Air-Stable Copper Derivatives as Efficient Catalysts for Controlled Lactide Polymerization: Facile Synthesis and Characterization of Well-Defined Benzotriazole Phenoxide Copper Complexes

Chen-Yu Li,[1] Shi-Jie Hsu,[1] Chin-lung Lin,[1] Chen-Yen Tsai,[1] Jun-Han Wang,[1] Bao-Tsan Ko,[1,2] Chia-Her Lin,[1] Hsi-Ya Huang[1]

[1]Department of Chemistry, Chung Yuan Christian University, Chung-Li 32023, Taiwan
[2]Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan
Correspondence to: B.-T. Ko (E-mail: btko@dragon.nchu.edu.tw) or C.-H. Lin (E-mail: chiaher@cycu.edu.tw)

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ABSTRACT: Air-stable copper catalysts supported by bis-**BTP** ligands (**BTP** = *N,O*-bidentate benzotriazole phenoxide) were synthesized and structurally characterized. The reactions of $Cu(OAc)_2{\cdot}H_2O$ with 2.0 molar equivalents of sterically bulky 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (^{CMe2Ph}**BTP**-H) and 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol ($^{t\text{-}Bu}$**BTP**-H) in refluxing ethanol solution afforded monomeric copper complexes **[(^{CMe2Ph}BTP)$_2$Cu]** (**1**) and **[($^{t\text{-}Bu}$BTP)$_2$Cu]** (**2**), respectively. The four-coordinated copper analogue **[(^{TMCl}BTP)$_2$Cu]** (**3**) resulted from treatment of 2-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (^{TMCl}**BTP**-H) as the ligand under the same synthetic method with ligand to metal precursor ratio of 2:1, but treatment of complex **3** in acetone gave five-coordinated monomeric complex **[(^{TMCl}BTP)$_2$Cu(Me$_2$CO)]** (**4**). X-ray diffraction of single crystals indicates that Cu complex **4** assumes a distorted square pyramidal geometry, penta-coordinated by two **BTP** ligands, and one Me_2CO molecule. Catalysis for lactide (LA) polymerization of **BTP**-containing Cu complexes in the presence of various alcohol initiators was investigated. Complex **3** initiated by 9-anthracenemethanol catalyzes the ring-opening polymerization effectively not only in a "living" fashion but also in an "immortal" manner, yielding polymers with the predictable molecular weights and narrow molecular weight distributions. Initiations from multifunctional alcohols were able to produce PLLAs with two-arm linear and three-arm star-shaped molecular architectures. The controlled character of Cu complex **3** also enabled us to synthesize the PEG-*b*-PLLA copolymer. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *00*, 000–000

KEYWORDS: benzotriazole phenoxide; biodegradable; catalysis; copper; lactide; polyesters; ring-opening polymerization (ROP)

INTRODUCTION Environmentally friendly polyesters such as poly(ε-caprolactone) (PCL) and poly(lactide) (PLA) as well as their copolymers have received considerable attention due to a promising alternative of conventional petrochemical based polymers.[1] Such polymers also have been widely utilized in the biomedical, pharmaceutical and environmental fields owing to their biodegradable, biocompatible, and permeable properties.[2] A convenient and useful synthetic route to PLA and other aliphatic polyesters is the ring-opening polymerization (ROP) of cyclic esters using metal-alkoxide initiators or catalysts derived from various main-group metal complexes. As a result, a variety of metal complexes including aluminum, calcium, lithium, magnesium, and tin(II) as well as zinc complexes have been developed to achieve great catalytic activities in a controlled manner.[3] Particularly, well-defined metal complexes supported by phenoxyimine ligands attract increasing attention because the metal center can be stabilized by *N,O*-bidentate chelation to realize the single active site catalyst. For instance, aluminum alkoxides bearing Salen-type ligands demonstrates not only good activities but also high stereoselectivity with P_m values up to 97% for stereoselective ROP of *rac*-lactide.[4] Although many catalytic systems have been reported for the preparation of polyesters with controlled molecular weights and narrow polydispersity indices (PDIs), moisture- and air-tolerant metal complexes with well-characterized structures that catalyze ROP effectively are rare.[5] For this reason, late transition metal complexes, such as nickel(II) and copper(II) complexes seem to be prospective candidates, and only a few studies of their catalytic performance toward ROP of cyclic esters have been reported.[6] With the exception of recently reported diketiminate copper isopropoxide catalyst,[6h] well-defined Cu complexes that previously studied catalyze LA polymerization

Additional Supporting Information may be found in the online version of this article.

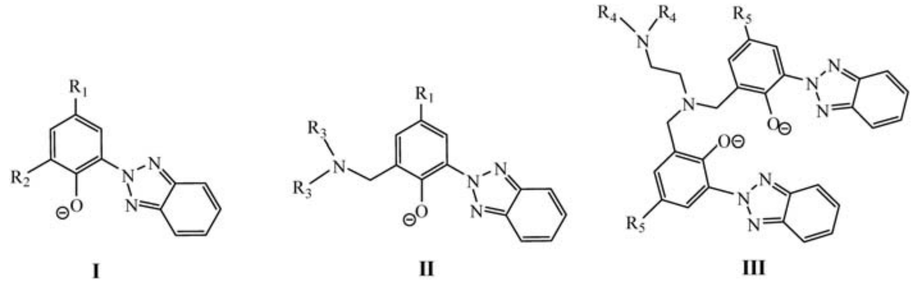


CHART 1 Several types of benzotriazole phenoxide (**BTP**) derivatives.

to produce PLA with poor controlled character and their catalytic activities are low. For instance, Cu(II) complexes[6b] of *N,O*-bidentate Schiff base ligands were demonstrated to be active catalysts for bulk ROP of L-lactide with moderate molecular weights and acceptable molecular weight distributions (M_n = 3000–16000; PDI = 1.08–1.58), but polymerizations with only maximum conversion yields of 70–80% and uncontrollable behaviors were observed.

Inspired by the successful catalytic systems of metal phenoxyimine complexes in the ROP, our current focus has been to design and to develop a new family of phenolate ligands containing nitrogen donors, benzotriazole phenoxide (**BTP**) derivatives (Chart 1). These unmodified-**BTP** ligands (type **I,** Chart 1) are commercially available, whereas amino-**BTP** ligands (type **II-III,** Chart 1) can be obtained with ease of modification via one-pot Mannich condensation.[7] The synthesis and catalysis of well-characterized **BTP**-containing Al,[5b,8] Zn[9] and Mg[10] complexes were reported recently, and the latter magnesium complexes incorporated by amine-**BiBTP** ligands have demonstrated to be efficient and bifunctional catalysts towards ROP of ε-caprolactone and cycloaddition of CO_2 with cyclohexene oxide.[10b] To extend studies for metal benzotriazole phenoxide complexes and to investigate differences of polymerization activity and controlled character with different metal systems, a direct reaction between commercially available **BTP**-H ligands and $Cu(OAc)_2{\cdot}H_2O$ as the metal precursor was approached. We envisaged the use of copper catalytic system to prepare PLAs and to explore the catalytic behavior of these Cu complexes bearing such ligands. In this article, we present the synthesis, structure and ROP catalysis of air-stable copper derivatives based on sterically bulky **BTP** ligands.

EXPERIMENTAL

General Considerations

Solvents and reagents were dried by refluxing for at least 24 h over sodium/benzophenone [hexane, toluene, tetrahydrofuran (THF)], or over phosphorus pentoxide (CH_2Cl_2). Deuterated solvents were dried over 4 Å molecular sieves. L-Lactide and *rac*-lactide were recrystallized from a toluene solution and sublimation twice prior to use. $Cu(OAc)_2{\cdot}H_2O$, 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol (**^{CMe2Ph}BTP**-H), 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol (**$^{t\text{-}Bu}$BTP**-H), 2-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (**^{TMCl}BTP**-H), poly(ethylene glycol) methyl ether (**PEG-OH**), *tert*-butyl bis(2-hydroxyethyl)carbamate (**BOC-2ROH**), triethanolamine (**TEA-3ROH**) and 9-anthracenemethanol (9-AnOH) were purchased from Aldrich and used without further purification. 2,2'-(hexadecylimino)diethanol (**$NC_{16}H_{33}$-2ROH**) was purchased, recrystallized by hexane. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Aveance (300 and 400 MHz) spectrometer with chemical shifts given in parts per million from the peak of internal TMS. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. Gel permeation chromatography (GPC) measurements were performed on a Jasco PU-2080 plus system equipped with a RI-2031 detector using THF (HPLC grade) as an eluent. The chromatographic column was Phenomenex Phenogel 5μ 103 Å and the calibration curve used to calculate M_n(GPC) was produced from polystyrene standards. The GPC results were calculated using the Scientific Information Service Corporation (SISC) chromatography data solution 3.1 edition. UV/Vis absorption spectra were taken on an Evolution 201 UV-Visible spectrophotometer.

Synthesis and Characterization of Copper Complexes 1–4

Synthesis of Complex [(^{CMe2Ph}BTP)$_2$Cu] (1)

To a mixture of 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)-phenol (1.78 g, 4.0 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.39 g, 2.0 mmol) were dissolved in ethanol (50 mL). The solution was heated under reflux for 24 h and then cooled to room temperature. After the reaction was completed, the dark brown precipitate occurred during the reaction was collected by filtration and then dried *in vacuo* to give dark brown solids. Yield: 1.55 g (81%). Anal. calc. for $C_{60}H_{56}CuN_6O_2$: N, 8.78; C, 75.33; H, 5.90%; Found: N, 9.01; C, 75.33; H, 6.24%.

Synthesis of Complex [($^{t\text{-}Bu}$BTP)$_2$Cu] (2)

To a mixture of 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol (1.30 g, 4.0 mmol), $Cu(OAc)_2{\cdot}H_2O$ (0.39 g, 2.0 mmol) were dissolved in ethanol (50 mL). The solution was heated under reflux for 24 h and then cooled to room temperature. After the reaction was completed, the dark green precipitate occurred during the reaction was collected by filtration and then dried in vacuo to give dark green solids. Yield: 0.71 g (50%). Anal. calc. for $C_{40}H_{48}CuN_6O_2$: N, 11.86; C, 67.82; H, 6.83%; Found: N, 11.86; C, 67.81; H, 6.82%.

Synthesis of Complex $[(^{TMCl}BTP)_2Cu]$ *(3)*

To a mixture of 2-*tert*-butyl-6-(5-chloro-2H- benzotriazol-2-yl)-4-methylphenol (1.26 g, 4.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (0.39 g, 2.0 mmol) were dissolved in ethanol (50 mL). The solution was heated under reflux for 24 h and then cooled to room temperature. After the reaction was completed, the dark green precipitate occurred during the reaction was collected by filtration and then dried in vacuo to give dark green solids. Yield: 0.83 g (60%). Anal. calc. for $C_{34}H_{34}Cl_2CuN_6O_2$: N, 12.12; C, 58.92; H, 4.94%; Found: N, 11.64; C, 59.20; H, 5.09%.

Synthesis of Complex $[(^{TMCl}BTP)_2Cu(Me_2CO)]$ *(4)*

To a solution of $[(^{TMCl}\mathbf{BTP})_2Cu]$ (**3**) (0.69 g, 1.00 mmol) was dissolved in acetone (30 mL). The solution was stirred at 25°C for 16 h and was removed the volatile components *in vacuo* to give pale green solids. Black crystals of 0.07 g (Yield: 10%) were obtained from the saturated acetone solution. Anal. calc. for $C_{37}H_{40}Cl_2CuN_6O_2$: N, 11.19; C, 59.16; H, 5.37%; Found: N, 11.18; C, 59.36; H, 5.45%.

General Procedure for Ring-Opening Polymerization

Polymerization of L-Lactide Catalyzed by Complex 3 in the Presence of 9-anthracenemethanol (9-AnOH)

A typical polymerization procedure was exemplified by the synthesis of PLLA-100 (the number 100 indicates the $[\text{L-LA}]_0/[\text{9-AnOH}]_0$ ratio). Polymerizations were carried out under a dry nitrogen atmosphere. To a solution of $[(^{TMCl}\mathbf{BTP})_2Cu]$ (**3**) (0.034 g, 0.05 mmol), 9-anthracenemethanol (9-AnOH, 0.020 g, 0.1 mmol) and L-lactide (1.44 g, 10.0 mmol) in toluene (10 mL) were stirred at 110 °C for 6 h. The conversion yield (93%) of PLLA-100 was analyzed by ^{1}H-NMR spectroscopic analysis. After the reaction was quenched by the addition of excess water (0.5 mL), the polymer was precipitated into hexane (100 mL). The final polymer was then dissolved in THF (20 mL) and purified upon precipitation again in MeOH (150 mL), collected and dried under vacuum. Yield: 1.20 g (90 %).

Polymerization of L-Lactide Catalyzed by Complex 3 in the Presence of Multifunctional Alcohol

Polymerization is similar to the procedure described for L-lactide polymerization with 9-anthracenemethanol. Polymerization with 2,2’-(hexadecylimino)bisethanol ($NC_{16}H_{33}$-2ROH) initiator in toluene (10 mL) were stirred at 110 °C for 6 h. The conversion yield (91%) of PLLA-100 (the number 100 indicates the $[\text{L-LA}]_0/[NC_{16}H_{33}\text{-2ROH}]_0$ ratio) was analyzed by ^{1}H-NMR spectroscopic analysis. ^{1}H-NMR ($CDCl_3$, ppm): δ 5.14 (q, -C*H*O(C═O)-), 4.30 (br, -CH_3C*H*OH(C═O)-), 4.11 (br, -OCH_2CH_2N-), 2.69 (br, -OCH_2CH_2N-), 2.43 (br, -CH_3CHO*H* (C═O)-), 1.75 (m, -NCH_2CH_2CH_2-), 1.56 (d, -CH_3CHO(C═O)-), 1.20 (s, -CH_2-), 0.82 (t, -CH_3-).

Polymerization with *tert*-butyl bis(2-hydroxyethyl)carbamate (BOC-2ROH) initiator in toluene (10 mL) were stirred at 110°C for 6 h. The conversion yield (93%) of PLLA-100 (the number 100 indicates the $[\text{L-LA}]_0/[\text{BOC-2ROH}]_0$ ratio) was analyzed by ^{1}H-NMR spectroscopic analysis. ^{1}H-NMR ($CDCl_3$, ppm): δ 5.14 (q, -C*H*O(C═O)-), 4.30 (br, -CH_3C*H*OH(C═O)-), 4.19 (br, -OCH_2CH_2N-), 3.40 (br, -OCH_2CH_2N-), 2.71 (br, -CH_3 CHO*H*(C═O)-), 1.75 (m, -NCH_2CH_2CH_2-), 1.56 (d, -CH_3CHO (C═O)-), 1.41 (s, -CH_3-).

Polymerization with triethanolamine (TEA-3ROH) initiator in toluene (10 mL) were stirred at 110°C for 48 h. The conversion yield (95%) of PLLA-150 (the number 150 indicates the $[\text{L-LA}]_0/[\text{TEA-3ROH}]_0$ ratio) was analyzed by ^{1}H-NMR spectroscopic analysis. ^{1}H-NMR (300 MHz, ppm, $CDCl_3$): δ 5.14 (q, -C*H*O(C═O)-), 4.33 (br, -CH_3C*H*OH(C═O)-), 4.12 (t, -OCH_2 CH_2N-), 2.77 (t, -OCH_2CH_2N-), 2.69 (br, -CH_3CHO*H*(C═O)-), 1.56 (d, -CH_3CHO(C═O)-).

Synthesis of PEG-b-PLLA Diblock Copolymer Catalyzed by the Complex 3

A typical polymerization procedure was exemplified by the synthesis of PEG(17)-*b*-PLLA(100) (the number 17 and 100 indicate the degree of polymerization of ethylene oxide and $[\text{L-LA}]_0/[\text{PEG-OH}]_0$). The living polymerization of L-LA was synthesized by a similar approach as described above, but poly(ethylene glycol) methyl ether (M_w = 750, 0.075 g, 0.1 mmol) in toluene (10.0 mL) was used as the initiator. The reaction mixture was stirred at 110°C for 6 h and was then quenched using the procedures described previously. Yield: 1.13 g (85%).

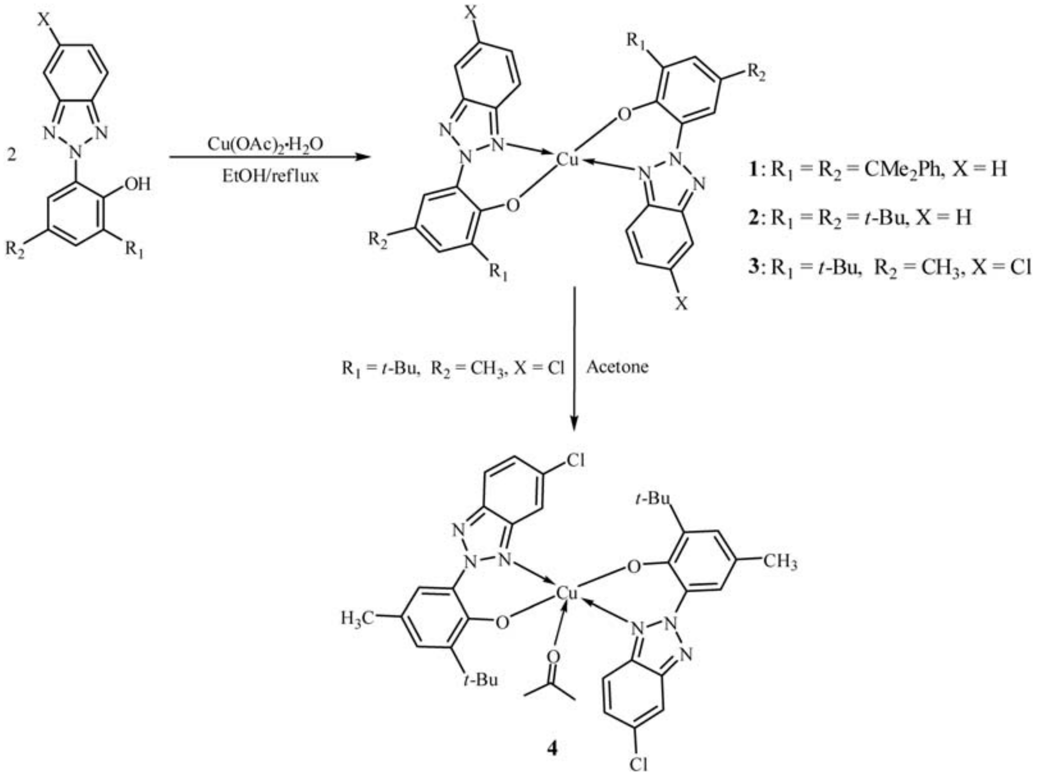
X-Ray Crystallographic Studies

Suitable crystals of **1** and **2** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on Bruker APEX2 diffractometer to collect diffraction data at 296K. Suitable crystals of complex **4** were mounted onto glass fiber using perfluoropolyether oil and cooled rapidly in a stream of cold nitrogen gas to collect diffraction data at 100 K using Bruker APEX2 diffractometer. Intensity data were collected in 1350 frames with increasing *w* (width of 0.5° per frame). The absorption correction was based on the symmetry-equivalent reflections using SADABS program.[11] The space group determination was based on a check of the Laue symmetry and systematic absence, and was confirmed by the structure solution. The structures were solved with direct methods using a SHELXTL package.[11] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were treated as a riding model on their parent C atoms. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H-atoms. Drawing of the molecules was done using Oak Ridge Thermal Ellipdoid Plots (ORTEP).[12] Crystallographic data of complexes **1, 2,** and **4** are summarized in Supporting Information Table S1.

RESULTS AND DISCUSSION

Syntheses and Crystal Structure Determination

The synthesis of copper complexes (**1**-**4**) containing sterically bulky benzotriazole phenoxide derivatives ($^{CMe2Ph}\mathbf{BTP}^-$, $^{t\text{-}Bu}\mathbf{BTP}^-$, and $^{TMCl}\mathbf{BTP}^-$) was shown in Scheme 1. Treatment of $Cu(OAc)_2 \cdot H_2O$ with 2.0 mol equiv. of 2-(2H-benzotriazol-2-yl)-4,6-bis(1-methyl-1-phenylethyl)phenol ($^{CMe2Ph}\mathbf{BTP}$-H) in refluxing ethanol (EtOH) solution gave tetra-coordinated



SCHEME 1 Synthetic route of copper complexes **1–4**.

copper complex **[(^{CMe2Ph}BTP)$_2$Cu]** (**1**) in high yield. Similarly, the monomeric copper analogue (**[($^{t\text{-}Bu}$BTP)$_2$Cu]** (**2**); **[(^{TMCl}BTP)$_2$Cu]** (**3**)) could also be synthesized by employing 2-(2H-benzotriazol-2-yl)-4,6-di-*tert*-butylphenol ($^{t\text{-}Bu}$**BTP**-H) or 2-*tert*-butyl-6-(5-chloro-2H-benzotriazol-2-yl)-4-methylphenol (^{TMCl}**BTP**-H) as the ligand according to the same synthetic route with metal precursor to ligand ratio of 1:2. Attempts to synthesize the mono-**BTP** Cu complexes have proved unsuccessful. Interestingly, complex **3** acetone adduct **[(^{TMCl}BTP)$_2$Cu(Me$_2$CO)]** (**4**) was obtained via recrystallization from acetone (Me$_2$CO) solution. It was further confirmed by X-ray structural analysis. No similar product was isolable

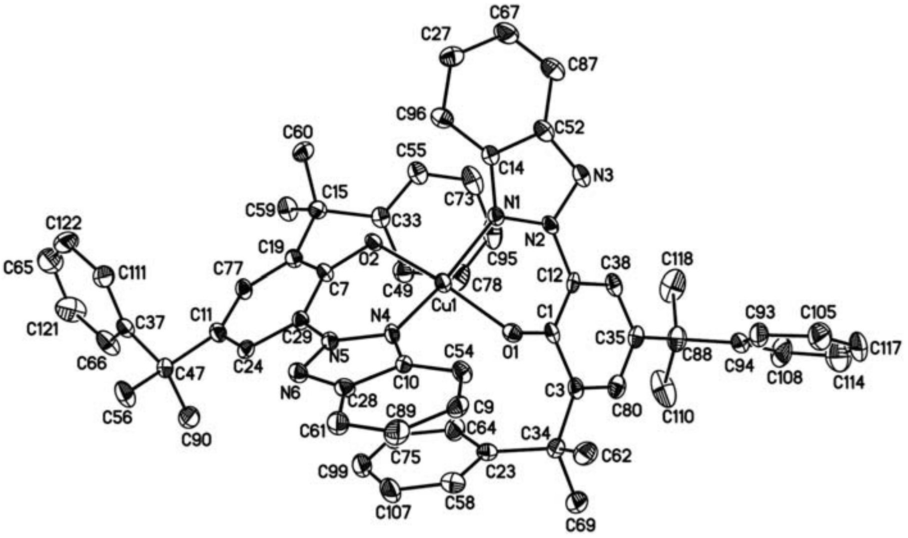


FIGURE 1 ORTEP drawing of complex **1** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-O(1) 1.875(3), Cu(1)-O(2) 1.876(3), Cu(1)-N(1) 1.973(3), Cu(1)-N(4) 1.966(3), O(1)-Cu(1)-O(2) 167.95(12), O(1)-Cu(1)-N(1) 89.43(13), O(1)-Cu(1)-N(4) 92.85(12), O(2)-Cu(1)-N(1) 92.35(12), O(2)-Cu(1)-N(4) 89.94(12), N(1)-Cu(1)-N(4) 158.07(14).

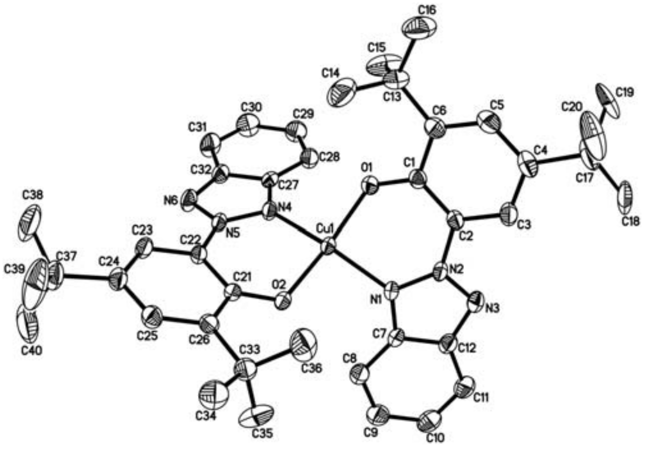


FIGURE 2 ORTEP drawing of complex **2** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-O(1) 1.8719(19), Cu(1)-O(2) 1.8750(18), Cu(1)-N(1) 1.976(2), Cu(1)-N(4) 1.9568(19), O(1)-Cu(1)-O(2) 165.36(9), O(1)-Cu(1)-N(1) 90.29(9), O(1)-Cu(1)-N(4) 91.80(8), O(2)-Cu(1)-N(1) 95.08(8), O(2)-Cu(1)-N(4) 90.25(8), N(1)-Cu(1)-N(4) 150.30(9).

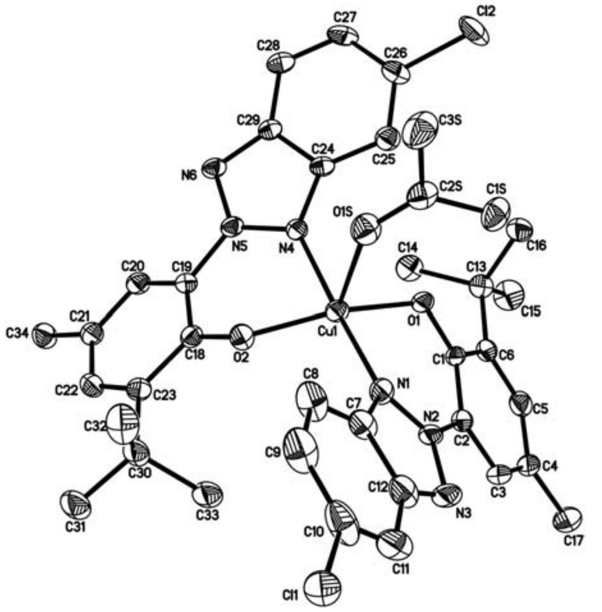
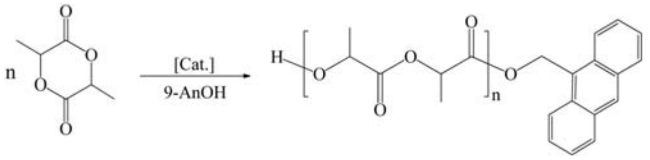


FIGURE 3 ORTEP drawing of complex **4** with thermal ellipsoids drawn at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)-O(1) 1.912(2), Cu(1)-O(2) 1.918(2), Cu(1)-N(1) 1.976(2), Cu(1)-N(4) 1.987(2), Cu(1)-O(1S) 2.452(3), O(1)-Cu(1)-O(2) 163.92(9), O(1)-Cu(1)-N(1) 87.82(10), O(1)-Cu(1)-N(4) 92.38(9), O(2)-Cu(1)-N(1) 93.11(9), O(2)-Cu(1)-N(4) 87.83(9), N(1)-Cu(1)-N(4) 175.91(11), O(1)-Cu(1)-O(1S) 98.47(8), O(2)-Cu(1)-O(1S) 97.61(8), N(1)-Cu(1)-O(1S) 87.66(10), N(4)-Cu(1)-O(1S) 88.28(10).

while complex **1** or **2** was recrystallized from Me_2CO. We believed that the effective electron-withdrawing ability of the -Cl moiety enhances the Lewis acidity of the copper(II) center and therefore leads to existence of weakly bonding between copper and oxygen atom from Me_2CO in **4**. All copper complexes were isolated as air-stable crystalline solids

TABLE 1 Ring-Opening Polymerization of Lactide (LA) Catalyzed by Complexes **1-3** in the Presence of 9-AnOH



Entry	Cat.	$[LA]_0/[Cat.]_0/[9\text{-}AnOH]_0$	*t* (h)	Conv. (%)[c]	M_n (calcd.)[d]	M_n (obsd.)[e]	M_n (NMR)[f]	PDI[g]	P_m[h]
1[a]	**1**	200/1/2	6	10	1,600	2,500(1,500)	1,440	1.10	–[i]
2[a]	**2**	200/1/2	6	92	13,500	18,700(10,800)	13,700	1.75	–[i]
3[a]	**3**	200/1/2	6	93	13,600	21,800(12,600)	14,400	1.13	–[i]
4[a]	**3**	50/1/2	6	95	3,600	5,300(3,100)	3,600	1.19	–[i]
5[a]	**3**	100/1/2	6	93	6,900	9,800(5,700)	6,500	1.18	–[i]
6[a]	**3**	300/1/2	6	93	20,300	39,800(23,000)	22,000	1.11	–[i]
7[a]	**3**	400/1/2	8	94	27,300	48,000(27,800)	29,700	1.19	–[i]
8[a]	**3**	400/1/8	6	93	69,00	14,400(8,300)	7,200	1.09	–[i]
9[a]	**3**	400/1/16	6	92	3,500	6,300(3,600)	3,600	1.12	–[i]
10[b]	**3**	200/1/2	6	94	13,700	23,900(13,800)	14,500	1.36	0.50

[a] $[Cat.]_0$ = 0.005M, 10 mL toluene, 110 °C.

[b] rac-LA as the monomer, 0.05 mmol complexes, 10 mL toluene, 110 °C.

[c] Obtained from ^{1}H-NMR determination.

[d] Calculated from the molecular weight of lactide times $[L\text{-}LA]_0/[9\text{-}AnOH]_0$ times conversion yield plus the molecular weight of 9-AnOH.

[e] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[20]

[f] Obtained from ^{1}H-NMR analysis.

[g] Obtained from GPC determination.

[h] P_m is the probability of meso linkages between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H-NMR spectrum.

[i] Not determination.

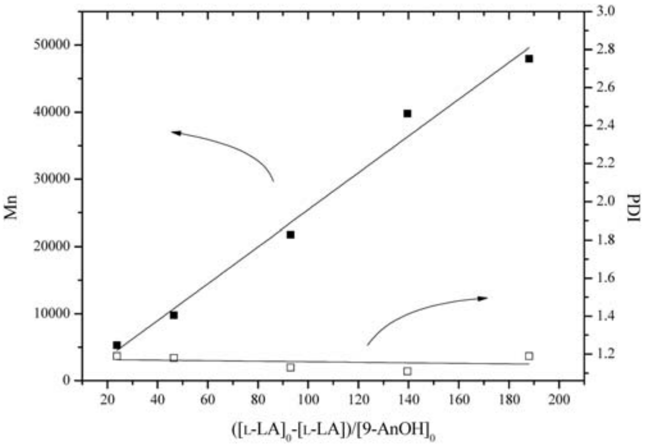


FIGURE 4 Polymerization of L-LA catalyzed by **3** in toluene at 110 °C. The relationship between M_n(■)/PDI(□) of polymer and the mole ratio ([L-LA]$_0$-[L-LA])/[9-AnOH]$_0$ is shown.

and were characterized on the basis of microanalyses and X-ray single crystal determinations.

Single crystals of complexes **1** and **2** suitable for X-ray structural analysis were obtained from their saturated Et_2O solutions. Oak Ridge Thermal Ellipsoid Plot (ORTEP) drawings displaying selected bond lengths and angles of the molecular structures of **1** and **2** are displayed in Figures 1 and 2, respectively. Both complexes crystallize in monoclinic space group $P2_1/c$ with two molecules of **[(BTP)$_2$Cu]** in the asymmetric unit. The molecular structures of complexes **1** and **2** are isostructural, except either a cumyl ($-CMe_2Ph$) or a *tert*-butyl ($-C_4H_9$) substituent at the 4- and 6-position of the phenoxy group. Complex **1** displays the monomeric and homoleptic features with a four-coordinated copper center incorporated by two *N,O*-bidentate **BTP** ligands, forming two six-membered chelating rings in a twisted conformation. The bond angles around Cu center in **1** are classified into two sets: one in a range 89.43(13)-92.85(12)° and the other in a range 158.07(14)-167.95(12)°, which indicate a distorted square planar geometry. The average bond lengths between the Cu atom and O(phenoxy) and N(benzotriazole) are, respectively, 1.876(3) and 1.968(3) Å for **1,** which are all comparable with those observed for the monomeric copper complexes bearing the *O,N*-chelating triazole-phenolate derivative.[13] In comparison, the Cu-containing bond distances and angles for **2** are similar to those found for complex **1** as shown in Supporting Information Table S2. The solid-state structure of **4** reveals a mononuclear species, pentacoordinated by two O atoms and two N atoms of the bidentate **BTP** ligands and one O atom of Me_2CO molecule (Fig. 3). The Cu center of complex **4** adopts a distorted square pyramidal geometry ($\tau = 0.20$)[14] with aryloxy oxygen atoms O(1), O(2), and benzotriazole nitrogen atoms N(1), N(4) occupying the square base, and the Cu(1) atom is about 0.0790 Å above the O(1)N(1)O(2)N(4) mean plane. The distances between the Cu atom and atoms O(1), O(2), N(1), and N(4) are 1.912(2), 1.918(2), 1.976(2), and 1.987(2) Å for **4,** which are slightly longer than the bond distances observed for complexes **1** and **2** as compared in Supporting Information Table S2. It is worth to note that the apical oxygen atom O(1S) from Me_2CO is coordinated to copper center with a Cu(1)-O(1S) bond distance of 2.452(2) Å, which is ~0.54 Å longer than the other Cu-O distances of 1.912(2)-1.918(2) Å,

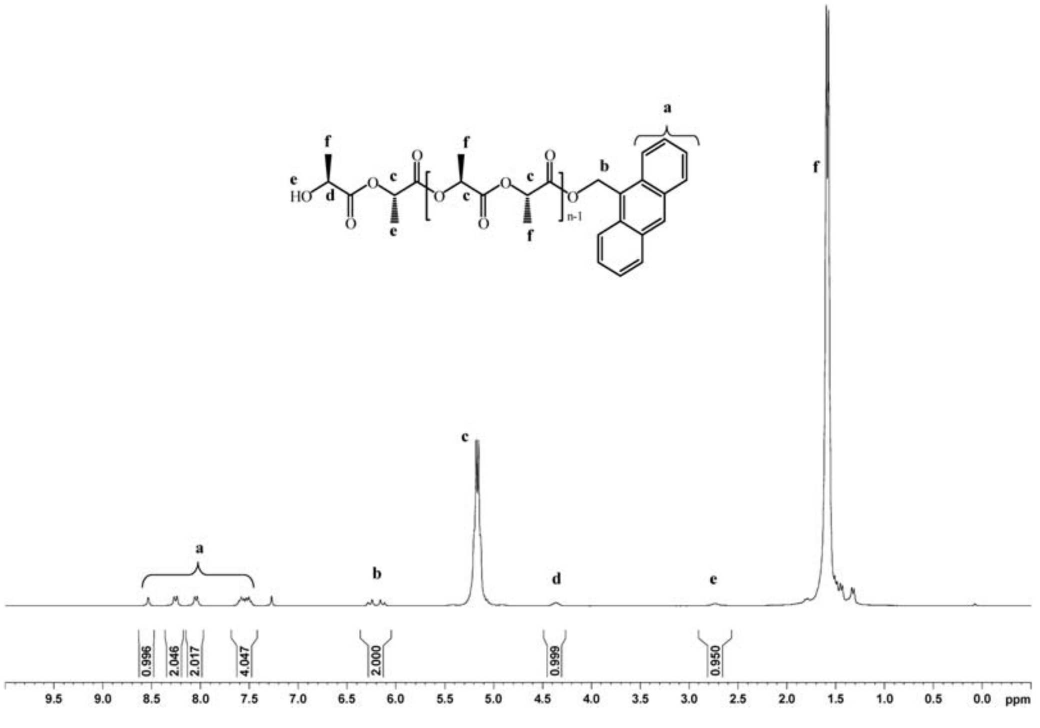


FIGURE 5 ^1H-NMR spectrum of PLLA-25 (Table 1, entry 4) in $CDCl_3$.

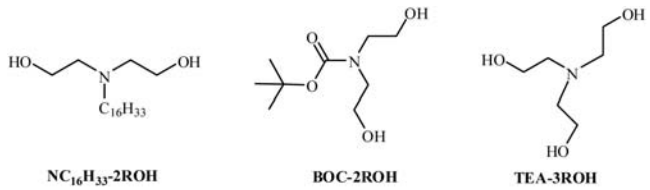


FIGURE 6 Multifunctional alcohol initiators used for the polymerization of L-LA.

indicating the weakly bonding between copper atom and oxygen atom of acetone. Similarly, a long Cu-O bond distance bonded by oxygen atom of O-donor solvent in the distorted square-pyramidal coordination was also reported in tetrahydrofuran(THF)-containing Cu(II) complex with the Cu-O(apical THF) distance of 2.476(5) Å.[15]

Ring-Opening Polymerization of Lactide

On the basis of our previous studies on controlled lactone polymerizations catalyzed by **BTP**-containing metal complexes (metal = Al, Mg, and Zn),[5b,8,9,10a] the benzotriazole phenoxide Cu derivatives have the potential to act as catalysts for the ROP of lactide (LA) in the presence of alcohol. ROP of L-LA catalyzed by Cu complexes **1**-**3** in the presence of 9-anthracenemethanol (9-AnOH) was first performed to evaluate their catalytic performances, and representative results are listed in Table 1. Optimized conditions were found to be the Cu catalyst concentration of 0.005 M with 9-AnOH (two molar equiv.) in toluene (10 mL) at 110°C. Experimental results revealed that Cu complex **3** is an active catalyst to give poly(L-LA)s with narrow molecular weight distributions (PDI < 1.20) among these copper complexes. Accordingly, different monomer-to-initiator ratios ([L-LA]$_0$/[9-AnOH]$_0$ = 25-200) catalyzed by **3** were systematically studied to probe "living" fashion under optimum conditions. It could be seen from Table 1, entries 3-7 that L-LA conversion was attained 92% within 8 h and the actual molecular weight M_n (M_n(GPC) value corrected by a factor of 0.58) of the yielded polymers is close to the molecular weight calculated from the molar ratio of L-LA to 9-AnOH. Figure 4 illustrates a linear relationship between observed M_n and ([L-LA]$_0$-[L-LA])/[9-AnOH]$_0$, and the PDIs of poly(L-LA)s catalyzed by **3** range from 1.11 to 1.19, indicating a "living" character of the polymerization. End group analysis from the ^{1}H-NMR spectrum (Fig. 5) of PLLA-25 ("25" indicates the [L-LA]$_0$/[9-AnOH]$_0$ ratio) reveals that the PLLA chain is capped by one 9-anthracenemethyl ester and one hydroxyl chain end with the integration ratio close to 9:2:1:1 between H$_a$, H$_b$, H$_d$, and H$_e$.[16] Based on the observed results from spectroscopic studies of PLLA, it implies that the $[(^{TMCl}\mathbf{BTP})_2\mathrm{Cu}]$/9-AnOH system might undergo an "activated-monomer" path, whereas L-LA is activated by **3** and 9-AnOH behaves as a nucleophile to proceed the insertion of an anthracenemethoxide group into the L-LA.[17] It is worthy of note that the structural investigation of complex **4** with an weakly bonding between copper and oxygen atom of Me$_2$CO suggested the behavior of "monomer activation" during the ROP of L-LA.

Not only the "living" character of complex **3** for L-LA polymerization has enabled, but also the "immortal" manner has provided an effective way by using only small amounts of catalyst to synthesize polyesters.[18] Consequently, ROP of L-LA catalyzed by copper complex **3** using excess equiv. ratios of 9-AnOH (up to 16 equiv.) as the chain transfer agent (entries 8-9) were examined. For instance, extra 9-AnOH can be added 16-fold amount to [L-LA]$_0$/[Cu]$_0$ = 400, giving a narrow PDI polymer with M_n that is similar to molecular weight from the addition of [L-LA]$_0$/[**3**]$_0$/[9-AnOH]$_0$ = 50/1/2 (Table 1, entry 9 vs. 4). The catalytic performance of copper catalyst **3** is slightly better than that of our previously reported benzotriazole-phenolate alumoxane catalysts, in which a prolonged period of time (48 h) is required to reach a high conversion yield under the same conditions.[5b] However, Cu complex **3** shows the lower catalytic activity than magnesium complex bearing the corresponding **BTP** ligands at the catalytic condition of 80°C for 5 h.[10a] In order to understand the microstructure of PLA catalyzed by **BTP**-modified Cu complexes, polymerization of *rac*-LA and the stereoselectivity catalyzed by Cu complex **3** were explored. It was found that the catalytic activity is not affected while rac-LA is used as the monomer and a virtually atactic polymer ($P_m = 0.50$) is obtained (Table 1, entry 10, Supporting Information Fig. S1).

To demonstrate further the versatility of Cu complex **3** for the L-LA polymerization, several multifunctional alcohol initiators such as 2, 2′-(hexadecylimino)diethanol (**NC$_{16}$H$_{33}$-2ROH**), *tert*-butyl bis(2-hydroxyethyl)carbamate (**BOC-2ROH**), and triethanolamine (**TEA-3ROH**) were employed to initiate polymerization of L-LA (Fig. 6). ROP of L-LA initiated

TABLE 2 Results of the ROP of L-LA with Various Multifunctional Initiators at 110 °C in Toluene Using Cu Complex **3**

Entry	ROH	[L-LA]$_0$/[**3**]$_0$/[ROH]$_0$	*t* (h)	Conv.(%)[a]	M_n (calcd.)[b]	M_n (obsd.)[c]	M_n (NMR)[d]	PDI[e]
1	NC$_{16}$H$_{33}$-2ROH	400/1/2	6	91	13,400	26,900 (15,000)	14,700	1.16
2	BOC-2ROH	400/1/2	6	93	13,600	25,000 (14,500)	14,400	1.15
3	TEA-3ROH	900/1/2	48	95	20,700	46,800 (27,100)	25,000	1.23
4	PEG$_{17}$-OH	200/1/2	6	92	14,000	23,800 (13,300)	14,100	1.13

[a] Obtained from ^{1}H-NMR determination.

[b] Calculated from the molecular weight of lactide times [L-LA]$_0$/[**3**]$_0$ times conversion yield plus the molecular weight of ROH.

[c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.

[d] Obtained from ^{1}H-NMR analysis.

[e] Obtained from GPC analysis.

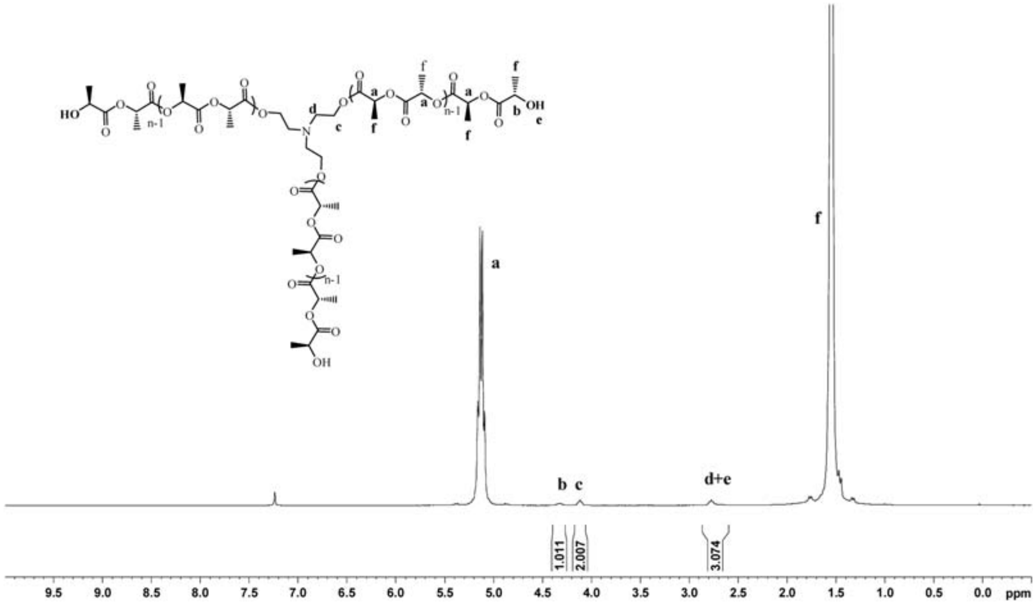
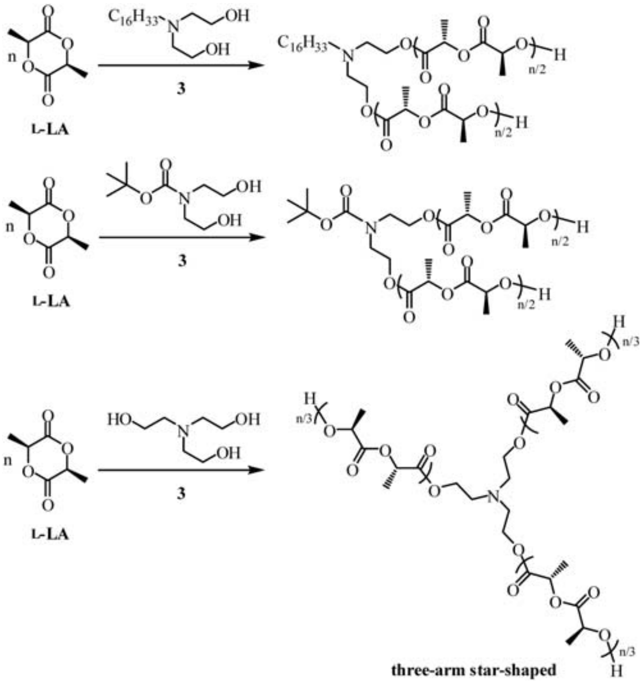


FIGURE 7 ^{1}H-NMR (400 MHz, $CDCl_3$) spectra of trihydroxylfunctionalized star-shaped PLLA (Table 2, entry 3).

from alcohols **$NC_{16}H_{33}$-2ROH** and **BOC-2ROH** gives two-arm linear PLLA while initiation from alcohol **TEA-3ROH** produces three-arm star-shaped PLLA (Scheme 2). Table 2 summarizes the conditions and results of Cu-catalyzed polymerization of L-LA in the presence of varied alcohol initiators. Relative to 9-AnOH as the initiator, the catalytic efficiency is little affected while **$NC_{16}H_{33}$-2ROH** or **BOC-2ROH** is altered as the initiator (Table 2, entries 1-2). For instance, the synthesized PLLA with two-arm linear architecture from **BOC-2ROH** exhibited the desired molecular weight (M_n = 14,500 g/mol) and low PDI (<1.20). However, initiating activities are drastically changed with alcohol **TEA-3ROH** as the initiator. As can be seen from Table 2, **$[(^{TMCl}BTP)_2Cu]$/TEA-3ROH** catalytic system also shows effective activity in a controlled fashion, but with duration of polymerization up to 48 h to attain conversion ~95%. To understand the chemical nature of three-armed polymer architecture initiated by **TEA-3ROH,** ^{1}H-NMR studies were conducted as shown in Figure 7. The ^{1}H-NMR spectrum of the resultant PLLA clearly displayed resonances from a triethanolamine-core and three HOCH(Me)CO chain ends for each macromolecule with the integration ratio ~2:1 between H_c and H_b, which was in agreement with a three-arm star-shaped PLA catalyzed by the Salan-ligated yttrium alkyl complex.[19]



SCHEME 2 Synthesis of two-arm linear and three-arm star-shaped PLLAs by L-LA polymerizations catalyzed by Cu complex **3** with various multifunctional alcohol initiators.

Encouraged by controlled catalysis of lactide polymerization initiated from multifunctional alcohol initiators, we also examined the capability of producing PEG-PLLA block copolymer with the controlled molecular weight and a narrow PDI. Block copolymer of PEG-*b*-PLLA was therefore synthesized by the ROP of L-LA in the presence of PEG-OH catalyzed by Cu complex **3,** and the results are shown in Table 2, entry 4. As expected, the catalytic activity and the controlled manner remained when PEG-OH is employed as the macroinitiator. The block nature of the PEG-*b*-PLLA copolymer was confirmed by its ^{1}H-NMR spectrum and GPC profile. ^{1}H-NMR spectrum (Fig. 8) of PEG-*b*-PLLA indicates that a sharp singlet of methylene protons (H_c, 3.60 ppm) for the PEG segment and a quartet signal of methine protons (H_a, 5.14 ppm) for the PLLA segment, suggesting the binary composition of the PEG-*b*-PCL copolymer. The GPC profiles are shown in Figure 9; peak A is relative to macroinitiator PEG-OH (M_n = 500 g/mol, PDI = 1.34) and peak B is to PEG-*b*-PLLA after

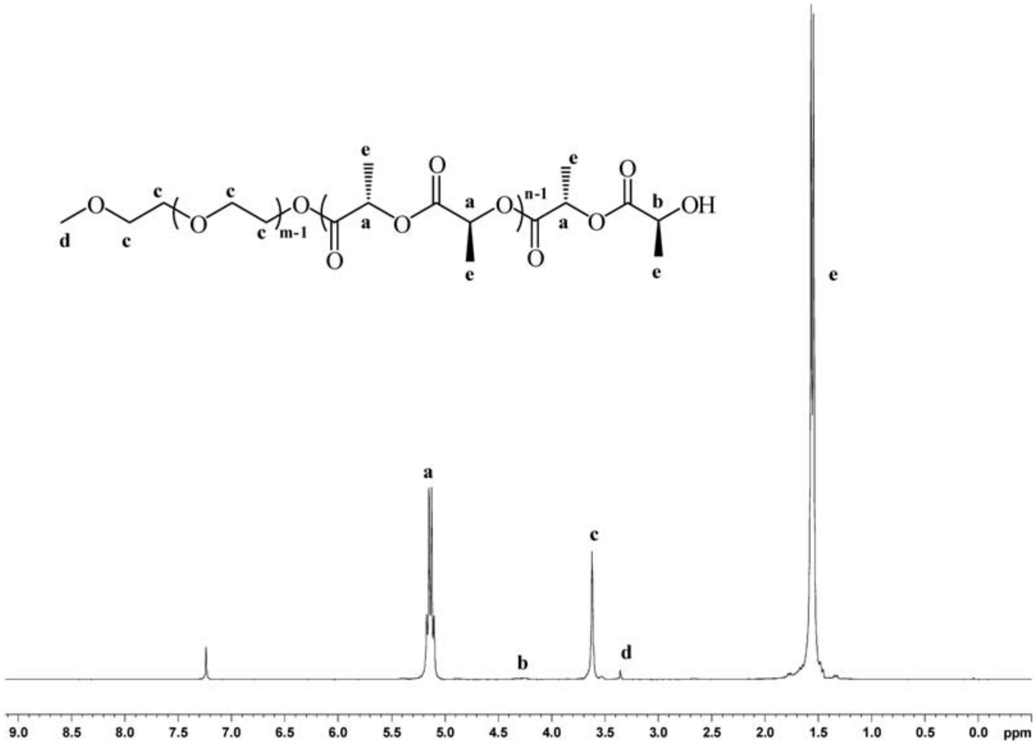


FIGURE 8 ^{1}H-NMR spectrum of PEG-*b*-PLLA (Table 2, entry 4) in $CDCl_3$.

copolymerization with L-LA at 100 equiv. An increased molecular weight and its narrow distribution (M_n = 23800 g/mol, PDI = 1.13) were observed (peak B), verifying the formation of the block copolymer.

CONCLUSIONS

Four new copper(II) complexes based on *N,O*-bidentate benzotriazole phenoxide ligands have been synthesized and characterized by Elem. Anal. as well as X-ray single crystal structural determination. On the basis of the crystal structure of **$[(^{TMCl}BTP)_2Cu(Me_2CO)]$** (**4**), the copper center is extra coordinated by one acetone molecule, suggesting the Cu center in four-coordinated complex **$[(^{TMCl}BTP)_2Cu]$** (**3**) can behave effectively as one active site to activate monomers during ring-opening polymerization (ROP). Experimental results indicate that **3**/9-anthracenemethanol catalytic system was able to catalyze ROP of L-lactide (L-LA) with "living" and "immortal" characters, giving polymers with the expected molecular weights and narrow molecular weight distributions. Initiations from multifunctional alcohols were able to produce polymers with diverse molecular architectures, such as two-arm linear and three-arm star-shaped PLLAs. The controlled fashion of complex **3** also enabled preparation of the PEG-*b*-PLLA copolymer, which were characterized by ^{1}H-NMR and GPC.

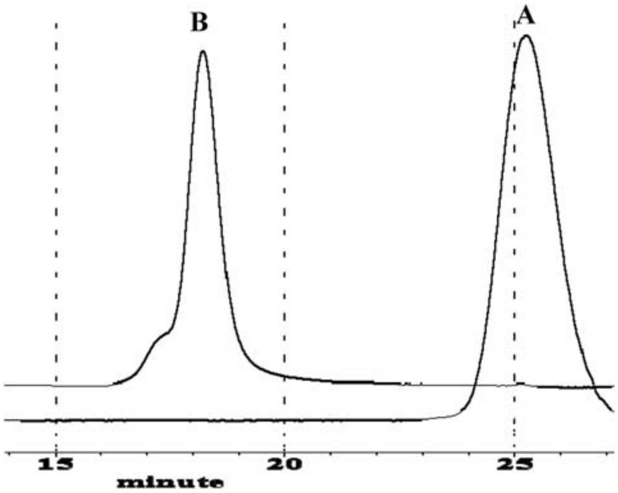


FIGURE 9 GPC profiles of copolymerization of PEG-*b*-PLLA: (peak A) the prepolymer (M_n = 500 g/mol, PDI = 1.34); (peak B) the block copolymer of PEG-*b*-PLLA (M_n = 23800 g/mol, PDI = 1.13).

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