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Supplemental Information to:

Tailoring molecular weight of isosorbide-derived polycarbonates via regulating the H-bond donor/acceptor ability of task-specific ionic liquid catalysts

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Content

1. Materials

Isosorbide (ISB, 98%) was obtained from Alfa Aesar and recrystallized with acetone before use. Dimethyl carbonate (DMC, 99%, anhydrous) and acetic acid (99.8%) were received from Aladdin Biochemical Technology Co., Ltd., (Shanghai, China). 1-ethyl-3-methylimidazolium chloride ([Emim]Cl, 98%), 1-ethyl-2,3-dimethylimidazolium chloride ([EMmim]Cl, 98%), 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl, 98%), and 1-decyl-3-methylimidazolium chloride ([Dmim]Cl, 99%) were purchased from Shanghai Macklin Biochemical Technology Co., LTD. 1-propyl-3-methylimidazolium chloride ([Pmim]Cl, 98%), 1-pentyl-3-methylimidazolium chloride ([$P_n$mim]Cl, 98%), and 1-octyl-3-methylimidazolium chloride ([Omim]Cl, 97%) were received from Shanghai Cheng Jie Chemical Co. Ltd. The anion exchange resin Ambersep 900(OH) was received from Alfa Aesar and was washed to neutral before use.

2. Synthesis of IL catalysts

These IL catalysts were prepared through the typical acid-base neutralization process referring to the previous work.[1,2] The synthesis of [Emim][OAc] was taken as an example and described as follows. Firstly, the proper amount of the anion exchange resin Ambersep® 900(OH) was loaded into the ion exchange column. Then, the appropriate amount of [Emim]Cl dissolved in CH_3OH flowed slowly through the ion exchange column. The obtained liquid was the solution [Emim]OH in methanol. Subsequently, an equimolar quantity of CH_3COOH was added into the solution of [Emim]OH in methanol and the mixture was stirred for 24 h at 25 ^oC. Next, the mixture was washed, and reduced pressure distillation. Finally, the colorless liquid [Emim][OAc] was vacuum-dried for 24 h at 55 ^oC.

3. Synthesis, separation, and analysis of PIC precursors

The synthesis and purification of MC-1, MC-2, and DC were according to the previous literature.[3,4] The specific process is as follows. The pre-polymerization stage was implemented in a 250 mL four-necked flask provided with a feed inlet, a N_2 inlet, a mechanical stirrer, and a rectifying column. Under the protection of N_2, ISB (10 g, 0.0684 mol), DMC (46.23 g, 0.5132 mol), and IL catalyst (0.88 mol% based on ISB) were added into the flask with stirring, and the oil bath temperature was increased gradually to 98 ºC. The fractionating head was maintained at 40~65 ºC. Several hours later, the reaction mixture was concentrated. Then the mixture was incorporated into a silica gel column chromatograph with gradient elution consisting of CH_2Cl_2 and CH_3OH. The volume ratio of CH_3OH gradually increased from 0 to 20%. Then, DC, MC-1, and MC-2 were obtained in order. HPLC analysis was implemented with a differential refraction detector (RID). The transesterification products were separated from the mobile phase of methanol and water. The calibration curves were implemented by using MC-1, MC-2, and DC concentrations between 20 and 2500 ppm with isosorbide 5-mononitrate as the internal standard. The reaction liquid of the transesterification stage was concentrated, and then an appropriate amount of the viscous product was dissolved in methanol, and isosorbide 5-mononitrate was added as an internal standard substance. Subsequently, the sample was injected into the HPLC and the selectivity of products was determined from the calibration curves. The characterization analysis of MC-1, MC-2, and DC has reported in our previous work.[1]

4. Characterization methods

Mass spectra data were collected on a Bruker micrQTOF-Q II mass spectrometer. The 1H NMR and ^{13}C NMR spectra analysis were dissolving in d_6-DMSO or $CDCl_3$ and tetramethylsilane (TMS) as the internal reference and carried out using a Bruker AVANCE III HD 600 MHz NMR spectrometer. The selectivity of transesterification products was analyzed on a SHIMADZU LC-20AT HPLC equipped with a differential refraction detector (RID) and an InertSustain C18 chromatographic column.[1] The ISB conversion was measured via a GC system (Agilent 7890B) using a TCD detector. The molecular weights of obtained PICs were measured on an Agilent PL-GPC 50 gel permeation chromatography (GPC). Polystyrene and the moving phase of dimethylformamide (DMF) were used to establish the calibration curve. Thermogravimetric Analysis (TGA) was analyzed on a Diamond TG/DTA6300 thermal analyzer with a heating rate of 10 °C/min under an N_2 atmosphere. The glass transition temperature was measured on a Mettler Toledo DSC 1 differential scanning calorimeter (DSC) with a heating rate of 10 °C/min. Scanning electron microscopy (SEM) images were acquired with JEM6700E, JEOL. Mass spectra data were determined on a Bruker micrQTOF-Q II electron spray ionization mass spectrometer. The intermediates were captured and analyzed by ESI-MS spectra as follows: Firstly, the obtained PIC multimers catalyzed by [Pmim][OAc] were sampled at 160 °C. Subsequently, the obtained PIC multimers were quenched with liquid nitrogen and stored in the refrigerator. Then, a proper sample was taken and dissolved in methanol for ESI-MS analysis.

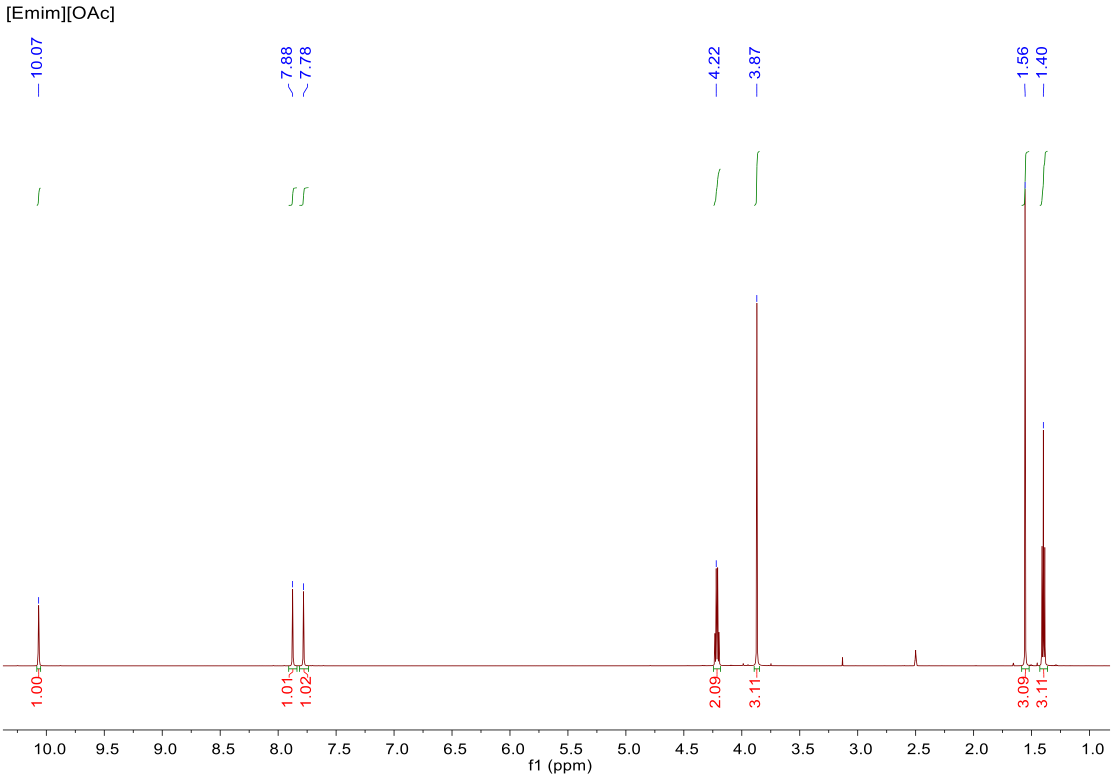
5. Computational details

All density functional theory calculations were performed in the Gaussian 09 package.[5] The structures were optimized at B3LYP/6-311+G* level.[6-12]

6. IL catalysts characterizations

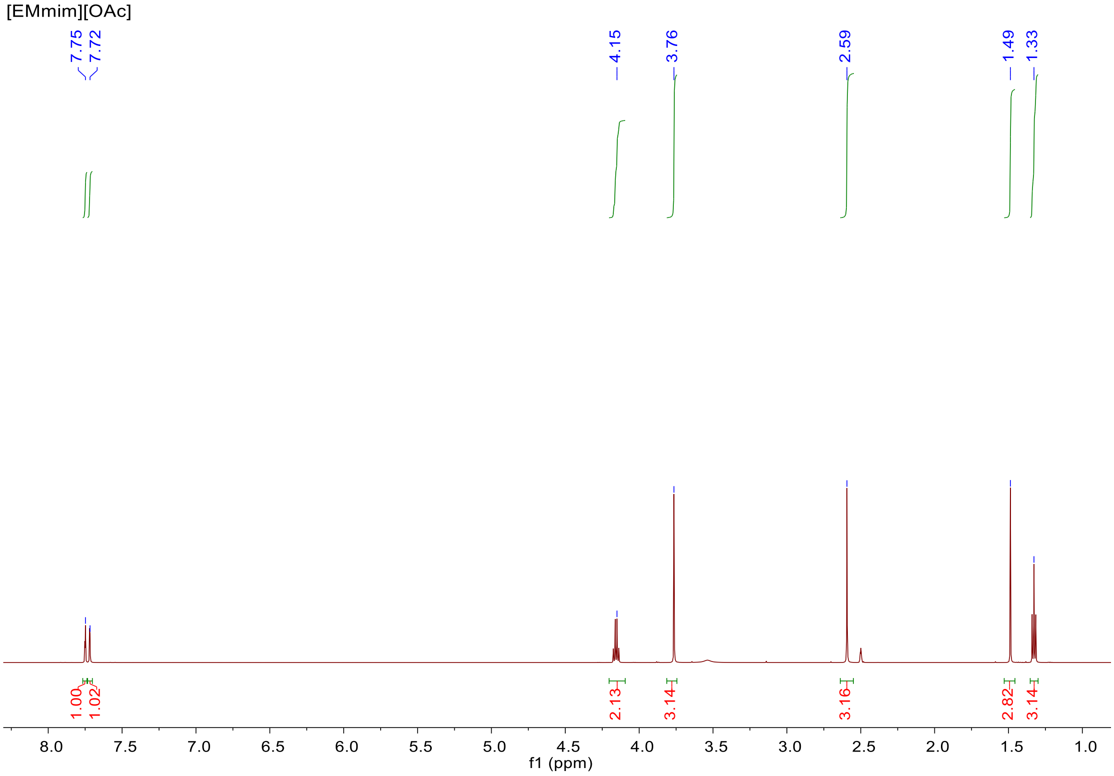
[Emim][OAc]:

^{1}H NMR (600 MHz, DMSO-d_6): δ 10.07 (s, 1H), 7.88 (t, 1H), 7.78 (t, 1H), 4.22 (m, 2H), 3.87 (s, 3H), 1.56 (s, 3H), 1.40 (t, 3H); MS (ESI): m/z: 111.14 [Emim], 281.25 $[Emim]_2[OAc]$.



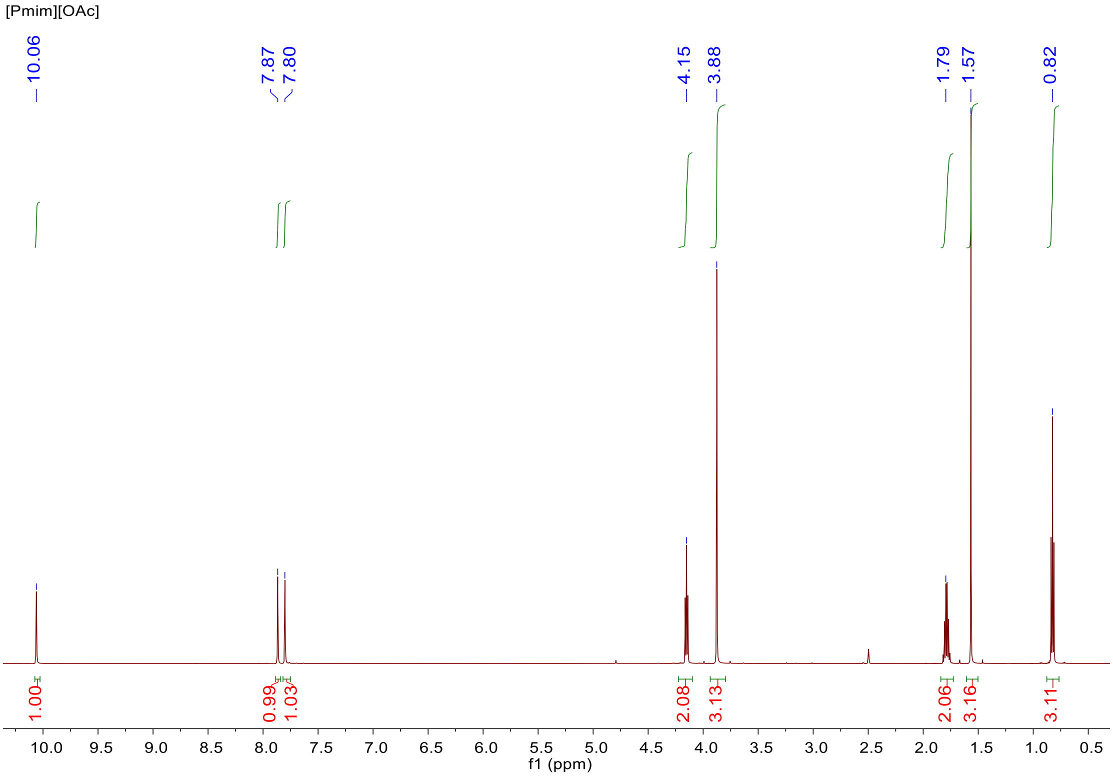
[EMmim][OAc]:

^{1}H NMR (600 MHz, DMSO-d_6): δ 7.75 (d, 1H), 7.72(d, 1H), 4.15 (m, 2H), 3.76 (s, 3H), 2.59 (s, 3H), 1.49 (s, 3H), 1.33 (t, 3H); MS (ESI): m/z: 125.13 [EMmim], 309.28 $[EMmim]_2[OAc]$.



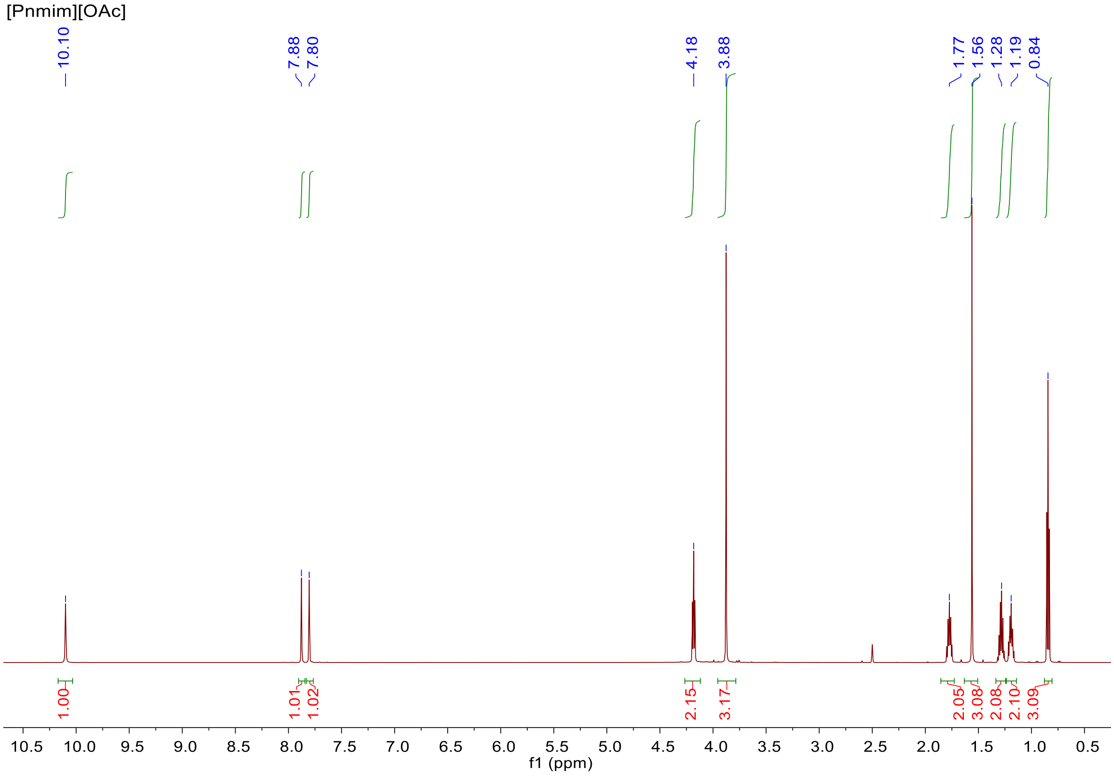
[Pmim][OAc]:

^{1}H NMR (600 MHz，DMSO-d$_6$): δ 10.06 (s, 1H), 7.87 (t, 1H). 7.80 (t, 1H), 4.15 (t, 2H), 3.88 (s, 3H), 1.79 (m, 2H), 1.57 (s, 3H), 0.82 (t, 3H); MS (ESI): m/z: 125.11 [Pmim], 309.23 [Pmim]$_2$[OAc].



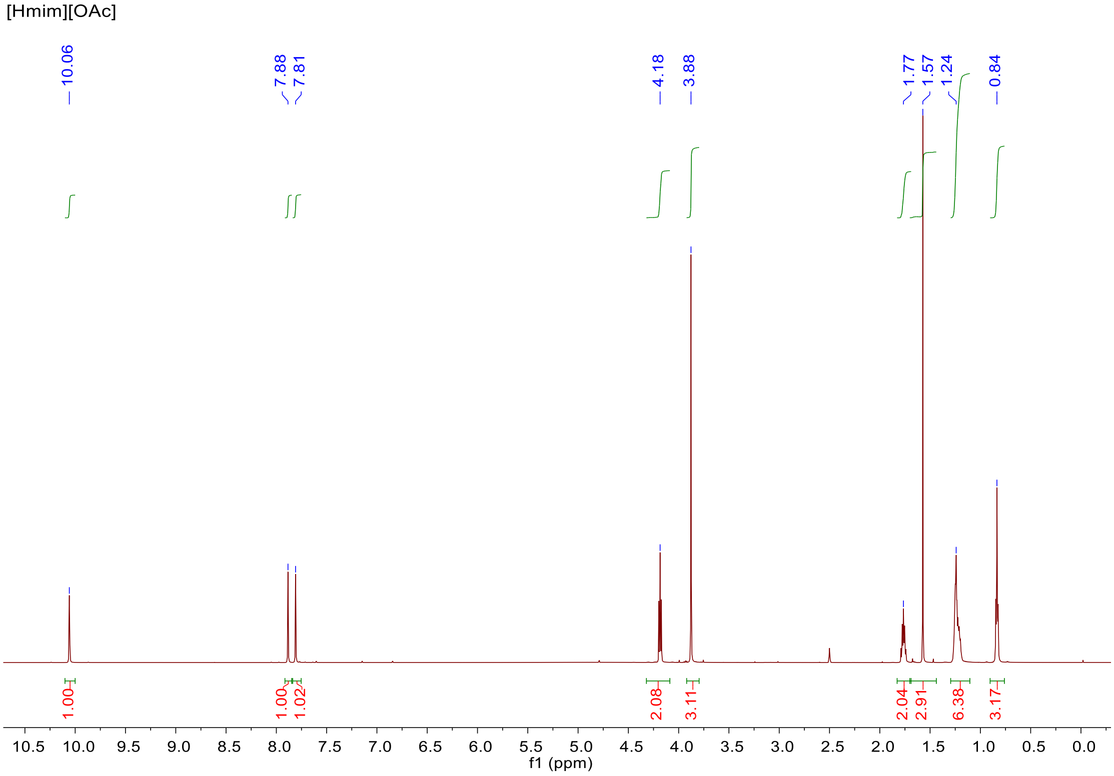
[P$_n$mim][OAc]:

^{1}H NMR (600 MHz, DMSO-d$_6$): δ 10.10 (s, 1H), 7.88 (s, 1H), 7.80 (s, 1H), 4.18 (t, 2H), 3.88 (s, 3H), 1.77 (m, 2H), 1.56 (s, 3H), 1.28 (m, 2H), 1.19 (m, 2H), 0.84 (t, 3H); MS (ESI): m/z: 153.17 [P$_n$mim], 365.39 [P$_n$mim]$_2$[OAc].



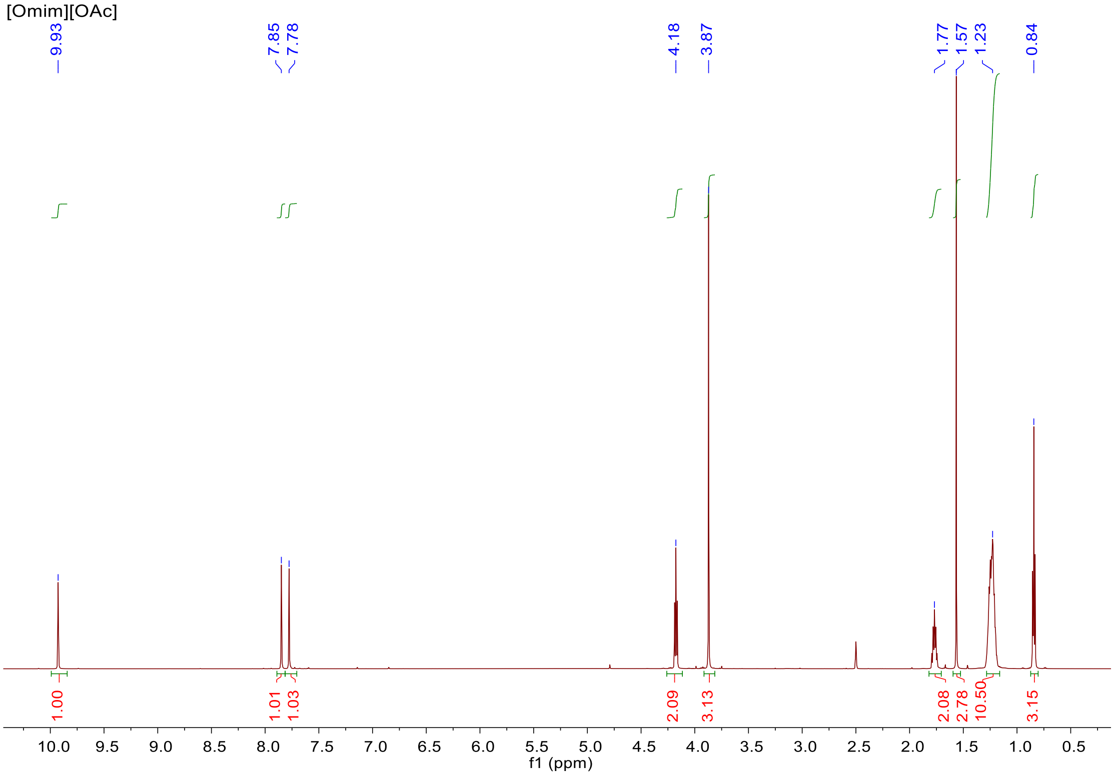
[Hmim][OAc]:

^{1}H NMR (600 MHz, DMSO-d$_6$): δ 10.06 (s, 1H), 7.88 (t, 1H), 7.81 (t, 1H), 4.18 (t, 2H), 3.88 (s, 3H), 1.77 (m, 2H), 1.57 (s, 3H), 1.24 (m, 6H), 0.84 (t, 3H); MS (ESI): m/z: 167.19 [Hmim], 393.39 [Hmim]$_2$[OAc].



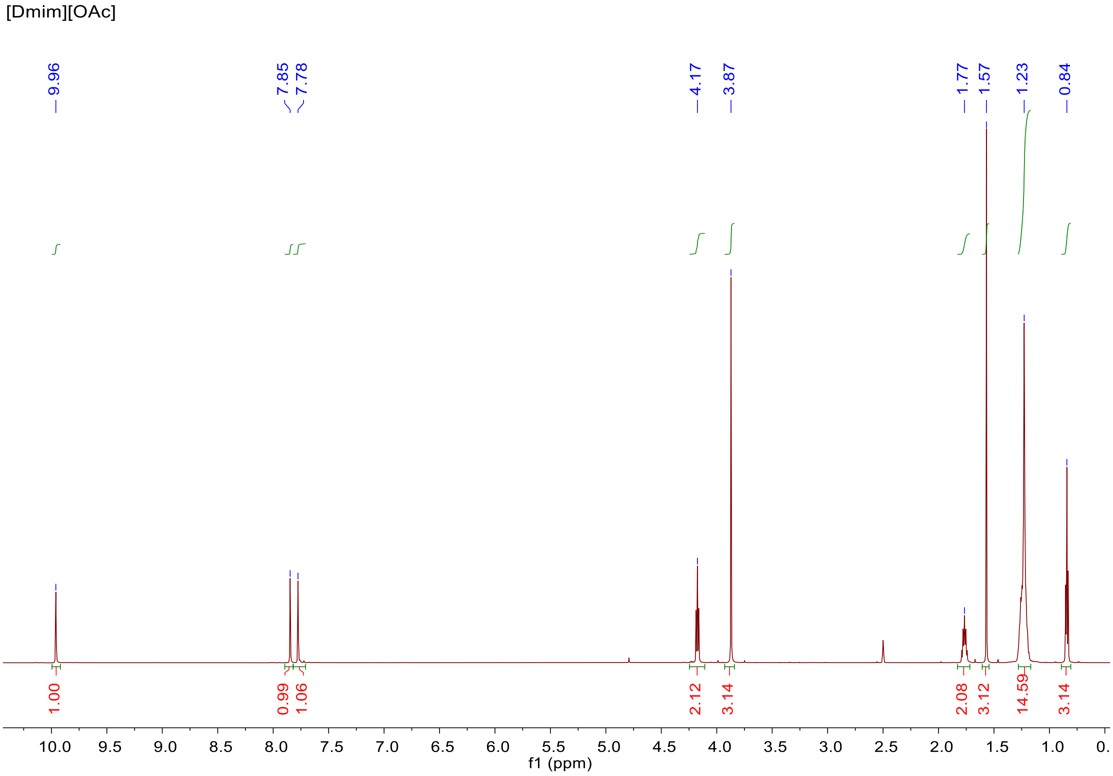
[Omim][OAc]:

^{1}H NMR (600 MHz, DMSO-d_6): δ 9.93 (s, 1H), 7.85 (t, 1H), 7.78 (t, 1H), 4.18 (t, 2H), 3.87 (s, 3H), 1.77 (m, 2H), 1.57 (s, 3H), 1.23 (m, 10H), 0.84 (t, 3H); MS (ESI): m/z: 195.19 [Omim], 449.39 $[Omim]_2[OAc]$.



[Dmim][OAc]:

^{1}H NMR (600 MHz, DMSO-d_6): δ 9.96 (s, 1H), 7.85 (t, 1H), 7.78 (t, 1H), 4.17 (t, 2H), 3.87 (s, 3H), 1.77 (m, 2H), 1.57 (s, 3H), 1.23 (m, 14H), 0.84 (t, 3H); MS (ESI): m/z: 223.25 [Dmim], 505.49 [Dmim]$_2$[OAc].



7. The thermostability of IL catalysts

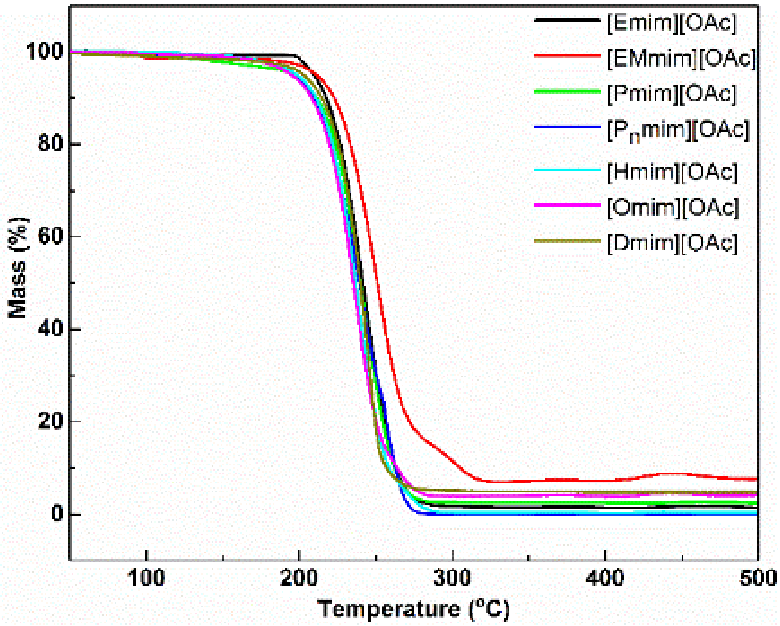


Fig.S1 The TGA curves of the synthesized IL catalyst.

8. The effects of transesterification time on the polymerization process

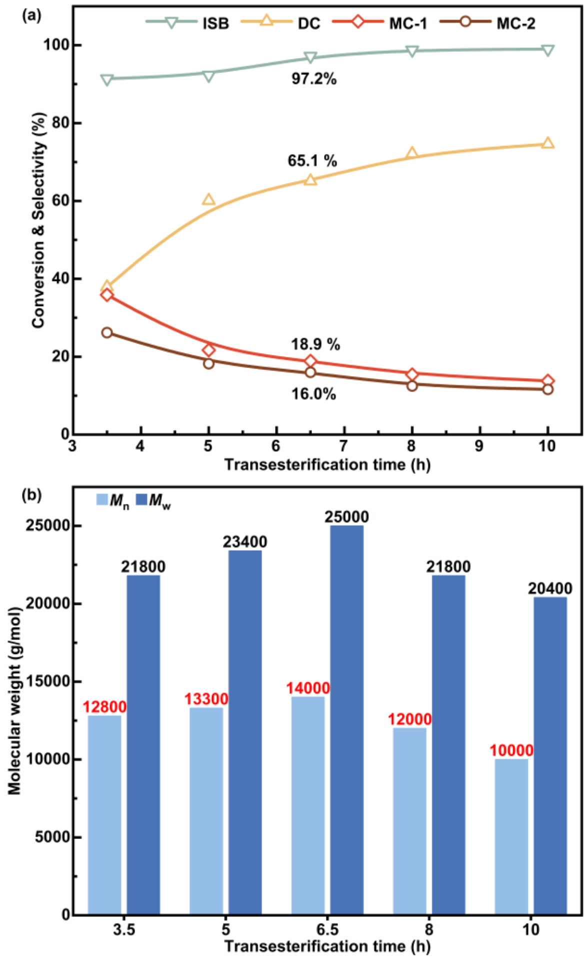


Fig.S2 Effect of transesterification time on (a) transesterification stage; (b) polycondensation stage. (Molar ratio DMC/ISB: 10/1; transesterification temperature: 98 °C; cat. amount: 4.4×10^{-3} equiv. mol based on ISB; polycondensation temperature: 200 °C; polycondensation time: 1.5 h.)

9. The effects of polycondensation temperature and time on PIC molecular weight

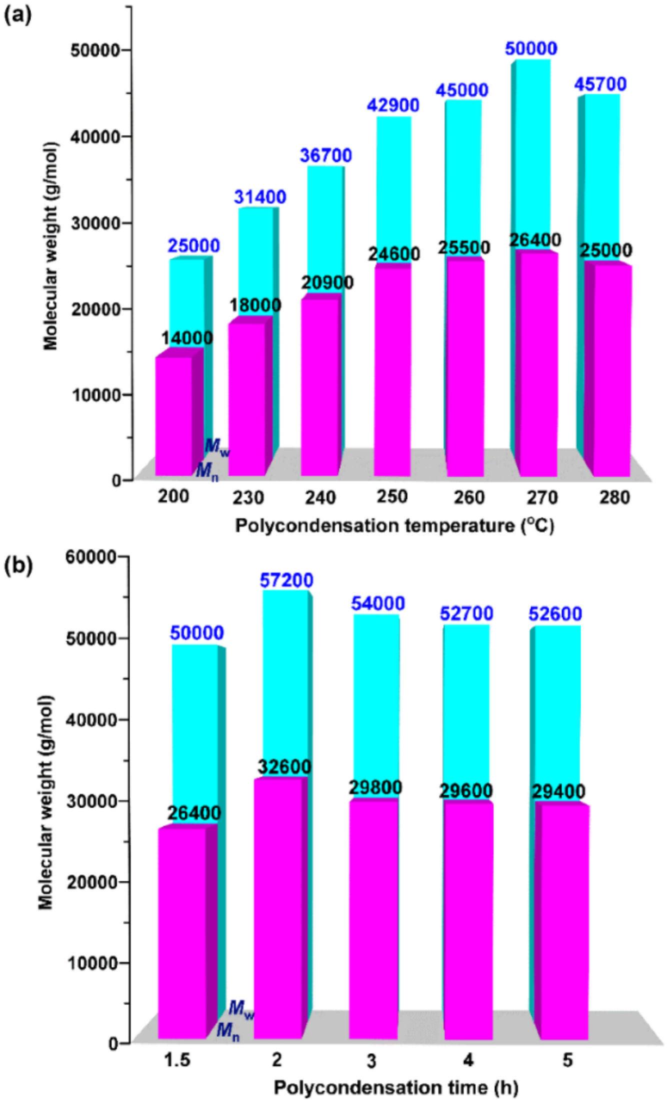


Fig.S3 Effect of (a) polycondensation temperature (Molar ratio DMC/ISB: 10/1; transesterification temperature: 98 °C; transesterification time: 6.5 h; cat. amount: 4.4×10^{-3} equiv. mol based on ISB; polycondensation time: 1.5 h.), and (b) polycondensation time on PIC molecular weight (Molar ratio DMC/ISB: 10/1; transesterification temperature: 98 °C; transesterification time: 6.5 h; cat. amount: 4.4×10^{-3} equiv. mol based on ISB; polycondensation temperature: 270 °C.).

10. The ^{13}C NMR spectra of the obtained PIC

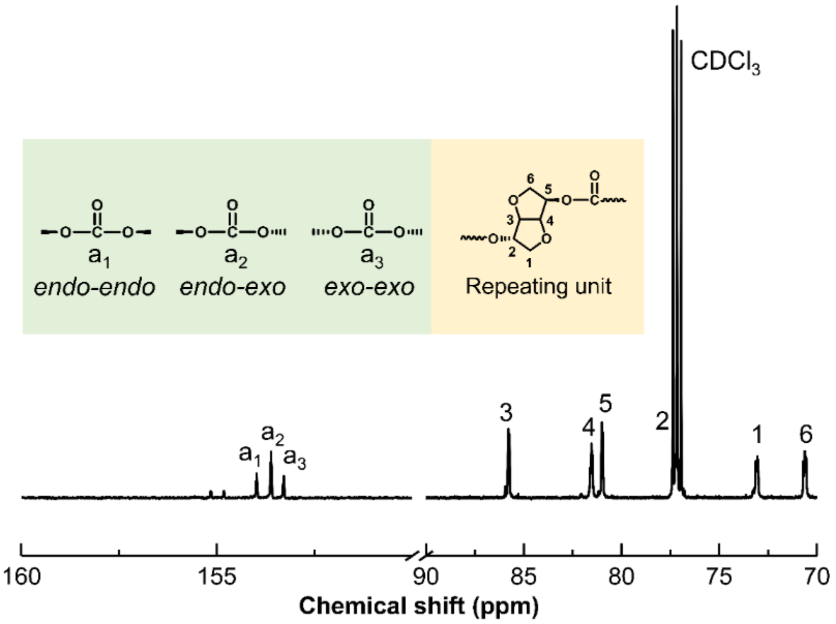


Fig.S4 ^{13}C NMR spectra of the obtained PIC catalyzed by [Pmim][OAc] (dissolved in CDCl$_3$).

11. The thermal properties of the obtained PIC

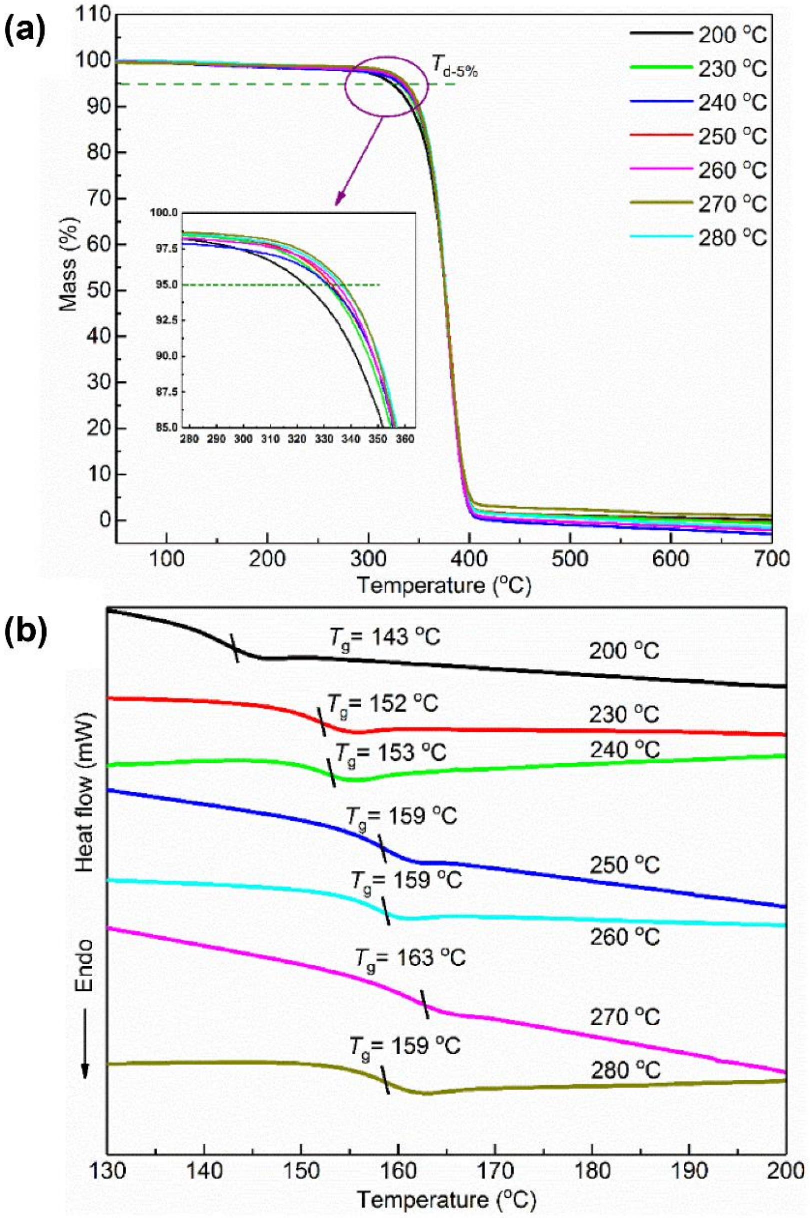


Fig.S5 Thermal properties of the PIC samples (a) TGA analysis; (b) DSC analysis.

12. DFT calculation for [Pmim][OAc]-DMC-*endo*-OH@ISB system

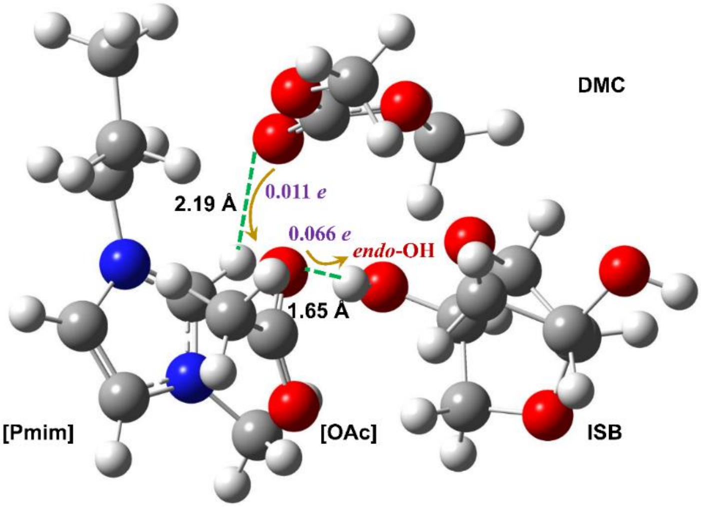


Fig.S6 Optimized structure of [Pmim][OAc]-DMC-*endo*-OH@ISB system. C atom (dark grey), H atom (light grey), O atom (red), N atom (blue).

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