Inorganica Chimica Acta 372 (2011) 88–93

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Phosphoroamidate compounds of 1,1′-Bi-2-napthol: Synthesis, structural characterization and solvent-free ring-opening polymerization of ε-caprolactone and L-lactide

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ARTICLE INFO

Article history:
Available online 4 February 2011

Dedicated to Prof. S.S. Krishnamurthy on the occasion of his 70th birthday.

Keywords:
Phosphorochloridate
Benzylphosphoroamidate
Ring-opening polymerization
ε-Caprolactone
L-Lactide

ABSTRACT

New phosphoroamidate compounds with 1,1′-Bi-2-napthol (binol) ligand were synthesized from the corresponding phosphorochloridate intermediates and benzyl amine or benzyl amine derivatives. They were completely characterized using different spectroscopic methods and single crystal X-ray diffraction studies. These compounds effectively catalyze the ring-opening polymerization of ε-caprolactone (CL) and L-lactide (LA). This methodology of polymer synthesis is green and environmental benign since phosphorus is a natural constituent of human anatomy and these polymers being completely biodegradable.

1. Introduction

Metal-free catalysts are attracting growing interest as more economical and environmentally friendly alternatives for classical organic transformations. To this end, enzymes (such as lipases) as well as organocatalysts (such as amines, phosphines, and *N*-heterocyclic carbenes) have recently been investigated for transesterification reactions [1–4], including lactide ring-opening polymerization [5–8]. These metal-free nucleophilic catalysts are particularly attractive for biomedical applications of the resulting polymers, since there is no concern of contamination, waste, and removal of metals. In this metal-free approach to ring-opening polymerization of cyclic ester and lactide monomers, enzymes, amines, phosphines, and carbenes all act as nucleophilic transesterification catalysts, requiring the presence of a protic agent (typically water for lipases and alcohols for organocatalysts) as an initiator. Although the precise mode of action of these catalysts remains obscure, it would seem likely that the polymerization occurs through an activated-monomer mechanism [9–15] involving a transient monomer–catalyst complex. Organophosphorus chemistry has been a popular area of research as a result of the application of such compounds in agriculture [16], pharmaceuticals [17–22], biology [23,24] and chemical agents [25–31]. Such compounds are known to be used extensively in chemical synthesis. These include the well known olefination reactions: Wittig reaction and Horner-Woodward-Emmons reaction [32]. In the recent years, we were interested in the chemistry of phosphorus (V) compounds [33]. One of our major objectives has been the use of such reagents for ring-opening polymerization reactions [34]. The work presented here reports the synthesis and complete characterization of new benzylphosphoroamidate compounds and scope of their utility in ring-opening polymerization reactions.

2. Experimental

2.1. General methods

The reactions concerning the synthesis of phosphoroamidates were performed under dry argon atmosphere using standard Schlenk techniques with rigorous exclusion of moisture and air. Methylene chloride was dried by stirring over calcium hydride overnight and distilled fresh prior to use. Phosphorous oxychloride, benzyl amine and its derivatives were purchased from Aldrich and used without subsequent purification. Hexane, ethyl acetate and methylene chloride were purchased from Ranchem India. $CDCl_3$ used for NMR spectral measurements was purchased from Aldrich and used as received.

2.2. Instrumentation

^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

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doi:10.1016/j.ica.2011.01.088

per million relative to $SiMe_4$. ^{31}P NMR spectra were recorded relative to 85% H_3PO_4 as an external standard. Mass spectra of the sample were recorded on a Micro mass QToF instrument, low resolution Electro-Spray Ionization (ESI) mass spectrometer using methanol solvent. Infrared spectra were recorded using a Nicolet 6700 FT-IR instrument. 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. Molecular weights (M_n) were corrected according to Mark–Houwink corrections [35]. CL and LA were purchased from Aldrich; the former dried over CaH_2 overnight and distilled fresh prior to use and the later sublimed before use.

2.3. Synthesis of benzylphosphoroamidate (**1**–**3**)

2.3.1. $P(O)(O_2C_{20}H_{12})(NHCH_2C_6H_5)$ (**1**)

Under a nitrogen atmosphere, to a stirred solution of binol (200 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added triethylamine (2 mL, 13.96 mmol). To the above reaction mixture, $POCl_3$ (0.07 mL, 0.69 mmol) was added dropwise. Reaction mixture stirred at 0 °C for 10 min followed by 4 h under ambient temperature. To the above, benzyl amine (0.38 mL, 3.49 mmol) was added at room temperature and the reaction mixture was stirred for 2.5 h and washed with water (5 mL) and saturated brine (5 mL). Organic layer dried over Na_2SO_4, filtered and evaporated to dryness to yield the crude product. This was further purified by column chromatography to yield a colorless solid compound (290 mg, 97%). M.p. = 49 °C. *Anal.* Calc. for $P(O)(O_2C_{20}H_{12})(NHCH_2C_6H_5)$ [M_r 437]: C, 74.14; H, 4.61; N, 3.20. Found: C, 74.18; H, 4.69; N, 3.24%. ESI-MS, $[P(O)(O_2C_{20}H_{12})(NHCH_2C_6H_5)]H^+$ m/z 438. IR (neat, cm^{-1}): 3210 (N–H), 1218 (P=O), 701 (P–N). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.97–7.18 (m, 17H, ortho, meta, para), 4.10 (m, 2H, CH_2Ph), 3.11 (br, 1H, NH). ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ 146.77 (Ar–O), 139.19 (Ar–C), 131.50 (Ar–C), 131.21 (Ar–C), 128.96 (Ar–C), 128.76 (Ar–C), 128.64 (Ar–C), 127.98 (Ar–C), 127.80 (Ar–C), 127.43 (Ar–C), 126.02 (Ar–C), 125.91 (Ar–C), 121.25 (Ar–C), 120.86 (Ar–C), 46.22 (CH_2Ph). $^{31}P\{^1H\}$ NMR (161 MHz $CDCl_3$, ppm): δ 13.37.

2.3.2. $P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}ClC_6H_4)$ (**2**)

Under a nitrogen atmosphere, to a stirred solution of binol (200 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added triethylamine (2 mL, 13.96 mmol). To the above reaction mixture, $POCl_3$ (0.07 mL, 0.69 mmol) was added dropwise. Reaction mixture stirred at 0 °C for 10 min followed by 4 h under ambient temperature. To the above, 4-chlorobenzyl amine (0.42 mL, 3.49 mmol) was added at room temperature and the reaction mixture was stirred for 2.5 h and washed with water (5 mL) and saturated brine (5 mL). Organic layer dried over Na_2SO_4, filtered and evaporated to dryness to yield the crude product. This was further purified by column chromatography to yield a colorless solid compound (310 mg, 96%). M.p. = 52 °C. *Anal.* Calc. for $P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}ClC_6H_4)$ [M_r 471]: C, 68.72; H, 4.06; N, 2.97. Found: C, 68.82; H, 4.12; N, 2.99%. ESI-MS, $[P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}ClC_6H_4)]^+$ m/z 471. IR (neat, cm^{-1}): 3204 (N–H), 1215 (P=O), 699 (P–N). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.88–6.91 (m, 16H, ortho, meta, para), 4.24 (m, 2H, CH_2Ph), 4.04 (br, 1H, NH). ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ 146.57 (Ar–O), 138.99 (Ar–C), 132.60 (Ar–C), 131.60 (Ar–C), 131.51 (Ar–C), 128.99 (Ar–C), 128.96 (Ar–C), 128.76 (Ar–C), 128.08 (Ar–C), 127.60 (Ar–C), 127.13 (Ar–C), 125.99 (Ar–C), 125.71 (Ar–C), 121.45 (Ar–C), 120.86, 45.99 (CH_2Ph). $^{31}P\{^1H\}$ NMR (161 MHz $CDCl_3$, ppm): δ 13.30.

2.3.3. $P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}OMeC_6H_4)$ (**3**)

Under a nitrogen atmosphere, to a stirred solution of binol (200 mg, 0.69 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added triethylamine (2 mL, 13.96 mmol). To the above reaction mixture, $POCl_3$ (0.07 mL, 0.69 mmol) was added dropwise. Reaction mixture stirred at 0 °C for 10 min followed by 4 h under ambient temperature. To the above, 4-methoxybenzyl amine (0.45 mL, 3.49 mmol) was added at room temperature and the reaction mixture was stirred for 2.5 h and washed with water (5 mL) and saturated brine (5 mL). Organic layer was dried over Na_2SO_4, filtered and evaporated to dryness to yield the crude product. This was further purified by column chromatography to yield a colorless solid compound (310 mg, 96%). M.p. = 55 °C. *Anal.* Calc. for $P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}OMeC_6H_4)$ [M_r 467]: C, 71.94; H, 4.74; N, 3.00. Found: C, 71.98; H, 4.79; N, 3.08%. ESI-MS, $[P(O)(O_2C_{20}H_{12})(NHCH_2\text{-}4\text{-}OMeC_6H_4)]^+$ m/z 467. IR (neat, cm^{-1}): 3208 (N–H), 1216 (P=O), 700 (P–N). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.95–6.80 (m, 16H, ortho, meta, para), 4.01 (m, 2H, CH_2Ph), 3.73 (s, 3H, ArOMe), 3.04 (br, 1H, NH). ^{13}C NMR (100 MHz $CDCl_3$, ppm): δ 157.61 (Ar–O), 146.54 (Ar–O), 138.91 (Ar–C), 131.55 (Ar–C), 131.50 (Ar–C), 128.97 (Ar–C), 128.86 (Ar–C), 128.75 (Ar–C), 128.01 (Ar–C), 127.40 (Ar–C), 127.23 (Ar–C), 125.88 (Ar–C), 125.74 (Ar–C), 121.47 (Ar–C), 55.71 (Ar–OMe), 45.92 (CH_2Ph). $^{31}P\{^1H\}$ NMR (161 MHz $CDCl_3$, ppm): δ 13.38.

2.4. X-ray crystallography

Single crystals of **2** and **3** suitable for structural studies were obtained by crystallization from 1:1 methylene chloride/hexane mixture at −10 °C over a period of 1 week. X-ray data collection was performed with a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with a graphite monochromated Mo Kα (λ = 0.7107 Å) radiation source. The data were collected with 100% completeness for θ up to 25°. ω and ϕ scans was employed to collect the data. The frame width for ω 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 [36]. 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.

2.5. General procedure for the bulk polymerization of CL and LA in 200:1 monomer catalyst ratio

For CL polymerization, 23.6 μmol of **1**–**3** were taken in a flask. The contents were stirred at 80 °C and 0.50 mL CL (0.54 g, 4.71 mmols) was added neat. The mixture was rapidly stirred at the given temperature. A rise in viscosity was observed and finally the stirring ceased. For LA polymerization, 17.3 μmol of **1**–**3** was used for 0.50 g (3.47 mmols) of monomer and the contents were heated to 150 °C. The LA melted slowly at this temperature. A rise in viscosity was observed and finally the stirring ceased. The polymerizations were quenched by pouring the contents into cold methanol. The polymer was isolated by subsequent filtration and dried till a constant weight was attained. A similar procedure was used for higher ratios between monomer and catalyst.

Table 1
The structures **2** and **3**.

Compound	**2**	**3**
Empirical formula	$C_{27}H_{19}ClNO_3P$	$C_{28}H_{22}NO_4P$
Formula weight	471.85	467.44
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
T (K)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073
a (Å)	13.9635(5)	14.1206(2)
b (Å)	11.1393(4)	11.0865(2)
c (Å)	14.9027(5)	15.0681(3)
α (°)	90	90
β (°)	111.032(2)	110.374(10)
γ (°)	90	90
V (Å^3)	2163.59(13)	2211.31(7)
Z	4	4
D_{calc} (g/cm^3)	1.449	1.404
Reflections collected	28 058	29 466
Number of unique reflections	5019	5247
Goodness-of-fit (GOF) on F^2	0.999	1.032
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0413$, $wR_2 = 0.1316$	$R_1 = 0.0347$, $wR_2 = 0.0961$
R indices (all data)	$R_1 = 0.0571$, $wR_2 = 0.1483$	$R_1 = 0.0419$, $wR_2 = 0.1056$

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

3. Results and discussion

3.1. Synthesis and characterization

Reaction of 1,1′-Bi-2-napthol (binol) ligand with $POCl_3$ in a 1:1 stoichiometric ratio in the presence of an acid scavenger like Et_3N afforded the corresponding phosphorochloridate compound which was subsequently quenched with benzyl amine or substituted benzyl amine derivatives, resulting in the formation of the corresponding benzylphosphoroamidate compounds **1**–**3**, respectively (Scheme 1). These compounds were isolated in high yield after column chromatography.

The ^1H NMR of **1**–**3** contains the signals for all moieties in the required ratio of integration. ^{13}C NMR reveals that the phenyl carbon atom directly bonded to oxygen is considerably deshielded with respect to the other aromatic peaks. These compounds showed only one signal in their $^{31}P\{1H\}$ NMR as expected from the structure. ESI-MS spectra recorded on these compounds reveal the molecular ion peaks. The IR spectra of **1**–**3** show peaks due to ν_{N-H}, $\nu_{P=O}$ and ν_{P-N} with prominent intensities. Finally, purity of these compounds was assured through the correct elemental analysis values.

3.2. Single-crystal X-ray diffraction studies

Single crystals of **2** and **3** suitable for X-ray diffraction studies were obtained by crystallization from 1:1 methylene chloride/hexane mixture at −10 °C over a period of 1 week. Both compounds crystallize in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. Selected bond lengths and angles are enumerated in Table 2 and the molecular structure is depicted in Figs. 1 and 2, respectively. Analysis of the crystal data reveals that phosphorus centers in **2** and **3** are in a distorted pyramidal environment. The

Table 2
Selected bond lengths (Å) and bond angles (°) for compounds **2** and **3**.

	2	**3**
P(1)–O(1)	1.5868(12)	1.5915(9)
P(1)–O(2)	1.6032(13)	1.6065(9)
P(1)–O(3)	1.4581(14)	1.4643(10)
P(1)–N(1)	1.6098(15)	1.6100(12)
O(2)–P(1)–O(3)	107.66(7)	106.79(5)
O(1)–P(1)–O(2)	102.64(6)	102.50(5)
O(2)–P(1)–N(1)	110.78(8)	111.74(6)
O(3)–P(1)–N(1)	114.27(8)	114.90(6)

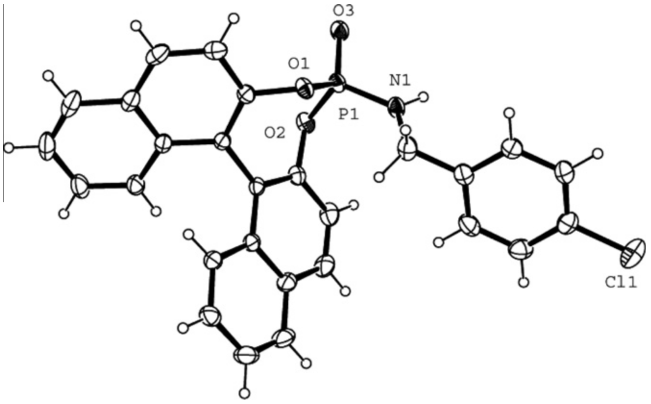


Fig. 1. Molecular structure of **2**; thermal ellipsoids were drawn at 30% probability level.

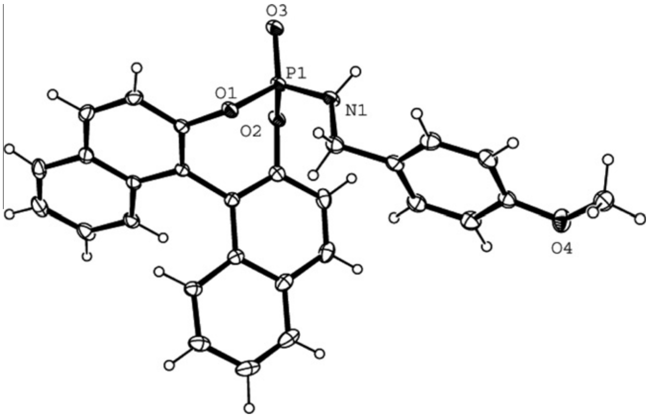
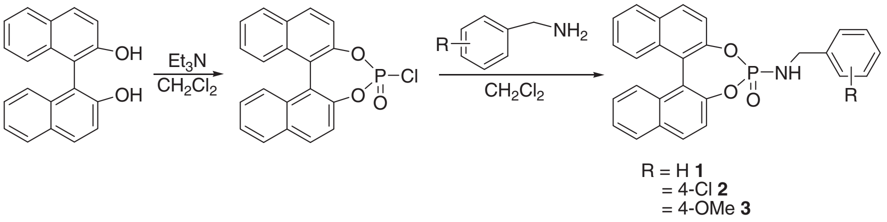


Fig. 2. Molecular structure of **3**; thermal ellipsoids were drawn at 30% probability level.



Scheme 1. Synthesis of benzylphosphoroamidate compounds.

P═O bond length is slightly shorter the P–O lengths. The P–N bond lengths in these compounds are nearly identical. All the bond lengths and angles are in agreement with literature precedents [33].

3.3. Polymerization studies

Compounds **1** – **3** were tested for their catalytic activity towards the ring-opening polymerization of CL and LA. The results are depicted in Tables 3 and 4, respectively.

Analyses of these results depicted reveal that these compounds are powerful initiators for the polymerization of CL and LA. The number average molecular weight (M_n) and molecular weight distribution (MWD) data are much superior to those obtained from conventional metal catalysts [37]. Good degree of control in the polymerization process was observed. Our polymerization results deserve special mention since we have been able to obtain good M_n and MWDs using this simple initiator system.

The variations of M_n with $[CL]_o/[Cat]_o$ ratio and $[LA]_o/[Cat]_o$ using **1**–**3** for CL and LA polymerizations were studied. The plots (Figs. 3 and 4) are linear indicating that there is a continual rise

Table 3
Results of CL polymerization with **1**–**3** at 80 °C.

Catalyst	$[CL]_o/[Cat]_o$	t^a (h)	10^3 M_n^{b} (g/mol)	MWD
1	200:1	29	21.63	1.18
1	400:1	32	22.89	1.24
1	800:1	38	24.66	1.55
1	1000:1	41	26.03	1.62
1	1200:1	44	27.15	1.50
2	200:1	33	34.64	1.41
2	400:1	36	35.98	1.81
2	800:1	43	38.32	1.30
2	1000:1	47	39.69	1.71
2	1200:1	50	40.96	1.39
3	200:1	25	35.10	1.67
3	400:1	27	37.81	1.33
3	800:1	32	42.45	1.17
3	1000:1	35	45.06	1.20
3	1200:1	37	47.57	1.45

[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.

Table 4
Results of LA polymerization with **1**–**3** at 150 °C.

Catalyst	$[CL]_o/[Cat]_o$	t^a (h)	10^3 M_n^{b} (g/mol)	MWD
1	200:1	32	26.69	1.14
1	400:1	35	27.59	1.19
1	800:1	41	29.40	1.28
1	1000:1	44	30.39	1.51
1	1200:1	48	31.29	1.15
2	200:1	35	42.37	1.31
2	400:1	38	48.13	1.64
2	800:1	45	57.57	1.41
2	1000:1	49	63.60	1.31
2	1200:1	52	67.73	1.37
3	200:1	29	38.99	1.55
3	400:1	31	43.82	1.70
3	800:1	36	53.89	1.61
3	1000:1	39	58.24	1.54
3	1200:1	42	63.78	1.50

[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.

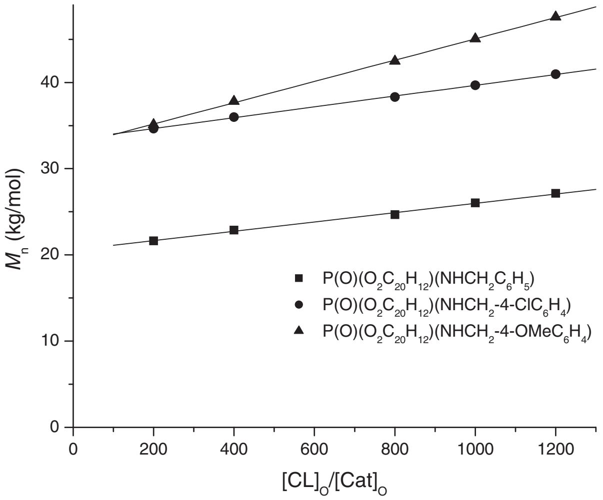


Fig. 3. Plot of M_n (vs. polystyrene standards) vs. $[CL]_o/[Cat]_o$ for CL polymerization at 80 °C using **1**–**3**.

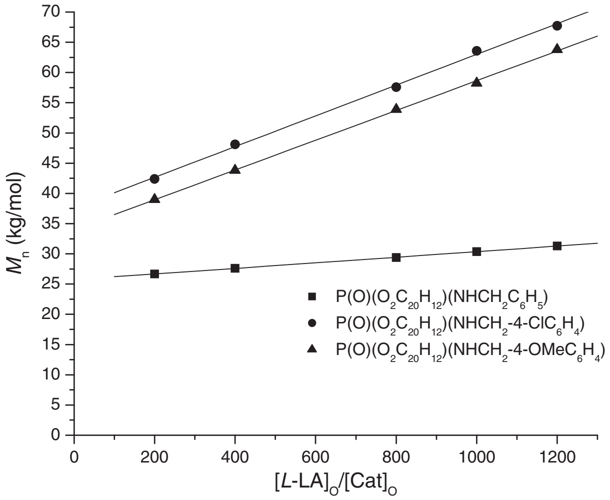


Fig. 4. Plot of M_n (vs. polystyrene standards) vs. $[LA]_o/[Cat]_o$ for LA polymerization at 150 °C using **1**–**3**.

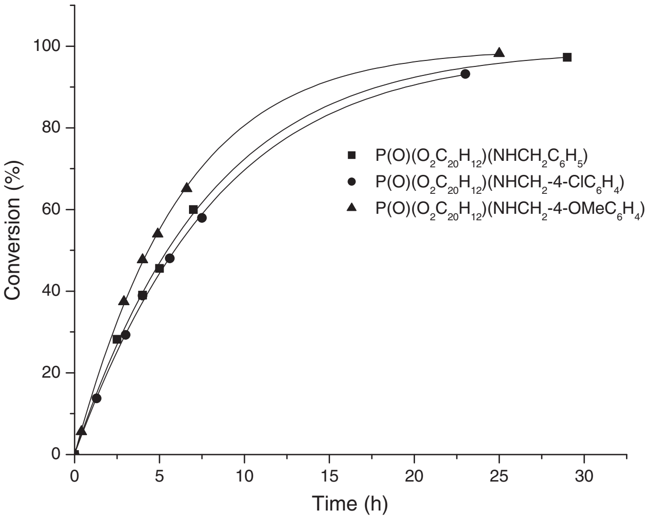


Fig. 5. CL conversion vs. time plot using **1**–**3**: $[CL]_o/[Cat]_o$ = 200 at 80 °C.

in M_n with an increase in $[CL]_o/[Cat]_o$ ratio and $[LA]_o/[Cat]_o$ ratio, respectively.

3.4. Polymerization kinetics

The kinetic studies for the polymerization of CL and LA using **1**–**3** in ratio $[M]_o/[Cat]_o = 200$ were performed (see Supplementary material). The results are depicted in Figs. 5 and 6, respectively.

The plots suggest the complete absence of induction period and there is a first-order dependence of rate of polymerization on monomer concentration. The $\ln[CL]_o/[CL]_t$ and $\ln[LA]_o/[LA]_t$ versus time plots (Figs. 7 and 8) exhibit linear variation. From the slope of the plots, the values of the apparent rate constant (k_{app}) for CL polymerizations initiated by **1**–**3** were found to be 0.1237, 0.1168 and 0.1607 h^{-1}. Similarly, values of the apparent rate constant (k_{app}) for LA polymerizations initiated by **1**–**3** were 0.1786, 0.1072 and 0.1990 h^{-1}, respectively. The orders of magnitude of k_{app} for CL and LA polymerization indicate that these behave in a similar manner like metal catalysts [37].

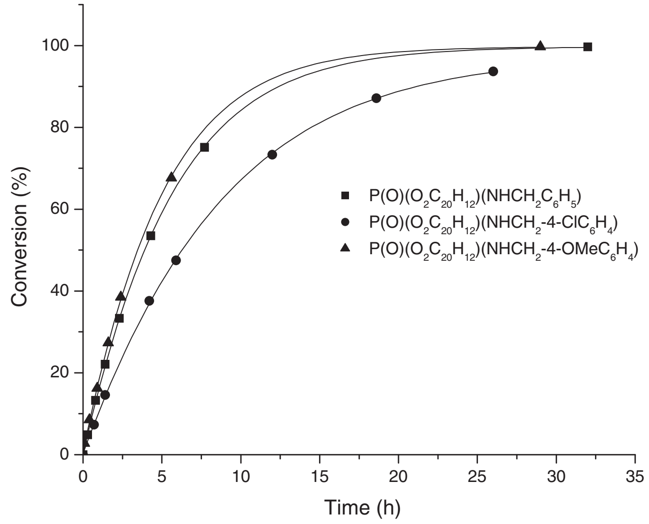


Fig. 6. LA conversion vs. time plot using **1**–**3**: $[LA]_o/[Cat]_o = 200$ at 150 °C.

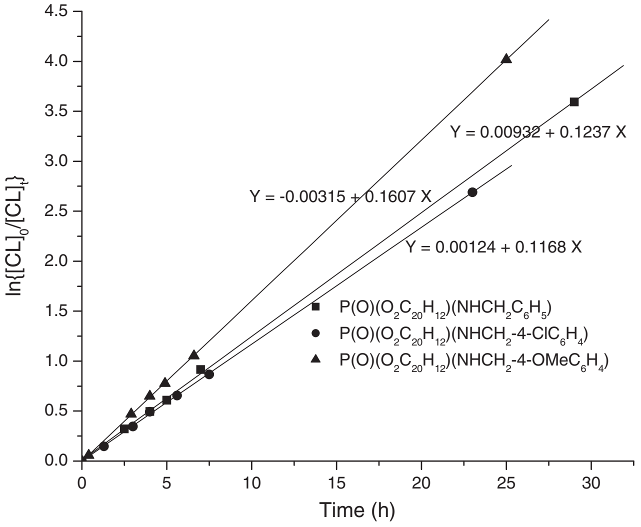


Fig. 7. Semilogarithmic plots of CL conversion in time initiated by **1**–**3**: $[CL]_o/[Cat]_o = 200$ at 80 °C.

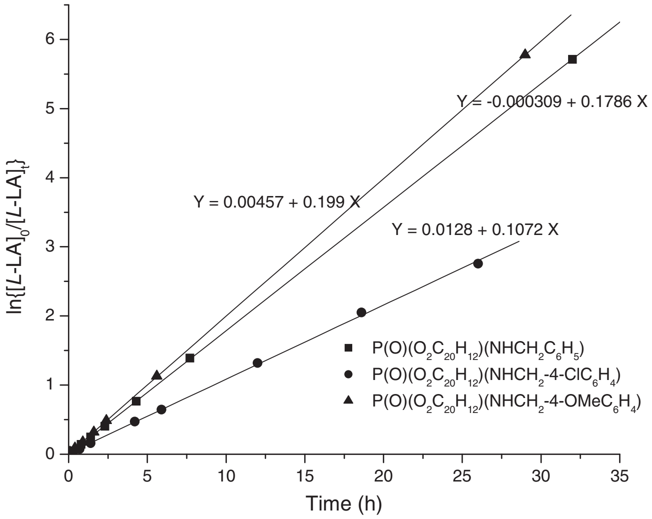


Fig. 8. Semilogarithmic plots of LA conversion in time initiated by **1** – **3**: $[LA]_o/[Cat]_o = 200$ at 150 °C.

4. Conclusions

In summary, **1**–**3** are potent towards the ring opening polymerization of CL and LA. This polymerization contributes to an economical process employing readily synthesized inorganics as catalysts and does not necessitate solvents. The overall system is green, eco-friendly and environmentally benign since phosphorus is a natural human constituent and these polymers being biodegradable. The achievement of obtaining good molecular weights without having to resort to elaborate ligands and metals is a noted feature for our system.

Acknowledgments

This work was supported by Department of Science and Technology, New Delhi. The services from the NMR facility purchased under the FIST program, sponsored by the Department of Science and Technology, New Delhi is gratefully acknowledged.

Appendix A. Supplementary material

CCDC 795746 and 795747 contain the supplementary crystallographic data for **2** and **3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.01.088.

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