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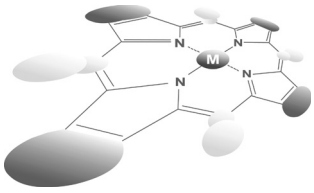

Synthesis of novel single site tin porphyrin complexes and the catalytic activity of tin tetrakis(4-fluorophenyl) porphyrin over ε-caprolactone

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ABSTRACT: Tin tetrakis(4-fluorophenyl)porphyrin, tin tetrakis(4-chlorophenyl)porphyrin and tin tetrakis(4-bromophenyl)porphyrin complexes were prepared by reaction of butyltin trichloride with tetrakis(4-fluorophenyl)porphyrin, tetrakis(4-chlorophenyl)porphyrin, and tetrakis(4-bromophenyl)porphyrin in tetrahydrofuran and toluene, respectively. These novel complexes were characterized by ^{1}H, ^{13}C NMR, FTIR, mass spectroscopy and elemental analysis. The single site tin complex including fluoride was tested as a catalyst in polymerization of ε-caprolactone and was very effective. Polycaprolactone was characterized by ^{1}H, ^{13}C NMR, and gel permeation chromatography.

KEYWORDS: butyltin trichloride; porphyrin; ring-opening; single site catalyst; ε-caprolactone.

INTRODUCTION

The complexes of porphyrins with different metals have been synthesized and characterized [1, 2]. Electron deficient metalloporphyrins such as Cr(TPP)Cl, Fe(TTP)OTf and Cr(TTP)OTf have been used as mild Lewis acid catalysts in polymerization reactions of lactides and caprolactone [2, 3]. Tin(IV) porphyrins have attracted attention in recent years due to successful utilization in catalysis, biomedicine and synthesis of biomaterials [4, 5]. The spectroscopic properties of tin(IV) porphyrin complexes make them convenient for chemical study. The Sn(IV) center is usually six-coordinate with two axial ligands and many derivatives have been synthesized with variety of anions such as carbanions, aryloxide, carboxylate and halides [6, 7]. We have previously shown that various tin compounds can be used for ring opening polymerization (ROP) of epoxides and caprolactone [8, 9]. However, there is no study about butyltin trichloride with tetrakis(4-fluorophenyl)porphyrin ($TFPPH_2$), tetrakis(4-chlorophenyl)porphyrin ($TCPPH_2$) and tetrakis(4-bromophenyl)porphyrin ($TBPPH_2$). The other tin(IV) porphyrin compounds have been used as mild Lewis acid catalysts in polymer synthesis. The single site catalyst is regio- and stereoselective in the ring opening polymerization of hetereocyclic compounds [10]. Therefore, it is important to prepare new single site tin porphyrin complexes having catalytic properties.

The first goal of the present work was to report the synthesis of single site tin(IV) porphyrin complexes. The second goal was their use as catalysts in a polymerization reaction of ε-caprolactone monomer.

EXPERIMENTAL SECTION

Materials and instruments

Butyltin trichloride (95%, Aldrich), pyrrole (97%, Merck), propionic acid (99%, Merck), ε-caprolactone (99%, Alfa Aesar), 4-fluorobenzaldehyde (98%, Sigma–Aldrich), 4-bromobenzaldehyde (99%, Sigma-Aldrich) and 4-chlorobenzaldehyde (97%, Sigma–Aldrich) were used as received. Tetrahydrofuran (THF) (99.9%, Merck), methanol (99.9%, Merck), and toluene (99.7%, Sigma-Aldrich) were dried over activated 4 Å molecular sieves before use. Polymer syntheses were carried out under nitrogen atmosphere. Tin porphyrin complexes and polymers were characterized by ^{1}HNMR (Bruker DPX, 400 MHz) and ^{13}C-NMR spectroscopy (Bruker DPX, 100 MHz). Infrared spectra of complexes were recorded on a Shimadzu 8201/86601 PC spectrometer. The elemental

◊ SPP full member in good standing

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analysis was carried out with a LECO CHNS-932 elemental analyzer. Bruker Microflex LT MALDI-TOF MS and Waters SYNAPT HRMS (ESI±) systems were used to obtain molecular weight of TXPP-Sn complexes. 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 50 µL. The calibration curve was made with seven polystyrene standards covering the molecular weight range from 162 to 67000 Da.

Preparation of 5,10,15,20-tetrakis(4-fluorophenyl) porphyrin ($TFPPH_2$)

$TFPPH_2$ was prepared according to the reported procedure by the reaction of 4-fluorobenzaldehyde (2.53 g, 20 mmol) with pyrrole (1.34 g, 20 mmol) in 20 mL of hot propionic acid [11, 12]. The reaction mixture was stirred for 30 min at reflux temperature. Then, the mixture was cooled at room temperature and filtered. The filtrate was washed with methanol and hot distilled water and then dried at furnace. The purple product was obtained with yield 20%. Elemental analysis ($C_{44}H_{26}F_4N_4$, M_w = 686.70 g/mol), Calcd.: C, 76.96; H, 3.82; N, 8.16%. Found: C, 77.13; H, 4.00; N, 8.29%. MALDI-MS: 687.20 Da for $[C_{44}H_{26}F_4N_4+H]^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.84 (s, 8H, porphyrin), 8.17 (s, 8H, Ph), 7.47 (s, 8H, Ph), -2.85 (s, 2H, N*H*, porphyrin). FTIR: ν, cm^{-1} 3307 (N-H, secondary amine), 3041 (C-H, phenyl), 1597, 1550, 1467 (C=C, C=N), 1348 (C-N), 966 (C-H, β-pyrrole), 788 (pyrrole).

Preparation of 5,10,15,20-tetrakis(4-chlorophenyl) porphyrin ($TCPPH_2$)

Reaction between 4-chlorobenzaldehyde (2.90 g, 20 mmol) and pyrrole (1.34 g, 20 mmol) was conducted similarly to that described above. The blue product was obtained with yield 20%. Elemental analysis ($C_{44}H_{26}Cl_4N_4$, M_w = 752.52 g/mol), Calcd.: C, 70.23; H, 3.48; N, 7.45%. Found: C, 71.46; H, 3.08; N 7.97%. MALDI-MS: 753.14 Da for $[C_{44}H_{26}Cl_4N_4+H]^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.87 (s, 8H, porphyrin), 8.15 (d, 8H, J = 7.96 Hz, Ph), 7.78 (d, 8H, J = 7.93 Hz, Ph), -2.82 (brd, 2H, N*H*, porphyrin). FTIR: ν, cm^{-1} 3312 (N-H, secondary amine), 3060 (C-H, phenyl), 1592, 1545, 1472 (C=C, C=N), 1346 (C-N), 966 (C-H, β-pyrrole), 796 (pyrrole).

Preparation of 5,10,15,20-tetrakis(4-bromophenyl) porphyrin ($TBPPH_2$)

Reaction between 4-bromobenzaldehyde (3.74 g, 20 mmol) and pyrrole (1.34 g, 20 mmol) was carried out similarly to the preceding reactions. The blue product was obtained with yield 25%. Microanalysis ($C_{44}H_{26}Br_4N_4$, M_w = 930.32 g/mol), Calcd.: C, 56.81; H, 2.82; N, 6.02%. Found: C, 56.74; H, 2.92; N 6.02%. MALDI-MS: 930.89 Da for $[C_{44}H_{26}Br_4N_4+H]^+$. HRMS, ESI(+): 930.89 Da for $[C_{44}H_{26}Br_4N_4+H]^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.86 (s, 8H, porphyrin), 8.08 (d, 8H, J = 8.26 Hz, Ph), 7.92 (d, 8H, J = 8.24 Hz, Ph), -2.84 (brd, 2H, N*H*, porphyrin). ^{13}C NMR ($CDCl_3$): δ_C, ppm 140.83, 135.83, 130.00, 122.65, 110.00. FTIR: ν, cm^{-1} 3310 (N-H, secondary amine), 3057 (C-H, phenyl), 1591, 1547, 1471 (C=C, C=N), 1344 (C-N), 966 (C-H, β-pyrrole), 796 (pyrrole).

Preparation of butyl(5,10,15,20-tetrakis(4-fluorophenyl)porphyrinato)tin(IV) chloride, [Bu(TFPP)SnCl]

Butyltin trichloride (0.073 g, 0.24 mmol) was added gradually to a solution of $TFPPH_2$ (0.11 g, 0.16 mmol) in 5 mL of THF. The reaction mixture was stirred for 3 h at reflux temperature under nitrogen atmosphere. Then the volatile parts were removed by vacuum evaporator at 40 °C and dried. The product was washed with hexane and then dried by vacuum evaporator. The blue product was obtained with yield 60%. Elemental analysis ($C_{48}H_{33}ClF_4N_4Sn$, M_w = 895.96 g/mol), Calcd.: C, 64.35; H, 3.71; N, 6.25%. Found: C, 64.01; H, 4.03; N 6.18%. MALDI-MS: 918.4 Da for $[C_4H_9SnCl(TFPP)+Na]^+$, 861.8 Da for $[C_4H_9Sn(TFPP)]^+$, 803.4 Da for $[Sn(TFPP)]^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.59 (brd, 8H, porphyrin), 8.59 (brd, 8H, Ph), 7.74 (t, 8H, J = 7.79 Hz, Ph), 1.40 (brd, 2H, Sn-$^{\alpha}$CH_2), 1.19 (brd, 2H, $^{\beta}$CH_2), 0.99 (brd, 2H, $^{\gamma}$CH_2), 0.65 (brd, 3H, $^{\delta}$CH_3). ^{13}C NMR ($CDCl_3$): δ_C, ppm 165.57, 163.56, 146.16, 140.45, 128.34, 115.81, 33.24, 27.82, 6.17. FTIR: ν, cm^{-1} 3041 (C-H, phenyl), 2958, 2928 (C-H, Bu), 1598, 1504, 1468 (C=C, C=N), 1319 (C-N), 987 (C-H, β-pyrrole), 798 (pyrrole). (Sn-$^{\alpha}$C$H_2$$^{\beta}CH_2$$^{\gamma}CH_2$$^{\delta}CH_3$; brd: broad).

Preparation of butyl(5,10,15,20-tetrakis(4-chlorophenyl)porphyrinato)tin(IV) chloride, [Bu(TCPP)SnCl]

Butyltin trichloride (0.07 g, 0.25 mmol) was added gradually to a solution of $TCPPH_2$ (0.12 g, 0.16 mmol) in 5 mL of toluene. The reaction mixture was stirred for 3 h at 90 °C under nitrogen atmosphere. Then, the volatile parts were removed by vacuum evaporator at 60 °C and dried. The product was washed with hexane and then dried by vacuum evaporator. The blue product was obtained with yield 50%. Microanalysis ($C_{48}H_{33}Cl_5N_4Sn$, M_w = 961.78 g/mol), Found: C, 59.94; H, 3.46; N, 5.83%. MS: 922.56 Da for $[C_4H_9(TCPP)Sn]^+$, 753.09 Da for $[(TCPP)+H]^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.68 (s, 8H, porphyrin), 8.58 (d, 8H, J = 8.14 Hz, Ph), 8.06 (d, 8H, J = 8.14 Hz, Ph), 1.34 (brd, 2H, Sn-$^{\alpha}$CH_2), 1.16 (brd, 2H, $^{\beta}$CH_2), 0.95 (m, 2H, $^{\gamma}$CH_2), 0.61 (t, 3H, $^{\delta}$CH_3). FTIR: ν, cm^{-1} 3032 (C-H, phenyl), 2958, 2928, 2874 (C-H, Bu),

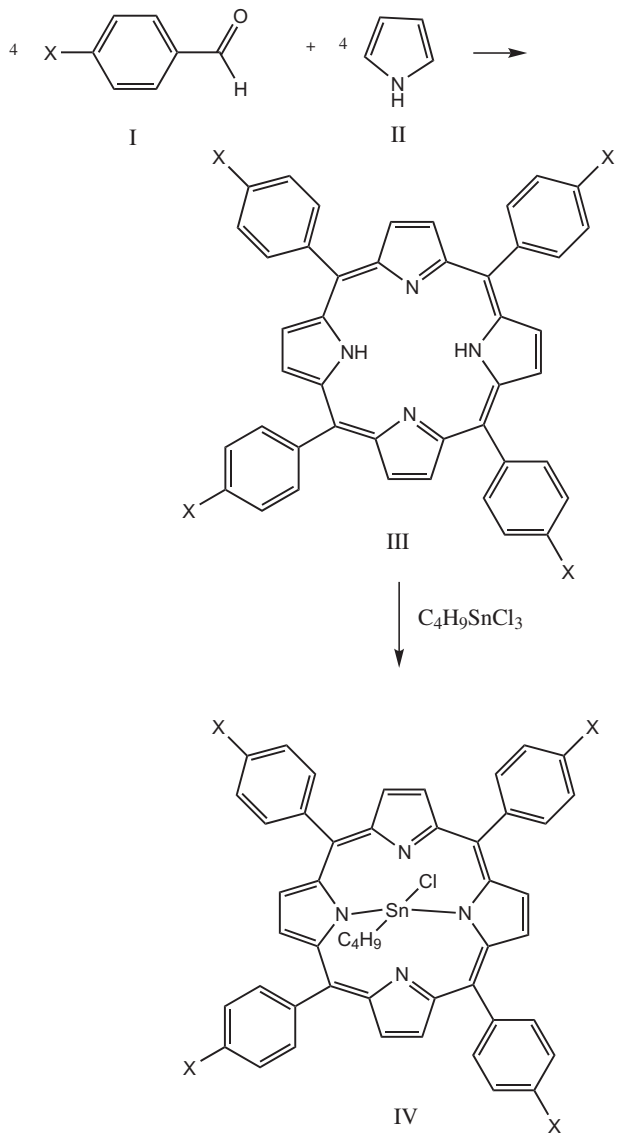
1588, 1482 (C=C, C=N), 1400, 1300 (C-N), 1093, 985 (C-H, β-pyrrole), 802 (pyrrole).

Preparation of butyl(5,10,15,20-tetrakis(4-bromophenyl)porphyrinato)tin(IV) chloride, [Bu(TBPP)SnCl]

Reaction between butyltin trichloride (0.07 g, 0.25 mmol) and $TBPPH_2$ (0.15 g, 0.16 mmol) was conducted similarly to that described above. The blue product was obtained with yield 50%. Microanalysis ($C_{48}H_{33}ClBr_4N_4Sn$, M_w = 1139.52 g/mol), Calcd.: C, 50.59; H, 2.92; N, 4.92%. Found: C, 50.23; H, 3.18; N 4.78%. HRMS ESI(+) (in methanol): 1171.29 Da for [Bu(TBPP)SnCl+CH_3OH+H]$^+$. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 8.65 (s, 8H, porphyrin), 8.49 (d, 8H, J = 7.09 Hz, Ph), 8.21 (d, 8H, J = 7.36 Hz, Ph), 1.35 (brd, 2H, Sn-$^{\alpha}CH_2$), 1.16 (brd, 2H, $^{\beta}CH_2$), 0.95 (m, 2H, $^{\gamma}CH_2$), 0.62 (t, 3H, $^{\delta}CH_3$). FTIR: ν, cm^{-1} 3037 (C-H, phenyl), 2954, 2930, 2872 (C-H, Bu), 1584, 1484 (C=C, C=N), 1400, 1302 (C-N), 1094, 986 (C-H, β-pyrrole), 801 (pyrrole).

Polymerization of ε-caprolactone with the [Bu(TFPP)SnCl] catalyst

The catalyst (Bu(TFPP)SnCl, 20 mg) was mixed with ε-caprolactone (1.0 mL) in a vial under nitrogen. The solvent free mixture was stirred at different temperatures and times as indicated in Table 1. ^{1}H NMR (400 MHz; $CDCl_3$; Me_4Si): δ_H, ppm 4.08 (t, J = 7.0 Hz, $^{\varepsilon}CH_2$-O), 2.30 (t, J = 7.0 Hz, $^{\alpha}CH_2$-C = O), 1.67 (m, J = 7.0 Hz, $^{\beta,\delta}CH_2$), 1.39 (m, J = 7.0 Hz, $^{\gamma}CH_2$). ^{13}C NMR ($CDCl_3$): δ_C, ppm 173.80 (C = O), 64.37 ($^{\varepsilon}CH_2O$), 34.34 ($^{\alpha}CH_2$), 28.56 ($^{\delta}CH_2$), 25.74 ($^{\beta}CH_2$), 24.80 ($^{\gamma}CH_2$). [O = C-$^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2{}^{\delta}CH_2{}^{\varepsilon}CH_2$O-].



Scheme 1. Synthesis reactions of Bu(TXPP)SnCl complexes. (**I**: 4-fluorobenzaldehyde, 4-chlorobenzaldehyde, and 4-bromobenzaldehyde when X is F, Cl, and Br **II**: pyrrole **III**: 5,10,15,20-tetrakis(4-halophenyl)porphyrins **IV:** butyl(5,10,15,20-tetrakis (4-halophenyl)porphyrinato)tin(IV) chloride complexes.

RESULTS AND DISCUSSIONS

In this study, novel single site tin porphyrin complexes were synthesized by reaction of $BuSnCl_3$ with 1.5:1 mol ratio of 5,10,15,20-tetrakis(4-fluorophenyl)porphyrin, 5,-10,15,20-tetrakis(4-chlorophenyl)porphyrin, and 5,10,-15,20-tetrakis(4-bromophenyl)porphyrin in THF at reflux temperature (or in toluene at 90 ºC) in accordance with the following reactions. The products were formulated to be butyl-5,10,15,20(tetrakis(4-fluorophenyl)porphyrinato) tin(IV) chloride, butyl(5,10,15,20-tetrakis(4-chlorophenyl) porphyrinato)tin(IV) chloride, and butyl(5,10,15,20-tetrakis(4-bromophenyl)porphyrinato)tin(IV) chloride (Scheme 1).

The formulations of tin porphyrin complexes were determined by elemental analysis, mass, FTIR, and NMR measurements. For example, the FTIR spectrum of free $TFPPH_2$ ligand exhibited band at 3307 cm^{-1} corresponding to stretching vibrations of N–H secondary amine [13]. After coordination of TFPP to butyltin trichloride, the band at 3307 cm^{-1} disappeared in the FTIR spectrum. In the FTIR spectrum of butyl-5,10,15,20-tetrakis(4-fluorophenyl)porphyrinatotin(IV) chloride complex, the bands at ~1598, 1504, 1468 cm^{-1} correspond to C=C, C=N vibrations. These values are consistent with those detected in a number of metal porphyrin complexes [14]. ^{1}H NMR spectrum of studied complex was given in the experimental section. The proton resonance signals for phenyl groups of the TFPP ligand appeared at 8.59 and 7.74 ppm as a broad singlet and a triplet while the porphyrin protons of the TFPP ligand appeared at 8.59 ppm as a broad singlet. These results are comparable to those published for the porphyrin-metal complexes [15]. The ^{13}C NMR spectrum of Bu(TFPP)SnCl complex showed characteristic peaks for ring carbon atoms of TFPP and butyl group. Carbons for both rings and butyl group appeared at

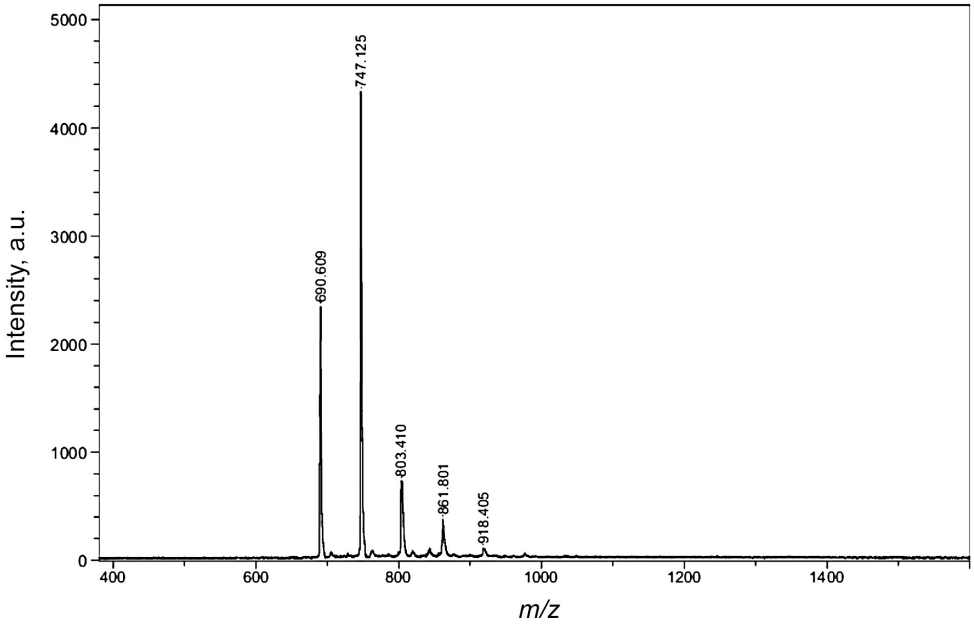


Fig. 1. MS spectrum of Bu(TFPP)SnCl complex

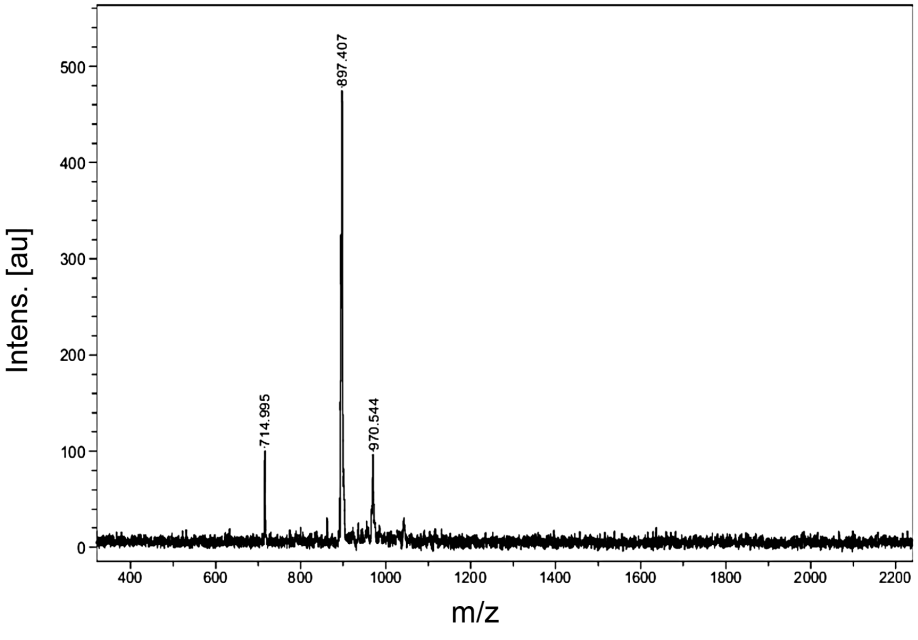
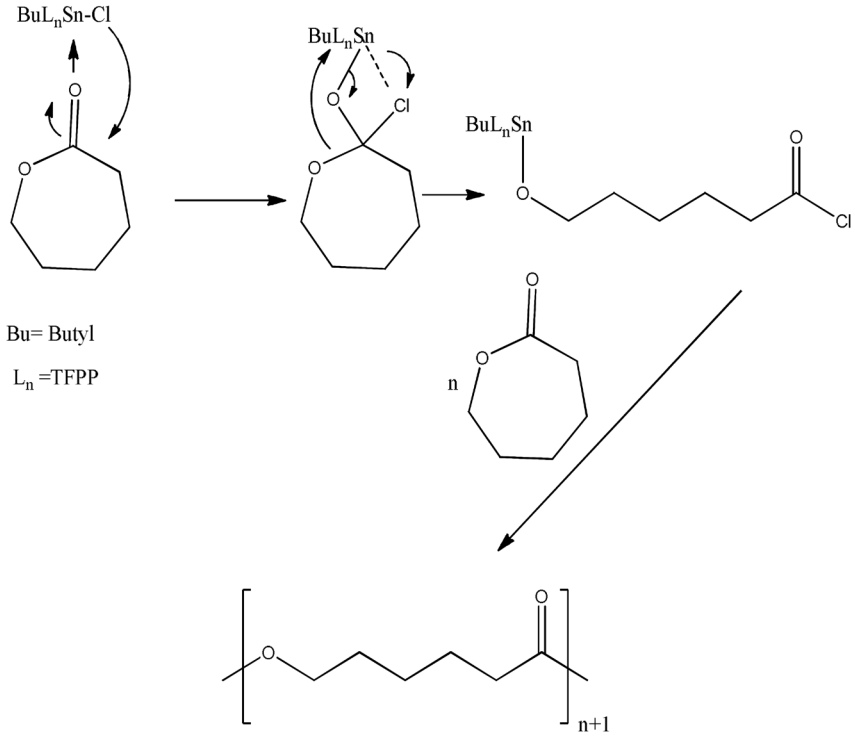


Fig. 2. MS spectrum of Bu(TFPP)SnCl complex (longer stirring times >3 h)

165.57, 163.56, 146.16, 140.45, 128.34, 115.81, 33.24, 27.82, 6.17 ppm. These values are very characteristic for metal-bonded substituted porphyrin complexes [16, 17]. MS measurement of Bu(TFPP)SnCl (M*w* = 895.96 g/mol) complex showed peaks at 918.4 Da for $[C_4H_9(TFPP)SnCl+Na]^+$, 861.8 Da for $[C_4H_9(TFPP)Sn]^+$, 803.4 Da for $[(TFPP)Sn]^+$, 747.1 Da for $[(TFPP)Sn\text{-}3F]^+$. MS spectrum of Bu(TFPP)SnCl complex is given in Fig. 1.

It is also important to note that when the stirring time increases from 3 h to longer stirring times at high temperature, solvent THF also bonds to the tin center as seen in the mass spectrum (Fig. 2). MS measurement of Bu(TFPP)SnCl complex showed peaks at 970.54 Da for $[C_4H_9(TFPP)SnCl+THF+H]^+$, and 897.41 Da for molecular ion $[C_4H_9(TFPP)SnCl+H]^+$. Similarly, the reactions between $BuSnCl_3$ and 5,10,15,20-tetrakis(4-chlorophenyl)porphyrin($TCPPH_2$) or 5,10,15,20-tetrakis-(4-bromophenyl)porphyrin($TBPPH_2$) in 1.5:1 mol ratio were conducted in toluene at 90 °C. The products, butyl-(5,10,15,20-tetrakis(4-chlorophenyl)porphyrinato)tin(IV)



Scheme 2. Reactions involved in the ring-opening polymerization of ε-caprolactone

chloride and butyl(5,10,15,20-tetrakis(4-bromophenyl) porphyrinato)tin(IV) chloride were obtained.

The formulations of these complexes Bu(TCPP)SnCl and Bu(TBPP)SnCl were also determined by elemental analysis, FTIR, NMR, and mass measurements. The comparison of the integral of the signals in ^{1}H-NMR spectra and the peak data in mass spectra confirmed the suggested formulas. The N-*H* secondary amine peak disappeared in the ^{1}H-NMR spectra of the tin porphyrin complexes while it was at ~ -2.82 ppm in free porphyrin ligand. The disappearance of N–*H* peak can be attributed to the formation of covalent bond between tin and nitrogen atoms. These bromo- and chloro-substituted porphyrin complexes were single-site catalysts, however, they were not very effective in the polymerization reactions of ε-caprolactone. For example, polymers of ε-caprolactone prepared with Bu(TCPP)SnCl by stirring at 100 °C for 10 h, the main peak appeared at 2300 Da for weight average molecular weight (M_w) with a conversion of 30%.

The development of ''single-site'' catalysts has been a key goal for producing polymers with controllable molecular weights and polydispersities [18]. The Bu(TFPP)SnCl complex was very effective in the polymerization reactions of ε-caprolactone when it was used as a catalyst (see Table 1). For example, ε-caprolactone polymers prepared with Bu(TFPP)SnCl by stirring at 100 °C for 10 h, the main peak appeared at 35790 Da for weight average molecular weight (M_w) with a conversion of 92%. This can be attributed solely to inductive effects of fluorine atoms. Due to the very large electronegativity of fluorine atoms, the electrons in the porphyrin ring and tin atom are pulled towards it, leading to the inductive effect over Sn–Cl bond. In other words, Sn(IV) center is more Lewis acidic with the fluorinated porphyrin. Polymer samples obtained from ring opening polymerization of ε-CL were characterized by ^{1}H, ^{13}C NMR, FTIR and gel permeation chromatography (GPC). In the ^{1}H NMR spectrum of polycaprolactone (PCL), signals are assigned as follows: δ_H, ppm 4.08 (t, H, ε-C*H*$_2$), 2.30 (t, H, α-C*H*$_2$), 1.67 (m, H, β-C*H*$_2$ + δ-C*H*$_2$), and 1.39 (m, H, γ-C*H*$_2$), which characterize the polymer chain. (ε-Caprolactone monomer: ^{1}H NMR ($CDCl_3$): δ_H, ppm 4.23 (m, ε-C*H*$_2$), 2.64 (m, α-C*H*$_2$), 1.86 (m, δ-C*H*$_2$), 1.77 (m, β-C*H*$_2$ + γ-C*H*$_2$). ^{13}C NMR($CDCl_3$): δ_H, ppm 176.66 (C=O), 69.50 ($^{\varepsilon}CH_2O$), 34.64 ($^{\alpha}CH_2$), 29.35 ($^{\delta}CH_2$), 29.00 ($^{\beta}CH_2$), 23.00 ($^{\gamma}CH_2$). In the ^{13}C NMR spectrum of PCL, signals are assigned as follows: 173.80 (C=O), 64.37 ($^{\varepsilon}CH_2O$), 34.34 ($^{\alpha}CH_2$), 28.56 ($^{\delta}CH_2$), 25.74 ($^{\beta}CH_2$), 24.80 ($^{\gamma}CH_2$) ppm, [O=C-$^{\alpha}CH_2{}^{\beta}CH_2{}^{\gamma}CH_2{}^{\delta}CH_2{}^{\varepsilon}CH_2$O-]. ^{13}C NMR data of PCL were different than data of ε-caprolactone monomer. For example, while ε-caprolactone monomer gave peaks at 176.66 for C=O and 69.50 for $^{\varepsilon}CH_2O$, PCL gave peaks at 173.80 for C=O and 64.37 ppm for $^{\varepsilon}CH_2O$ respectively. These values are consistent with those in the literature [19, 20]. Butyl(TFPP)tin chloride is an octahedral complex. Only the axial chloride ligand participates in the ring opening polymerization process when it is used as a catalyst. The coordination of the

Table 1. Data for PCL obtained from GPC measurements

Catalyst	T, °C	Time, h	M_w	M_n	(M_w/M_n)	Conversion (%)
Butyl(5,10,15,20-tetrakis(4-fluorophenyl) porphyrinato)tin(IV) chloride, Bu(TFPP)SnCl	40	2	420	420	1.00	38
	40	24	430	430	1.00	63
	60	2	425	420	1.00	42
	60	10	2130	1990	1.10	26
	60	24	4130	3820	1.10	44
	60	48	7170	6380	1.10	57
	80	2	2460	2290	1.10	13
	80	4	5660	5030	1.10	32
	80	6	7840	7170	1.10	40
	80	8	9410	9000	1.00	48
	80	10	12450	10780	1.15	61
	80	24	30640	21940	1.40	86
	80	48	37780	25980	1.45	89
	100	2	11800	10550	1.10	63
	100	4	27580	21050	1.30	63
	100	6	32270	24860	1.30	77
	100	8	32820	21740	1.50	83
	100	10	35790	24010	1.50	>92

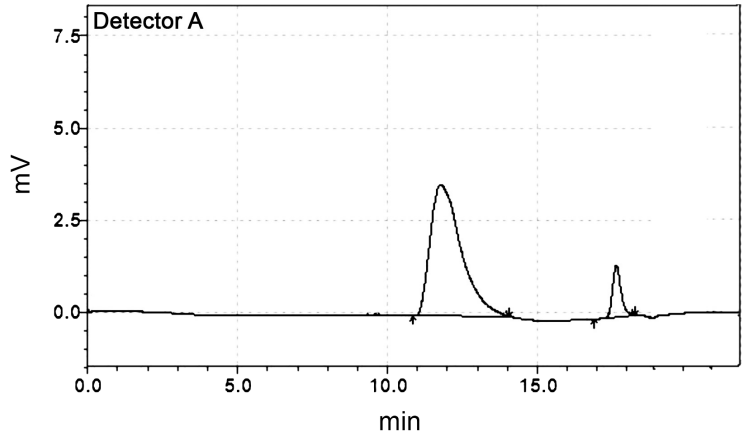


Fig. 3. Gel permeation chromatogram of ε-CL polymer prepared at 100 °C for 10 h with the catalyst Bu(TFPP)SnCl

ε-caprolactone to the tin center is one of the key steps. Coordination to the Lewis acidic tin center (large ionic radius) facilitates ring opening by both an S_N2 and S_N1 reaction pathways [17, 21, 22]. Transition metal and tin compounds carry out ROP of lactides, epoxides, and ε-caprolactone *via* a coordination-insertion mechanism [18, 23]. As seen from Scheme 2, in the S_N2 mechanism the tin ion first allows coordination of the ε-caprolactone to the tin center through the carbonyl oxygen atom. Then, the labile chloride ligand attacks the activated carbonyl group, leading to oxygen-acyl scission. Subsequently, ε-caprolactone molecules coordinate to the tin center and insert in to the tin-chloride bond, resulting in the formation of polycaprolactone. In the S_N1 mechanism, the leaving group chloride first leaves, whereupon a tin cation compound forms that is attacked by the ε-caprolactone.

As seen from Table 1, the conversion of monomer to polymer depends on times and temperatures. For short times and low temperatures, low conversions were

obtained. The conversion increased with the temperature rising from 80 °C (60%) to 100 °C (92%) after 10 h stirring (Fig. 3). Since the polymerization reactions were conducted without solvent, it was difficult to reach 100% conversion because of difficult stirring of viscous PCL. As expected for acidic catalysts, the medium molecular weights of polymers (~35000 Da) were obtained.

CONCLUSION

In this work, novel single site tin porphyrin complexes were synthesized and characterized by a combination of elemental analysis, FTIR, NMR and mass spectroscopic methods. The fluoro-substituted porphyrin tin complex (Bu(TFPP)SnCl) was used as a catalyst for the polymerization of ε-caprolactone at different temperatures and time intervals. Polymers with narrow molecular weight distribution (M_w/M_n = 1.0–1.5) were obtained by using this single site tin catalyst. The structure of polymers was characterized by NMR, FTIR spectroscopy and GPC. In summary, this new fluoro-substituted porphyrin tin complex was good catalyst for ring opening polymerization of ε-caprolactone when compared to the known acid catalysts. In other words, ε-caprolactone polymers were produced with controllable molecular weights and polydispersities by using this single site tin porphyrin catalyst.

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REFERENCES

1. Barbe JM, Ratti C, Richard P, Lecomte C, Gerardin R and Guilard G. *Inorg. Chem.* 1990; **29**: 4126–4130.
2. Rafiemanzelat F, Abdollahi E, Moghadam M, Mirkhani V, Tangestaninejad S and Mohammadpoor-Baltork I. *J. Appl. Polym. Sci.* 2012; **124**: 638–646.
3. Chatterjee C and Chisholm MH. *Inorg. Chem.* 2011; **50**: 4481–4492.
4. Moghadam M, Tangestaninejad S, Mirkhani V, Shaibani R, *Tetrahedron* 2004; **60**: 6105–6111.
5. Berg K, Selbo PK, Weyergang A, Dietze A, Prasmickaite L, Bonsted A, Engesaeter BØ, Angell-Petersen E, Warloe T, Frandsen N and Høgset A, *J. Microsc.* 2005; **218**: 133–147.
6. Kumar AA, Giribabu L, Reddy DR and Maiya BG. *Inorg. Chem.* 2001; **40**: 6757–6766.
7. Arnold DP and Blok J. *Coord. Chem. Rev.* 2004; **248**: 299–319.
8. Yalçın G and Kayan A. *Des. Monomers Polym.* 2012; **15**: 405–416.
9. Kayan A. *Des. Monomers Polym.* 2015; **18**: 545–549.
10. Kayan A. *J. Appl. Polym. Sci.* 2012; **123**: 3527–3534.
11. Adler AD, Sklar L, Longo FR, Finarelli JD and Finarelli MG. *J. Heterocyclic. Chem.* 1968; **5**: 669–678.
12. Lindsey JS, Schreiman IC, Hsu HC, Kearnay PC and Marguerettaz AM. *J. Org. Chem.* 1987; **52**: 827–836.
13. Hayvalı M, Gündüz H, Gündüz N, Kılıç Z and Hökelek T. *J. Molec. Struc.* 2000; **525**: 215–226.
14. Sharma RK, Ahuja G and Sidhwani IT. *Green Chem. Lett. Rev.* 2009; **2**: 101–105.
15. Banfi S, Montanari F and Quici S. *J. Org. Chem*. 1988; **53**: 2863–2866.
16. Hirohara S, Obata M, Alitomo H, Sharyo K, Ando T, Yano S and Tanihara M. *Bioconjugate Chem.* 2009; **20**: 944–952.
17. Chen P, Chisholm MH, Gallucci JC, Zhang X and Zhou Z, *Inorg. Chem.* 2005; **44**: 2588–2595.
18. Aida T and Inoue S. *Acc. Chem. Res.* 1996; **29**: 39–48.
19. Yildiz BC and Kayan A, *Des. Monomers Polym.* 2017; **20**: 89–96.
20. Contreras JM, Medina D, López-Carrasquero F and Contreras RR. *J. Polym. Res.* 2013; **20**: 1–6.
21. Coates GW and Moore DR. *Angew. Chem. Int. Ed.* 2004; **43**: 6618–6639.
22. Moghadam M, Tangestaninejad S, Mirkhani V, Mohammadpoor-Baltork I and Taghavi SA. *Catal. Commun.* 2007; **8**: 2087–2095.
23. Balasanthiran V, Chatterjee C, Chisholm MH, Harrold ND, RajanBabu TV and Warren GA. *J. Am. Chem. Soc.* 2015; **137**: 1786–1789.