Preparation of single-site tin(IV) compounds and their use in the polymerization of ε-caprolactone

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ABSTRACT
Butyltin(IV) carboxylate compounds were obtained by reactions of butyltrichlorotin(IV) with potassium pivalate, perfluoroheptanoate, methacrylate, 2,6-pyridinedicarboxylate, and phthalate. The synthesized complexes were fully characterized by nuclear magnetic resonance (1H-, 13C-NMR), Fourier transform infrared (FTIR), mass spectroscopies (MS) and elemental analysis. These tin complexes were used as catalysts for the ring opening polymerization of ε-caprolactone and the conversion of monomers to polymers was completed in just 1 h. The structures of polymers were characterized by a combination of spectroscopic techniques (NMR, FTIR, MS), differential scanning calorimeter (DSC) and gel permeation chromatography. In this study, the ε-caprolactone polymers with different average molecular weights between 5000 and 40,000 Da having a regular structure were obtained.

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Single-site tin catalyst; carboxylates; ε-caprolactone; ring-opening; NMR

1. Introduction
Organotin(IV) derivatives show variety of applications ranging in all sorts of biological activities as anticancer, antiviral, antibacterial and antifungal agents, wood preservatives, pesticides, etc., precursors for hybrid inorganic–organic nano and non-linear optical materials, catalysts for organic carbon–carbon coupling and ring opening processes.[1–5] Despite their broad utilities, it is surprising that there is very little information about the synthesis of single-site organotin derivatives and their usage as catalysts in the ring opening of cyclic esters such as ε-caprolactone or L-lactide.[6,7] The single-site catalyst has a general formula of LnRMX (M: Metal, R: alkyl or aryl). The steric and electronic properties of the ancillary ligands (Ln) adjust the bonding of the metal center to the ligands and influence the activity and stereo-selectivity of the catalysts. The initiating group, X, affects the polymerization activity of the compounds.[8–10] Therefore, it is important to synthesize new organotin derivatives by appropriate combinations of Ln and X to produce efficient catalysts which can precisely control the polymerization rate, molecular weight and polymer stereo-chemistry in polymerization reactions. In order to see their catalytic activity in the ring opening polymerization (ROP) of cyclic esters, ε-caprolactone or lactide was chosen as a monomer because of their applications in versatile areas such as drug delivery systems, medical devices, dentistry, bone and tissue engineering.[11–13] Poly-ε-caprolactones (PCL) is a hydrophobic and semi-crystalline polymer which has good solubility, low melting point (59–64 °C) and exceptional blend-compatibility. These properties have stimulated extensive research into its potential application in the medical field.[11–13]

Firstly in this context, the synthesis and characterization of a family of single-site butyltin(IV) pivalate, perfluoroheptanoate, methacrylate, phthalate, and 2,6-pyridinedicarboxylate compounds were reported. Secondly, the study of the title compounds in the ROP of ε-caprolactone was included. Finally, the obtained PCL were fully characterized by Fourier transform infrared (FTIR), 1H-NMR, 13C-NMR, mass spectroscopies (MS) and gel permeation chromatography (GPC).

2. Experimental
2.1. Materials and instruments
Butyltrichlorotin(IV) (BuSnCl3, 95%, Alfa Aesar), potassium hydroxide reagent (KOH, 85% min, Merck), pivalic acid (PivH, 99%, Merck), methacrylic acid (MAcH, 98%, Fluka), perfluoroheptanoic acid (PFHH, 99%, Sigma), phthalic acid

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(PHH, 100%, Merck), 2,6-pyridinedicarboxylic acid, (PyDH, 99%, Aldrich), ε-caprolactone (ε-CL, 99%, Alfa Aesar) were used as received. Ethanol (99.8%, Sigma-Aldrich) and toluene (99.7% Sigma-Aldrich) were dried over activated 4Å molecular sieves before use.

The infrared spectra of butyltin(IV) compounds, potassium carboxylates and PCL were recorded on a Bruker Tensor 27 FTIR spectrophotometer using single reflection ATR universal plate of diamond crystal. The K-, Sn-compounds, and PCL were scanned from 400 to 4000 cm⁻¹ with a resolution of 4 cm⁻¹. The elemental analysis was carried out with the Costech ECS 4010 CHNS-O elemental analyzer. Differential scanning calorimeter (DSC, Metler Toledo DSC 1 Star System) analysis was performed to obtain thermal properties of PCL. The films were heated from −10 to 100 °C at a heating rate of 10 °C/min under a nitrogen gas in order to prevent oxidative degradation. GPC analysis was performed at 30 °C on a Shimadzu prominence GPC system equipped with a RID-10A refractive index detector, a LC-20AD solvent delivery unit, a CTO-10AS column oven and a set of two columns, PSS SDV 5 μL 1000 Å and PSS SDV 5 μL 50 Å. THF (HPLC grade) was used as the mobile phase at 1.0 mL/min. The sample concentration was 2 mg/mL and the injection volume was 20 μL. The calibration curve was made with polystyrene standards covering the molecular weight range from 162 to 67,000 Da.

3. Preparation of potassium carboxylates

3.1. Preparation of potassium phthalate

Phthalic acid (6.0 mmol, 1.0 g) was added to the solution of KOH (12.0 mmol, 0.79 g) in 15 ml distilled water. The reaction was stirred at RT for 30 min and then the solvent water was removed at 65 °C by vacuum evaporator. The white solid was washed two times with ethanol and one time with toluene and dried under vacuum. Elemental analysis, C₉H₅O₄K₂. Found: C, 38.85; H, 1.60%. Calculated: C, 39.65; H, 5.04%. TOF MS + (solvent-ethanol): 873.05 Da [(CH₃COO)₂SnCl₂(C₆H₄OH)₂ + H]^+. 756.96 Da [(CH₃COO)₂Sn(C₆H₄OH)₂ + H]^+. 538.93 Da [(CH₃COO)₂Sn(C₆H₄)(C₆H₅CH₂ + H)]^+. 1H-NMR, CDCl₃, ppm: δ: 0.94 (t, 6H, −CH₃), 1.21 (s, 36H, C(CH₃)₃), 1.45 (m, 4H, γ-CH₂), 1.69 (m, 4H, β-CH₂), 1.83 (m, 4H, α-CH₂). 13C-NMR, CDCl₃, ppm: δ: 13.64 (CH₃), 25.52 (γ-CH₂), 27.11 (β-CH₂), 27.19 (α-CH₂), 27.41 (C(CH₃)₃), 188.3 (COO terminal-bidentate), 186.9 (COO bridging-bidentate). FTIR (cm⁻¹): 2965, 2930, 2870, 1553, 1484, 1423, 1371, 1227, 880, 786, 686. [Sn−CH₂CH₂−CH₂−CH₂−Sn]₂.

4. Preparation of butyltin(IV) carboxylates

4.1. Preparation of butylchlorobis(pivalato)tin(IV) compound

2(CH₃)₂CCOOK + BuSnCl₃ → 1/2[But(CH₃)₂CCOO]₂SnCl₂

Potassium pivalate (1.68 g, 12.0 mmol) was added to the solution of butyltrichlorotin (1.79 g, 6.0 mmol) in 30 ml of ethanol and then solution was refluxed for 3 h. After refluxing, the solvents were removed under vacuum at 50 °C to give a colorless liquid. To remove KCl, the liquid product was dissolved in ~20 ml of toluene and then the white solid was removed by filtration. The solvent toluene was removed from filtrate under vacuum at 65 °C to give colorless liquid product. Elemental analysis: (C₅H₁₀O₄Sn)₂Mw = 827.04 g/mol. Calculated: C, 40.66; H, 6.58%. Found: C, 40.10; H, 6.40%. TOF MS + (solvent-ethanol): 1242, 948, 827.

4.2. Preparation of butylchlorobis(methacrylato)tin(IV) compound

2(CH₃)₂CCOOK + BuSnCl₃ → 1/2[But(CH₃)₂CCOO]₂SnCl₂

By a similar procedure to 4.1, potassium methacrylate (0.37 g, 3.0 mmol) and butyltrichlorotin (0.44 g, 1.5 mmol) gave [But(CH₃)₂CCOO]₂SnCl₂ as a colorless liquid. Elemental analysis (C₅H₁₀O₄Sn)₂Mw = 762.88 g/mol. Calculated: C, 37.79; H, 5.02%. Found: C, 37.26; H, 5.04%. TOF MS + (solvent-ethanol): 801.0 Da [(CH₂=CH(CH₃)COO)₂SnCl₂(C₆H₄OH)₂ + C₆H₄OH + H]^+, 522.8 Da [(CH₂=CH(CH₃)COO)₂Sn(C₆H₄OH)₂ + H]^+. 374.2 Da [(CH₂=CH(CH₃)COO)₂Sn(C₆H₄)(C₆H₅CH₂ + H)]^+. 1H-NMR, CDCl₃, ppm: δ: 0.93 (t, 6H, −CH₃), 1.25 (m, 4H, γ-CH₂), 1.43 (m, 4H, β-CH₂), 1.82 (t, 4H, α-CH₂), 1.94 (s, 12H, =CCH₃), 5.68 (d, 2H, =CH₂), 6.25 (d, 2H, =CH₂). 13C-NMR, CDCl₃, ppm: δ: 13.58 (−CH₂), 18.04 (γ-CH₂), 18.18 (γ-CH₂), 25.57 (β-CH₂), 27.00 (α-CH₂), 128.35 (−CH₂ bridging), 129.87 (−CH₂, terminal), 136.30 (−CH₂, bridging), 137.54 (−CH₂, terminal), 174.46 (COO, bridging-bidentate), 175.88 (COO, terminal-bidentate). FTIR (cm⁻¹): 2960, 2930, 2867, 1639 (C=C), 1543 (COO), 1453, 1413 (COO), 1242, 948, 827.
Under the same reaction condition, the product \( [(\text{CH}_3=\text{C(C}_2\text{H}_5)\text{COO})_{\text{Sn}}\text{Cl}_2(\text{C}_4\text{H}_9)]_{\text{HOOC(C}_6\text{F}_13\text{COO})=\text{CH}_2}]_2 \) formed when methacrylic acid was used as a ligand instead of potassium methacrylate. TOF MS ES+(solvent-ethanol): 862.87, 864.87, 866.87 Da \((\text{[CH}_3=\text{C(C}_2\text{H}_5)\text{COO})_{\text{Sn}}\text{Cl}_2(\text{C}_4\text{H}_9)]_{\text{HOOC(C}_6\text{F}_13\text{COO})=\text{CH}_2} + \text{C}_2\text{H}_5\text{OH}]^+ \). FTIR (cm\(^{-1}\)): 2967, 2936, 2870, 1710, 1548, 1403, 1081, 750, 695, 472.

4.3. Preparation of butylchlorobis(perfluoroheptanoato)tin(IV) compound

\[ 2\text{CF}_3(\text{C}_2\text{F}_5)_2\text{COOK} + \text{BuSnCl}_3 \rightarrow [\text{Bu}(\text{CF}_3(\text{C}_2\text{F}_5)_2\text{COO})_{\text{Sn}}\text{Cl}_2]_{\text{SnCl}} \]

By a similar procedure to 4.1, potassium perfluoroheptanoate (1.21 g, 3.0 mmol) and butylchlorotin (0.44 g, 1.5 mmol) gave \([\text{Bu}(\text{CF}_3(\text{C}_2\text{F}_5)_2\text{COO})_{\text{Sn}}\text{Cl}_2]_{\text{SnCl}}\) as a colorless liquid.

Elemental analysis: \((\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{O}_4\text{Sn}), M_w = 937.38 \text{ g/mol})\): Calculated: C, 35.10; H, 3.49%. Found: C, 37.40, H, 3.58%. TOF MS ES+(solvent-ethanol): 938.9 \text{ Da} \([\text{C}_6\text{F}_{13}\text{COO})_{\text{Sn}}(\text{C}_4\text{H}_9)_{\text{SnCl}}\) + H\(^+\). 1H-NMR, CDCl\(_3\), ppm, δ: 0.82 (t, 3H, -CH\(_3\)), 1.10 (m, 2H, β-CH\(_2\)), 1.35 (t, 2H, α-CH\(_2\)), 7.4 (d, 2H, C\(_6\text{H}_4\)), 7.5 (d, 2H, C\(_6\text{H}_4\)). 13C-NMR, CDCl\(_3\), ppm: 162 (COO), 147, 141, 128 (C\(_6\text{H}_4\)), 38 (α-CH\(_3\)), 28 (β-CH\(_2\)), 26 (γ-CH\(_2\)), 13 (β-CH\(_3\)). FTIR (cm\(^{-1}\)): 2957, 2928, 2870, 1710, 1548, 1403, 1081, 750, 695, 472.

4.4. Preparation of butylchloro(2,6-pyridinedicarboxylato)tin(IV) compound

\[ \text{C}_6\text{H}_4(\text{COOK})_2 + \text{BuSnCl}_3 \rightarrow [\text{Bu}(\text{C}_6\text{H}_4(\text{COO})_{\text{Sn}}\text{Cl}_2]_{\text{SnCl}} \]

By a similar procedure to 4.4, potassium phthalate (0.73 g, 3.0 mmol) and butyltrichlorotin (0.89 g, 3.0 mmol) produced \([\text{Bu}(\text{C}_6\text{H}_4(\text{COO})_{\text{Sn}}\text{Cl}_2]_{\text{SnCl}}\) as a white solid. Elemental analysis: \((\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8\text{Sn}_2\text{Cl}_2), M_w = 375.4 \text{ g/mol})\): Calculated: C, 38.39%. Found: C, H 3.49%. TOF MS ES+(solvent-ethanol): 376.9 \text{ Da} \([\text{C}_{12}\text{H}_{13}\text{ClO}_4\text{Sn} + \text{H}]^+\). 1H-NMR, CDCl\(_3\), ppm, δ: 4.05 (t, J = 7.0 Hz, C\(_6\text{H}_4\text{O}–\)), 2.30 (t, J = 7.0 Hz, C\(_6\text{H}_4\text{C}–\)), 1.64 (m, δ-CH\(_2\)), 1.37 (m, γ-CH\(_2\)). 13C-NMR, CDCl\(_3\), ppm, δ: 173.6 (C=O), 64.2 (C\(_6\text{H}_4\text{O}\)), 34.1 (C\(_6\text{H}_4\)), 28.3 (C\(_6\text{H}_4\)), 25.5 (C\(_6\text{H}_4\)), 24.6 (C\(_6\text{H}_4\)). FTIR (cm\(^{-1}\)): 2943 (CH\(_2\), asym str), 2865 (CH\(_2\), sym str), 1722 (C=O), 169 (COO), 133, 130, 128, 127 (C\(_6\text{H}_4\)), 28 (C=O), 26 (β-CH\(_2\)), 25 (γ-CH\(_2\)), 13 (δ-CH\(_2\)).

5. Polymerization of ε-caprolactone with butyltin carboxylates

The catalyst \([\text{Bu}(\text{C}_6\text{H}_4\text{O}_2)_{\text{Sn}}\text{Cl}_2]_{\text{SnCl}}\) (15 mg) was mixed with ε-caprolactone (1.4 mL) in a vial under nitrogen atmosphere. The solvent free mixture was stirred at 80 °C for 1 h. GPC results: \(M_w = 29,600 \text{ Da}, M_n = 26,510 \text{ Da}, M_w/M_n = 1.12\). 1H NMR, CDCl\(_3\), ppm, δ: 4.05 (t, J = 7.0 Hz, C\(_6\text{H}_4\text{O}–\)), 2.30 (t, J = 7.0 Hz, C\(_6\text{H}_4\text{C}–\)), 1.64 (m, δ-CH\(_2\)), 1.37 (m, γ-CH\(_2\)). 13C-NMR, CDCl\(_3\), ppm, δ: 173.6 (C=O), 64.2 (C\(_6\text{H}_4\text{O}\)), 34.1 (C\(_6\text{H}_4\)), 28.3 (C\(_6\text{H}_4\)), 25.5 (C\(_6\text{H}_4\)), 24.6 (C\(_6\text{H}_4\)). FTIR (cm\(^{-1}\)): 2943 (CH\(_2\), asym str), 2865 (CH\(_2\), sym str), 1722 (C=O), 1471 (CH\(_2\), bending), 1367 (CH\(_2\), bending), 1293 (C–C), 1241 (C–O–C), 1167 (C–O–C, sym), 1047, 962, 732. [O=C–CH\(_2\)CH\(_2\)CH\(_2\)CH\(_2\)O–]

The polymerization reactions of ε-caprolactone with other butyltin(IV) carboxylates were carried out under similar conditions to the reaction above. They were also very effective in the ring opening of ε-caprolactone.

6. Results and discussion

As mentioned in the experimental section, firstly potassium salts of phthalate, 2,6-pyridinedicarboxylate, methacrylate, pivalate, and perfluoroheptanoate were prepared as in literatures.[14–16] The known structures of these potassium carboxylates were confirmed by elemental analysis and FTIR measurements. Secondly, the single-site
tin compounds described in this study were prepared by ligand substitution reactions as shown in Scheme 1.

To our knowledge, tin pivalate, methacrylate, and perfluoroheptanoate compounds in these compositions were synthesized for the first time and therefore, they should be fully characterized. The structures of these single-site tin(IV) compounds were characterized using a combination of elemental analysis and spectroscopic techniques such as $^1$H-, $^{13}$C-NMR, FTIR, and MS. Colorless liquid monocarboxylate-tin compounds and white solid dicarboxylate-tin compounds were relatively air and moisture stable. Their elemental analysis results were in good agreement with the proposed formulations as shown in Scheme 1.

The FTIR absorption bands provided information about the formation of tin-carboxylate compounds and the mode of coordination of each carboxylate ligand in its compounds. The peaks of all potassium and tin carboxylates shown in the FTIR spectra belonged to the coordinated carboxyl groups not the free carboxylic acid groups. For example, the FTIR spectrum of free pivalic acid exhibited intense band at 1697 cm$^{-1}$ corresponding to asymmetrical stretching vibrations of the carboxyl group.[17] After the reaction of pivalic acid with KOH, the band shifted the low wave numbers ~1542 for $\nu$COO$_{\text{asym}}$ and ~1360 cm$^{-1}$ for $\nu$COO$_{\text{sym}}$. As it was expected, FTIR spectrum of tin(IV) pivalate compound showed peaks at different wave numbers and regions. In the FTIR spectrum of tin(IV) pivalate compound, the bands at ~1553 and 1371 cm$^{-1}$ indicated the bonding of carboxylate group as bidentate chelating mode. These values are consistent with those detected in a number of carboxylate–metal compounds.[18]

The $^1$H NMR spectra of all tin compounds exhibited signals corresponding to the organic-carboxylate groups as well as those of butyl group attached to the tin(IV) atom. The $^1$H-NMR spectrum of [Bu((CH$_3$)$_3$CCOO)$_2$SnCl]$_2$ showed peaks 0.94 (t, 6H, $\delta$-CH$_3$)$_2$, 1.45 (m, 4H, $\gamma$-CH$_2$), 1.69 (m, 4H, $\beta$-CH$_2$), 1.83 (t, 4H, $\alpha$-CH$_2$) ppm for n-butyl group and at 1.21 (s, 36H, C(CH$_3$)$_3$) ppm for tert-butyl group. The $^{13}$C NMR spectrum of [Bu((CH$_3$)$_3$CCOO)$_2$SnCl]$_2$ showed four resonances at 13.64 ($\delta$-CH$_3$), 25.52 ($\gamma$-CH$_2$), 27.11 ($\beta$-CH$_2$), 27.19 ($\alpha$-CH$_2$) ppm for n-butyl groups and three resonances at 24.85, 25.52, 27.11 ppm for tert-butyl groups.

Figure 1. Mass spectrum of [Bu((CH$_3$)$_3$CCOO)$_2$SnCl]$_2$.

Figure 2. The dimeric structure of [Bu((CH$_3$)$_3$CCOO)$_2$SnCl]$_2$.
butyltin(IV) moiety was an important factor to give activity to the complexes when they were used as catalysts in the ring opening of \(\varepsilon\)-caprolactone. The tin-carboxylate compounds were more active than tin-dicarboxylate compounds in the polymerization reactions. The tin-carboxylate compounds have aliphatic substituents (pivalate, methacrylate, and perfluoroheptonate); whereas tin-dicarboxylate compounds have aryl substituents (phthalate and 2,6-pyridinedicarboxylate).

The synthesized tin carboxylate compounds were used as catalysts in the polymerization reactions of \(\varepsilon\)-caprolactone and the obtained PCL were fully characterized by FTIR, \(^1\)H-NMR, \(^{13}\)C-NMR, MS and GPC. The chloride ligand on the tin catalyst was active group in the ring opening of \(\varepsilon\)-CL which was supported by mass data. MS measurements of PCL showed that chloride atom moved on to the \(\varepsilon\)-CL unite (the peak at 149.0 Da, PCL-Cl) (Figure 4). This MS measurement was performed after the first few minutes of polymerization reactions.

FTIR spectrum of PCL displayed characteristic peaks of C=O stretching vibrations at 1722 cm\(^{-1}\), CH\(_2\) bending modes at 1471 and 1367 cm\(^{-1}\) and CH\(_2\) asymmetric stretching at 2943 and symmetric stretching at 2865 cm\(^{-1}\). The C–O–C stretching vibrations gave peaks at 1047, 1167, and 1241 cm\(^{-1}\). The bands at 1167 and 1293 cm\(^{-1}\) were assigned to C–O and C–C stretching in the amorphous and in the crystalline phases, respectively.[24,25]

The \(^{13}\)C-NMR spectrum (Figure 5) of PCL showed six peaks that each carbon atom of PCL appeared at only one region 173.6 (C=O), 64.2 (\(\varepsilon\)-CH\(_2\)O), 34.1 (\(\delta\)-CH\(_3\)), 28.3 (\(\gamma\)-CH\(_2\)), 25.5 (\(\beta\)-CH\(_2\)), 24.6 (\(\alpha\)-CH\(_2\)) ppm. These data are the evidence of

Figure 3. The dimeric structure of [BuSnCl(OOC)\(_2\)C\(_6\)H\(_3\)N\(_2\)]

Figure 4. TOF MS ES+ spectrum of PCL prepared with [Bu(PFH)\(_2\)SnCl].

Figure 5. \(^{13}\)C-NMR spectrum of PCL prepared with [Bu(PFH)\(_2\)SnCl].
weights to the number average molecular weights ($M_w/M_n$) was 1.07 (Table 1).

When compared with other acidic or basic catalysts, these single-site tin catalysts were very effective in the ROP of ε-caprolactone in short times.[29–31] It is also important

regular polymerization of ε-CL and are consistent with the literature data.[26]

These data suggest that first ε-caprolactone attacks to tin(Sn) center and then the nucleophile Cl⁻ ion attacks C=O carbon atom in the ε-caprolactone unit as seen in Scheme 2.[27] Then, lactone exocyclic oxygen coordinates to the tin atom. Propagation step involves successive ring-opening by an anionic coordination–insertion mechanism.[28]

GPC was also used to determine molecular weight and molecular weight distribution index of polymers. By varying the reaction times, temperatures and the catalysts, the CL polymers with different average molecular weights or number average molecular weights were obtained. These tin catalysts were very active for ε-CL polymerization at and above 60 °C. The polymerization of ε-CL was completed within 17 h at 60 °C. Therefore, polymerization reaction was accelerated by the increasing of temperature from 60 to 80 °C as seen in Table 1. For polymers of ε-CL prepared with [Bu(PFH)₂SnCl] by stirring at 80 °C for 1 h, the peak appeared at 34,120 Da for weight average molecular weight ($M_w$) and at 31,640 Da for number average molecular weight ($M_n$) (Figure 6). The ratio of average molecular

Figure 6. Gel permeation chromatogram of PCL prepared at 80 °C with the compound [Bu(PFH)₂SnCl].
7. Conclusion

In this study, it was shown that carboxylates derivatives were effective ligands for modification of butyltrichlorosn(IV). Five tin carboxylate compounds were prepared, characterized, and used as catalysts for the polymerization of ε-caprolactone at 80 °C and have somewhat different influence on the conversion of ε-caprolactone. The new liquid tin pivalate, methacrylate and perfluoroheptanoate compounds were more active catalysts than solid tin dicarboxylate compounds and other known tin catalysts in the polymerization of ε-CL. The conversion of ε-caprolactone was completed in just 1 h under solvent free condition by tin carboxylates. The structures of polymers were characterized by GPC, DSC, NMR, FTIR, and MS spectroscopies. As seen from 13C NMR experimental data, there was just one peak for each carbon atom. There was just one narrow molecular weight distribution peak with ratio of \( M_w / M_n = 1.0 \) in the gel permeation chromatogram. DSC measurements showed that there is one crystalline phase. All these data were evidence of the regular polymerization of ε-CL and indicating the characteristic of single site tin catalysts.

Disclosure statement

No potential conflict of interest was reported by the authors.

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