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# Preparation and characterization of poly(ε-caprolactone)-*b*-polyacrylonitrile (PCL-*b*-PAN) and poly(L-lactide)-*b*-polyacrylonitrile (PLLA-*b*-PAN) copolymers by aluminum and lithium alkoxides containing double-headed initiators

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## Abstract

Three new metal alkoxides, $[(MMPEP)Al(\mu\text{-}OCH_2C_6H_4CH_2Cl)]_2$ (**1**), $[(MMPEP{-}H)Li\cdot(BnOH)]_2$ (**2**) and $[(MMPEP{-}H)Li\cdot(HOCH_2C_6H_4CH_2Cl)]_2$ (**3**) ($MMPEP{-}H_2$: 2,2′-methylene-bis{4,6-di(1-methyl-1-phenylethyl)phenol}) have been synthesized and characterized. Complex **1** was prepared by the reaction of $[(MMPEP)Al(CH_3)(Et_2O)]$ with *p*-(chloromethyl)benzyl alcohol. Followed by the reaction of $MMPEP{-}H_2$ with $^{n}$BuLi, BnOH or *p*-(chloromethyl)benzyl alcohol was added to give complexes **2** and **3**, respectively. Complex **1** has shown excellent catalytic activity towards ring-opening polymerization (ROP) of ε-caprolactone. Both complexes **2** and **3** are active for ROP of L-lactide. Block copolymers of poly(ε-caprolactone)-*b*-polyacrylonitrile (PCL-*b*-PAN) and poly(L-lactide)-*b*-polyacrylonitrile can be synthesized by combining a technique of atom transfer radical polymerization (ATRP) and ROP using a double-headed initiator. Microphase-separated morphology of PCL-*b*-PAN has been observed by transmission electron microscopy, indicating the formation of self-assembled nanostructure.

*Keywords:* Double-headed initiator; ε-Caprolactone; L-Lactide

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## 1. Introduction

Nowadays, carbon materials have been used for a wide range of applications such as for chemistry, chemical engineering or material science. These materials can be applied in separation processes, electrochemistry, catalysis, energy/conversion devices, etc. [1]. Polyacrylonitrile (PAN) is one of the many materials used for manufacturing activated carbon [2] and is an important source for carbon fibers and carbon materials. Over the last decades, carbon material has played an important role in nanoapplications. The formation of carbon nanotube with regular textured and with proper orientations is expensive, tricky and complicate procedures, however, it is generally prepared either by physical/chemical vapor deposition techniques [3]. Recently, demands for developing new carbon materials have dramatically increased with high performance-to-price ratio. Therefore, it is a great challenge to explore an easy and cheap alternative method by adopting a mild reaction condition to synthesize carbon nanomaterials. Many technologies have been evolved for creating nanotemplates which have a great potential for the preparation of many nanomaterials. One of the most convenient ways for the preparation of nanotemplates is by self-assembling of diblock copolymers [4]. A variety of nanotemplates with different applications have received great interest nowadays, in general they can be obtained by simply controlling the fraction of constituted building blocks [5].

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Block copolymers with biodegradable polyester and polyacrylonitrile are good precursors for the preparation of carbon nanomaterials. A novel route based on block copolymer constituting a well-known carbonization precursor, such as poly(acrylonitrile), has been developed to generate a well-defined nanostructured carbon materials [6–9]. Copolymer of poly(ε-caprolactone) and poly(styrene-*co*-acrylonitrile) has been synthesized by blending method [10]. The preparation of homo- and copolymer polyacrylonitrile was typically carried out via free radical polymerization and anionic polymerization without having control on the molecular weight and its polydispersity indexes as well as other functional properties [11]. Matyjaszewski and coworkers have recently communicated the synthesis of polyacrylonitrile by using atom transfer radical polymerization (ATRP) technique. ATRP has more advantages for controlling polymer properties as compared to other analogue synthetic methods [12]. The typical method to synthesize poly(cyclic esters) is by the ring-opening polymerization [13–18]. With the help of this method, the molecular weight of the polymer can be controlled, and the PDIs are in a narrow range [19]. Therefore, we report herein the synthesis of aluminum and lithium complexes containing double-headed initiators [20] for the preparation of block copolymers with well-defined architectural properties.

## 2. Experimental section

### 2.1. General

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing at least for 24 h over sodium/benzophenone (toluene, *n*-hexane and diethyl ether), phosphorus pentoxide ($CH_2Cl_2$), or over anhydrous magnesium sulfate (benzyl alcohol) and then freshly distilled prior to use. Deuterated solvents were dried over 4 Å molecular sieves. [(MMPEP)Al($CH_3$)($Et_2O$)] [19c] and *p*-(chloromethyl)benzyl alcohol [21] were prepared according to literature method. Copper(I) bromide was purified by washing with pure acetic acid. Acrylonitrile, 2,2′-bipyridine, ethylene carbonate, NaOH, EDTA, MeOH and aluminum oxide (standard grade, ~150 mesh, 58 Å) were purchased and used as such without further purification. $^1$H and $^{13}$C NMR spectra were recorded on a Varian Mercury-400 (400 MHz) or a Varian Unity Inova 600 MHz (the $^{13}$C NMR spectra of complex **3**) spectrometer with chemical shifts given in parts per million from the internal standard TMS. Microanalyses were performed by using a Heraeus CHN-O-RAPID instrument. Infrared spectra were obtained from a Bruker Equinox 55 spectrometer. The GPC measurements were performed on a Hitachi L-7100 system equipped with a differential Bischoff 8120 RI detector using THF (HPLC grade) as an eluent (for PCL and PLLA) or a Postnova PN1122 Solvent Delivery system equipped with a RI Detector PN3110 using DMF (HPLC grade) as an eluent (for PCL-*b*-PAN). Molecular weight and its distributions were calculated by using polystyrene as standard.

### 2.2. [(MMPEP)Al(μ-$OCH_2C_6H_4CH_2Cl$)]$_2$ (**1**)

To an ice cold solution (0 °C) of [(MMPEP)Al($CH_3$)($Et_2O$)] (1.57 g, 2 mmol) in toluene (20 mL) was added the solution of *p*-(chloromethyl)benzyl alcohol (0.312 g, 2 mmol) in toluene (10 mL). The mixture was stirred for 3 h while the temperature increased from 0 °C to room temperature and the volatile materials were removed under vacuum. The residue was redissolved in hot toluene and then concentrated to ca. 10 mL. The solution was allowed to cool to room temperature affording colorless crystalline solids after 24 h. Yield: 1.13 g (66%). $^1$H NMR ($CDCl_3$, ppm): $\delta$ 6.69–7.28 (m, 56H, Ph), 4.27 (s, 4H, C$H_2$Cl), 3.19 (s, 4H, OC$H_2$), 2.37 (d, 2H, PhC$H_2$Ph, $J_{H-H} = 14.8$ Hz), 2.04 (d, 2H, PhC$H_2$Ph, $J_{H-H} = 14.8$ Hz), 1.82, 1.58, 1.57, 1.44 (s, 48H, C$H_3$). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 151.50, 151.13, 150.70, 140.48, 137.33, 136.47, 135.74, 129.24, 128.55, 128.22, 128.00, 127.82, 126.61, 126.51, 125.82, 125.64, 125.35, 125.30, 124.74 (Ph), 66.09 (O$CH_2$), 45.60 ($CH_2$Cl), 43.00, 42.25 (Ph*C*($CH_3$)$_2$Ph), 33.73, 31.04, 31.02, 30.73(C($CH_3$)$_2$), 27.98 (Ph*C*$H_2$Ph). IR (KBr, cm$^{-1}$): 3025 (m), 2965 (s), 2873 (m), 1597 (m), 1478 (s), 1373 (m), 1276 (s), 1203 (m), 1149 (m), 1093 (m), 1027 (m), 923 (m), 834 (m). Anal. Calcd. for $C_{114}H_{116}Al_2O_6Cl_2$: C, 80.21; H, 6.85. Found: C, 79.64; H, 6.22%. Mp = 184–186 °C.

### 2.3. [(MMPEP–H)Li·(BnOH)]$_2$ (**2**)

To an ice cold solution (0 °C) of 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP–$H_2$) (2.70 g, 4.0 mmol) in diethyl ether (30 mL) was added benzyl alcohol (0.42 mL, 4 mmol). $^n$BuLi (2 mL, 5 mmol in *n*-hexane) was then injected into the solution and the resulting mixture was stirred at room temperature for 3 h. The volatile materials were removed under vacuum and the residue was extracted in toluene (30 mL). The extract was concentrated to ca. 5 mL and *n*-hexane (ca. 50 mL) was added slowly. On keeping at room temperature for 24 h, white solid was obtained. Yield: 2.04 g (65%). $^1$H NMR ($CDCl_3$, ppm): $\delta$ 6.78–7.37 (m, 58H, Ph), 5.10 (Br, 2H, PhO*H*), 4.63 (s, 4H, PhC$H_2$OH), 3.59 (s, 4H, PhC$H_2$Ph), 1.63, 1.54 (s, 48H, C$H_3$). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 151.67, 140.57, 139.37, 134.91, 129.50, 128.66, 128.39, 127.76, 127.51, 127.10, 127.00, 126.73, 126.43, 125.68, 125.23, 123.16 (Ph), 66.03 (O$CH_2$), 42.38, 42.10 (Ph*C*($CH_3$)$_2$Ph), 32.73, 31.07 (C($CH_3$)$_2$), 29.83 (Ph*C*$H_2$Ph). IR (KBr, cm$^{-1}$): 3500 (br), 2868 (m), 1599 (m), 1492 (s), 1462 (s), 1441 (s), 1381 (m), 1361 (m), 1319 (m), 1202 (m), 1030 (m). Anal. Calcd. for $C_{112}H_{118}Li_2O_6$: C, 85.46; H, 7.56. Found: C, 85.59; H, 7.55%. Mp = 143–145 °C.

### 2.4. [(MMPEP–H)Li·($HOCH_2C_6H_4CH_2Cl$)]$_2$ (**3**)

To an ice cold solution (0 °C) of 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP–$H_2$) (2.70 g, 4.0 mmol) and *p*-(chloromethyl)benzyl alcohol (0.624 g, 4.0 mmol) in diethyl ether (30 mL) was added slowly $^n$BuLi

(2.0 mL, 5.0 mmol in *n*-hexane). The reaction mixture was stirred at room temperature for 3 h and the volatile materials were removed under vacuum to give white powder. The residue was extracted with toluene. The extract was concentrated to ca. 5 mL and *n*-hexane (ca. 50 mL) was added slowly. On keeping at room temperature for 24 h, white solid was obtained. Yield: 2.40 g (72%). $^1$H NMR ($CDCl_3$, ppm): $\delta$ 6.64–7.38 (m, 56H, Ph), 5.13 (Br, 2H, PhO*H*), 4.66 (s, 4H, PhC*H*$_2$OH), 4.60 (s, 4H, PhC*H*$_2$Cl), 3.58 (br, 4H, PhC*H*$_2$Ph), 1.64, 1.49 (s, 48H, C*H*$_3$). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 152.11, 151.53, 136.67, 134.92, 128.75, 127.93, 127.81, 127.56, 127.19, 126.72, 126.35, 125.94, 125.17, 124.54, 123.75, 123.08 (Ph), 64.87 (O*C*H$_2$), 46.04 (*C*H$_2$Cl), 42.40, 42.03 (Ph*C*(CH$_3$)$_2$Ph), 31.04 (C(*C*H$_3$)$_2$), 29.75 (Ph*C*H$_2$Ph). IR (KBr, cm$^{-1}$): 3527 (s), 3482 (s), 2961 (s), 2866 (m), 1599 (s), 1492 (m), 1459 (s), 1440 (s), 1382 (m), 1319 (s), 1264 (m), 1218 (m), 1028 (m), 987 (m). Anal. Calcd. for $C_{114}H_{120}O_6Li_2Cl_2$: C, 81.94; H, 7.24. Found: C, 81.58; H, 6.95%. Mp = 148–149 °C.

### 2.5. Synthesis of p-(chloromethyl)benzyl end-functionalized PCLs

A typical polymerization procedure was exemplified by the synthesis of PCL100 (the number 100 indicates the designed $[M]_0/[I]_0$). To a rapidly stirred solution of [(MMPEP)Al ($\mu$-OCH$_2$C$_6$H$_4$CH$_2$Cl)]$_2$ (0.0854 g, 0.05 mmol) in toluene (15 mL) was added ε-CL (0.53 mL, 5.0 mmol). The reaction mixture was stirred at 50 °C for 1 h and the reaction was quenched by the addition 10 mL $H_2O$. The polymer was precipitated out by the addition of *n*-hexane (50 mL). The resulting white precipitate was extracted in dichloromethane and then precipitated into *n*-hexane. Finally the white precipitate was dried under vacuum to give a white solid. $M_n$ (NMR) for PCL was calculated based on the comparison of integral between peaks at 5.12 (–OC*H*$_2$Ph–), 4.58 (–OC*H*$_2$Cl), 4.05 (–C*H*$_2$OC(=O)–) and at 3.65 (–C*H*$_2$OH) ppm.

### 2.6. Preparation of PLLAs

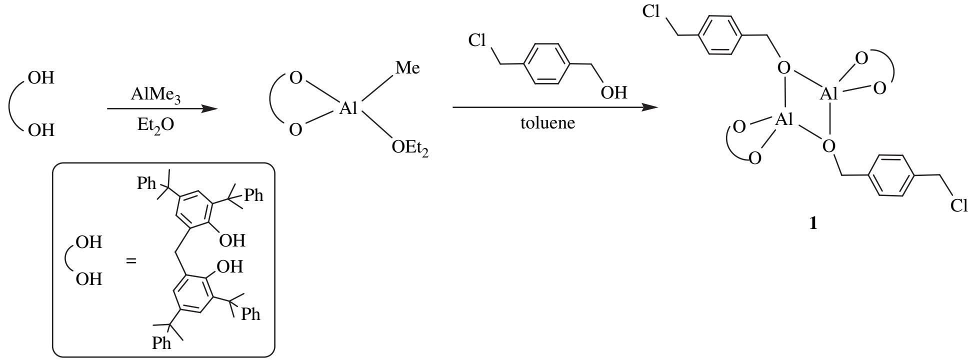
A typical polymerization procedure was exemplified by the synthesis of PLLA30 (the number 30 indicates the designed $[M]_0/[I]_0$). To a rapidly stirred solution of [(MMPEP–H)Li·(BnOH)]$_2$ (0.0787 g, 0.05 mmol) in $CH_2Cl_2$ (4.0 mL) was added L-LA (0.216 g, 1.5 mmol) in $CH_2Cl_2$ (6.0 mL). The reaction mixture was stirred at 0 °C for 5 h and the volatile materials were removed in vacuum. The residue was then redissolved in toluene (10 mL) and $H_2O$ (10 mL) was added into it to quench the polymerization. The polymer was precipitated out by pouring the mixture into *n*-hexane. The white precipitate was redissolved in dichloromethane and then precipitated out in *n*-hexane again. The resulting powder was dried under vacuum to give a white solid. $M_n$ (NMR) for PLLA was calculated based on the comparison of integral between peaks at 7.27–7.37 (–CH$_2$*Ph*) 5.18 (–OC*H*MeC(O)–), and at 4.36 (–C*H*MeOH) ppm.

### 2.7. Synthesis of p-(chloromethyl)benzyl ester end-functionalized PLLAs

A typical polymerization procedure was exemplified by the synthesis of PLLA50 (the number 50 indicates the designed $[M]_0/[I]_0$). To a rapidly stirred solution of [(MMPEP–H)Li·(HOCH$_2$C$_6$H$_4$CH$_2$Cl)]$_2$ (0.0835 g, 0.05 mmol) in $CH_2Cl_2$ (3.0 mL) was added L-LA (0.36 g, 2.5 mmol) in $CH_2Cl_2$ (7.0 mL). The reaction mixture was stirred at 0 °C for 5.5 h and the volatile materials were removed in vacuum. The residue was then redissolved in toluene (10 mL) and $H_2O$ (10 mL) was added into it to quench the polymerization. The polymer was precipitated out by pouring the mixture into *n*-hexane. The white precipitate was redissolved in dichloromethane and then precipitated out in *n*-hexane again. The resulting powder was dried under vacuum to give a white solid. $M_n$ (NMR) for PLLA was calculated based on the comparison of integral between peaks at 7.27–7.37 (–CH$_2$*Ph*–) 5.18 (–OC*H*MeC(O)–), 4.58 (–PhC*H*$_2$Cl) and at 4.36 (–C*H*MeOH) ppm.

### 2.8. Synthesis of poly(ε-caprolactone)-b-polyacrylonitrile copolymer

CuBr of 0.33 g (2.25 mmol), 0.71 g (4.5 mmol) 2,2-bipyridine and 25 g ethylene carbonate were taken in a flask which was vacuumed for 1 h. The color of the reaction mixture



Scheme 1.

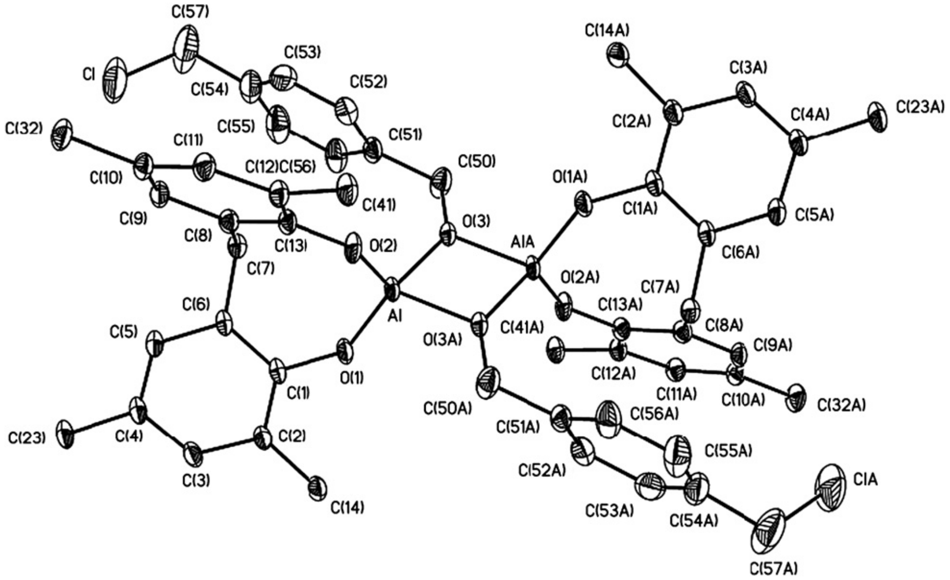
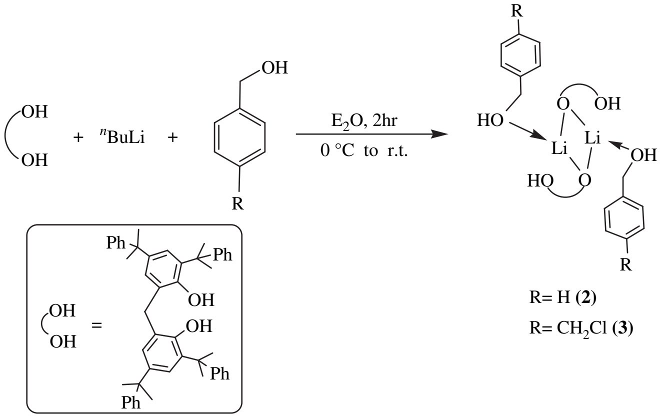


Fig. 1. Molecular structure of **1** as 20% ellipsoids (methyl and phenyl carbons of the ethyl groups and all of the hydrogen atoms are omitted for clarity).

changes to dark brown. The flask was heated to 70 °C under nitrogen atmosphere. When the ethylene carbonate was dissolved, the temperature of the flask was decreased to room temperature and then *p*-(chloromethyl)benzyl ester end-functionalized PCL (PCL2350, 3.53 g, 1.5 mmol) was added into it. The solid mixtures were dissolved in 14.31 g (270 mmol) acrylonitrile. The reaction mixture was stirred at 70 °C for 24 h. Methyl alcohol was added to quench the reaction with overnight stirring and the resulting residue was filtered to give dark yellow powder. The powder was dissolved in DMF and the solution was added with ca. 1 mM EDTA/NaOH aqueous solution (ca. 1 L) to obtain light yellow powder. The yellow powder was redissolved in DMF and the resulting solution was filtered through a column of aluminum oxide with MeOH (aq) (the ratio of MeOH and $H_2O$ is ca. 1:1, 1 L) as an eluent. The eluent was then evaporated to dryness giving grey solid. The solid was washed with hot MeOH many times and then finally dried under vacuum to obtain a copolymer. Yield: 9.92 g (55.6%). $M_n$ (NMR) for PCL-*b*-PAN was calculated based on the comparison of integral between peaks at 7.23–7.29 ($-CH_2$*Ph*$-$) 5.03 ($-C$*$H_2$*Ph$-$), 3.97 ($-C$*$H_2$*$OC(=O)-$) and 3.12 ($-C$*H*(CN)$-$) ppm in DMSO-*$d_6$*.



Scheme 2.

## 2.9. Synthesis of polylactide-b-polyacrylonitrile copolymer

CuBr of 0.218 g (1.52 mmol), 0.467 g (2.95 mmol) 2,2′-bipyridine and 20 g ethylene carbonate were added in a flask which was vacuumed for 1 h. The color of the mixture was changed to dark brown. The flask was heated to 70 °C in nitrogen atmosphere. When ethylene carbonate dissolved completely the temperature of the flask was cooled to room temperature and then *p*-(chloromethyl)benzyl ester end-functionalized PLLA (PLLA4300, 4.3 g, 1.0 mmol) in 5.3 g (100 mmol) acrylonitrile was added to it. The reaction mixture was stirred at 70 °C for 24 h. The methyl alcohol was added to quench the reaction and dark-white powder can be obtained in good yield.

## 2.10. The morphological study of PCL-b-PAN

Bulk samples of block copolymers were prepared by solution casting from *N*,*N*-dimethylformamide ($HCON(CH_3)_2$, DMF) solution (100 mg/mL of PAN-*b*-PCL) at temperature above the melting temperature of PCL for 3 days. After solution casting, sample was annealed at 160 °C for 12 h in vacuum oven. The specimens for TEM are embedded in epoxy and subsequently sectioned by ultra-cryomicrotomy using a Reichert Ultracut microtome. Bright field TEM images were obtained by mass-thickness contrast on a JEOL TEM-1200× transmission electron microscopy, at an accelerating voltage of 120 kV. Staining was accomplished by exposure of the samples to the vapor of a 4% aqueous $RuO_4$ solution

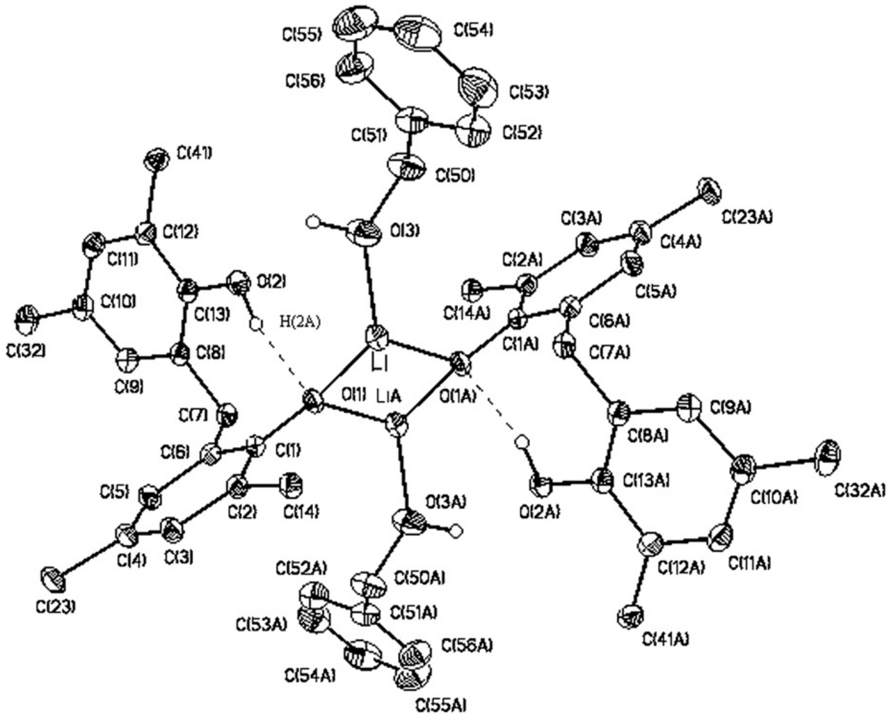


Fig. 2. Molecular structure of **2** as 20% ellipsoids (methyl and phenyl carbons of the ethyl groups and all of the hydrogen atoms are omitted for clarity).

for 3 h. Bright field images of mass-thickness contrast were obtained from the stained samples.

### 2.11. X-ray crystallographic studies

Suitable crystals of **1**–**3** were sealed in thin-walled glass capillaries under dry nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing $\omega$ (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct

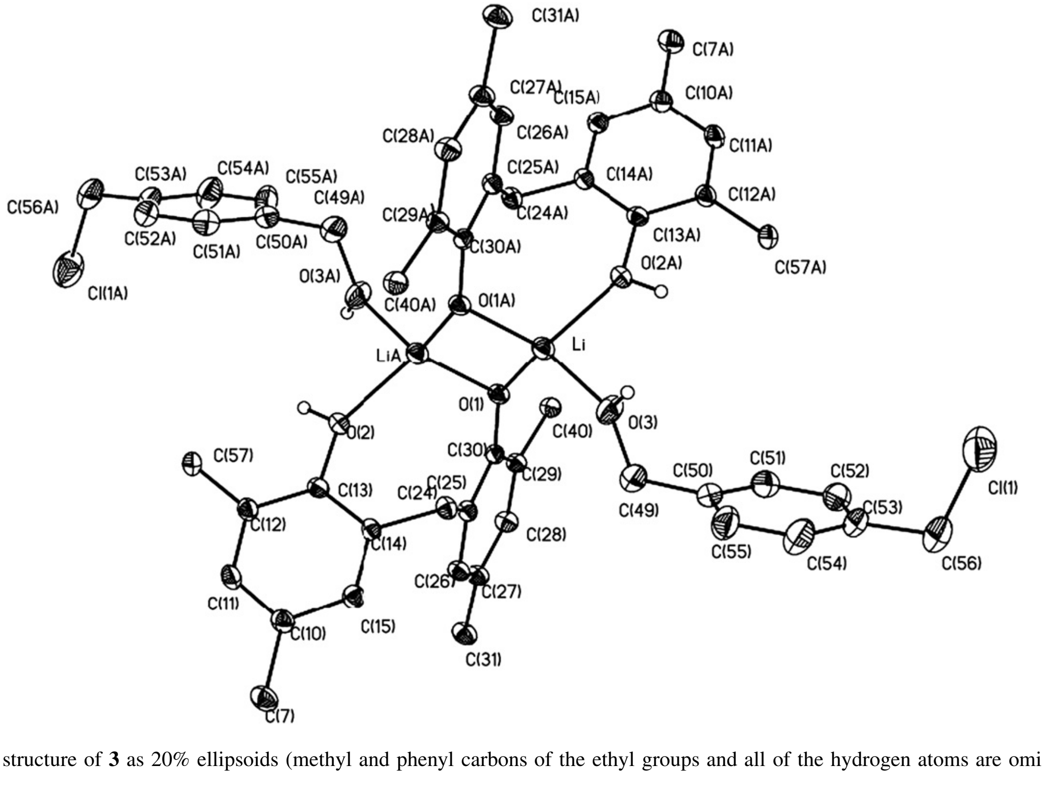


Fig. 3. Molecular structure of **3** as 20% ellipsoids (methyl and phenyl carbons of the ethyl groups and all of the hydrogen atoms are omitted for clarity).

Table 1
Ring-opening polymerization of ε-CL initiated by **1**[a]

| Entry | $[M]_0$:[**1**]$_0$:[ROH][b] | $t$ (h) | $M_n$ (Calcd)[c] | $M_n$ (NMR)[d] | $M_n$ (GPC)[e] | PDI[e] | Conv[d] (%) |
|---|---|---|---|---|---|---|---|
| 1 | 100:1:0 | 1 | 5800 | 6700 | 13 900 | 1.08 | 99 |
| 2 | 200:1:0 | 1 | 10 400 | 10 600 | 19 600 | 1.07 | 90 |
| 3 | 300:1:0 | 3 | 15 700 | 16 100 | 29 400 | 1.08 | 91 |
| 4 | 400:1:0 | 5 | 22 700 | 23 200 | 42 100 | 1.18 | 99 |
| 5 | 100(100):1:0 | 1(1) | 11 200 | 11 100 | 19 200 | 1.07 | 99(95) |
| 6 | 800:1:14 | 2 | 5700 | 6550 | 11 100 | 1.05 | 97 |
| 7 | 800:1:78 | 1 | 1300 | 1350 | 1950 | 1.20 | 93 |

[a] Reaction conditions: 15 mL toluene, 50 °C, 0.05 mmol of **1**.

[b] ROH is *p*-(chloromethyl)benzyl alcohol.

[c] Calculated from the molecular weight of ε-CL × $[M]_0/2[I]_0$ × conversion yield + $M_w$(BnOH).

[d] Obtained from $^1$H NMR analysis.

[e] Obtained from GPC analysis.

methods using a Siemens SHELXTL PLUS package. All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms and fixed isotropic parameters were used for H atoms. Crystallographic data of **1**–**3** are listed in Supplementary data.

## 3. Results and discussion

### 3.1. Synthesis and characterization

[(MMPEP)Al(μ-$OCH_2C_6H_4CH_2Cl$)]$_2$ (**1**) was obtained by the reaction of [(MMPEP)Al($CH_3$)($OEt_2$)] [19c] with an equal equivalent of *p*-(chloromethyl)benzyl alcohol in toluene (Scheme 1). $^1$H NMR studies of **1** reveal two singlets at 4.27 ($CH_2$Cl) and 3.19 ($OCH_2$) consistent with the expected structure. The structure of **1** was further confirmed by X-ray single crystal determination. Suitable crystals of **1** were obtained at room temperature by slow cooling a hot toluene solution, and its ORTEP was shown in Fig. 1. The molecular structure of **1** shows a dimeric feature containing an $Al_2O_2$ core bridging through the benzyl alkoxy oxygen atoms with the center of the $Al_2O_2$ core sitting on the crystallographic center. The geometry around Al was distorted from tetrahedral and the bond distances between bridging oxygen atom and two Al centers are almost symmetric with the bond distances Al–O(1) 1.700(2), Al–O(2) 1.689(3) (phenoxy), Al–O(3) 1.816(2) and Al–O(3A) 1.822(2) (bridging oxygen).

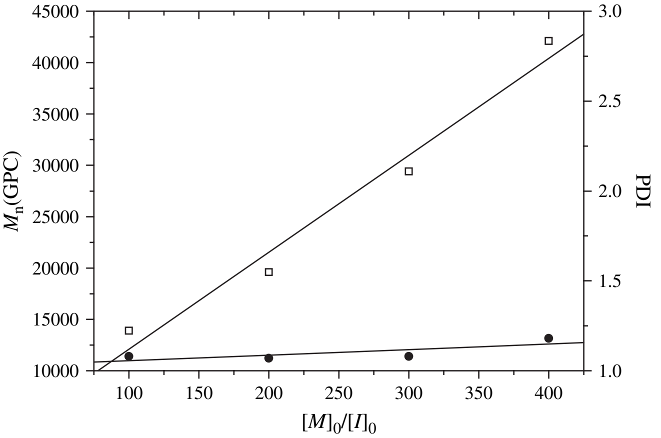


Fig. 4. Polymerization of ε-CL initiated by **1** in toluene at 50 °C. The relationship between $M_n$ (GPC) (□) (PDI (●)) of the polymer and the monomer-to-initiator ratio $[M]_0/[I]_0$ is shown.

Two novel lithium alkoxides, [(MMPEP–H)Li·(BnOH)]$_2$ (**2**) and [(MMPEP–H)Li·($HOCH_2C_6H_4CH_2Cl$)]$_2$ (**3**) were synthesized in similar procedures (Scheme 2). Complex **2** was obtained by the addition of 1 molar equiv of $^n$BuLi to the mixture of 2,2′-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP–$H_2$) and benzyl alcohol (BnOH) in diethyl ether. Complex **3** was prepared by similar method in which $HOCH_2C_6H_4CH_2Cl$ was used. Suitable crystals of **2** and **3** were obtained from a mixed solution of dichloromethane and *n*-hexane, and their ORTEPs are shown in Figs. 2 and 3, respectively. The molecular structure of **2** shows a dimeric feature containing an $Li_2O_2$ core bridging through the phenoxy oxygen atoms. Lithium atom was tri-coordinated by the oxygen atom of benzyl alcohol and two bridging phenoxy oxygens with the bond distances Li–O(1) 1.868(3), Li–O(1A) 1.918(3) (bridging phenoxy) and Li–O(3) 1.888(4) (the oxygen of benzyl alcohol). It is interesting to note that an intramolecular hydrogen bonding was observed between the phenoxy oxygen and phenol group of the MMPEP–$H^-$ with H(2A)···O(1) 1.924 Å, and the nearly linear O(2)–H(2A)···O(1) angle at 162.8°. The dimeric complex **3** consists of an $Li_2O_2$ core bridging through the phenoxy oxygen of the MMPEP–$H^-$ group. However, Li is tetra-coordinated with bond distances of Li–O(1) 1.839(5), Li–O(1A) 1.900(5) (bridging phenoxy), Li–O(2A) 2.068(5) (the oxygen of the phenol on the other phenoxy), and Li–O(3) 2.009 (5) (the oxygen of *p*-(chloromethyl)benzyl alcohol).

### 3.2. Ring-opening polymerization of ε-caprolactone initiated by *1*

The catalytic behavior of **1** towards ROP of ε-caprolactone (ε-CL) has been systematically examined and found that the polymerization of ε-CL proceeds smoothly as shown in Table 1. GPC analyses reveal that poly(ε-caprolactone) formed with the help of initiator **1** with "controlled" polymer properties and the PDIs of PCL ranging from 1.07 to 1.20. The linear relationship between the number-average molecular weight ($M_n$) and the monomer-to-initiator ratio

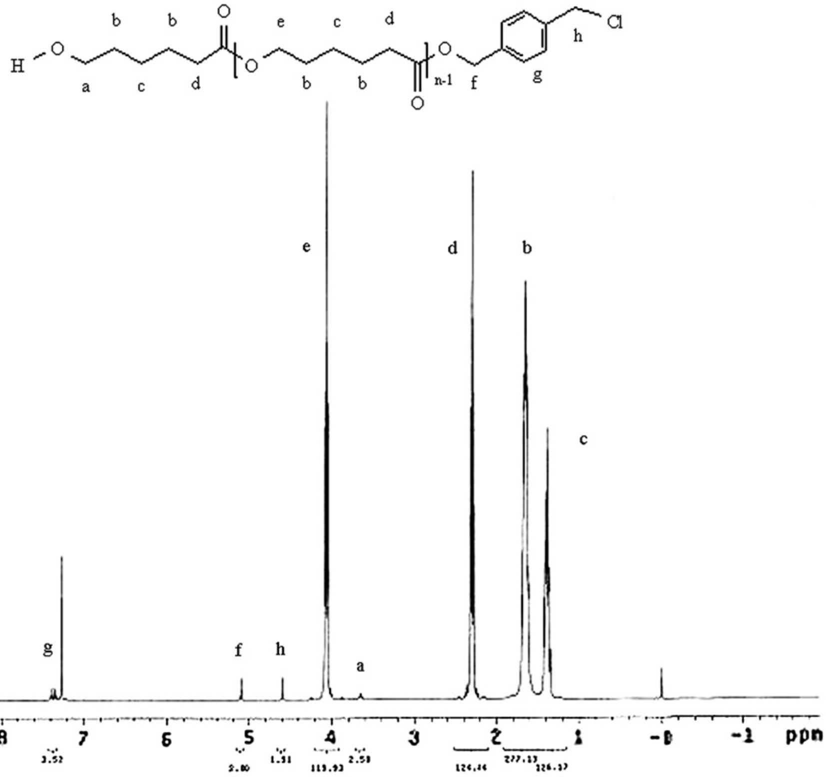


Fig. 5. The $^1$H NMR spectrum of PCL100 in $CDCl_3$.

($[M]_0/[I]_0$) is shown in Fig. 4. In the experiment (entry 5), another portion of 100 equiv of ε-CL monomer was added after the polymerization of the first addition of 100 equiv had gone to completion. The molecular weight obtained in this process was similar to that of polymer obtained by the polymerization of 200 molar equiv of ε-CL catalyzed by **1** (entry 2). It was worth noting that as much as 78 folds of *p*-(chloromethyl)benzyl alcohol can be added which results in a low PDI index with a smaller $M_n$ (entry 7). These properties are useful for fabrication of biomedical material due to the presence of less metal content. It was also found that when the reaction was performed in the higher [*p*-(chloromethyl)benzyl alcohol/initiator] ratio, the conversion rate is much faster. The $^1$H NMR spectrum of PCL100 (the number 100 indicates the designed $[M]_0/[I]_0$ ratio) gives an intensity ratio closed to **1** between $H_e$ ($CH_2$ from ε-CL at the benzylalkoxide chain end) and $H_a$ ($CH_2$ from ε-CL at the hydroxy end) (Fig. 5). This result shows that the initiation occurs through insertion of a *p*-(chloromethyl)benzyl alkoxy group from compound **1** to ε-caprolactone, giving an aluminum alkoxide as an intermediate product, which further reacts with excess lactones to give polyesters. These results further agree with our expectation that the polymer chain should be capped with one ester

Table 2
Ring-opening polymerization of L-LA initiated by **2** and **3**[a]

| Entry | Ini. | $[M]_0$:$[I]_0$ | *t* (h) | $M_n$ (Calcd)[b] | $M_n$ (NMR)[c] | $M_n$ (GPC)[d] | PDI[d] | Conv[c] (%) |
|---|---|---|---|---|---|---|---|---|
| 1 | **2** | 30:1 | 5 | 2150 | 2050 | 3150 | 1.14 | 95 |
| 2 | **2** | 50:1 | 5.5 | 3450 | 2900 | 4650 | 1.16 | 93 |
| 3 | **2** | 100:1 | 7 | 6450 | 5250 | 7600 | 1.07 | 88 |
| 4 | **2** | 150:1 | 8 | 8750 | 6900 | 8600 | 1.06 | 80 |
| 5 | **3** | 50:1 | 5.5 | 3600 | 2850 | 4900 | 1.16 | 96 |
| 6 | **3** | 100:1 | 6.5 | 6700 | 5500 | 7100 | 1.10 | 91 |
| 7 | **3** | 150:1 | 7.5 | 10 200 | 8750 | 11 300 | 1.06 | 93 |
| 8 | **3** | 200:1 | 8.5 | 13 400 | 11 700 | 15 400 | 1.07 | 92 |

[a] The condition of the polymerization is in 10 mL $CH_2Cl_2$ at 0 °C, 0.05 mmol of **2** and **3** was used in each entry.

[b] Calculated from the molecular weight of L-lactide × $[M]_0/2[I]_0$ × conversion yield + the molecular weight of benzyl alcohol/*p*-(chloromethyl)benzyl alcohol.

[c] Obtained by $^1$H NMR.

[d] Obtained by GPC analysis.

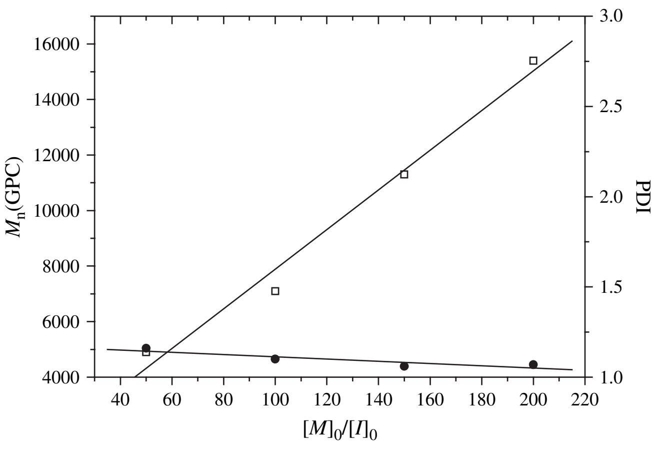


Fig. 6. Polymerization of L-LA initiated by **3** in toluene at 0 °C. The relationship between $M_n$ (GPC) (□) (PDI (●)) of the polymer and the monomer-to-initiator ratio $[M]_0/[I]_0$ is shown.

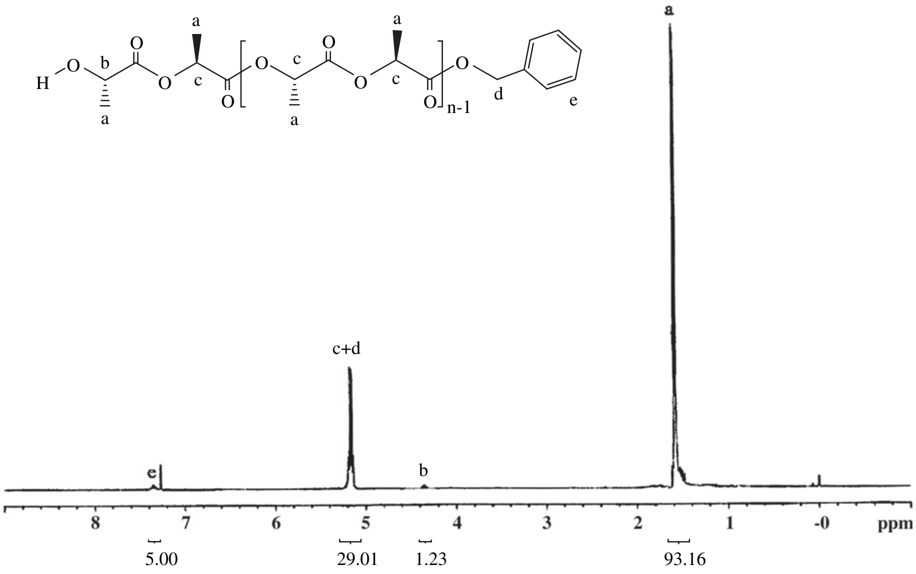


Fig. 7. The $^1$H NMR spectrum of PLLA30 initiated by **2** in $CDCl_3$.

group and with one hydroxyl group. These results are consistent with that found for [(MMPEP)Al(OBn)]$_2$ [19c].

### *3.3. Ring-opening polymerization of benzyl and p-(chloromethyl)benzyl L-lactide initiated by **2** and **3***

Polylactide (PLA) was considered to be a good substitute for replacing nonbioresorbable polymers due to its excellent chemical and mechanical properties [22]. Ring-opening polymerization of L-lactide (L-LA) initiated by complexes **2** and **3** was examined (Table 2). Experimental results indicate that both complexes **2** and **3** are efficient initiators for the ROP of L-lactide. Polymerization goes to completion within 8–8.5 h at 0 °C by using **2** and **3** as an initiator, respectively, and with polydispersity indexes (PDIs) ranging from 1.06 to 1.16 in PLLA with controlled properties. The low PDIs along with a linear relationship between the number-average molecular weight ($M_n$) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) (Fig. 6), suggest that back-biting reactions are negligible. These reactions were further verified with the help of $^1$H NMR spectroscopic study. $^1$H NMR spectrum of PLLA30 and PLLA50 (the numbers 30 and 50 indicate the designed $[M]_0/[I]_0$ ratio) (Figs. 7 and 8, respectively) reveals the polymer chain is capped with a hydroxy group in one end and with benzylalkoxyl or *p*-(chloromethyl)benzyl ester in the other end, respectively.

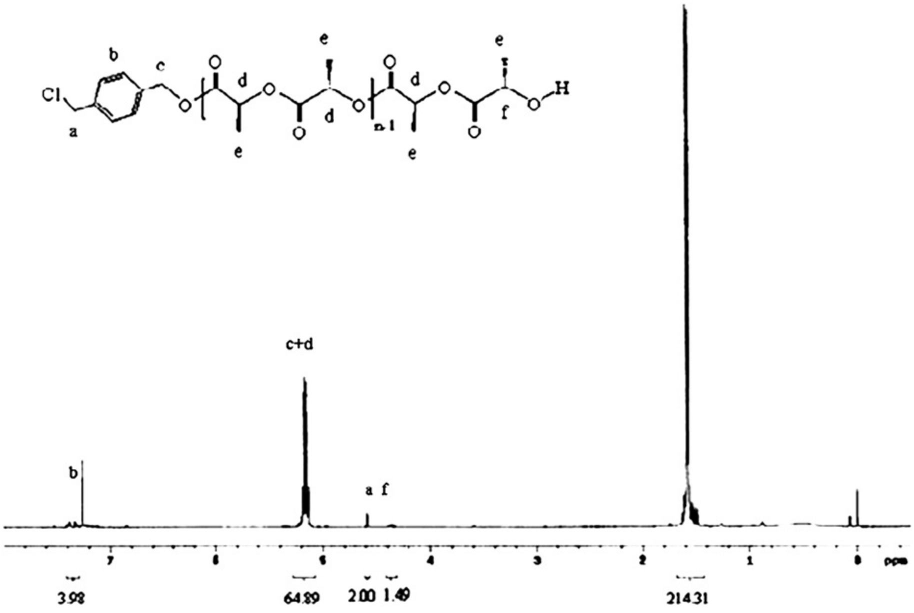


Fig. 8. The $^1$H NMR spectrum of PLLA50 initiated by **3** in $CDCl_3$.

Table 3
Polymerization of PCL-*b*-PAN copolymer[a]

| Entry | PCL | | [AN]/[PCL] | PCL-*b*-PAN | | PAN | $V_{PAN}$:$V_{PCL}$[d] |
|---|---|---|---|---|---|---|---|
| | $M_n$ (NMR)[b] | PDI[c] | | $M_n$ (GPC)[c] | PDI[c] | $M_n$ (NMR)[b] | |
| 1 | 2350 | 1.10 | 270/1 | 58 200 | 1.24 | 96 00 | 78:22 |
| 2 | 1350 | 1.20 | 29/1 | 18 000 | 1.24 | 2000 | 57:43 |
| 3 | 1350 | 1.20 | 58/1 | 24 100 | 1.31 | 4450 | 74:26 |
| 4 | 1350 | 1.20 | 145/1 | 44 620 | 1.34 | 8150 | 84:16 |

[a] The reaction was performed in 25 g (entry 1), 10 g (entry 2) and 20 g (entries 3 and 4) ethylene carbonate at 70 °C, 24 h.

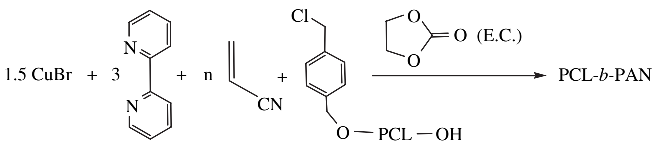
[b] Obtained by $^1$H NMR.

[c] Obtained by GPC.

[d] PCL amorphous density = 1.08 (g/cm$^3$), PAN density = 1.23 (g/cm$^3$) [23].

### 3.4. Preparation of PCL-b-PAN and PLLA-b-PAN copolymers

In this study, a series of PCL-*b*-PAN block copolymers (Table 3) were prepared by the polymerization of acrylonitrile with atom transfer radical polymerization (ATRP) technique developed by Matyjaszewski group by using CuBr/2,2′-bipyridine as a catalyst and functionalized poly(ε-caprolactone) with the number-average molecular weight ($M_n$) 2350 (PDI = 1.10) or 1350 (PDI = 1.20) as a macroinitiator in ethylene carbonate at 70 °C (Scheme 3) [12]. $^1$H NMR spectrum of PCL2350-*b*-PAN9600 (the numbers 2350 and 9600 indicate the molecular weight determined by $^1$H NMR) (Fig. 9) reveals that acrylonitrile has been polymerized and the GPC studies demonstrate the formation of the block copolymer (PDI = 1.24). The large difference between $M_n$ (NMR) and $M_n$ (GPC) is most likely attributable to the character of the PAN segment. The $V_{PAN}$:$V_{PCL}$ ratios were calculated based on the $M_n$ (NMR) results.



Scheme 3.

The synthesis of PLLA-*b*-PAN copolymer was carried out similarly to the method used for the preparation of PCL-*b*-PAN. PLLA50 (the number 50 indicates the designed $[M]_0/[I]_0$ ratio) was obtained by ring-opening polymerization of L-lactide using **3** as an initiator (PDI = 1.26). The $^1$H NMR spectrum (Fig. 10) shows that the peak shown at 4.47 ppm corresponds to ethylene carbonate and the peaks shown at 3.33 and 2.59 ppm are the peaks of DMSO-$d_6$. Further detailed studies for the synthesis of polyacrylonitrile with better stereochemical yields, distribution and morphology are undertaking.

### 3.5. The morphological study for PCL1350-b-PAN2000

Fig. 11 shows the TEM micrograph of PCL1350-*b*-PAN2000 ($f_{PAN}{}^v$ = 57%) [24]. The stained PAN microdomains appear

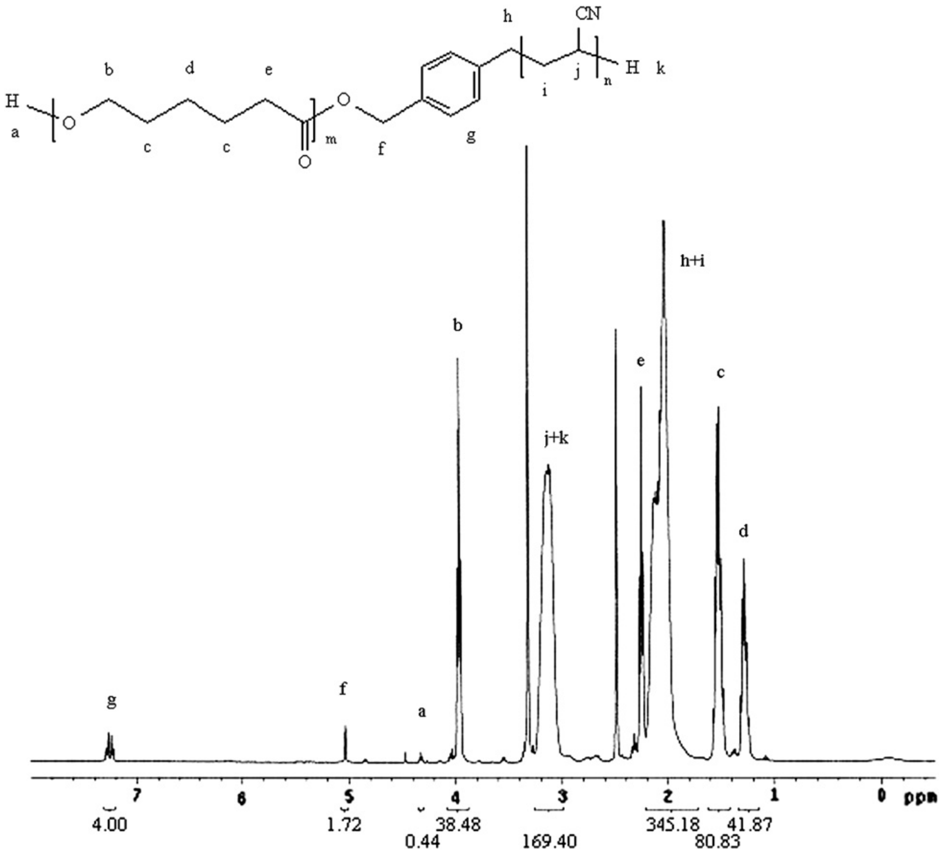
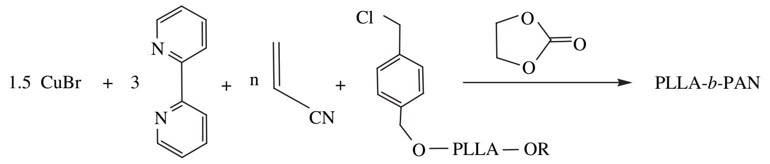


Fig. 9. The $^1$H NMR spectrum of PCL2350-*b*-PAL9600 in DMSO-$d_6$.



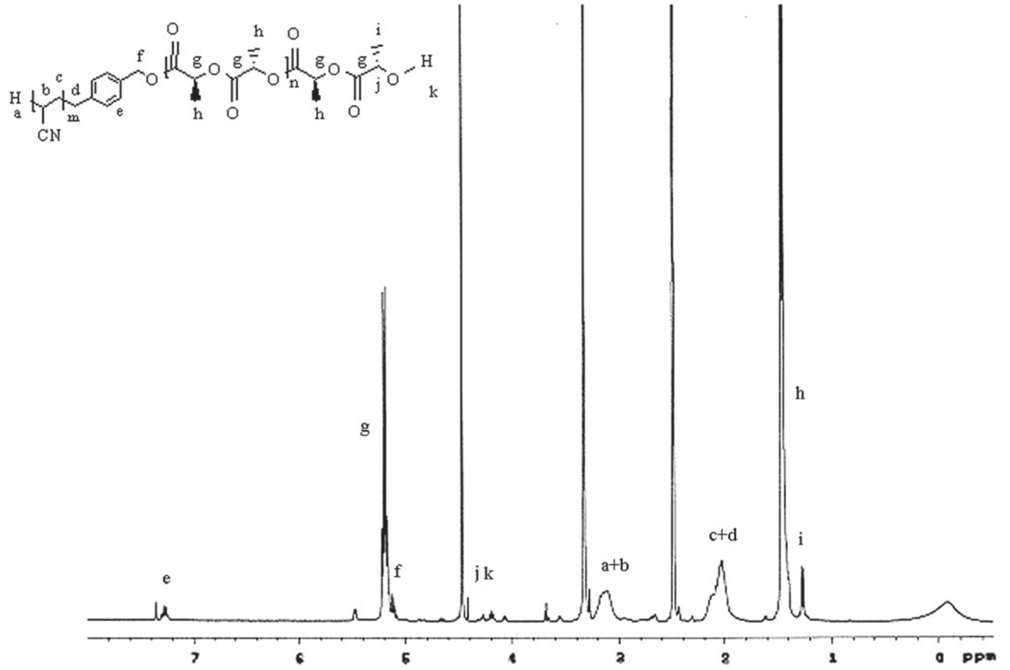


Fig. 10. The $^1$H NMR spectrum of PLLA4300-*b*-PAN in DMSO-$d_6$.

dark while the PCL microdomains appear light. The TEM image of PCL1350-*b*-PAN2000 exhibits typical microphase-separated lamellar morphology with *d*-spacing measured as around 9 nm. Further details of the experimental results are published elsewhere [23].

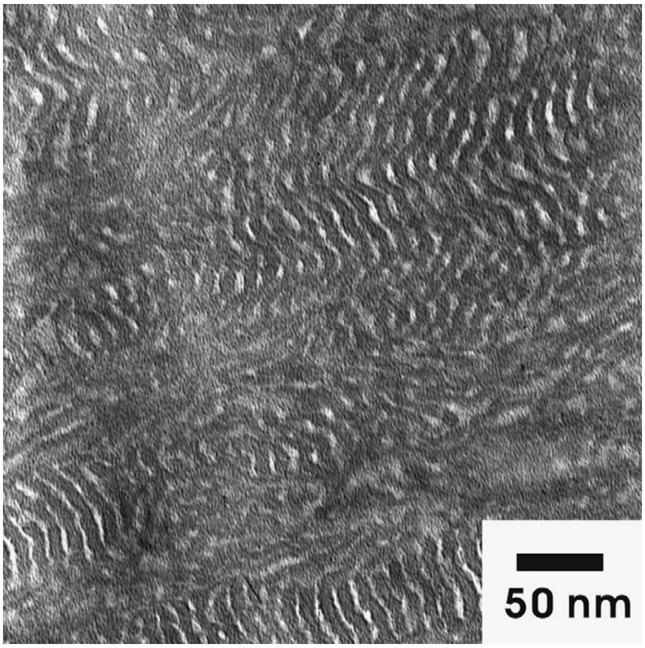


Fig. 11. TEM micrograph of PCL1350-*b*-PAN2000 sample.

## 4. Conclusion

We have designed and synthesized three interesting metal alkoxides **1**–**3** and have demonstrated these alkoxides as efficient catalytic initiators for the ROP of ε-caprolactone or L-lactide. $^1$H NMR studies of polyesters confirm that the initiation occurs through the insertion of the *p*-(chloromethyl)benzyl alkoxy group to ε-caprolactone/L-lactide. The catalytic behavior of complex **1** paved the new way to synthesize as much as 40 folds polymer chains with low PDI. Novel block copolymers, PCL-*b*-PAN and PLLA-*b*-PAN have been prepared and well characterized with GPC and $^1$H NMR studies. Consequently, the self-assembly of PAN-*b*-PCL block copolymer giving microphase-separated nanostructures has been observed by TEM. This method may provide a promising and convenient way for the manufacturing of mesoporous carbon materials.

## Acknowledgement

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## Appendix. Supplementary data

Further details of the crystal structure determination of **1–3** and the GPC figure about PCL2350-*b*-PAN9600 are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2007.05.044.

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[24] $f_{PAN}{}^{v} = V_{PAN}/(V_{PAN} + V_{PCL})$.