Supporting Information

Tailoring molecular weight of bio-derived polycarbonates *via* bifunctional ionic liquids catalysts under metal-free conditions

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Totals – 12 pages, 7 figures, 3 tables and 3 equations

Content

1. Specific data of Figure 1

Table S1 Effect of electronegativity and HB formation ability of ILs anions on catalysis performance

Entry	Catalysts	Yield (%)	M_n (g/mol)	M_w (g/mol)	PDI	Charge
1	$[Bmim]_2[Succinate]$	96	27,500	49,600	1.80	-0.4948
2	$[Bmim][C_6H_5COO]$	96	45,500	79,500	1.75	-0.7370
3	[Bmim][HCOO]	96	47,800	86,100	1.80	-0.7857
4	$[Bmim][CH_3COO]$	97	50,300	89,500	1.78	-0.7891
5	$[Bmim][C_2H_5COO]$	97	53,800	86,600	1.61	-0.7932
6	$[Bmim][C_3H_7COO]$	97	57,000	94,100	1.65	-0.8049
7	$[Bmim]_2[Tartrate]$	97	44,100	78,900	1.79	-0.4333
8	$[Bmim][OHCH_2COO]$	95	53,000	83,500	1.57	-0.7484
9	$[Bmim][CH_3CHOHCOO]$	99	61,700	105,800	1.71	-0.7681

2. Kinetic Measurements

Method

The detailed experimental procedures for kinetic study were performed as follows. Under nitrogen atmosphere, 35.78 g (0.25 mol) isosorbide and 53.5 g (0.25 mol) of DPC were charged into a three-necked flask. The temperature was gradually increased and stabilized at 100 °C.[1] Then the catalyst (15 ppm mol) was added into the melt solution. At different reaction time, small amount (0.1-0.2ml) of the reaction melt was sampled and introduced into ampoules, closed and cooled immediately.[1] The concentration of phenol was estimated by Gas chromatography (GC) (Agilent 6820) with a Flame Ionization Detector (FID) detector. Biphenyl was used as the internal standard and dichloromethane was used as the solvent.

Kinetic study of different catalysts

The transesterification reaction rate is significantly affected by the activity of catalyst. Kinetic study on the transesterification of isosorbide and DPC catalyzed by three different ILs were conducted by using the following equations reported by Ignatov et al.[2]

$$k't = [P]/([I]_0^{\,2} - [P][I]_0)$$

$$k = k'/[Cat]$$

where k' is the effective reaction rate constant; [P] is the concentration of phenol; k is the reaction rate; [Cat] is the concentration of catalyst; [I] is the initial concentration of the functional groups (hydroxy groups or carbonyl groups).

By plotting $[P]/([I]_0^{\,2}-[P][I]_0)$ versus time, k' can be obtained by the slope of the linear fitting of the experimental data. Figure S1 showed the activities of the three different catalysts, [Bmim][$CH_3CHOHCOO$], [Bmim][HCOO] and [Bmim][Succinate]. The results are listed in Table S1.

As illustrated by Fig S1 and Table S2, it is confirmed that the reaction rate catalyzed by [Bmim][$CH_3CHOHCOO$] is much higher than that of the other two ILs. The consequence of catalytic activity is in accordance with that of the molecular weight. It makes sense that higher-molecular-weight PIC can be obtained in the presence of a catalyst with higher activity. Therefore, the kinetic study is also a dependable method to evaluate the efficiency of various catalysts.[2]

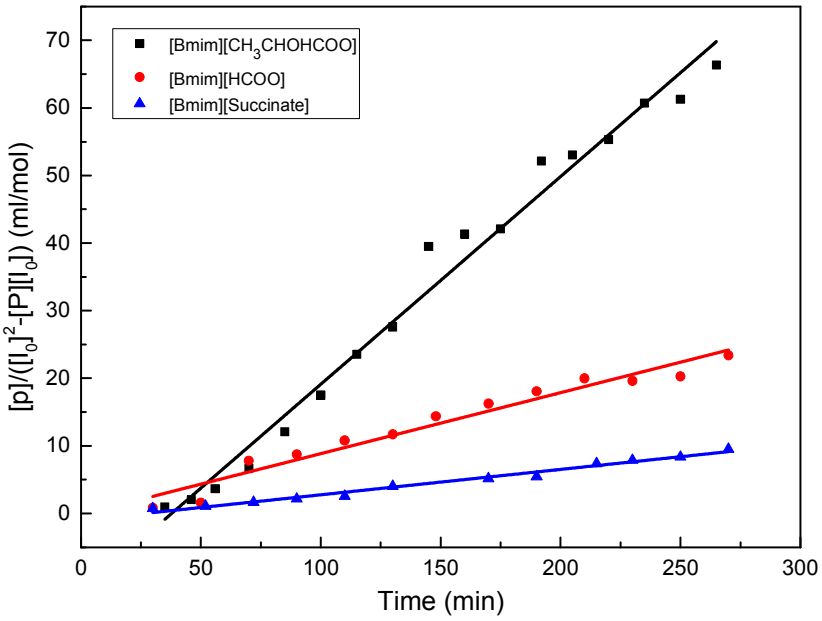

Figure S1. Kinetic curves of the transesterification of isosorbide and DPC with different catalysts.

Table S2 Catalyst activity of the three catalysts

Catalyst	k'	[Cat]	k
[Bmim][$CH_3CHOHCOO$]	0.30732	1.72	178,251
[Bmim][HCOO]	0.09022	1.72	52,328
[Bmim][Succinate]	0.03757	1.72	21,791

3. Characterization of synthesized ILs

[Bmim][HCOO]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.53 (s, 1H), 8.49 (s, 1H), 7.83 (s, 1H), 7.75 (m, 1H), 4.18 (m, 2H), 3.91 (m, 3H), 1.78 (m, 2H), 1.27 (m, 2H), 0.89 (m, 3H).

[Bmim][CH_3COO]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.30 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 4.16 (t, 2H), 3.88(m, 3H), 1.75 (m, 2H), 1.57 (s, 3H), 1.25 (m, 2H), 0.89 (m,3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1228; m/z calcd for $C_2H_3O_2^-$: 59.0139 $[M]^-$, found: 59.0146.

[Bmim][C_2H_5COO]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.23 (s, 1H), 7.77 (s, 1H), 7.71 (s, 1H), 4.16 (t, 2H), 3.85 (s, 2H), 1.88 (m, 2H), 1.76 (m, 2H), 1.27 (m, 2H), 0.91 (t, 3H), 0.87 (m, 3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1218; m/z calcd for $C_3H_5O_2^-$: 73.0295 $[M]^-$, found: 73.0273.

[Bmim][C_3H_7COO]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.41 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 4.17 (t, 2H), 3.85 (s, 3H), 1.79 (t, 2H), 1.76 (m, 2H), 1.38 (m, 2H), 1.25 (m, 2H), 0.89 (m, 3H), 0.79 (t, 3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1221; m/z calcd for $C_4H_7O_2^-$: 87.0452 $[M]^-$, found: 87.0457.

[Bmim][$OHCH_2COO$]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.37 (s, 1H), 7.80 (s, 1H), 7.71 (s, 1H), 4.18 (t, 2H), 3.86 (s, 3H), 3.33 (s, 2H), 1.77 (m, 2H), 1.27 (m, 2H), 0.90 (t, 3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1224; m/z calcd for $C_2H_3O_3^-$: 75.0088 $[M]^-$, found: 75.0076.

[Bmim][$CH_3CHOHCOO$]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.31 (s, 1H), 7.79 (s, 1H), 7.72 (s, 1H), 4.17 (t, 2H), 3.86 (s, 3H), 3.47 (m, 1H), 1.77 (m, 2H), 1.26(m, 3H), 1.06 (d, 3H), 0.90 (t, 3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1222; m/z calcd for $C_3H_5O_3^-$: 89.0244 $[M]^-$, found: 89.0248.

[Bmim][C_6H_5COO]:

^{1}H NMR (700 MHz, DMSO-d_6, δ/ppm relative to TMS): 9.41 (s, 1H), 7.81 (m, 2H), 7.78 (m, 1H), 7.70 (m, 1H), 7.21 (m, 3H), 4.17 (t, 2H), 3.86 (s, 3H), 1.76 (m, 2H), 1.26 (m, 2H), 0.88 (m, 3H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1228; m/z calcd for $C_7H_5O_2^-$: 121.0295 $[M]^-$, found: 121.0298.

[Bmim]$_2$[Tartrate]:

^{1}H NMR (700 MHz, D_2O, δ/ppm relative to TMS): 8.61 (s, 2H), 7.38 (m, 2H), 7.33 (m, 2H), 4.25 (s, 2H), 4.18 (t, 4H), 3.79 (s, 6H), 1.76 (m, 4H), 1.22 (m, 4H), 0.85 (m, 6H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230$[M]^+$, found: 139.1226; m/z calcd for $C_4H_5O_6^-$: 149.0092 $[M]^-$, found: 149.0035.

[Bmim]$_2$ [Succinate]:

^{1}H NMR (700 MHz, D_2O, δ/ppm relative to TMS): 8.61 (s, 2H), 7.37 (t, 2H), 7.33 (t, 2H), 4.10 (t, 4H), 3.79 (s, 6H), 2.31 (s, 4H), 1.75 (m, 4H), 1.22 (m, 4H), 0.83 (t, 6H). HRMS (ESI): m/z calcd for cation $C_8H_{15}N_2^+$: 139.1230 $[M]^+$, found: 139.1221; m/z calcd for $C_4H_5O_4^-$: 117.0193 $[M]^-$, found: 117.0139.

Bmim-2-CO_2:

Bmim-2-CO_2 was prepared using the reported procedures.[3] The mixture of 1-n-buthylimidazole, dimethyl carbonate and methanol was introduced into a Schlenk tube under nitrogen atmosphere, followed by transferring the mixture to a batch reactor. In the reactor, the mixture was heated to 135 °C and reacted for 7 h with stirring. The methanol was evaporated under reduced pressure. Then the obtained residue was washed by dry diethyl ether for 3 times.

^{1}H NMR (600 MHz, D_2O, δ/ppm relative to TMS): 7.37 (d, 1H), 7.32 (d, 1H), 4.31 (t, 2H), 3.84 (s, 3H), 1.74 (m, 2H), 1.22 (m, 2H), 0.83 (m, 3H). ^{13}C NMR (151 MHz, D_2O) δ 158.49, 139.96, 123.38, 122.13, 49.26, 36.38, 31.83, 18.73, 12.59.

TEAI:

TEAI was prepared using the reported procedures.[4] The equimolar amount of imidazole and NaOH were mixed in isopropyl alcohol and refluxed for 30 min. Then tetraethylammonium bromide was added into the above mixture, following by refluxing for 6 h. Next, through filtration and evaporation under reduced pressure, the product could be obtained.

^{1}H NMR (600 MHz, D_2O, δ/ppm relative to TMS): 7.62 (s, 1H), 7.00 (d, 2H), 3.09 (m, 8h), 1.12 (m, 12H)

4. Characterization of PIC and PAICs

PIC: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.10 (m, 2H, H2, H5, isosorbide), 4.88 (m, 1H, H3, isosorbide), 4.53 (m, 1H, H4, isosorbide), 4.15 – 3.81 (m, 4H, H1, H6, isosorbide). ^{13}C NMR (176 MHz, $CDCl_3$) δ 153.93, 153.56, 153.24 (C=O), 85.72 (C3, isosorbide), 81.46 (C4, isosorbide), 80.93 (C5, isosorbide), 77.13 (C2, isosorbide), 73.03 (C1, isosorbide), 70.56 (C6, isosorbide).

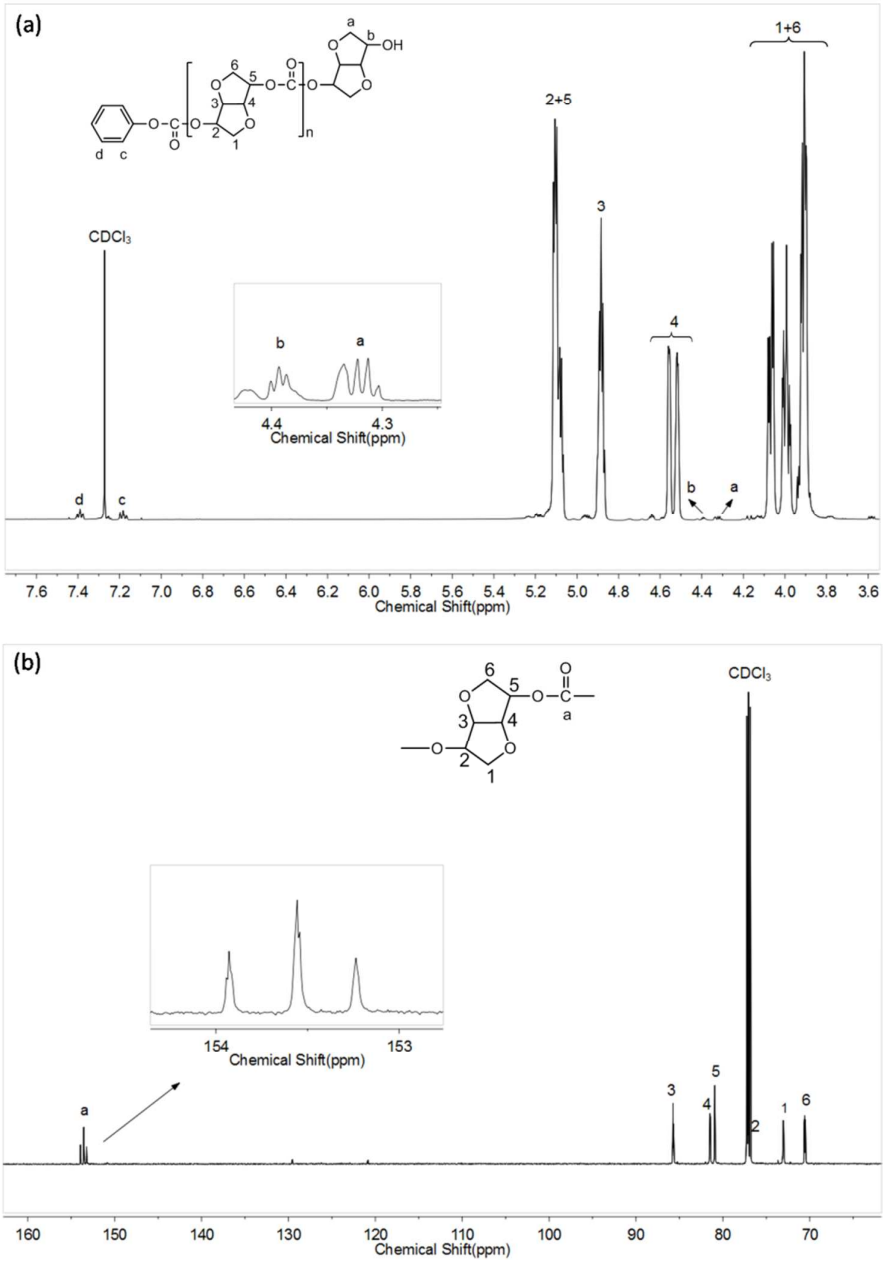

Figure S2. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PIC-1.

PBIC: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.14–5.03 (m, 2H, H2, H5, Isosorbide), 4.94–4.83 (m, 1H, H3, isosorbide), 4.59–4.49 (m, 1H, H4, isosorbide), 4.30–4.11 (m, 4H), 4.11–3.84 (m, 4H, H1, H6, isosorbide), 1.94–1.63 (m, 4H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.91–152.48 (C=O), 85.78 (C3, isosorbide), 81.55 (C4, isosorbide), 80.99 (C5, isosorbide), 76.67 (C2, isosorbide), 73.11 (C1, isosorbide), 70.53 (C6, isosorbide), 67.51 (-<u>C</u>H_2-CH_2-CH_2-<u>C</u>H_2-), 25.09 (-CH_2-<u>C</u>H_2-<u>C</u>H_2-CH_2-).

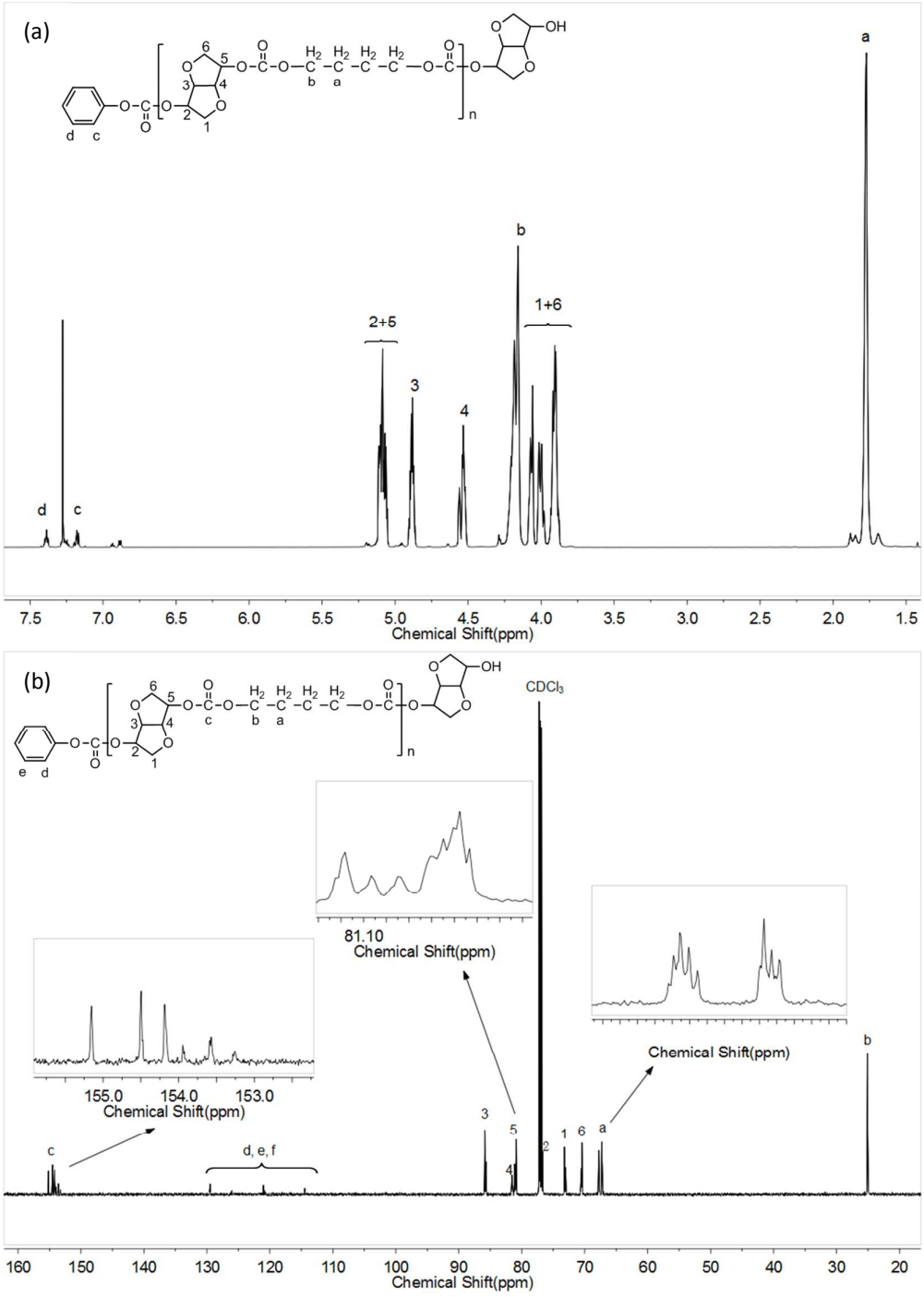

Figure S3. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PBIC.

PHIC: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.18 – 4.99 (m, 2H, H2, H5, Isosorbide), 4.94 – 4.80 (m, 1H, H3, isosorbide), 4.60 – 4.46 (m, 1H, H4, isosorbide), 4.15 (m, 4H), 4.08 – 3.84 (m, 4H, H1, H6, isosorbide), 1.70 (m, 4H), 1.42 (t, 4H). ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.33-153.58 (C=O), 85.77 (C3, isosorbide), 81.54 (C4, isosorbide), 80.96 (C5, isosorbide), 77.18, 76.58 (C2, isosorbide), 73.25, 73.04 (C1, isosorbide), 70.50 (C6, isosorbide), 68.32, 67.76(-CH_2-CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2-CH_2-), 28.49 (-CH_2-$\underline{C}H_2$-CH_2-CH_2-$\underline{C}H_2$-CH_2-), 25.32 (-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2-$\underline{C}H_2$-).

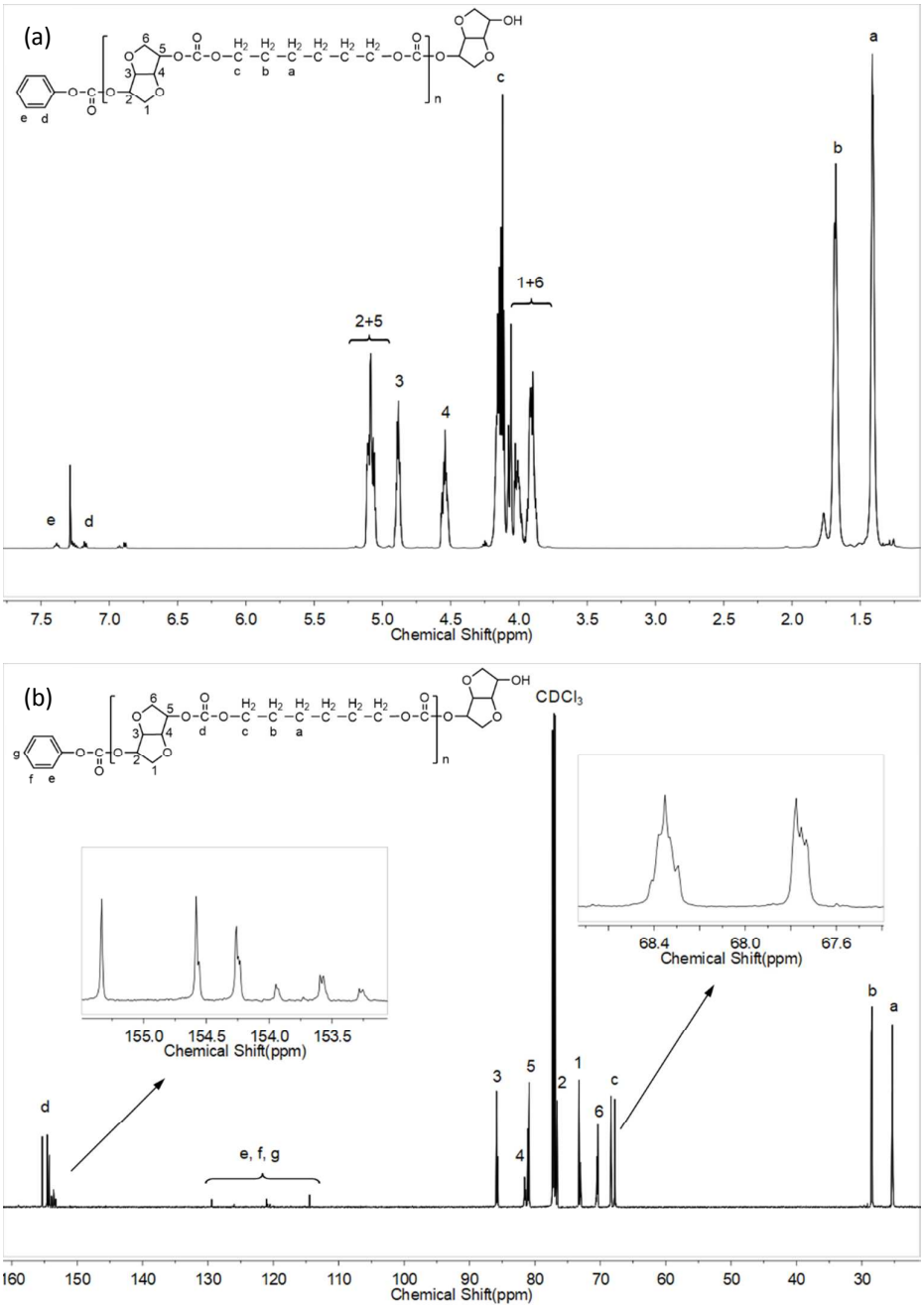

Figure S4. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PHIC.

PGIC: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.22–4.99 (m, 2H, H2, H5, Isosorbide), 4.89 (d, 1H, H3, isosorbide), 4.59–4.46 (m, 1H, H4, isosorbide), 4.31 (m, 4H, -C$\underline{H_2}$-CH2-O-CH2-C$\underline{H_2}$-), 4.11–3.82 (m, 4H, H1, H6, isosorbide), 3.73(t, 4H, -CH2-C$\underline{H_2}$-O-C$\underline{H_2}$-CH2-). ^{13}C NMR (176 MHz, $CDCl_3$) δ 155.78–152.57 (C=O), 85.81 (C3, isosorbide),81.37 (C4, isosorbide), 80.90 (C5, isosorbide), 77.12, 76.80 (C2, isosorbide), 73.09 (C1, isosorbide), 70.48 (C6, isosorbide), 68.80 (-$\underline{C}H_2$-CH_2-O-CH_2-$\underline{C}H_2$-), 67.23, 66.93 (-CH_2-$\underline{C}H_2$-O-$\underline{C}H_2$-CH_2-).

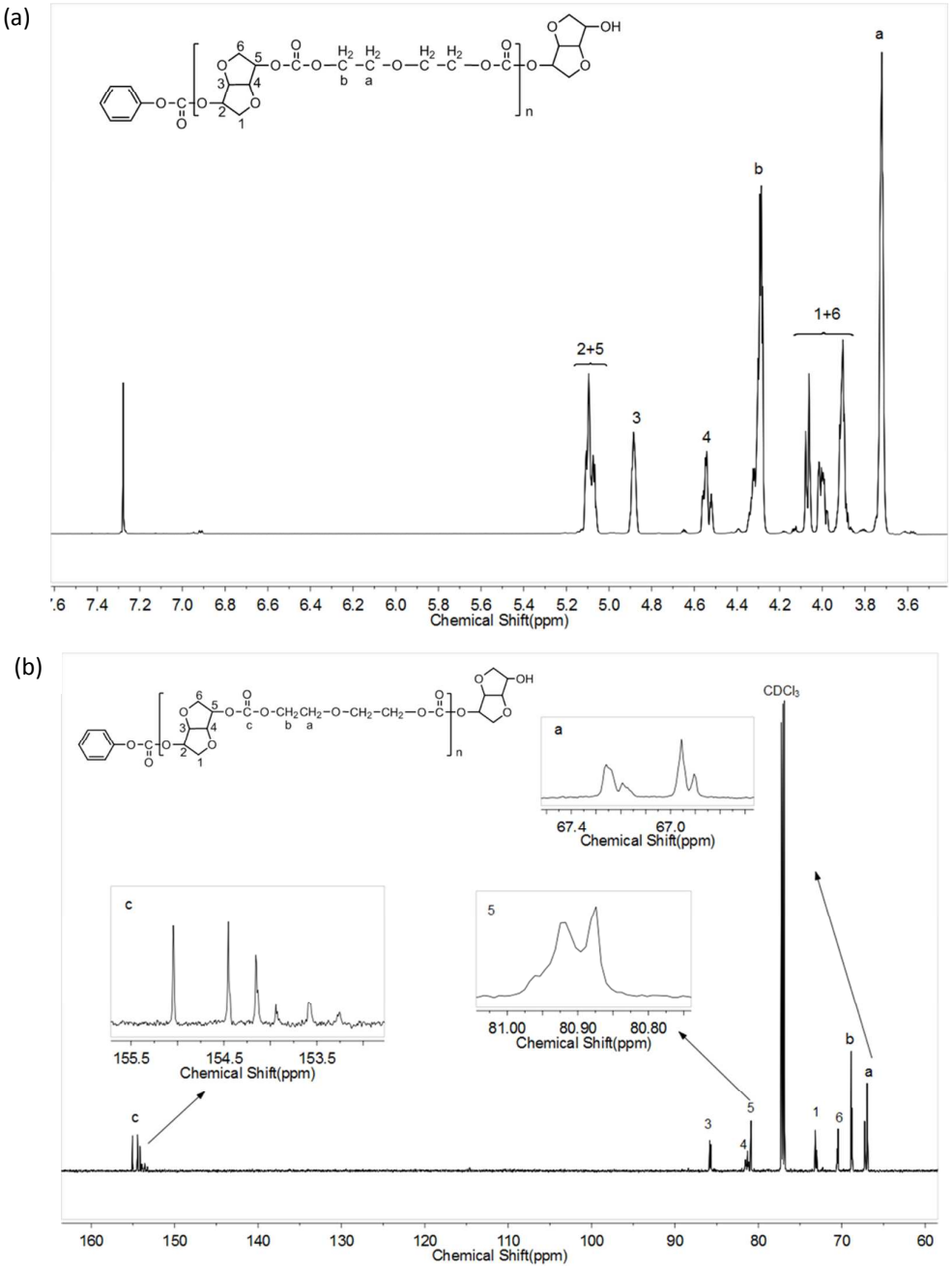

Figure S5. The ^{1}H NMR (a) and ^{13}C NMR (b) spectra of PGIC.

PCIC: ^{1}H NMR (700 MHz, $CDCl_3$) δ 5.18–4.98 (m, 2H, H2, H5, Isosorbide), 4.87 (m, 1H, H3, isosorbide), 4.62–4.44 (m, 1H, H4, isosorbide), 4.13–3.96 (m, 4H, -O-CH_2-C-ring), 3.96–3.85 (m, 4H, H1, H6, isosorbide), 2.01–0.86 (m, 10H, H1-H6, cyclohexane group (C-ring)). ^{13}C NMR (176 MHz, $CDCl_3$) δ 156.07–152.39 (C=O), 85.78 (C3, isosorbide), 81.54 (C4, isosorbide), 80.97 (C5, isosorbide), 76.63 (C2, isosorbide), 73.01 (C1, isosorbide), 71.06 (-O-CH_2-C-ring), 70.63 (C6, isosorbide), 36.95, 34.45, (C1, C4, C-ring), 28.49,25.04, (C2, C3, C5, C6, C-ring).

The microstructure of PAICs was characterized by ^{13}C NMR. The carbonyl carbon was split to sextuple peaks according to its expanded spectrum from Figure S6. The signals were donated as AA, AIs (or IsA), and IsIs respectively to present the different ways of connection. The microstructure of PAICs were analyzed through integration of the sextuple peaks. Based on the integration area of split peaks, the degree of randomness (B) and the number-average sequence length (L_n) were obtained by the following equations:[5]

$$L_{nAC} = \frac{f_{AC/IsC} + 2f_{AC/AC}}{f_{AC/IsC}} \quad (1)$$

$$L_{nIsC} = \frac{f_{AC/IsC} + 2f_{IsC/IsC}}{f_{AC/IsC}} \quad (2)$$

$$B = \frac{1}{L_{nAC}} + \frac{1}{L_{nIsC}} \quad (3)$$

where f represents the molar fraction, AC and IsC are aliphatic carbonate unit and isosorbide carbonate unit, respectively. When B equals to 1, the repeating units of AC and IsC present irregular distribution and the polymer is defined as random copolymer. When B equals to 0, the polymer is the simple blending of homopolymers. When B equals to 2, the polymer is alternating copolymer. The calculated results were summarized in Table S3. It can be known that the B values are all approximate equal to 1, which indicates that the synthesized PAICs are all random copolymers.

Table S3 Microstructure of PAICs based on ^{13}C NMR

PAICs	Dyads (mol %)[a]			L_n		B
	AA	AIs/IsA	IsIs	L_{nAc}	L_{nIsc}	
PCIC	21.64	53.90	24.46	1.80	1.91	1.08
PHIC	20.79	56.13	23.08	1.74	1.82	1.12
PGIC	22.99	54.48	22.53	1.84	1.83	1.09
PBIC	21.41	53.53	25.06	1.80	1.94	1.07

[a]Obtained from the ^{13}C NMR integration peak area.

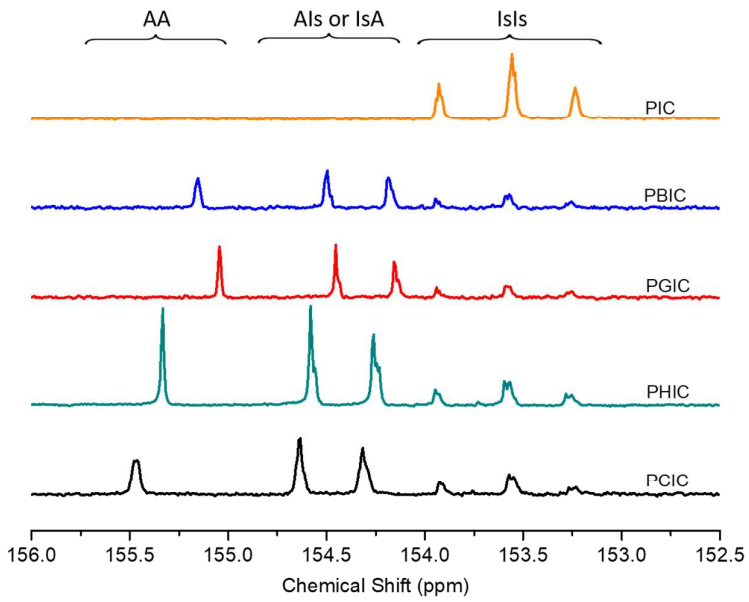

Figure S6. Expanded ^{13}C NMR spectrum of PAICs for carbonyl carbon.

5. Chemical shift of isosorbide

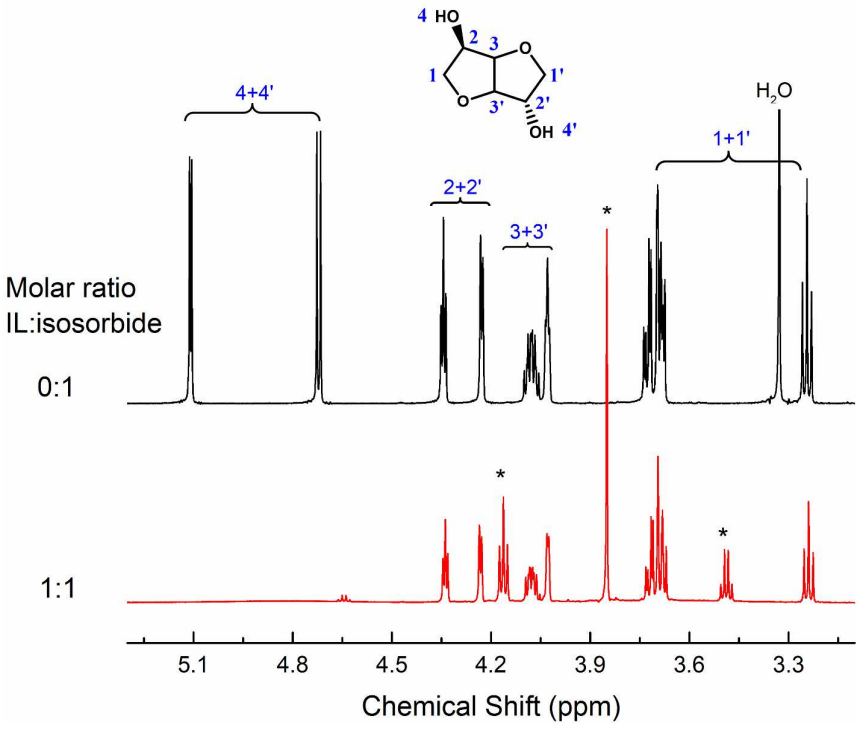

Figure S7. The chemical shift of isosorbide with the molar ratio of [Bmim][$CH_3CHOHCOO$] to isosorbide from 0:1 to 1:1 in the ^{1}H NMR spectrum. The peak with * means the corresponding protons from [Bmim][$CH_3CHOHCOO$].

Reference

1. Eo, Y. S.; Rhee, H.-W.; Shin, S., Catalyst screening for the melt polymerization of isosorbide-based polycarbonate. *J. Ind. Eng. Chem.* **2016,** *37*, 42-46. DOI: 10.1016/j.jiec.2016.03.007.
2. Ignatov, V. N.; Tartari, V.; Carraro, C.; Pippa, R.; Nadali, G.; Berti, C.; Fiorini, M., New Catalysts for Bisphenol A Polycarbonate Melt Polymerisation, 1. Kinetics of Melt Transesterification of Diphenylcarbonate with Bisphenol A. *Macromol. Chem. Phys.* **2001,** *202* (9), 1941-1945. DOI: 1022-1352/2001/0906-1941$17.50+.50/0.
3. Naik, P. U.; Refes, K.; Sadaka, F.; Brachais, C.-H.; Boni, G.; Couvercelle, J.-P.; Picquet, M.; Plasseraud, L., Organo-catalyzed synthesis of aliphatic polycarbonates in solvent-free conditions. *Polym. Chem.* **2012,** *3* (6), 1475-1480. DOI: 10.1039/c2py20056b.
4. Sun, W.; Xu, F.; Cheng, W.; Sun, J.; Ning, G.; Zhang, S., Synthesis of isosorbide-based polycarbonates via melt polycondensation catalyzed by quaternary ammonium ionic liquids. *Chinese J. Catal.* **2017,** *38* (5), 908-917. DOI: 10.1016/S1872-2067(17)62822-5.
5. Li, Q.; Zhu, W.; Li, C.; Guan, G.; Zhang, D.; Xiao, Y.; Zheng, L., A non-phosgene process to homopolycarbonate and copolycarbonates of isosorbide using dimethyl carbonate: Synthesis, characterization, and properties. *J. Polym. Sci., Part A: Polym. Chem.* **2013,** *51* (6), 1387-1397. DOI: 10.1002/pola.26507.