Arabian Journal of Chemistry (2014) 7, 209–218

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

Synthesis and characterization of alkoxy derivatives with double-headed initiators for the preparation of poly(ε-caprolactone)-β-polyacrylonitrile (PCL-β-PAN) and poly(L-lactide)-β-polyacrylonitrile (PLLA-β-PAN) copolymers

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Received 13 July 2010; accepted 26 October 2010
Available online 3 November 2010

KEYWORDS

Alkoxy based initiator;
ε-Caprolactone;
L-Lactide;
Polymerization

Abstract The synthesis of simple single source molecular precursor based on metal alkoxides of the type, [(MMPEP)Al(μ-OBnCH_2Cl)]$_2$ (**1**), [(MMPEP-H)Li·(BnOH)]$_2$ (**2**) and [(MMPEP-H)Li·(HOB-*n*CH_2Cl)]$_2$ (**3**) has been reported herein. Complex **1** was prepared by the reaction of [(MMPEP)Al(CH_3)(Et_2O)] with *p*-(chloromethyl)benzyl alcohol. The reaction of 2,2′-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP-H_2) with ″BuLi, BnOH or *p*-(chloromethyl)benzyl alcohol was added to give complexes **2** and **3,** respectively. Among them, only complex **1** shows excellent catalytic properties towards ring-opening polymerization (ROP) of ε-caprolactone. However, complexes **2** and **3** are active for ROP of L-lactide only. Block copolymers of poly(ε-caprolactone)-β-polyacrylonitrile and poly(L-lactide)-β-polyacrylonitrile were synthesized by using a technique known as atom transfer radical polymerization (ATRP) and the ring opening polymerization (ROP). TEM micrograph of PCL-β-PAN shows the microphase property with the help of self-assembly.

1. Introduction

For last one decade, demands for developing new materials have dramatically increased due to their high performance-versus-price ratio (Burchell, 1999). Polyacrylonitrile (PAN) is one of the many reagents used for manufacturing activated carbon materials (Yang and Yu, 1998). The formation of well-oriented nanotube with regular textured is considered to be most expensive, tricky and complicated, it is prepared either by vapor deposition process (Fan et al., 1999). It is a great

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Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.arabjc.2010.10.026

challenge to the synthetic chemist to explore an easy and cheap eco-friendly method by using a mild reaction conditions. Many nanotemplates has been used as a building blocks for their potential applications in polymerization (Rzayev and Hillmyer, 2005; Ha et al., 2004; Zalusky et al., 2002; Bates and Fredrickson, 1999).

A novel, synthetic route, based on block copolymer has been designed to generate nanostructured materials with well-defined properties (Kowalewski et al., 2002, 2003; Tang et al., 2004). Copolymer of poly(ε-caprolactone) and polyacrylonitrile has been reported by blending method (Runt and Rim, 1982; Keroack et al., 1998; Tsarevsky et al., 2002). The preparation of homo- and copolymer polyacrylonitrile was carried out via free radical and anionic polymerization method without having control in the molecular weight and its polydispersites (Nuyken et al., 1992). Matyjaszewski and co-workers reported the synthesis of polyacrylonitrile by using atom transfer radical polymerization (ATRP) technique (Matyjaszewski et al., 1999; Trofimoff et al., 1987; Duda et al., 1990, 2000; Chisholm et al., 2000, 2001, 2005; Chisholm and Delbridge, 2003a,b; Jhurry et al., 2001; Ma et al., 2003, 2005; Taden et al., 2000; Hormnirun et al., 2004; Ishii et al., 2004; Nomura et al., 2002; Zhong et al., 2002; Sawhney et al., 1993; Zhang et al., 1994; Kricheldorf et al., 2000; Aubrecht et al., 2002; Dove et al., 2001; Majerska et al., 2000; Chamberlain et al., 2001; Simic et al., 1997; Spassky et al., 2000; Dittrich and Schulz, 1971; Williams et al., 2002, 2003; Rieth et al., 2002; Webster, 1991; Aida and Inoue, 1996; Meyer et al., 2002). Herein the clean synthesis of complexes has been reported via soft chemical approach for the preparation of block copolymers with well defined catalytic properties (Hawker et al., 1998).

2. Experimental

2.1. General

All manipulations were carried out in a dry nitrogen atmosphere. Solvents used for the synthesis of initiators of PCL and PLLA were dried by refluxing for at least 24 h over sodium/benzophenone (toluene, *n*-hexane and diethyl ether), phosphorus pentaoxide (CH_2Cl_2), or magnesium sulfate (benzyl alcohol). Deuterated solvents were dried over 4 Å molecular sieves. $[(MMPEP)Al(CH_3)(Et_2O)]$ and *p*-(chloromethyl)benzyl alcohol (Pierce et al., 1996) were prepared as reported in the literature. Copper(I) bromide was purified by washing with 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. ^1H 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 by reporting a chemical shifts given in ppm by using the internal standard TMS. Microanalysis was performed by using a Heraeus CHN-O-RAPID instrument. An infrared spectrum was recorded 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-β-PAN). Molecular weight and its distributions were calculated by using polystyrene as standard.

2.2. $[(MMPEP)Al(\mu\text{-}OBnCH_2Cl)]_2$ (**1**)

At 0 °C $[(MMPEP)Al(CH_3)(Et_2O)]$ (1.56 g, 2 mmol) was added into the solution of *p*-(chloromethyl)benzyl alcohol (0.32 g, 2 mmol) in toluene, the reaction mixture was stirred at room temperature for 3 h. After removal of volatile materials under vacuum and the residue was redissolved in toluene and then concentrated. It was heated till the solution become clear. The solution was allowed to cool at room temperature, colorless crystalline solids were obtained after 24 h. Yield: 1.13 g (66%). ^1H NMR ($CDCl_3$, ppm): δ 6.69–7.28 (m, Ph), 4.27 (s, CH_2Cl), 3.19 (s, OCH_2), 2.37 (d, $PhCH_2Ph$, J_{H-H} = 14.8 Hz), 2.04 (d, $PhCH_2Ph$, J_{H-H} = 14.8 Hz), 1.82, 1.58, 1.57, 1.44 (s, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 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 (OCH_2), 45.60 (CH_2Cl), 43.00, 42.25 ($PhC(CH_3)_2Ph$), 33.73, 31.04, 31.02, 30.73($C(CH_3)_2$), 27.98 ($PhCH_2Ph$). 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. $[(MMPEP\text{-}H)Li\cdot(BnOH)]_2$ (**2**)

At 0 °C 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) ($MMPEP\text{-}H_2$) (2.71 g, 4.0 mmol) was taken in diethyl ether, and benzyl alcohol (0.42 mL, 4 mmol) mixture followed by the addition of BuLi (2 mL, 5 mmol in *n*-hexane). The resulting mixture was stirred for 3 h. Removal of volatile materials was undertaken in vacuum and the residue was extracted in toluene. The extract was concentrated, followed by the addition of *n*-hexane. Keeping for 24 h. at room temperature the white solid was obtained. Yield: 2.04 g (65%).

2.4. $[(MMPEP\text{-}H)Li\cdot(HOBnCH_2Cl)]_2$ (**3**)

At 0 °C 2,2-methylene-bis(4,6-di(1-methyl-1-phenylethyl)-phenol) ($MMPEP\text{-}H_2$) (2.71 g, 4.0 mmol) and *p*-(chloromethyl)benzyl alcohol (0.63 g, 4 mmol) were added slowly into ^{n}BuLi (2 mL, 5 mmol in *n*-hexane) in ethyl ether and then the reaction mixture was stirred for 3 h. The volatile materials were removed under vacuum and the residue was redissolved in toluene and then concentrated. On keeping for 24 h a white solid was obtained. Yield: 2.40 g (72%).

2.5. Synthesis of *p*-(chloromethyl)benzyl end-functionalized PCL

The synthesis of PCL-50 (the number 50 indicates the designed $[M]_0/[I]_0$) was carried out. To a stirring solution of $[(MMPEP)Al(\mu\text{-}OBnCH_2Cl)]_2$ (0.09 g, 0.05 mmol) was added ε-CL (0.53 mL, 5.0 mmol) in toluene. The reaction mixture was stirred for 1 h at 50 °C. The reaction was quenched with H_2O; the polymer was precipitated out in *n*-hexane. White precipitate was redissolved in dichloromethane and then precipitated into *n*-hexane and then dried under vacuum to give a white solid. The peaks at 5.12 (–OCH_2Ph–), 4.58 (–OCH_2Cl), 4.05 (–$CH_2OC(=O)$–) and at 3.65 (–CH_2OH) ppm in $CDCl_3$.

2.6. Preparation of PLLA

A [(MMPEP-H)Li·(BnOH)]$_2$ (0.08 g, 0.05 mmol) was added L-LA (0.22 g, 1.5 mmol) in CH_2Cl_2. The reaction mixture was stirred at 0 °C for 5 h. After the removal of volatile materials the residue was redissolved in toluene and then quenched with H_2O. The polymer was precipitated out in *n*-hexane and then redissolved in dichloromethane and then precipitated as a white solid. The peaks at 7.27–7.37 (–CH_2*Ph*) 5.18 (–OC*H* MeC(O)–), and 4.36 (–C*H*MeOH) ppm in $CDCl_3$.

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

A [(MMPEP-H)Li·(HOBnCH_2Cl)]$_2$ (0.09 g, 0.05 mmol) was added with L-LA (0.36 g, 2.5 mmol) in CH_2Cl_2. The reaction mixture was stirred at 0 °C for 5.5 h. After the removal of volatile materials the residue was redissolved in toluene followed by quenching with H_2O. The white polymer was precipitated out in *n*-hexane and then redissolved in dichloromethane and again precipitated out as white solid in *n*-hexane. The peaks at 7.27–7.37 (–CH_2*Ph* –), 5.18 (–OC*H*MeC(O)–), 4.58 (–OCH_2Cl) and 4.36 (–C*H*MeOH) ppm in $CDCl_3$.

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

A 0.33 g (2.25 mmol) CuBr, 0.71 g (4.5 mmol) 2,2-bipyridine and 25 g ethylene carbonate were taken together in a flask and then dried for 1 h. The color of the reaction mixture changes to dark-brown followed by the addition of ethylene carbonate and then heated at 70 °C. By cooling with an addition of *p*-(chloromethyl)benzyl ester end-functionalized PCL (PCL-2350, 3.53 g, 1.5 mmol) in 14.31 g (270 mmol) acrylonitrile and stirred at 70 °C for 24 h. The reaction was quenched with MeOH followed by overnight stirring. The dark yellow powder was obtained after filtration. The powder was dissolved in DMF and then followed by addition of 1 mM EDTA/alkali solution to give light yellow powder. The powder was redissolved in DMF and then filtered through a mixture of MeOH–H_2O (1:1) of Al_2O_3 and the grey solid was obtained. The solid was washed with hot MeOH many times and then finally dried under vacuum to obtain a copolymer. The peaks at 7.23–7.29 (–CH_2*Ph* –), 5.03 (–CH_2Ph–), 3.97 (–$CH_2OC(=O)$–) and 3.12 (–C*H*(CN)–) ppm in DMSO-d_6.

2.9. Synthesis of polylactide-β-polyacrylonitrile copolymer

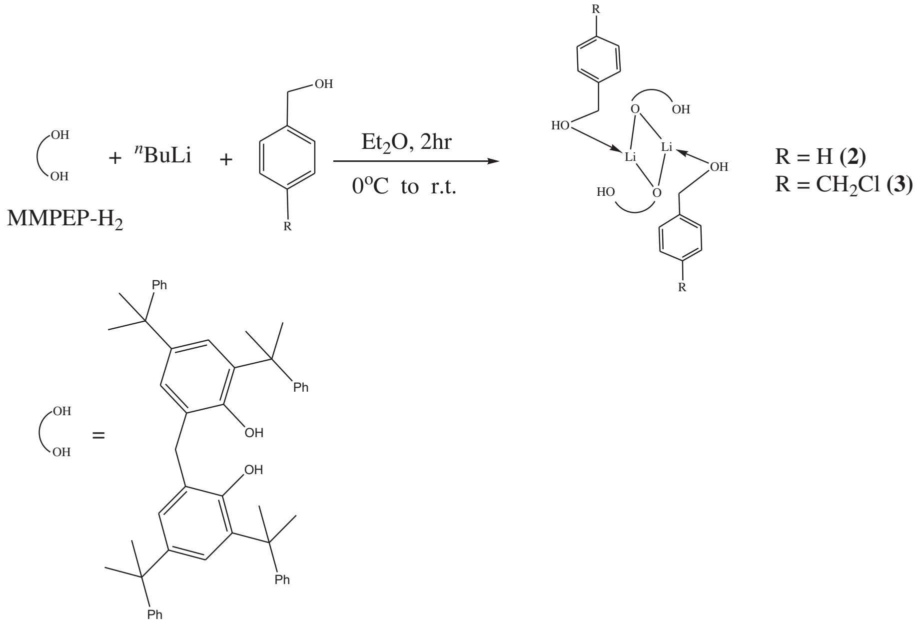
Add 0.22 g (1.5 mmol) CuBr, 0.47 g (3.0 mmol) 2,2′-bipyridine and 20 g ethylene carbonate was taken and then heated to 70 °C in nitrogen atmosphere then cooled to room temperature. Followed by the addition of *p*-(chloromethyl)benzyl ester end-functionalized PLLA in acrylonitrile. The reaction mixture was stirred at 70 °C for 24 h. after quenching the reaction with MeOH a dark-white powder was obtained in good yield.

3. Results and discussion

3.1. Synthesis and characterization

[(MMPEP)Al(μ-OBnCH_2Cl)]$_2$ (**1**) was obtained by the reaction of [(MMPEP)Al(CH_3)(OEt_2)] with an equivalent amount of *p*-(chloromethyl)benzyl alcohol (Pierce et al., 1996) in toluene. ^{1}H NMR studies of **1** reveal two singlet at 4.27 (CH_2Cl) and 3.19 (OCH_2) consistent with the expected structure.

Alkoxy derivatives of lithium were synthesized [(MMPEP-H)Li·(BnOH)]$_2$ (**2**) and [(MMPEP-H)Li·(HOBnCH_2Cl)]$_2$ (**3**). Complex **2** was obtained by the reaction of ^{n}BuLi to the mixture of 2,2′-methylene-bis(4,6-di(1-methyl-1-phenylethyl)phenol) (MMPEP-H_2) with an equal equivalent of



Scheme 1

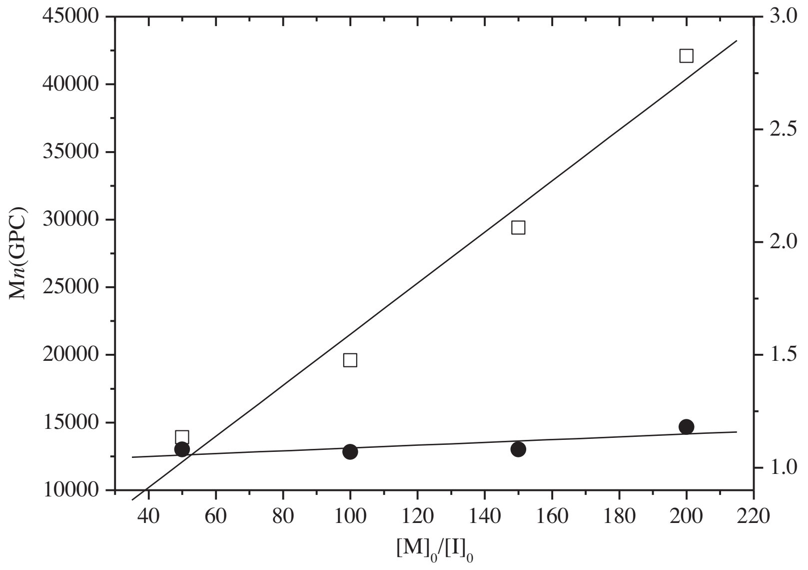


Figure 1 Polymerization of ε-CL initiated by **1** in toluene at 50 °C. The relationship between M_n (GPC) (□) (PDI (●)) of the polymer and the initial ratio $[M]_0/[I]_0$ is shown.

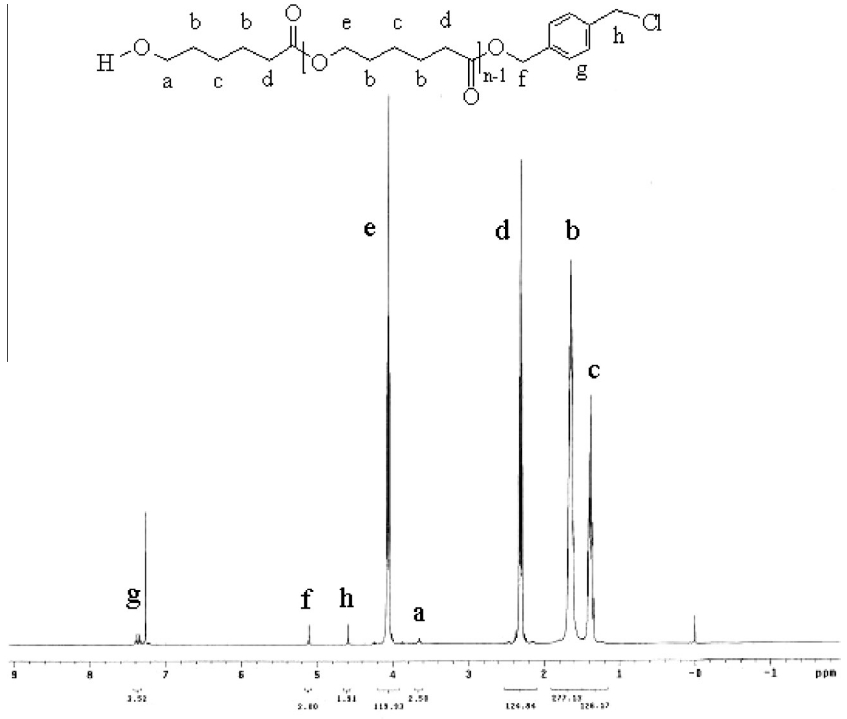


Figure 2 The ^{1}H NMR spectrum of PCL-50 in $CDCl_3$.

BnOH in diethyl ether. ^{1}H NMR ($CDCl_3$, ppm): δ 6.78–7.37 (m, Ph), 5.10 (br, PhO*H*), 4.63 (s, BnO*H*), 3.59 (s, PhCH_2Ph), 1.63, 1.54 (s, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 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*C*H_2), 42.38, 42.10 (Ph*C*$(CH_3)_2$Ph), 32.73, 31.07($C(CH_3)_2$), 29.83 (Ph*C*H_2Ph). 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.

Complex **3** was synthesized by similar method that was used for the preparation of **2** (Scheme 1). ^{1}H NMR ($CDCl_3$, ppm): δ 6.64–7.38 (m, Ph), 5.13 (br, PhO*H*), 4.66 (s, BnO*H*), 4.60 (s, PhCH_2Cl), 3.58 (br, PhCH_2Ph), 1.64, 1.49 (s, CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ 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_2Cl), 42.40, 42.03 (Ph*C*$(CH_3)_2$Ph), 31.04 ($C(CH_3)_2$), 29.75 (Ph*C*H_2Ph). IR (KBr, cm^{-1}): 3527 (s), 3482 (s), 2961 (s), 2866 (m), 1599

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

Entry	$[M]_0$:$[I]_0$:[ROH][b]	Time (h)	M_n (Calcd)[c]	M_n (NMR)[d]	M_n (GPC)[e]	PDI[e]	Conv (%)[d]
1	100:2:0	1	5800	6700	13,900	1.08	99
2	200:2:0	1	10,400	10,600	19,600	1.07	90
3	300:2:0	3	15,700	16,100	29,400	1.08	91
4	400:2:0	5	22,700	23,200	42,100	1.18	99
5	100(100):2:0	1(1)	11,200	11,100	19,200	1.07	99(95)
6	800:2:14	2	5700	6550	11,100	1.05	97
7	800:2:78	1	1300	1350	1950	1.15	93

[a] The reaction condition is in 15 mL toluene at 50 °C and **1** was used 0.05 mmol in each entry.

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

[c] Calculated from the molecular weight of ε-CL times $[M]_0/[I]_0$ times conversion yield.

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

[e] Obtained from GPC analysis.

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

Entry	Initiator	$[M]_0$:$[I]_0$[b]	Time (h)	M_n (Calcd)[c]	M_n (NMR)[d]	M_n (GPC)[e]	PDI[e]	Conv (%)[d]
1	**2**	30:2	5	2150	2050	3150	1.14	95
2	**2**	50:2	5.5	3450	2900	4650	1.16	93
3	**2**	100:2	7	6450	5250	7600	1.07	88
4	**2**	150:2	8	8750	6900	8600	1.06	80
5	**3**	50:2	5.5	3600	2850	4900	1.16	96
6	**3**	100:2	6.5	6700	5500	7100	1.10	91
7	**3**	150:2	7.5	10,200	8750	11,300	1.06	93
8	**3**	200:2	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, **2**and **3** was used 0.05 mmol in each entry.

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

[c] Obtained by ^{1}H NMR.

[d] Obtained by GPC.

[e] Obtained from GPC analysis.

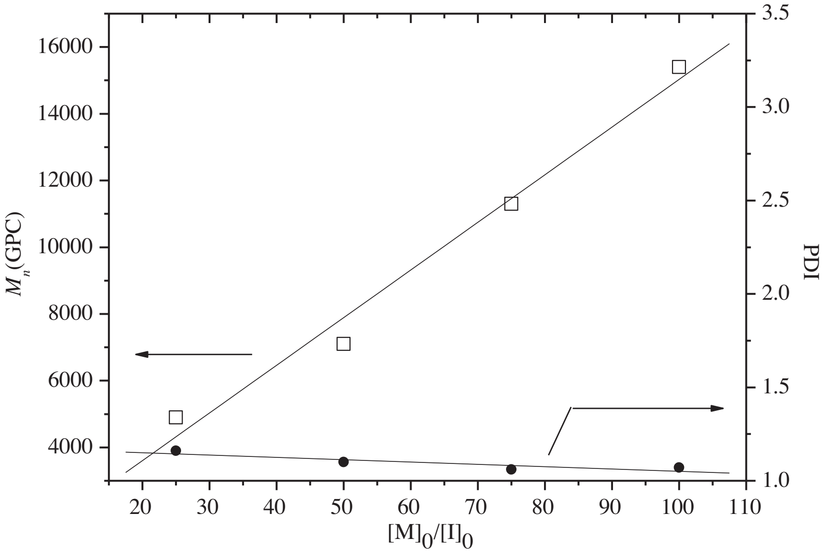


Figure 3 Polymerization of L-LA initiated by **3** in toluene at 0 °C. The relationship between M_n (GPC) (□) (PDI (●)) of the polymer and the initial ratio $[M]_0/[I]_0$ is shown.

(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.

3.2. Ring-opening polymerization ε-caprolactone initiated by 1

The catalytic behavior of **1** towards ROP of ε-caprolactone (ε-CL) has been systematically examined and it was observed that

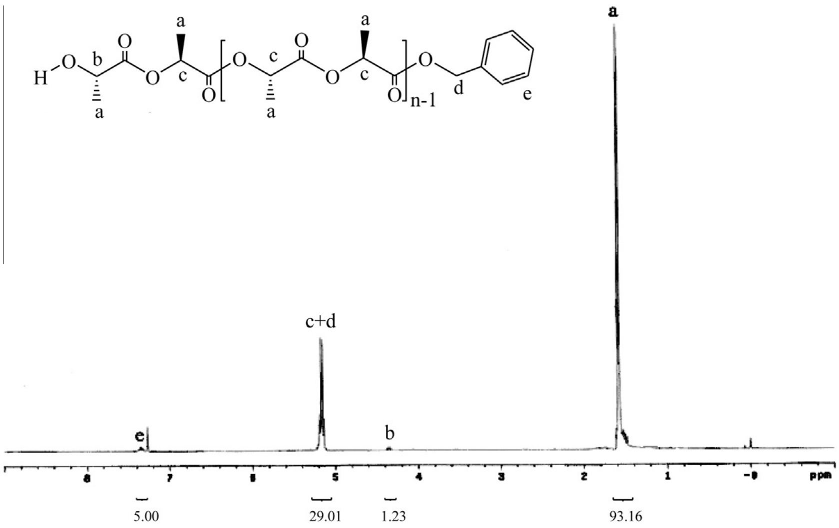


Figure 4 The ^{1}H NMR spectrum of PLLA-15 in $CDCl_3$.

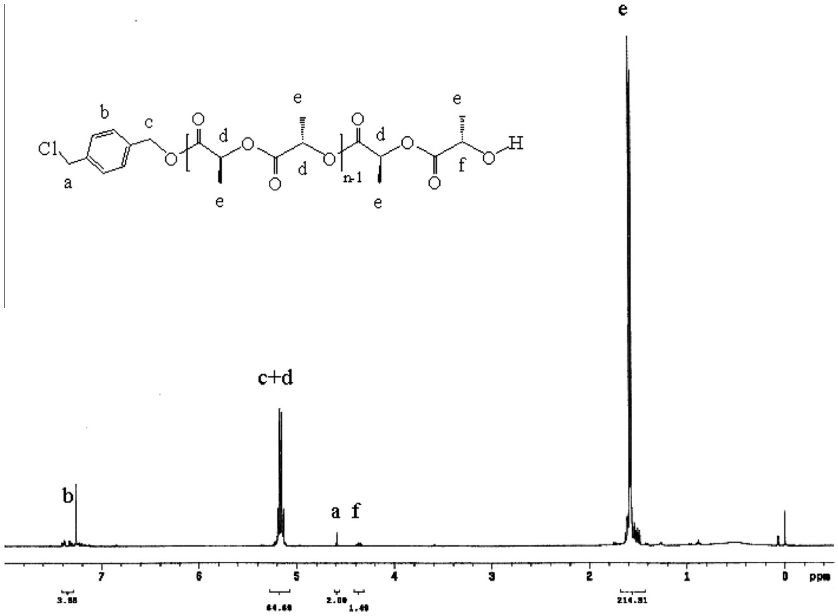


Figure 5 The ^{1}H NMR spectrum of PLLA-50 in $CDCl_3$.

Table 3 Polymerization of acrylonitrile and PCL by ATRP.[a]

Entry	Temp. (°C)/time (h)	PCL		[PCL]/[AN]	PCL-PAN		PAN	V_{PAN}:V_{PCL}[d]
		M_n (NMR)[b]	PDI[c]		M_n (GPC)[c]	PDI[c]	M_n (NMR)[b]	
1	70/24	2350	1.10	1/270	58,200	1.24	9600	78:22
2	70/24	1350	1.20	1/29	18,000	1.24	2000	57:43
3	70/24	1350	1.20	1/58	24,100	1.31	4450	74:26
4	70/24	1350	1.20	1/145	44,620	1.34	8150	84:16

[a] The reaction was in 25 g, (entry 1) 10 g (entry 2) and 20 g (entry 3 and 4) ethylene carbonate.

[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.

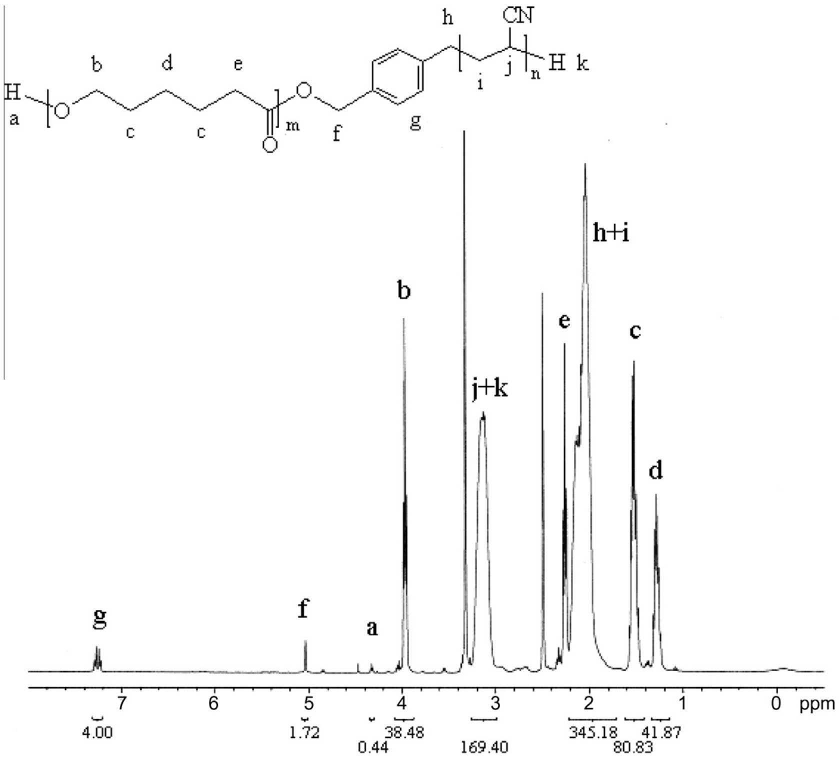


Figure 6 The ^{1}H NMR spectrum of PCL-β-PAL in $CDCl_3$.

the polymerization of ε-CL proceed smoothly. GPC analyses reveal that poly(ε-caprolactone) formation takes place with the help of initiator **1** having PDI value ranging from 1.07 to 1.18, with controlled polymer properties. The linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) has been shown in Fig. 1. These reactions are useful for designing of biomedical material due to the presence of limited amount of metal content. It was found that when the reaction was performed in the higher [*p*-(chloromethyl)benzyl alcohol/initiator] ratio, the conversion rate is much faster. ^{1}H NMR spectrum of PCL-50 gives an intensity ratio close to **1** between H_e (CH_2 from ε-CL at the benzyloxide chain end) and H_a (CH_2 from ε-CL at the hydroxy end) (Fig. 2). These result support that the initiation occurs through insertion of a *p*-(chloromethyl)benzyl alkoxy group from compound **1** to ε-caprolactone, giving an alkoxide as an intermediate product (see Table 1).

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

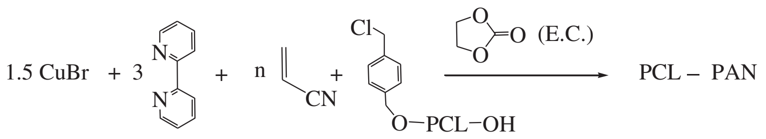
Due to excellent chemico-mechanical properties of PLA are considered to be a good substitute for nonbioresorbable polymers (Vert et al., 1995). Ring-opening polymerization of L-lactide (L-LA) by complexes **2** and **3** was examined (Table 2). Experimental results indicate that both complexes **2** and **3** are used as efficient initiators for the ROP of L-lactide. Polymerization goes to completion within 8 h at 0 °C with polydispersity indexes (PDIs) range from 1.06 to 1.16 with controlled properties in PLLA. The low PDIs value support a linear relationship between the number-average molecular weight (M_n) and the monomer-to-initiator ratio ($[M]_0/[I]_0$) (Fig. 3), suggesting the absence of back-biting reactions. These reactions were further verified with the help of ^{1}H NMR studies. ^{1}H NMR spectrum of PLLA-15,50 (the number of 15,50 indicates the designed $[M]_0/[I]_0$ ratio) (Fig. 4) indicates that the polymer chain is capped with benzyl alcohol in one end, *p*-(chloromethyl)benzyl ester and other end with hydroxyl end, respectively (see Fig. 5).

3.4. *Preparation of PCL-β-PAN*

PCL-β-PAN was prepared by the polymerization of acrylonitrile with atom transfer radical polymerization (ATRP) technique by using CuBr/2,2-bipyridine as a catalyst which leads to the formation of poly(ε-caprolactone) with an average molecular weight (M_n) 2350 (PDI = 1.10) by using ethylene carbonate as a macroinitiator at 70 °C (Matyjaszewski et al., 1999) (see Table 3). ^{1}H NMR spectrum of PCL-β-PAN was determined by ^{1}H NMR (Fig. 6) shows that acrylonitrile has been polymerized and the GPC studies support the formation of block copolymer (PDI = 1.24) (see Scheme 2).

3.5. *Preparation of PLLA-β-PAN*

The synthesis of PLLA-β-PAN was carried out in a similar fashion as used for the preparation of PCL-β-PAN. PLLA-50 was obtained by ring-opening polymerization of L-lactide by using **3** as an initiator (PDI = 1.26). The PDI value of PLLA-β-PAN was compared with PCL-β-PAN. The ^{1}H NMR (Fig. 7) shows the peak at 4.47 ppm which corresponds to ethylene carbonate and the peaks at 3.33 and 2.59 ppm are due to the presence of DMSO-d_6. Depending on the



Scheme 2

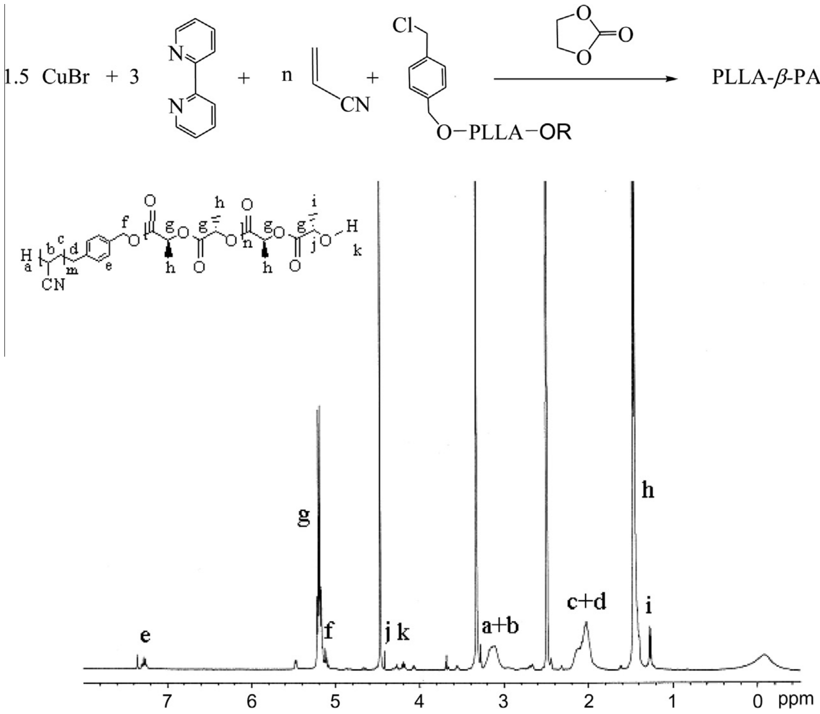
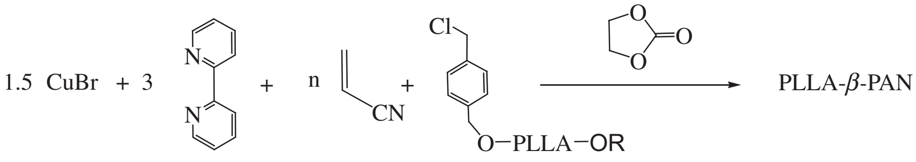


Figure 7 The ^{1}H NMR Spectrum of PLLA-β-PAN in *d*-DMSO.



Scheme 3

concentration of precursor, temperature and reaction time, the synthesis of polyacrylonitrile is underway with good stereochemical yield (see Scheme 3).

3.6. The morphological study for PCL-β-PAN

Fig. 8 shows the TEM micrograph of PCL-β-PAN ($f^{V}_{PAN} = 78\%$). Bulk samples of the block copolymers were prepared by solution casting. The PAN-β-PCL was taken in DMF with 100 mg/mL, for 3 days. After solvent removal the samples was annealed in vacuum oven at 160 °C for 12 h. The carbonization procedure was carried out for 2 h at 260 °C in an Ar atmosphere. The specimens for TEM are embedded in epoxy and subsequently sectioned by ultramicrotome with specimen were stained by RuO$_4$. The stained PAN microdomains appear dark while the PCL microdomains appear light. TEM image exhibits a typical microphase-separated by lamellar morphology with d-spacing around 19 nm in the microphase.

4. Conclusion

The synthesis of metal alkoxy derivative **1**–**3** has demonstrated their use as efficient catalytic initiators for the ROP of ε-caprolactone/L-lactide. ^{1}H NMR studies supports that the initiation occurs with the help of insertion of the *p*-(chloromethyl)benzyl alkoxy group to ε-caprolactone/L-lactide. The catalytic properties help to synthesize polymer-chains with low PDI with good stereochemical properties. Novel block copolymers have been prepared and well characterized. TEM studies support the formation of block copolymer of PCL-β-PAN with good morphological properties having good compatibility and phase distribution.

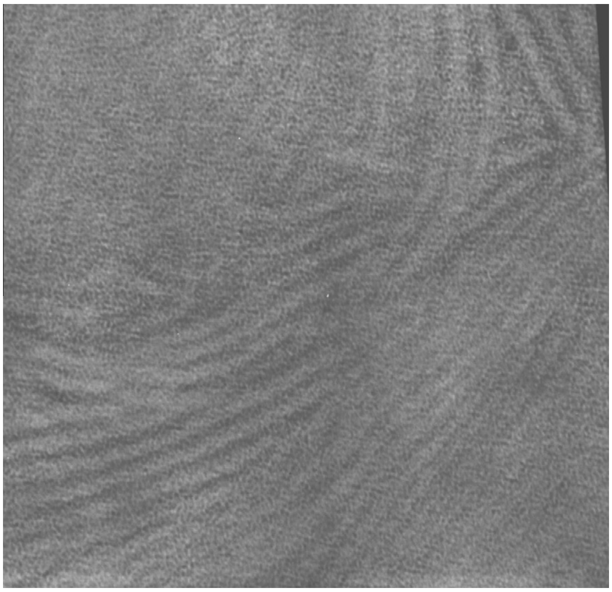


Figure 8 TEM micrograph of PCL-β-PAN samples.

References

Aida, T., Inoue, S., 1996. Metalloporphyrins as initiators for living and immortal polymerizations. Acc. Chem. Res. 29, 39.

Aubrecht, K.B., Hillmyer, M.A., Tolman, W.B., 2002. Polymerization of lactide by monomeric Sn(II) alkoxide complexes. Macromolecules 35, 644.

Bates, F.S., Fredrickson, G.H., 1999. Block copolymers – designer soft materials. Phys. Today 52, 32.

Burchell, T.D. (Ed.), 1999. Carbon Materials for Advanced Technologies. Pergamon, Amsterdam, Oxford.

Chamberlain, B.M., Cheng, M., Moore, D.R., Ovitt, T.M., Lobkovsky, E.B., Coates, G.W., 2001. Polymerization of lactide with zinc and magnesium β-diiminate complexes: stereocontrol and mechanism. J. Am. Chem. Soc. 123, 3229.

Chisholm, M.H., Delbridge, E.E., 2003a. A study of the ring-opening of lactides and related cyclic esters by Ph_2SnX_2 and Ph_3SnX compounds ($X = NMe_2$, OR). New J. Chem. 27, 1167.

Chisholm, M.H., Delbridge, E.E., 2003b. A study of the ring-opening polymerization (ROP) of L-lactide by Ph_2SnX_2 precursors ($X = NMe_2$, OPri): the notable influence of initiator group. New J. Chem. 27, 1177.

Chisholm, M.H., Eilerts, N.W., Huffman, J.C., Iyer, S.S., Pacold, M., Phomphrai, K., 2000. Molecular design of single-site metal alkoxide catalyst precursors for ring-opening polymerization reactions leading to polyoxygenates. 1. Polylactide formation by achiral and chiral magnesium and zinc alkoxides, (η^3-L)MOR, where L = trispyrazolyl- and trisindazolylborate ligands. J. Am. Chem. Soc. 122, 11845.

Chisholm, M.H., Huffman, J.C., Phomphrai, K., 2001. Monomeric metal alkoxides and trialkyl siloxides: (BDI)Mg(OtBu)(THF) and (BDI)Zn(OSiPh3)(THF). Comments on single site catalysts for ring-opening polymerization of lactides. J. Chem. Soc., Dalton Trans., 222.

Chisholm, M.H., Patmore, N.J., Zhou, Z.P., 2005. Concerning the relative importance of enantiomorphic site vs. chain end control in the stereoselective polymerization of lactides: reactions of (R,R-salen)- and (S,S-salen)-aluminum alkoxides $LAlOCH_2R$ complexes ($R = CH_3$ and S-CHMeCl). Chem. Commun. 1, 127.

Dittrich, W., Schulz, R.C., 1971. Angew. Makromol. Chem. 15, 109.

Dove, A.P., Gibson, V.C., Marshall, E.L., White, A.J.P., Williams, D.J., 2001. A well defined tin(II) initiator for the living polymerisation of lactide. Chem. Commun., 283.

Duda, A., Florjanczyk, Z., Hofman, A., Slomkowski, S., Penczek, S., 1990. Living pseudoanionic polymerization of ε-caprolactone poly(ε-caprolactone) free of cyclics and with controlled end groups. Macromolecules 23, 1640.

Duda, A., Penczek, S., Kowalski, A., Libiszowski, J., 2000. Polymerizations of ε-caprolactone and L,L-dilactide initiated with stannous octoate and stannous butoxide—a comparison. Macromol. Symp. 153, 41.

Fan, S., Chapline, M.G., Franklin, N.R., Tombler, T.W., Cassell, A.M., Dai, H., 1999. Self-oriented regular arrays of carbon nanotubes and their field emission properties. Science 283, 512.

Ha, J.M., Wolf, J.H., Hillmyer, M.A., Ward, M.D., 2004. Polymorph selectivity under nanoscopic confinement. J. Am. Chem. Soc. 126, 3382.

Hawker, C.J., Hedrick, J.L., Malmström, E.E., Trollsås, M., Mecerreyes, D., Moineau, G., Jérôme, R., 1998. Dual living free radical and ring opening polymerizations from a double-headed initiator. Macromolecules 31, 213.

Hormnirun, P., Marshall, E.L., Gibson, V.C., White, A.J.P., Williams, D.J., 2004. Remarkable stereocontrol in the polymerization of racemic lactide using aluminum initiators supported by tetradentate aminophenoxide ligands. J. Am. Chem. Soc. 126, 2688.

Ishii, R., Nomura, N., Kondo, T., 2004. Stereoselective bulk polymerization of racemic lactide for stereo block poly(racemic lactide) using an achiral aluminum complex. Polym. J. 36 (3), 261.

Jhurry, D., Bhaw-Luximon, A., Spassky, N., 2001. Synthesis of polylactides by new Al-Schiff's base complexes. Macromol. Symp. 175, 67.

Keroack, D., Zhao, Y., Prud'homme, R.E., 1998. Molecular orientation in crystalline miscible blends. Polymer 40, 243.

Kowalewski, T., Tsarevsky, V.N., Matyjaszewski, K., 2002. Nanostructured carbon arrays from block copolymers of polyacrylonitrile. J. Am. Chem. Soc. 124, 10632.

Kowalewski, T., McCullough, R.D., Matyjazawski, K., 2003. Complex nanostructured materials from segmented copolymers prepared by ATRP. Eur. Phys. J. E 10, 5.

Kricheldorf, H.R., Kreiser-Saunders, I., Stricker, A., 2000. Polylactones 48. $SnOct_2$-initiated polymerizations of lactide: a mechanistic study. Macromolecules 33, 702.

Ma, H.Y., Spaniol, T.P., Okuda, J., 2003. Rare earth metal complexes supported by 1,ω-dithiaalkanediyl-bridged bis(phenolato) ligands: synthesis, characterization and ring-opening polymerization catalysis of L-lactide. J. Chem. Soc., Dalton Trans., 4770.

Ma, H.Y., Melillo, G., Oliva, L., Spaniol, T.P., Englert, U., Okuda, J., 2005. Aluminium alkyl complexes supported by [OSSO] type bisphenolato ligands: synthesis, characterization and living polymerization of rac-lactide. J. Chem. Soc., Dalton Trans., 721.

Majerska, K., Duda, A., Penczek, S., 2000. Kinetics and mechanism of cyclic esters polymerisation initiated with tin(II) octoate. 4. Influence of proton trapping agents on the kinetics of ε-caprolactone and L,L-dilactide polymerization. Macromol. Rapid Commun. 21, 1327.

Matyjaszewski, K., Jo, S.M., Paik, H.-J., Shipp, D.A., 1999. An investigation into the CuX/2,2′-bipyridine (X = Br or Cl) mediated atom transfer radical polymerization of acrylonitrile. Macromolecules 32, 6431.

Meyer, U., Palmans, A.R.A., Loontjens, T., Heise, A., 2002. Enzymatic ring-opening polymerization and atom transfer radical polymerization from a bifunctional initiator. Macromolecules 35, 2873.

Nomura, N., Ishii, R., Akakura, M., Aoi, K., 2002. Communication stereoselective ring-opening polymerization of racemic lactide using aluminum-achiral ligand complexes: exploration of a chain-end control mechanism. J. Am. Chem. Soc. 124, 5938.

Nuyken, O., Latterman, W., Dannhorn, G., Vogel, R., 1992. Modifizierung von homo- und copolymeren des epichlorhydrins durch polymeranaloge umsetzungen. Makromol. Chem. 193, 1057.

Pierce, M.E., Harris, G.D., Islam, Q., Radesca, L.A., Storace, L., Waltermire, R.E., Wat, E., Jadhav, P.K., Emmett, G.C., 1996. Stereoselective synthesis of HIV-1 protease inhibitor, DMP 323. J. Org. Chem. 61, 444.

Rieth, L.R., Moore, D.R., Lobkovsky, E.B., Coates, G.W., 2002. Single-site β-diiminate zinc catalysts for the ring-opening polymerization of β-butyrolactone and β-valerolactone to poly(3-hydroxyalkanoates). J. Am. Chem. Soc. 124, 15239.

Runt, J., Rim, P.B., 1982. Effect of preparation conditions on the development of crystallinity in compatible polymer blends: poly(styrene-co-acrylonitrile)/poly(ε-caprolactone). Macromolecules 15, 1018.

Rzayev, J., Hillmyer, M.A., 2005. Nanoporous polystyrene containing hydrophilic pores from an ABC triblock copolymer precursor. Macromolecules 38, 3.

Sawhney, A., Pathak, C.P., Hubbell, J.A., 1993. Bioerodible hydrogels based on photopolymerized poly(ethylene glycol)-co-poly(alpha-hydroxy acid) diacrylate macromers. Macromolecules 26, 581.

Simic, V., Spassky, N., Hubert-Pfalzgraf, I.G., 1997. Ring-opening polymerization of D,L-lactide using rare-earth μ-oxo isopropoxides as initiator systems. Macromolecules 30, 7338.

Spassky, N., Simic, V., Montaudo, M.S., Hubert-Pfalzgraf, L.G., 2000. Inter- and intramolecular ester exchange reactions in the ring-opening polymerization of (D,L)-lactide using lanthanide alkoxide initiators. Macromol. Chem. Phys. 201, 2432.

Taden, I., Kang, H.C., Massa, W., Spaniol, T.P., Okuda, J., 2000. Alcoholysis of aluminum alkyls supported by bulky phenoxide ligands: synthesis, characterization, and ε-caprolactone polymerization activity of two dimeric aluminum isopropoxides. Eur. J. Inorg. Chem., 441.

Tang, C., Qi, K., Wooley, K.L., Matyjazawski, K., Kowalewski, T., 2004. Well-defined carbon nanoparticles prepared from water-soluble shell cross-linked micelles that contain polyacrylonitrile cores. Angew. Chem. 43, 2783.

Trofimoff, L., Aida, T., Inoue, S., 1987. Formation of poly(lactide) with controlled molecular weight. Polymerization of lactide by aluminum porphyrin. Chem. Lett., 991.

Tsarevsky, N.V., Sarbu, T., Göbelt, B., Matyjaszewski, K., 2002. Synthesis of styrene–acrylonitrile copolymers and related block copolymers by atom transfer radical polymerization. Macromolecules 35, 6142.

Vert, M., Schwarch, G., Coudane, J., 1995. Present and future of PLA polymers. J. Macromol. Sci., Pure Appl. Chem. A32, 787.

Webster, O.W., 1991. Living polymerization methods. Science 251, 887.

Williams, C.K., Brooks, N.R., Hillmyer, M.A., Tolman, W.B., 2002. Metalloenzyme inspired dizinc catalyst for the polymerization of lactide. Chem. Commun., 2132.

Williams, C.K., Breyfogle, L.E., Choi, S.K., Nam, W., Young, V.G., Hillmyer, M.A., Tolman, W.B., 2003. A highly active zinc catalyst for the controlled polymerization of lactide. J. Am. Chem. Soc. 125, 11350.

Yang, M.-C., Yu, D.-G., 1998. Influence of activation temperature on the properties of polyacrylonitrile-based activated carbon hollow fiber. J. Appl. Polym. Sci. 68, 1331.

Zalusky, A.S., Roberto Olayo-Valles, R., Wolf, J.H., Hillmyer, M.A., 2002. Ordered, nanoporous polymers from polystyrene–polylactide block copolymers. J. Am. Chem. Soc. 124, 12761.

Zhang, X., MacDonald, D.A., Goosen, M.F.A., McAuley, K.B., 1994. Mechanism of lactide polymerization in the presence of stannous octoate: the effect of hydroxy and carboxylic acid substances. J. Polym. Sci., Part A: Polym. Chem. 32, 2965.

Zhong, Z.Y., Dijkstra, P.J., Feijen, J., 2002. [(salen)Al]-mediated, controlled and stereoselective ring-opening polymerization of lactide in solution and without solvent: synthesis of highly isotactic polylactide stereocopolymers from racemic D,L-lactide. Angew. Chem., Int. Ed. 41, 4510.