-7.30 (d, 1H, I = 8.0 Hz, Ar-H), 7.34–7.37 (t, 5H, I = 8.0 Hz, Ar-H), 7.41–7.43 (d, 1H, J = 8.0 Hz, Ar-H), 7.76–7.78 (d, 7H, J = 8.0 Hz, Ar-H), 7.90–7.92 (d, 1H, J = 8.0 Hz, Ar-H), 8.54 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 96.68, 115.02, 117.71, 118.13, 120.30, 123.51, 127.20, 128.10, 128.36, 128.71, 129.64, 131.96, 132.48, 133.83, 134.98, 137.57, 139.22, 155.91, 162.72, 163.32, 183.97. FTIR (solid KBr) v (cm⁻¹): 3059.10, 1591.27, 1523.76, 1024.20, 754.17, 680.87, 620.05, 516.92. Anal. Calc. for C43H31NO6Zr: C, 68.96; H, 4.17; N, 1.87; Zr, 12.18. Found: C, 68.89; H, 4.12; N, 1.85; Zr, 12.13%.

3.3.3. Synthesis of the complex [($CH_3COCHCOCH_3$)₂ZrL²] **3**

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^2 (2.92 g, 10 mmol) and acetylacetone (2.00 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 5.70 g, 98.4%. Mp: 208–210 °C. ¹H

NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 1.84 (s, 11H, *CH*₃), 1.96 (s, 1H, *CH*₃), 5.42, 5.60 (s, 2H, *CH*), 6.50–6.52 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 6.57–6.59 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 6.61–6.65 (t, 1H, *J* = 8.0 Hz, Ar-*H*), 6.99–7.03 (t, 1H, *J* = 8.0 Hz, Ar-*H*), 7.22–7.24 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 7.29–7.30 (d, 1H, *J* = 4.0 Hz, Ar-*H*), 7.40–7.41 (d, 1 H *J* = 4.0 Hz, Ar-*H*), 8.41 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 24.86, 26.62, 100.46, 104.17, 108.95, 114.68, 117.71, 117.79, 122.06, 124.40, 129.82, 135.28, 137.05, 138.30, 154.34, 162.18, 162.42, 190.68, 191.20. FTIR (solid KBr) ν (cm⁻¹): 3064.05, 2982.53, 1583.20, 1526.44, 1019.74, 736.92, 618.45, 524.31. *Anal.* Calc. for C₂₃H₂₂BrNO₆Zr: C, 47.67; H, 3.83; N, 2.42; Zr, 15.74. Found: C, 47.71; H, 3.80; N, 2.39; Zr, 15.69%.

3.3.4. Synthesis of the complex $[(C_6H_5COCHCOC_6H_5)_2ZrL^2]$ 4

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^2 (2.92 g, 10 mmol) and dibenzoylmethane (4.48 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 8.05 g, 97.3%. Mp: 225–227 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 6.49–6.52 (d, 1H, J = 8.0 Hz, Ar-H), 6.59–6.61 (d, 1H, J = 8.0 Hz, Ar-H), 6.68–6.71 (t, 1H, J = 8.0 Hz, Ar-H), 7.02-7.06 (t, 1H, J = 8.0 Hz, Ar-H), 7.10 (s, 2H, C-H), 7.25-7.29 (t, 9H, J=8.0 Hz, Ar-H), 7.36-7.40 (t, 4H, J = 8.0 Hz, Ar-H), 7.42–7.44 (d, 1H, J = 8.0 Hz, Ar-H), 7.47–7.48 (d, 1H, J = 4.0 Hz, Ar-H), 7.76–7.78 (d, 7H, J = 8.0 Hz, Ar-H), 7.91–7.93 (d, 1H, J = 8.0 Hz, Ar-H), 8.45 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 93.18, 96.78, 109.07, 115.08, 115.08, 117.87, 117.94, 122.36, 125.14, 127.19, 128.07, 128.42, 128.71, 130.14, 132.12, 132.47, 135.31, 135.59, 137.23, 137.41, 138.82, 154.35, 162.45, 162.79, 184.04, 185.79. FTIR (solid KBr) v (cm⁻¹): 3053.21, 1591.27, 1525.69, 1072.42, 750.31, 675.09, 607.58, 518.85. Anal. Calc. for C₄₃H₃₀BrNO₆Zr: C, 62.39; H, 3.65; N, 1.69; Zr, 11.02. Found: C, 62.42; H, 3.69; N, 1.70; Zr, 11.10%.

3.3.5. Synthesis of the complex $[(CH_3COCHCOCH_3)_2ZrL^3]$ 5

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^3 (2.43 g, 10 mmol) and acetylacetone (2.00 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 5.22 g, 98.4%. Mp: 214–216 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 1.85 (s, 11H, *CH*₃), 1.97 (s, 1H, *CH*₃), 3.07 (s, 3H, *CH*₃), 5.42, 5.60 (s, 2H, *CH*), 6.57–6.66 (m, 3H, Ar-H), 6.87–6.89 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.95–6.97 (d, 1H, *J* = 8.0 Hz, Ar-H), 6.98–7.02 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.23–7.25 (d, 1H, Ar-H), 8.51 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 24.85, 26.60, 57.10, 100.45, 104.15, 114.52,

117.27, 117.42, 117.67, 118.71, 123.17, 126.23, 128.35, 129.35, 138.63, 149.92, 154.56, 156.01, 162.41, 163.17, 190.65, 191.20. FTIR (solid KBr) ν (cm $^{-1}$): 3042.02, 2978.43, 1595.17, 1521.34, 1026.78, 755.15, 637.67, 516.31. Anal. Calc. for $C_{24}H_{25}NO_7Zr$: C, 54.32; H, 4.75; N, 2.64; Zr, 17.19. Found: C, 54.19; H, 4.68; N, 2.67; Zr, 17.25%.

3.3.6. Synthesis of the complex $[(C_6H_5COCHCOC_6H_5)_2ZrL^3]$ 6

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^3 (2.43 g, 10 mmol) and dibenzoylmethane (4.48 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 7.58 g, 97.4%. Mp: 225–227 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 3.50 (s, 3H, CH₃), 6.59–6.61 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 6.66–6.69 (t, 2H, *J* = 8.0 Hz, Ar-*H*), 6.86–6.88 (d, 1H, *J* = 8.0 Hz, Ar-*H*), 7.00–7.05 (m, 2H, Ar-*H*), 7.09 (s, 2H, C-*H*), 7.22–7.26 (t, 8H, *J* = 8.0 Hz, Ar-*H*), 7.34–7.50 (m, 5H, Ar-*H*), 7.77–7.79 (d, 7H, *J* = 8.0 Hz, Ar-*H*), 7.91–7.92 (d, 1H, *J* = 4.0 Hz, Ar-*H*), 8.55 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm) 57.44, 96.77, 115.05, 117.58, 117.68, 117.73, 120.27, 124.04, 126.69, 127.20, 128.12, 128.35, 128.71, 129.68, 131.95, 137.55, 139.23, 149.97, 154.87, 156.09, 162.80, 184.02. FTIR (solid KBr) ν (cm⁻¹): 3046.04, 1592.24, 1524.14, 1039.87, 751.28, 618.58, 514.52. *Anal.* Calc. for C₄₄H₃₃NO₇Zr: C, 67.84; H, 4.27; N, 1.80; Zr, 11.71. Found: C, 67.69; H, 4.15; N, 1.73; Zr, 11.67%.

3.3.7. Synthesis of the complex $[(CH_3COCHCOCH_3)_2ZrL^4]$ 7

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^4 (2.63 g, 10 mmol) and acetylacetone (2.00 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 5.41 g, 98.3%. Mp: 225–227 °C. ¹H NMR (400 MHz, DMSO d₆, 25 °C) δ (ppm): 1.68 (s, 8H, CH₃), 1.84 (s, 1H, CH₃), 2.03 (s, 2H, CH₃), 2.14 (s, 1H, CH₃), 5.55, 5.63, 5.70 (s, 2H, CH), 6.42–6.57 (m, 1H, Ar-H), 6.67–6.80 (m, 1H, Ar-H), 6.92–7.08 (m, 2H, Ar-H), 7.55–7.59 (t, 1H, *J* = 8.0 Hz, Ar-H), 7.78–7.94 (m, 3H, Ar-H), 8.48–8.57 (m, 2H, Ar-H), 9.61, 9.70 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 24.87, 26.62, 100.46, 103.97, 114.53, 117.59, 117.63, 120.01, 123.17, 127.62, 128.57, 129.14, 135.44, 139.78, 151.05, 162.07, 164.79, 190.53, 191.21. FTIR (solid KBr) ν (cm⁻¹): 3043.12, 2964.65, 1582.14, 1525.28, 1024.07, 751.64 615.27, 519.45. *Anal.* Calc. for C₂₇H₂₅NO₆-Zr: C, 58.89; H, 4.58; N, 2.54; Zr, 16.56. Found: C, 58.72; H, 4.55; N, 2.46; Zr, 16.62%.

3.3.8. Synthesis of complex $[(C_6H_5COCHCO C_6H_5)_2ZrL^4]$ 8

Zirconium(IV) isopropoxide (3.87 g, 10 mmol), Schiff's base H_2L^4 (2.63 g, 10 mmol) and dibenzovlmethane (4.48 g, 20 mmol). Stoichiometry: 1:1:2. (Yield: 7.81 g, 97.7%. Mp: 258–260 °C. ¹H NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 6.74–6.79 (m, 3H, Ar-H), 6.89–6.91 (d, 1H, J = 8.0 Hz, Ar-H), 7.08 (s, 2H, C-H), 7.14–7.16 (d, 6H, J = 8.0 Hz, Ar-H), 7.29–7.30 (d, 3H, J = 4.0 Hz, Ar-H), 7.34 (s, 1H, Ar-H), 7.42–7.48 (m, 4H, Ar-H), 7.72–7.74 (d, 9H, J = 8.0 Hz, Ar-H), 7.91-7.93 (d, 2H, J = 8.0 Hz, Ar-H), 8.10-8.13 (d, 1H, J = 12.0 Hz, Ar-H), 9.50 (s, 1H, N=CH). ¹³C NMR (100.65 MHz, CDCl₃, 25 °C) δ (ppm): 96.64, 114.91, 115.05, 117.57, 117.87, 120.03, 123.12, 123.31, 127.19, 127.64, 127.86, 128.06, 128.29, 128.70, 128.94, 129.06, 131.94, 132.45, 133.99, 135.66, 137.46, 140.29, 151.22, 164.94, 183.99, 185.79. FTIR (solid KBr) v (cm⁻¹): 3056.10, 1614.42, 1590.96, 1524.31, 1038.73, 750.85, 669.62, 623.47, 520.26. Anal. Calc. for C₄₃H₃₁NO₆Zr: C, 68.96; H, 4.17; N, 1.87; Zr, 12.18. Found: C, 68.89; H, 4.12; N, 1.85; Zr, 12.13%.

3.4. Polymerization of ε-caprolactone

Typically, to a solution of the catalyst (0.2 mmol) in DCM (5 mL), another solution of benzyl alcohol (0.4 mmol) in 5 mL DCM was added. After stirring the solution for 10 min, a measured amount of ϵ -CL dissolved in 5 mL of DCM was transferred and kept in an oil bath for stirring at 50 °C for the required individual

duration for each set of reactions (Table 2). Since screw-capped reaction tubes were employed to carry out all the polymerization reactions, a bit of pressure was experienced due to overheating of the dichloromethane solvent in the tubes concerned, but the process got completed safely and successfully. After quenching the polymerization by addition of methyl alcohol, the reaction mixture was poured into *ca.* 50 mL of methanol for precipitation of PCL as a white solid. The obtained polymer was purified by dissolving it in DCM and by re-precipitating it with methanol. Afterwards, the polymer was dried in a vacuum oven at 50 °C until a constant weight was obtained.

3.5. Single crystal XRD

Single crystals of the new zirconium(IV) complexes were obtained by keeping a solution of the concerned derivatives in a benzene-DCM mixture overnight. Intensity data were collected on a single-crystal Bruker SMART APEX2 diffractometer and processed using Saint-Plus [49]. The structure was solved by the application of the direct phase-determination technique using SHELXS-97. and anisotropically refined by full-matrix least-square on F^2 using SHELXL-2014/7 [50]. All structural calculations were performed with the WinGX suit (Version 2013.3) [51]. Hydrogens were placed in geometrically expected positions and refined with riding options. The torsion angles for the methyl group hydrogen atoms were set with reference to a local difference Fourier calculation. The distances to hydrogen atoms are: aromatic C—H = 0.93 Å, methyl C—H = 0.96 Å and U_{iso} = 1.2 $U_{eq}(C_{ar})/1.5 U_{eq}(CH_3)$. Unlike **3** and **5** (asymmetrical methoxy and bromo-substitutions in H_2L^1), the structures of 1 and 2 are disordered. There are two different orientations of the H_2L^1 residues, related by a two-fold axis passing through the Zr(IV) center. The two alternative orientations of the molecule with equal occupancy led to C2 point group symmetry and the asymmetric unit comprises half of the molecule, with one acac/dbm and half of H₂L¹ (with half occupancy of Schiff's base -C=N-). The phenol ring in H₂L¹ of **2** possesses an additional positional disorder of equal occupancy. The refinement involved a series of trials to arrive at the optimum refinement and in the final cycle notable restraints were applied. In complex 1, for the Schiff's base bond distances, the restraints were as follows: -C=N-, 1.28 (1) Å, –C_{ar}–C–, 1.47(1) Å and –C_{ar}–N–, 1.45(1) Å. In structure **2**, other than Schiff's base bond restrains, additional Car-Car, 1.39 (1) Å bond restraints for the benzene and the phenol rings were applied [52]. To deal with the positional disorder in the phenol ring (in **2**), the same distance restrains (SADI) was applied for the C_{ar} -O bond, and ring atoms were restrained with an effective standard deviation (0.02 Å) to have the same Uij components (SIMU restraints) and approximating to isotropic behavior (ISOR restraint). In the final cycle of refinement, reflections, (100) in 1, (020) in **2** and (200) in **3** were omitted, which were affected by the beam-stop. Essential crystal data are listed in Table 1.

4. Conclusion

Hepta-coordination around zirconium(IV) with a pentagonal bipyramidal geometry for the new derivatives was evident from the single crystal XRD of complexes **1**, **2**, **3** and **5**. Derivative **1** was confirmed to be moisture stable from UV–Vis and ¹H NMR spectroscopy. Further, all the synthesized complexes were tested for the ROP of ε -CL. It could be considered as an encouraging observation that the polymerization of ε -CL occurred exclusively by complexes **1**, **3**, **5** and **7**, incorporating acetylacetone, while the derivatives **2**, **4**, **6** and **8**, associated with dibenzoylmethane, exhibit their reluctance towards this activity. The "living" character of complex **3** in polymerizing ε -CL was evidenced by the linear

relationship between $M_{\rm p}$ and $[M]_{\rm o}$: $[Zr]_{\rm o}$. While performing kinetic studies, derivative **3** displayed the highest rate of polymerization compared to its analogs due to the enhanced lewis acidity of the zirconium(IV) center, fabricated by the electron withdrawing bromine substituent on the Schiff's base ligand.

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Appendix A. Supplementary data

CCDC 1402390, 1402391, 1402389 and 1402388 contains the supplementary crystallographic data for 1, 2, 3 and 5. These data can be obtained free of charge via http://www.ccdc.cam.ac. uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2016.01.035.

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