Electronic supplementary information (ESI)

Synthesis of Chlorostannate (Ⅱ) Ionic Liquids and Their Novel Application in Preparation of High-quality L-Lactide

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Raman spectra

Raman spectra of the needle-shaped precipitate in [Bmim]Cl−SnCl$_2$ ($x_{\mathrm{SnCl_2}}$ = 0.67) were recorded using a RENISHAW InVia Reflex Raman spectrometer, with a 785 nm focused laser beam.

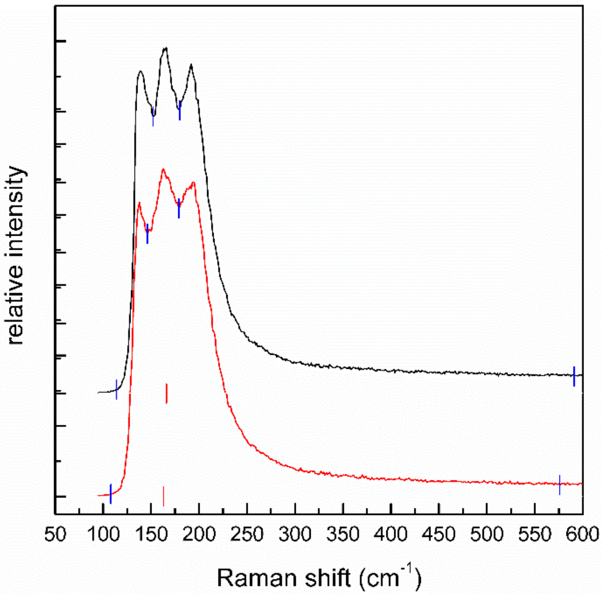

Figure S1. Raman spectra of the needle-shaped precipitate in [Bmim]Cl−SnCl$_2$ ($x_{\mathrm{SnCl_2}}$ = 0.67) and neat tin (II) chloride (Aladdin, ≥99.0%)

Molecular weight determination of O-PLLA.

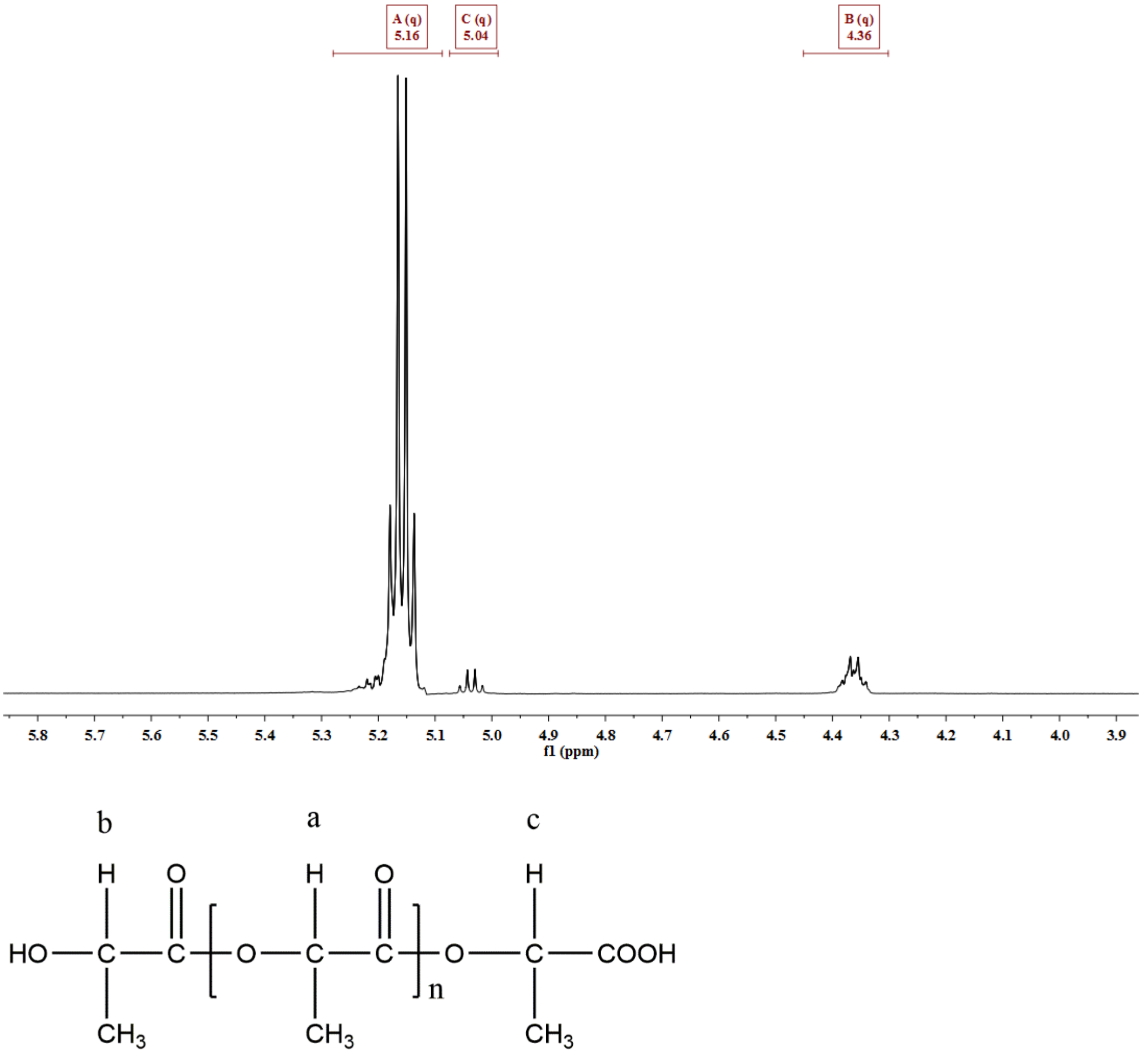

Figure S2. (a) ^{1}H NMR spectra of O-PLLA in $CDCl_3$; (b) Labeling of the different constitutive units of lactic acid oligomers

The number average molecular mass of O-PLLA was determined by ^{1}H NMR. Figure S2 shows the ^{1}H NMR spectra of O-PLLA in $CDCl_3$. There was a quartet locating at 5.16 ppm, which representing the CH proton (a) of repeated chain segments. The quartet occurring at 5.04 ppm was CH proton (c) at carboxyl end units, while the quartet at 4.36 ppm was the CH proton (b) at hydroxyl end units.

The number molecular weight of O-PLLA can be calculated by integrating the peak area of the signal at about 5.16 ppm, 5.04 ppm and 4.36 ppm. The average degree of polymerization (DP) is calculated by eq. (1) derived from the theory that the length of a polymer molecule can be determined from the number of protons in a molecule per proton positioned in its end group. [1-3] After analysis and calculation, the DP of O-PLLA was 12.

$$DP_n = \frac{(a+b+c)}{b} \tag{1}$$

Calculation the fractional amount of *D,L* –lactide.

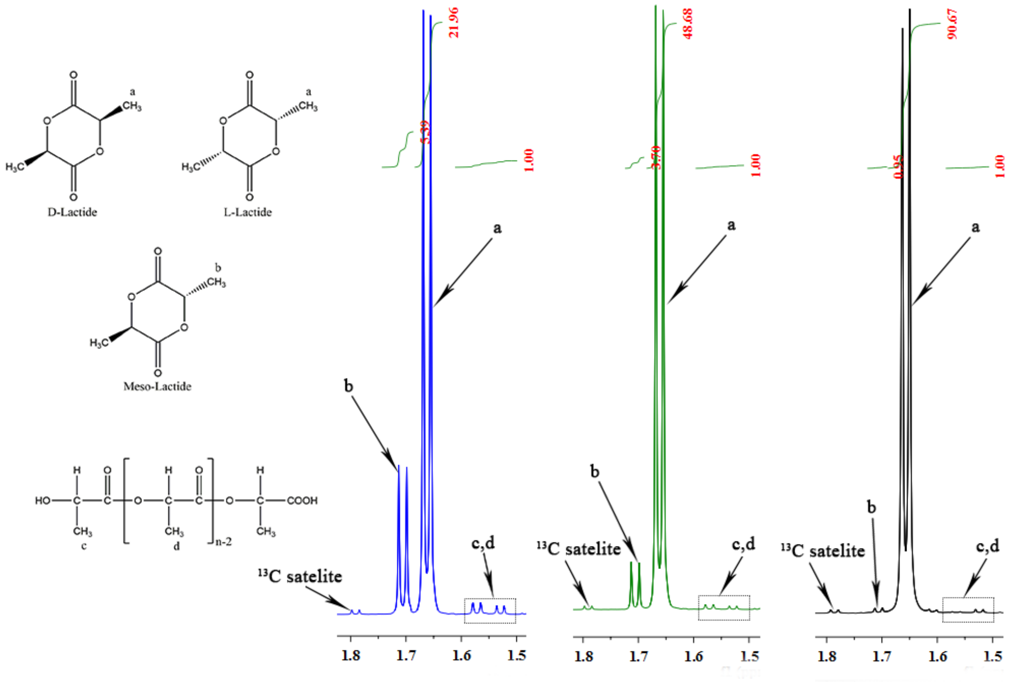

Figure S3. ^{1}H NMR spectra of crude lactide obtained from O-PLLA by different catalyst systems using $SnCl_2$ (a), [Bmim]Cl (b) and [Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.63, c), respectively.

Figure S3 shows the typical ^{1}H NMR spectra of crude lactide obtained by different catalyst systems using $SnCl_2$ (a), [Bmim]Cl (b) and [Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.63, c), respectively. The signals in the ^{1}H NMR spectrum were assigned to the chemical structure of lactide, as shown in Figure S3. [4, 5] The CH_3 signal of *D,L* -lactide was observed at 1.66 ppm. *D,L* -lactide means a minute amount of *D*-lactide in addition to *L* -lactide. However, the CH_3 signal t of *meso*-lactide was shifted downfield at 1.71 ppm, due to higher deshielding effect. The fractional amount of *D,L* -lactide in the product were calculated by comparing the integral areas of these signals.

Isotacticity measured with ^{13}C NMR.

Figure S4 shows typical ^{13}C NMR spectra of the residual PLLAr, and the enlarged carbonyl signals of the residual PLLAr catalyzed by using $SnCl_2$ (a), [Bmim]Cl (b) and [Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.63, c), respectively. The extent of racemization was examined at δ=169.8 ppm where is the carbonyl carbon. As is shown in figure 3, the spectra exhibited five peaks. The isotacticity of the residual PLLAr was calculated by comparing the integral areas of these signals. [1, 6, 7]

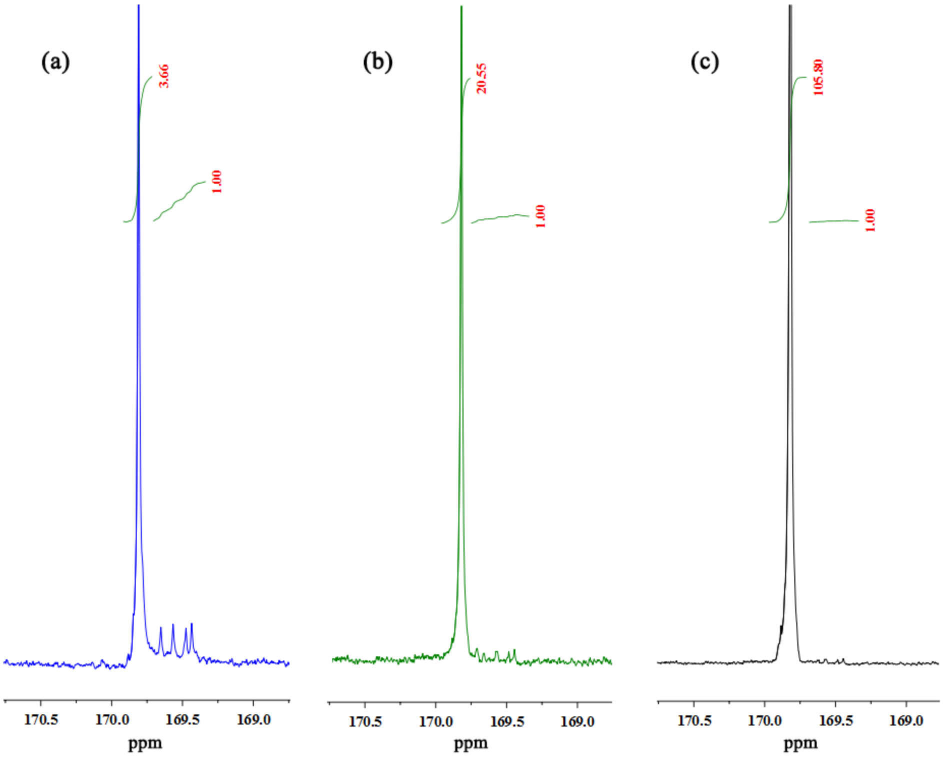

Figure S4. ^{13}C NMR characterization of the residual PLLAr by different catalyst systems using SnCl$_2$ (a), [Bmim]Cl (b) and [Bmim]Cl–SnCl$_2$ ($x_{\mathrm{SnCl_2}}$ = 0.63, c), respectively.

Synthesis of PLLA by using ILs catalysts

When the synthesis of PLLA was carried out by using ILs catalysts, the yield and average degree of the polymerization of PLLA was studied (see Table S1). The *L*-lactic acid vapor is expelled easily by distillation from the reaction part for the synthesis of PLLA. Thus, the synthesis of prepolymer was proceed in three phases (*eg.* 100 ℃, 1h, N$_2$ atmosphere; 130 ℃, 1h, 100 torr; 150 ℃, 1h, 50 torr; 120rpm). Obviously, the loss in the oligomer yield was due to vaporization of the unreacted *L*-lactic acid and oligomer with low molecular weight.

Table S1. Synthesis of PLLA by prepolymerization of *L*-lactic acid (*L*-LA)

No.	Catalyst	Yield %	DP
1	No catalyst [a]	92.2%	12.02
2	No catalyst [a]	92.8%	4.77
3	SnCl2 [c]	91.0%	8.46
4	[Bmim]Cl [c]	93.7%	7.42
5	[Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.33) [c]	92.7%	8.96
6	[Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.50) [c]	93.8%	10.36
7	[Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.60) [c]	92.0%	11.86
8	[Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.63) [c]	94.2%	12.43

a 100 ℃, 1 h, N_2 atmosphere; 130 ℃, 1 h, 100 torr; 150 ℃, 1 h, 50 torr; 120 rpm.

b 100 ℃, 30 min, N_2 atmosphere; 130 ℃, 30 min, 100 torr; 150 ℃, 30 min, 50 torr; 120 rpm.

c 100 ℃, 30 min, N_2 atmosphere; 130 ℃, 30 min, 100 torr; 150 ℃, 30 min, 50 torr; 120 rpm, Catalyst 0.1 mol% relative to *L*-LA.

Molecular weight determination of Residues

Figure S5 shows ^{1}H NMR spectra of PLLA residues in $CDCl_3$ catalyzed by using $SnCl_2$ (a), [Bmim]Cl (b) and [Bmim]Cl−$SnCl_2$ (x_{SnCl_2} = 0.63, c), respectively. The number molecular weight of PLLA residues can be calculated by integrating the peak area of signals. After calculation, the DP of PLLAr was 56 by using $SnCl_2$ catalyst; the DP of PLLAr was 52 by using [Bmim]Cl catalyst; the DP of PLLAr was 49 by using [Bmim]Cl−$SnCl_2$ catalyst.

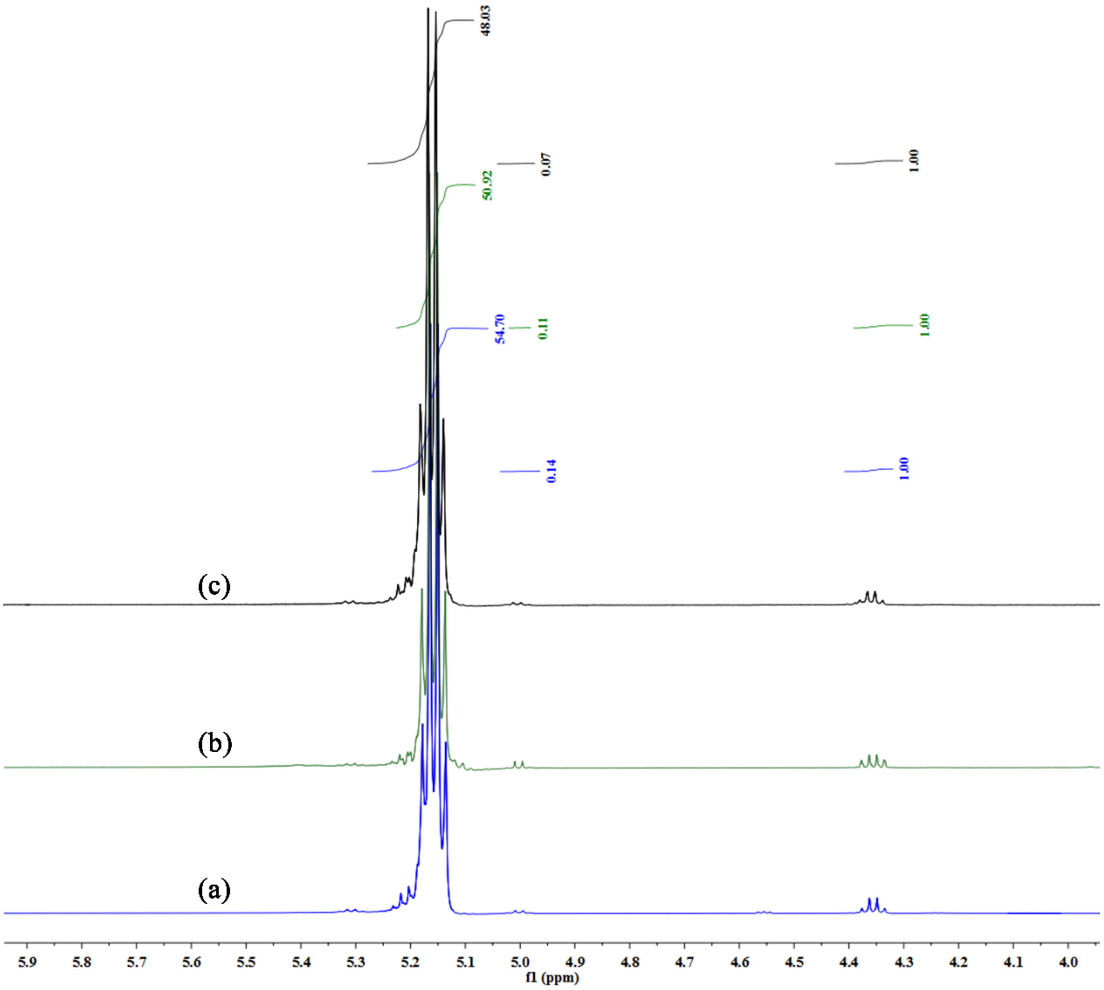

Figure S5. ^{1}H NMR spectra of PLLA residues in $CDCl_3$ by using different catalysts

(a) $SnCl_2$; (b) [Bmim] Cl; (c) [Bmim] Cl - $SnCl_2$ ($x_{SnCl_2} = 0.63$)

References.

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