Synthesis of Bioderived Polycarbonates with Molecular Weight Adjustability Catalyzed by Phenolic-derived Ionic Liquids

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Content

1. Materials

Dimethyl carbonate (DMC, anhydrous, 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 99%), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%), 1,1,3,3-tetramethylguanidine (TMG, 99%), and tetrabutylammonium hydroxide ($[N_{4444}]OH$, 25 wt% in H_2O) were purchased from Aladdin biochemical technology Co., Ltd., (Shanghai, China). Isosorbide (IS, 98%) and anion exchange resin Ambersep 900(OH) were received from Alfa Aesar. Trihexyl(tetradecyl)phosphonium bromide ($[P_{66614}]Br$, 97%) was obtained from J&K Scientific Ltd., (Beijing, China). Phenol (4-H-Phen, AR), 4-fluorophenol (4-F-Phen, 99%), 4-chlorophenol (4-Cl-Phen, 99%), 4-bromophenol (4-Br-Phen, 98%), 4-iodophenol (4-I-Phen, 98%), and isosorbide 5-mononitrate (98%) were provided by Shanghai Macklin Biochemical Co., Ltd. The compound of 1-Butyl-3-methylimidazolium hydroxide ([Bmim]OH, 20 wt% in ethanol) was received from Shanghai Cheng Jie Chemical Co. Ltd. Additionally, exchange resin Ambersep 900(OH) was rinsed to neutral using deionized water and isosorbide was recrystallized with acetone. The others were used as received without further purification.

2. Synthesis and separation of PIC precursors and HPLC analysis

The synthesis and separation of isosorbide carboxymethyl products are according to the previous literature.[1,2] The transesterification stage was operated in a 250 mL four-necked round-bottom flask equipped with a feeding funnel, a nitrogen inlet, a mechanical stirrer, and a dephlegmator connected to a liquid dividing head. In a specific experiment, under an N_2 atmosphere, isosorbide (10 g, 0.0684 mol), DMC (46.23 g, 0.5132 mol), and $[P_{66614}]$[4-H-Phen] (0.346 g, 0.88 mol% based on isosorbide) were added into the flask with stirring, and the oil bath temperature was increased gradually to 98 ^{o}C. The temperature of the column top was maintained between 40 and 65 ^{o}C. 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. 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 selectivities of products were determined from the calibration curves.

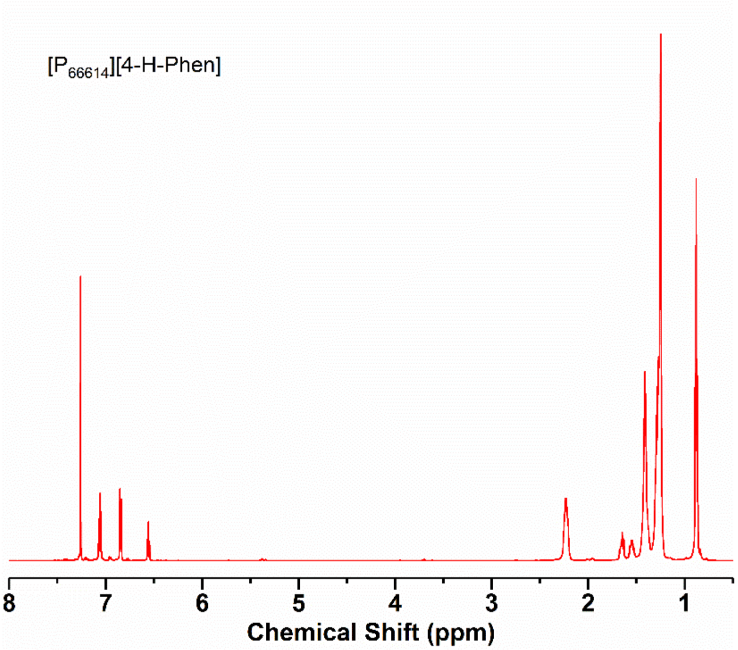
3. Computational details

All DFT calculations were carried out with the Gaussian 09 package.[3] The structures were optimized at the B3LYP level of theory[4] in conjunction with the 6-311+G* basis set[5,6] assigned to C, H, O, N and P, whereas LanL2DZ assigned to I.[7]

4. Characterization of synthesized ILs[1]

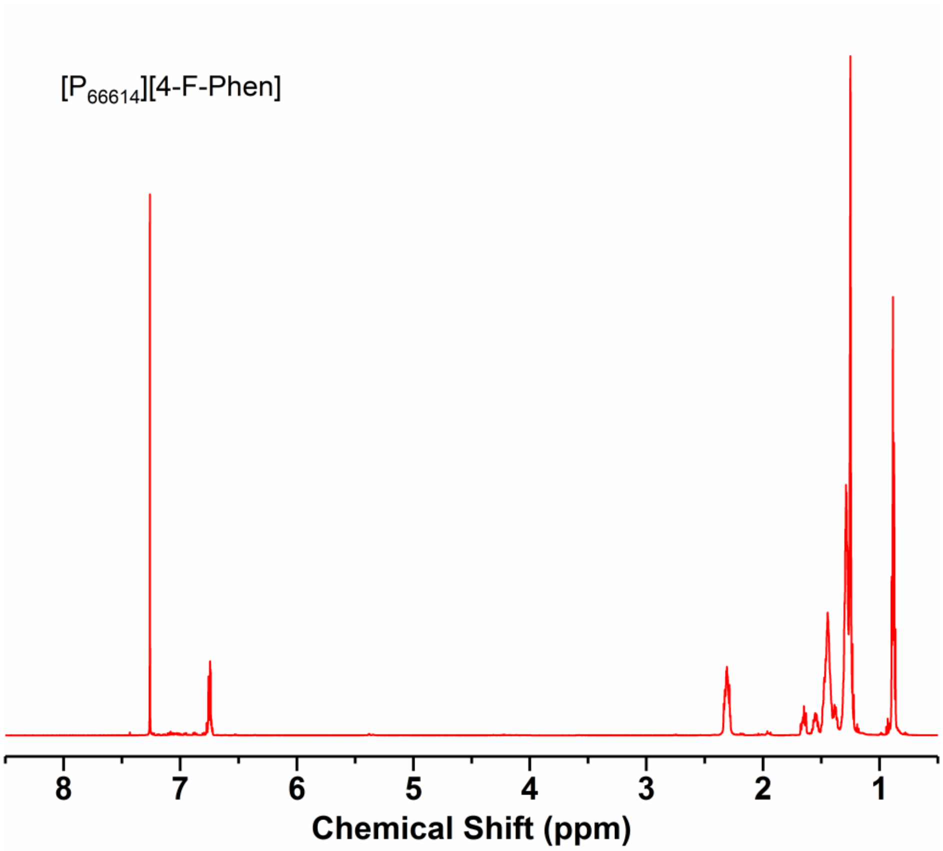
Trihexyl(tetradecyl)phosphonium phenolate ([P_{66614}][4-H-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.06 (m, 2H), 6.85 (d, 2H), 6.57 (m, 1H), 2.23 (m, 8H; 4×PCH_2), 1.68 – 1.25 (m, 48H; 24×CH_2), 0.88 ppm (m, 12H; 4×CH_3); MS (ESI): m/z: 483.51 [P_{66614}], 93.02 [4-H-Phen].



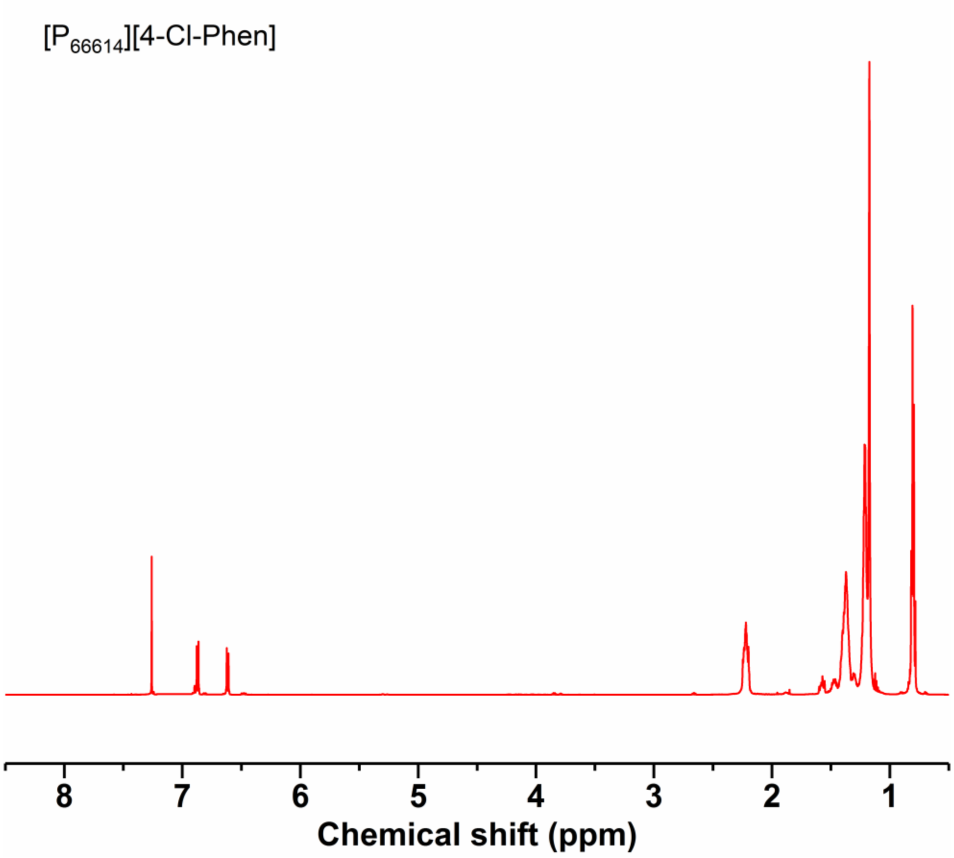
Trihexyl(tetradecyl)phosphonium 4-fluorophenolate ([P_{66614}][4-F-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.74 (m, 4H), 2.31 (m, 8H; 4×PCH_2), 1.68 – 1.25 (m, 48H; 24×CH_2), 0.86 ppm (m, 12H; 4×CH_3); MS (ESI): m/z: 483.51 [P_{66614}], 111.01 [4-F-Phen].



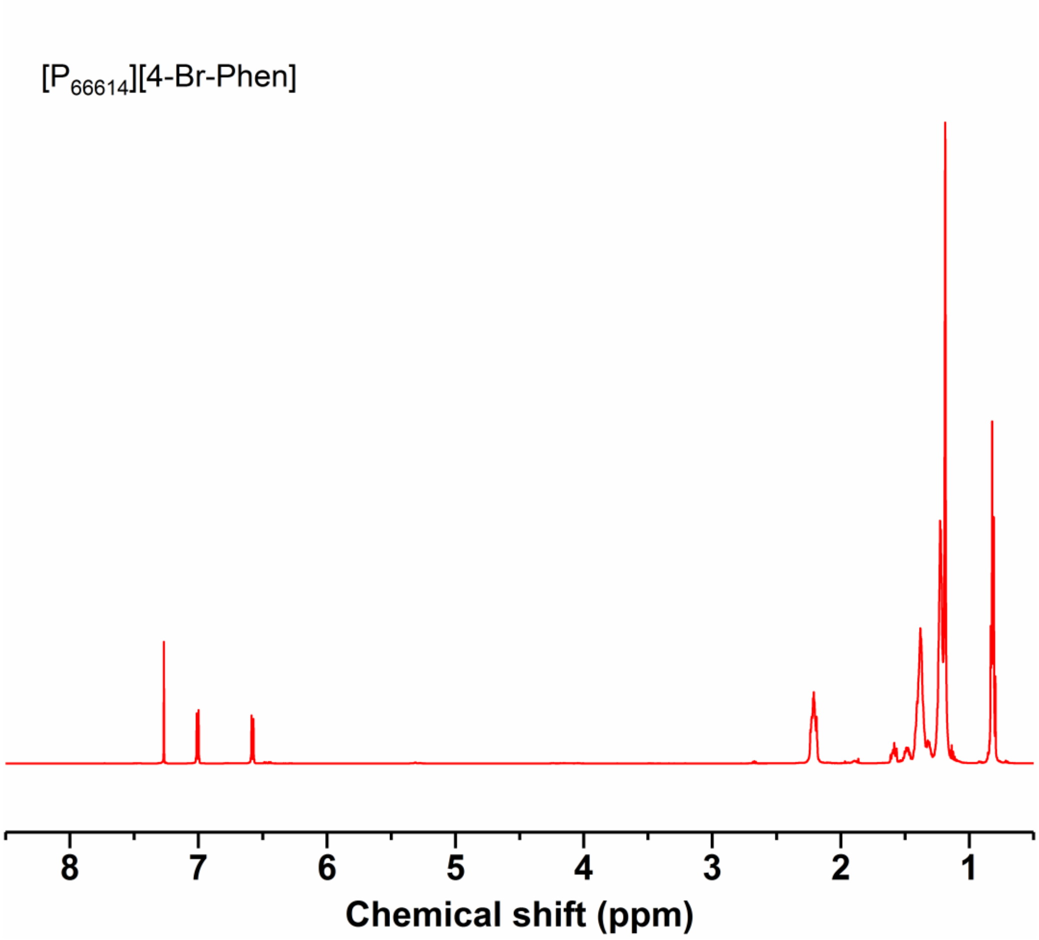
Trihexyl(tetradecyl)phosphonium 4-chlorophenolate ([P_{66614}][4-Cl-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.86 (d, 2H), 6.61 (d, 2H), 2.22 (m, 8H; 4×PCH_2), 1.57 – 1.17 (m, 48H; 24×CH_2), 0.81 ppm (m, 12H; 4×CH_3); MS (ESI): m/z: 483.51 [P_{66614}], 126.98 [4-Cl-Phen].



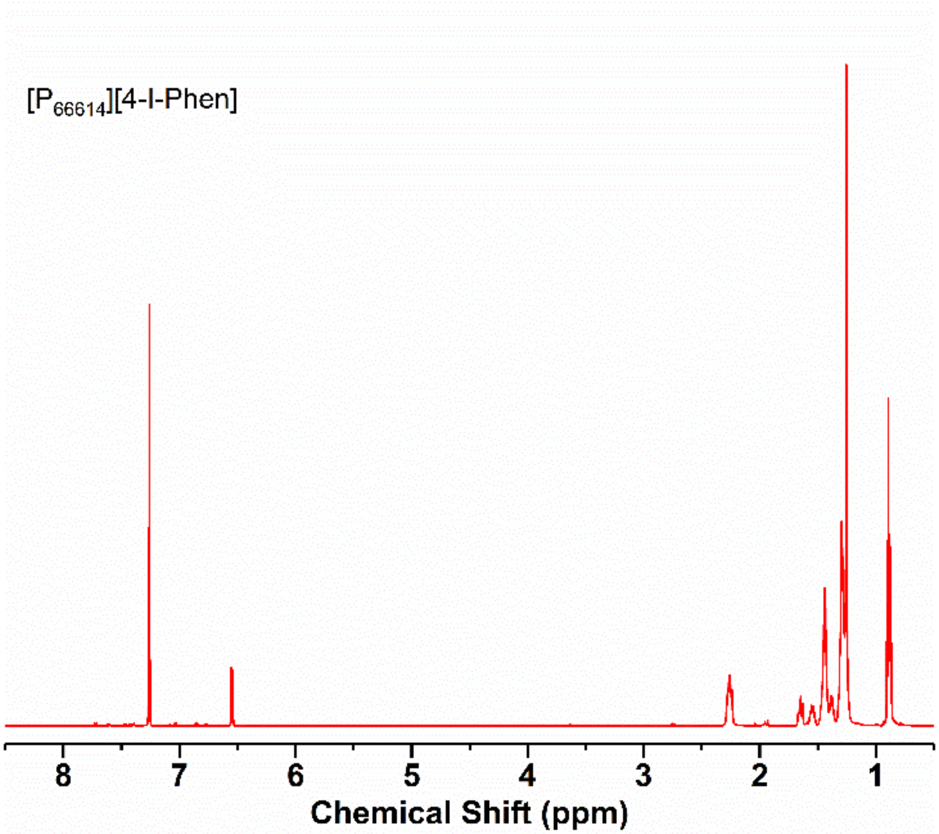
Trihexyl(tetradecyl)phosphonium 4-bromophenolate ([P_{66614}][4-Br-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.00 (d, 2H), 6.58 (d, 2H), 2.20 (m, 8H; 4×PCH_2), 1.58 – 1.18 (m, 48H; 24×CH_2), 0.81 ppm (m, 12H; 4×CH_3); MS (ESI): m/z: 483.50 [P_{66614}], 172.93 [4-Br-Phen].



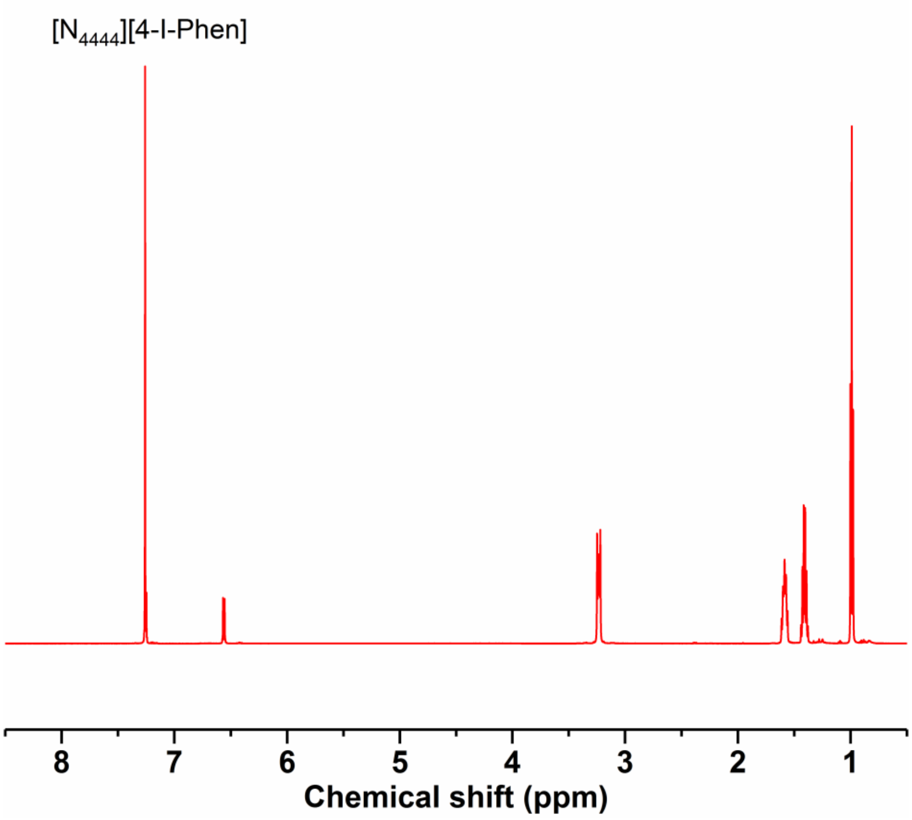
Trihexyl(tetradecyl)phosphonium 4-iodophenolate ([P_{66614}][4-I-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.27 (d, 2H), 6.55 (d, 2H), 2.26 (m, 8H; 4×PCH_2), 1.68–1.25 (m, 48H; 24×CH_2), 0.89 ppm (m, 12H; 4×CH_3); MS (ESI): m/z: 483.50 [P_{66614}], 218.92 [4-I-Phen].



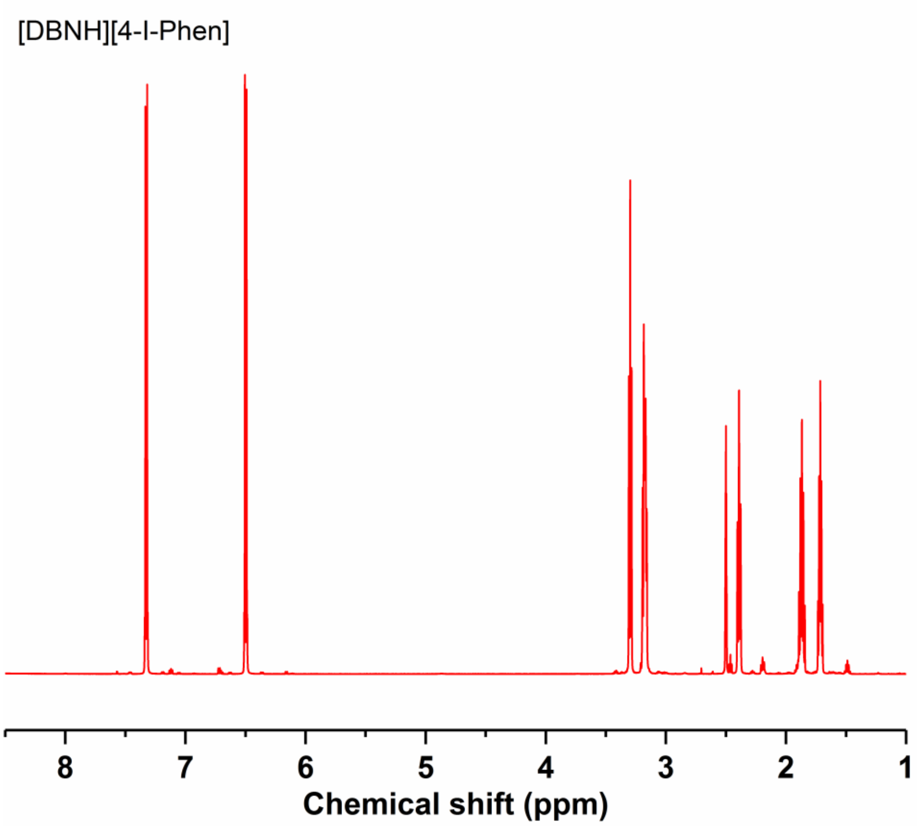
Tetrabutylammonium 4-iodophenolate ($[N_{4444}]$[4-I-Phen]):

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (d, 2H), 6.57 (d, 2H), 3.23 (m, 8H; 4×NCH_2), 1.59 (m, 8H; 8×CH_2), 1.41 (m, 8H; 8×CH_2), 0.99 ppm (m, 4×CH_3); MS (ESI): m/z: 242.51 [N_{4444}], 218.92 [4-I-Phen].



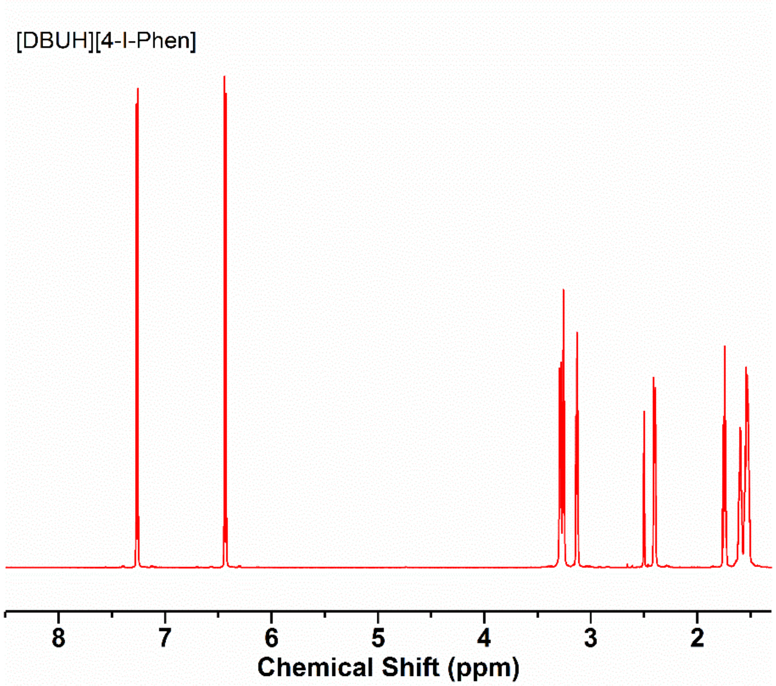
1,5-Diazabicyclo[4.3.0]non-5-enium 4-iodophenolate ([DBNH][4-I-Phen])

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.33 (d, 2H), 6.51 (d, 2H), 3.30 - 3.18 (m, 6H), 2.39 (m, 2H), 1.87 (m, 2H), 1.71 ppm (m, 2H); MS (ESI): m/z: 125.28 [DBNH], 218.92 [4-I-Phen].



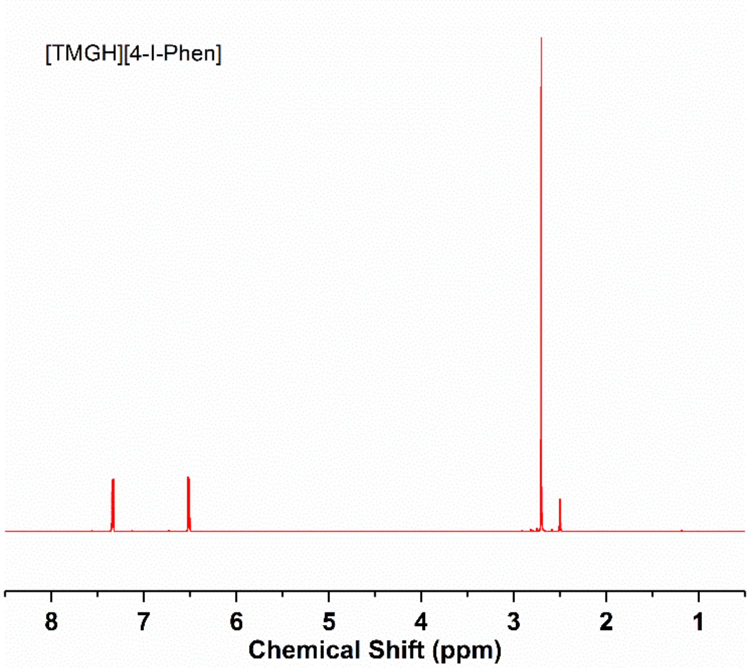
1,8-Diazabicyclo[5.4.0]undec-7-ene-8-ium 4-iodophenolate ([DBUH][4-I-Phen])

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.32 (d, 2H), 6.50 (d, 2H), 3.43 (m, 1H), 3.23 (m, 4H), 3.11 (m, 2H), 2.33 (m, 2H), 1.71 (m, 2H), 1.52 ppm (m, 6H); MS (ESI): m/z: 153.32 [DBUH], 218.92 [4-I-Phen].



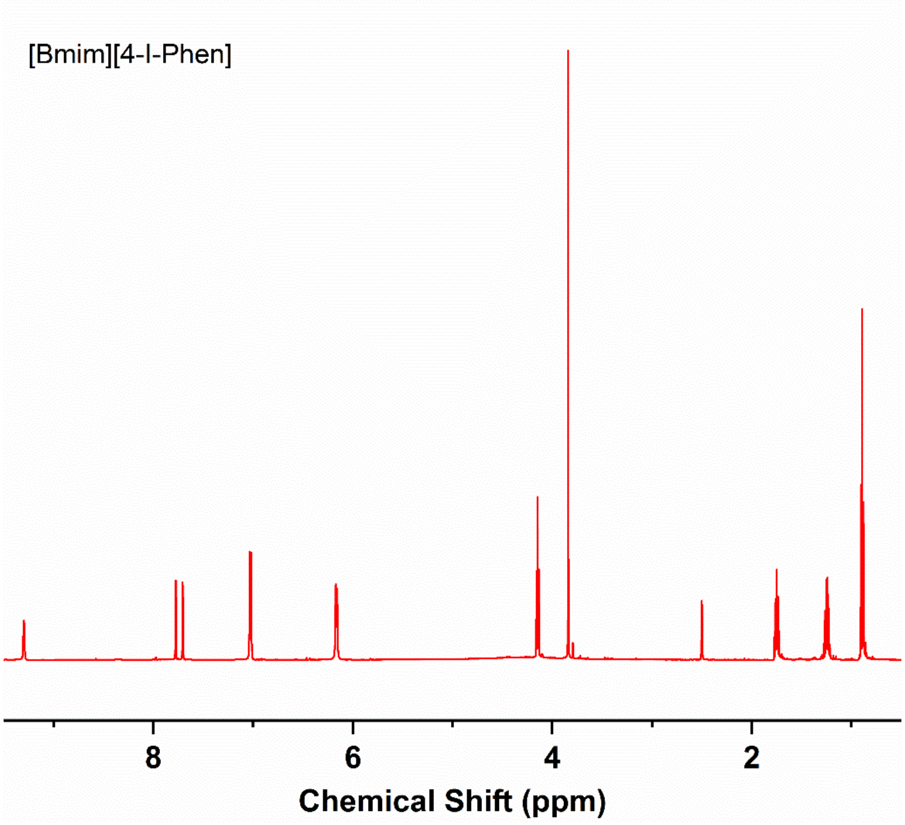
1,1,3,3-Tetramethylguanidinium 4-iodophenolate ([TMGH][4-I-Phen])

^{1}H NMR (600 MHz, DMSO-d_6): δ = 7.36 (d, 2H), 6.58 (d, 2H), 2.77 ppm (s, 12H); MS (ESI): m/z: 116.28 [TMGH], 218.92 [4-I-Phen].



1-Butyl-3-methylimidazolium 4-iodophenolate ([Bmim][4-I-Phen]):

^{1}H NMR (600 MHz, DMSO-d_6): δ = 9.30 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 7.03 (d, 2H), 6.17 (d, 2H), 4.15 (t, 2H), 3.84 (s, 3H), 1.75 (m, 2H), 1.24 (m, 2H), 0.89 ppm (t, 3H); MS (ESI): m/z: 139.30 [Bmim], 218.92 [4-I-Phen].



5. Characterization of carboxymethyl products[1]

DC: $C_{10}H_{14}O_8$; isolated yield: 6.4 g; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.10 – 5.05 (m, 2 H), 4.88 (t, 1 H), 4.54 (d, 1H), 4.08 – 4.00 (m, 2 H), 3.93 – 3.87 (m, 2H), 3.81 (s, 3 H), 3.80 ppm (s, 3 H); ^{13}C NMR (600 MHz, $CDCl_3$): δ = 155.24, 154.91, 86.00, 81.36, 80.98, 76.90, 73.39, 70.61, 55.28, 55.24 ppm; MS (ESI): m/z: 262.24; elemental analysis calcd (%) for $C_{10}H_{14}O_8$: C 45.81, H 5.38, O 48.81; found: C 45.72, H 5.41, O 48.75.

MC-1: $C_8H_{12}O_6$; isolated yield: 0.4 g; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 5.13 (d, 1 H), 4.64 (t, 1 H), 4.53 (d, 1H), 4.33 – 4.30 (m, 1H), 4.02 – 4.00 (dd, 1 H), 3.90 – 3.88 (m, 1 H), 3.81 (s, 3 H), 3.56–3.59 (m, 1 H), 2.48 ppm (s, 1H); ^{13}C NMR (600 MHz, $CDCl_3$): δ =154.87, 85.51, 82.11, 81.71, 73.78, 73.42, 72.41, 55.28 ppm; MS (ESI): m/z: 227.05 $[MC\text{-}1+Na]^+$; elemental analysis calcd (%) for $C_8H_{12}O_6$: C 47.06, H 5.92, O 47.02; found: C 47.08, H 5.88, O 46.98.

MC-2: $C_8H_{12}O_6$; isolated yield: 0.2 g; ^{1}H NMR (600 MHz, $CDCl_3$): δ =5.05 – 5.02 (m, 1H), 4.87 (t, 1H), 4.38 (d, 1H), 4.31 (d, 1H), 3.91 – 3.82 (m, 4H), 3.80 (s, 3H), 2.41 ppm (s, 1H); ^{13}C NMR (600 MHz, $CDCl_3$): δ = 155.41, 88.57, 80.63, 77.46, 76.28, 75.86, 70.54, 55.32 ppm; MS (ESI): m/z: 227.05 $[MC\text{-}2+Na]^+$; elemental analysis calcd (%) for $C_8H_{12}O_6$: C 47.06, H 5.92, O 47.02; found: C 47.09, H 5.87, O 47.05.

6. The thermostability of synthesized IL catalysts

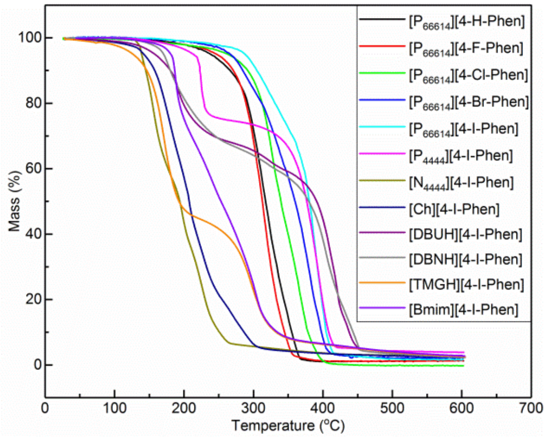


Fig. S1 The TGA curves of synthesized IL catalysts.[1]

7. The typical ^{1}H NMR spectra of the different stages of the isosorbide moiety construction

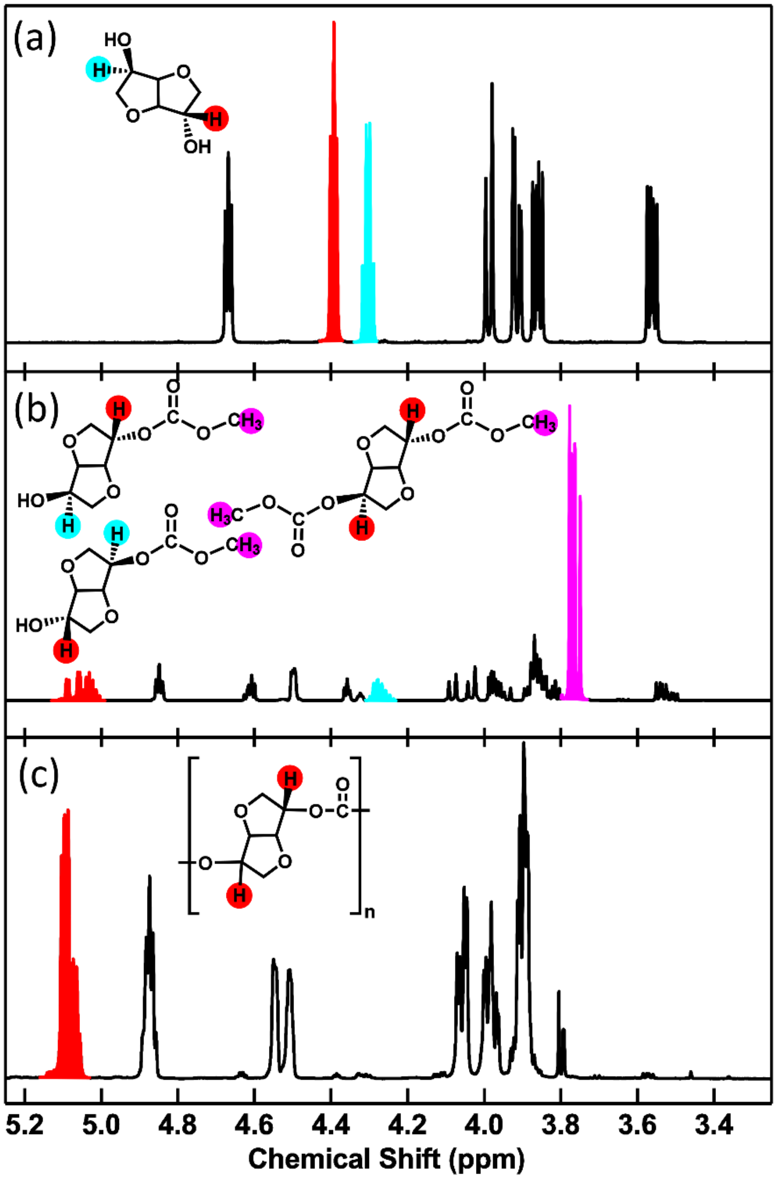


Fig. S2 Selected regions in the ^{1}H NMR spectra ($CDCl_3$) of the reaction process: (a) isosorbide; (b) transesterification products, and (c) final product.

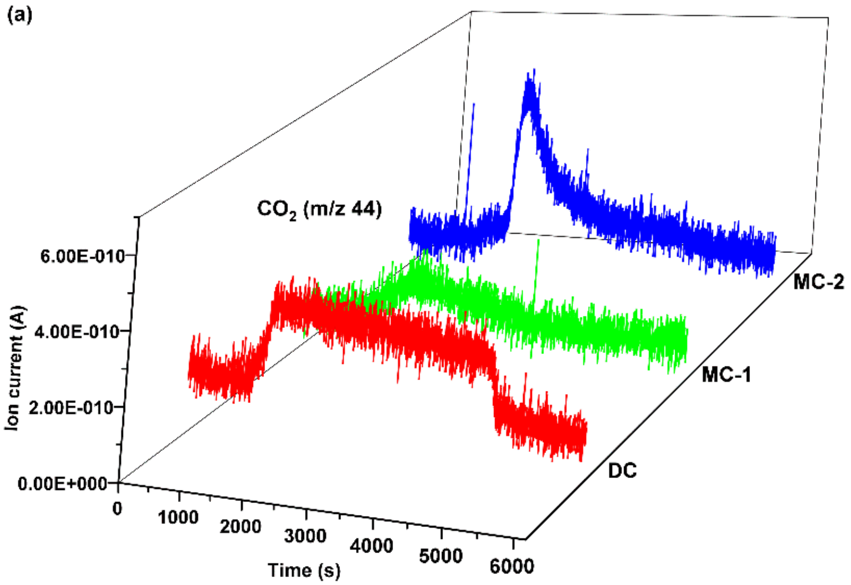
8. The ^{1}HNMR signals of PIC catalyzed by IL catalysts

Table S1 The relative ratio of repeating unit and end groups of PIC catalyzed by IL catalysts

Catalyst	Repeating Unit (100%)	End groups (100%)			Total end groups (100%)	M_w (×10^3 g/mol)
		Total -OH	-OCH$_3$	-OCOOCH$_3$		
[P$_{66614}$][4-H-Phen]	1	0.041	0.005	0.135	0.181	16.5
[P$_{66614}$][4-F-Phen]	1	0.057	0.007	0.112	0.176	17.8
[P$_{66614}$][4-Cl-Phen]	1	0.054	0.010	0.111	0.175	18.7
[P$_{66614}$][4-Br-Phen]	1	0.082	0.017	0.095	0.194	15.5
[P$_{66614}$][4-I-Phen]	1	0.017	0.007	0.103	0.127	28.4
[N$_{4444}$][4-I-Phen]	1	0.015	0.008	0.100	0.123	29.2
[DBNH][4-I-Phen]	1	0.174	0.002	0	0.176	17.3
[DBUH][4-I-Phen]	1	0.334	0.001	0	0.335	9.3
[TMGH][4-I-Phen]	1	0.594	0.007	0	0.601	3.7
[Bmim][4-I-Phen]	1	0.046	0.004	0.049	0.099	39.6

Reaction conditions: DMC/IS=7.5. Transesterification time: 3.5 h. Polycondensation time: 4 h. Cat. amount is 4.4×10^{-3} equiv. mol based on IS. The relative amount of terminal groups determined by ^{1}H NMR. The peak integration at δ 4.87 ppm in a repeating unit normalized to be 1. *PT* denotes polycondensation temperature. The ^{1}H NMR information is similar to **Figure 5a**.

9. The TG-MS analysis and ^{1}HNMR spectra of transesterification product of DC before and after undergo decarboxylation reaction



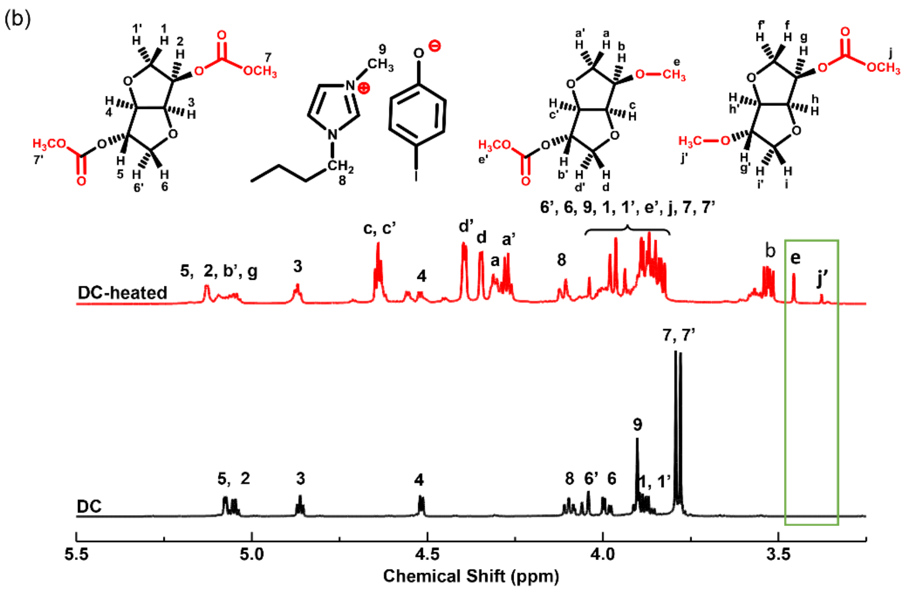
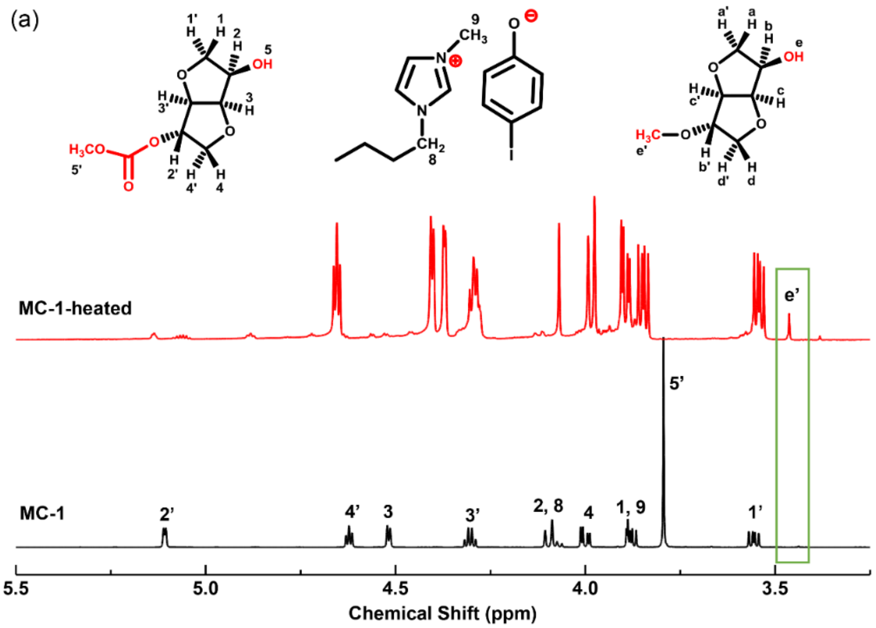


Fig. S3 (a) TG-MS analysis of transesterification products kept at 190 °C; (b) ^{1}H NMR spectra of DC before and after heated at 190 °C for 1 h under an N_2 atmosphere in the presence of [Bmim][4-I-Phen].

10. The ^{1}HNMR spectra of transesterification products before and after undergo decarboxylation reaction



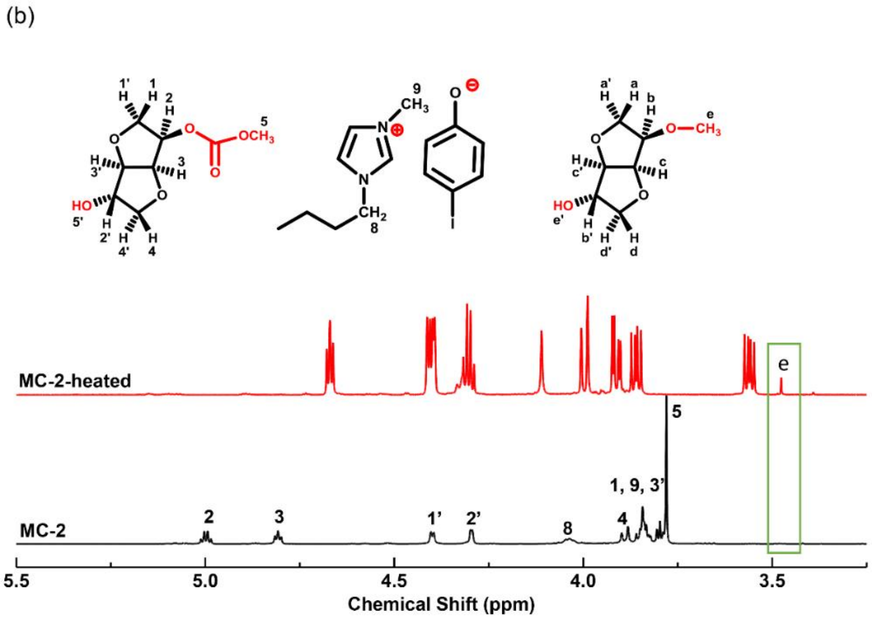
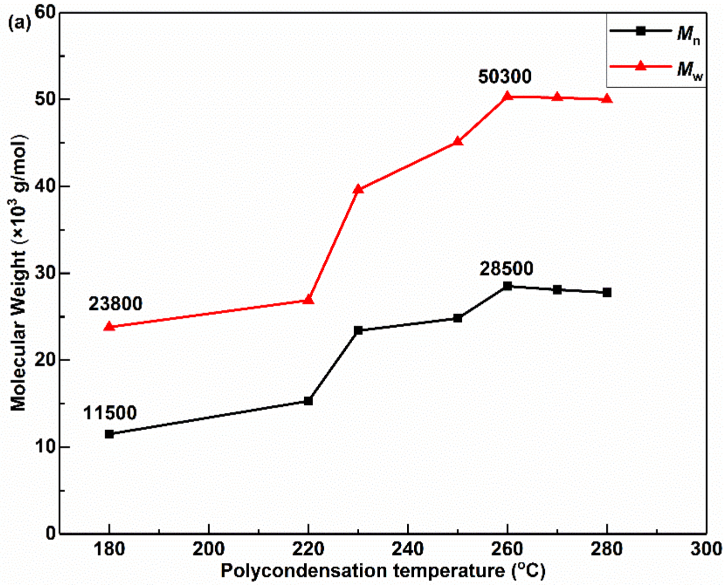


Fig. S4 The ^{1}HNMR spectra of transesterification products before and after heating at 190 °C (a) MC-1; (b) MC-2 in the presence of [Bmim][4-I-Phen].

11. The influences of various reaction parameters on the polymerization reaction



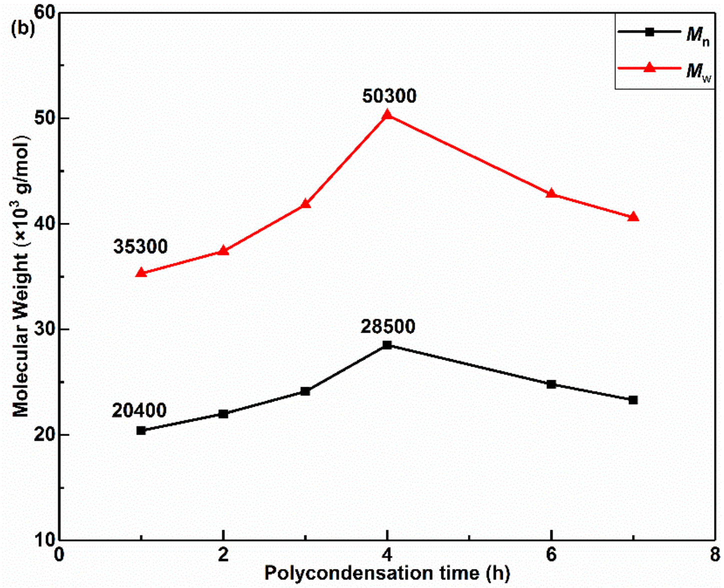


Fig. S5 Influences of reaction conditions (a) polycondensation temperature; (b) polycondensation time on the M_n and M_w of PIC.

12. The thermal stability of DC and the PIC sample obtained at 180 °C.

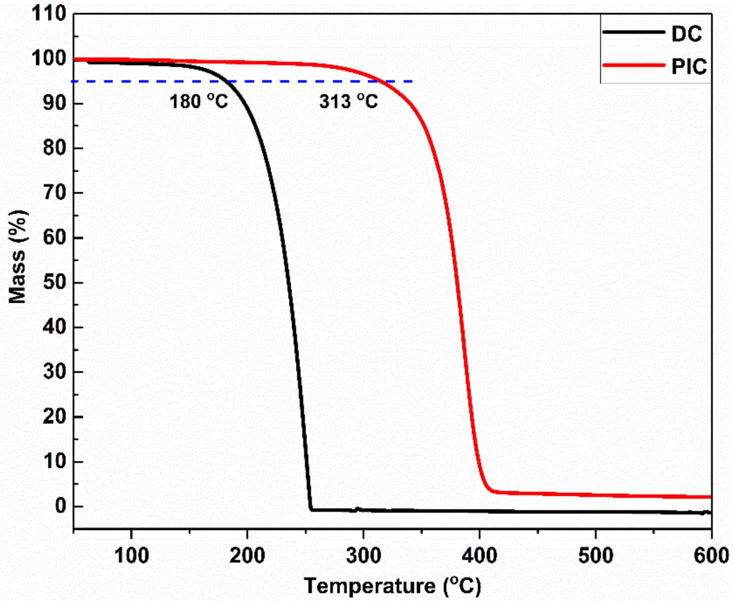
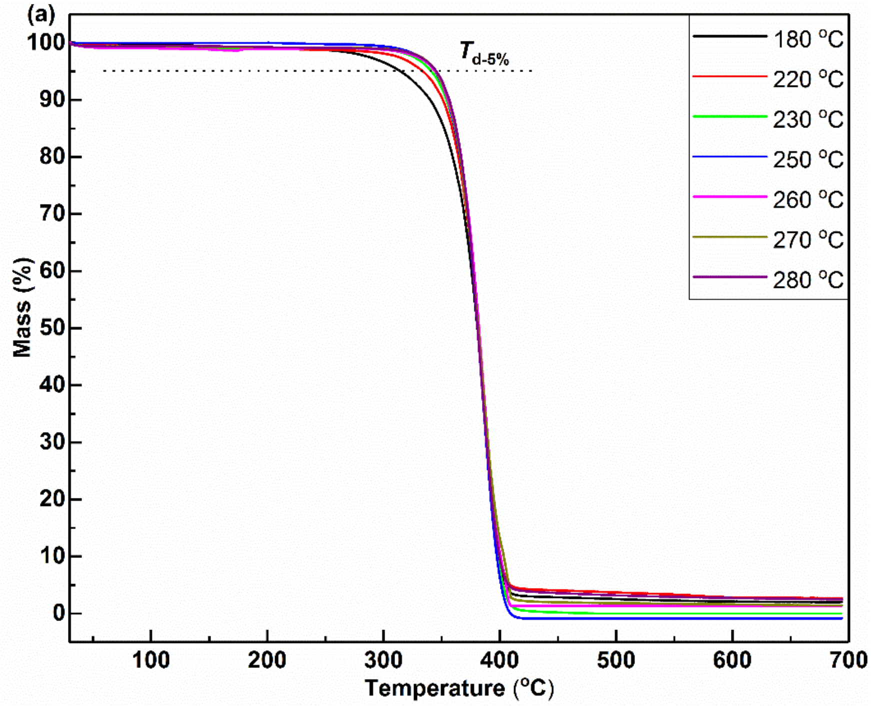
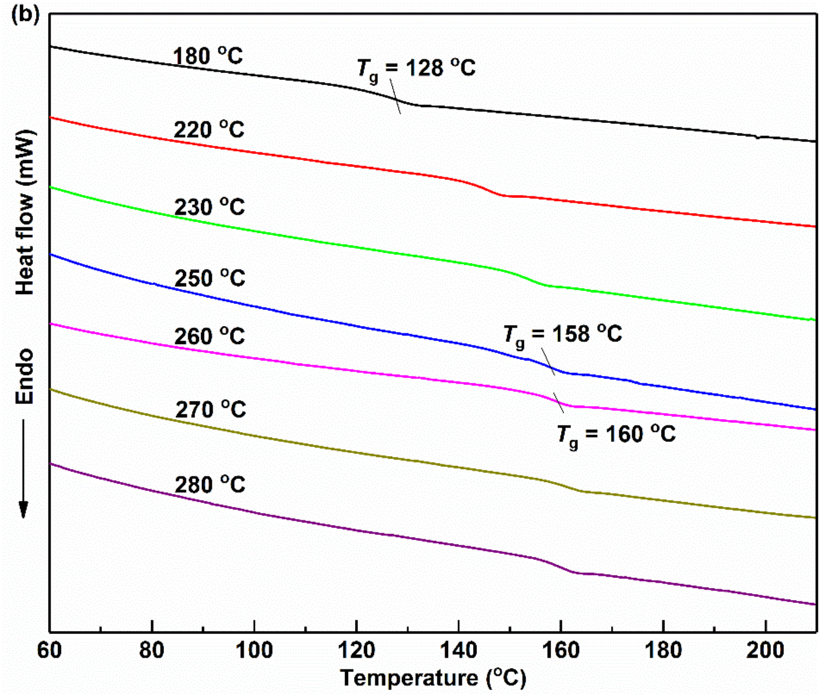


Fig. S6 The thermal stability of DC and the PIC sample obtained at 180 °C.

13. The thermal properties of synthesized PIC





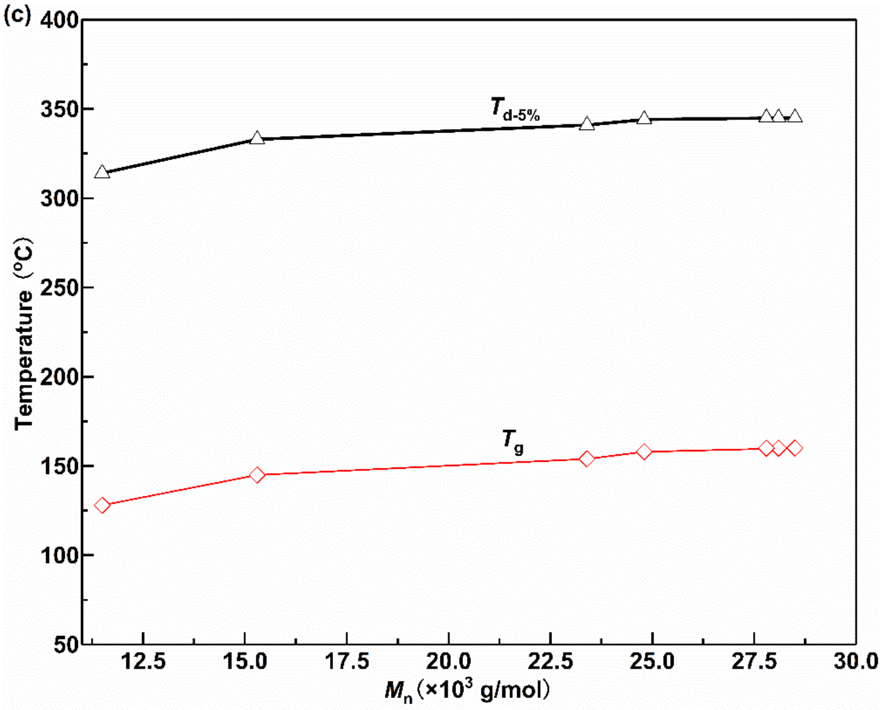


Fig. S7 Thermal properties of PIC samples (a) TGA curves; (b) DSC curves; (c) the relationship with molecular weight (M_n).

Table S2. The relationship of molecular weight with the thermal properties

Entry	*PT* (°C)	$T_{d\text{-}5\%}$ (°C)	T_g (°C)	M_n (g/mol)	M_w (g/mol)
1	180	314	128	11500	23800
2	220	333	145	15300	26900
3	230	341	154	23400	39600
4	250	344	158	24800	45100
5	260	345	160	28500	50300
6	270	345	160	28100	50200
7	280	345	160	27800	50000

PT denotes polycondensation temperature.

14. The reaction mechanism analysis

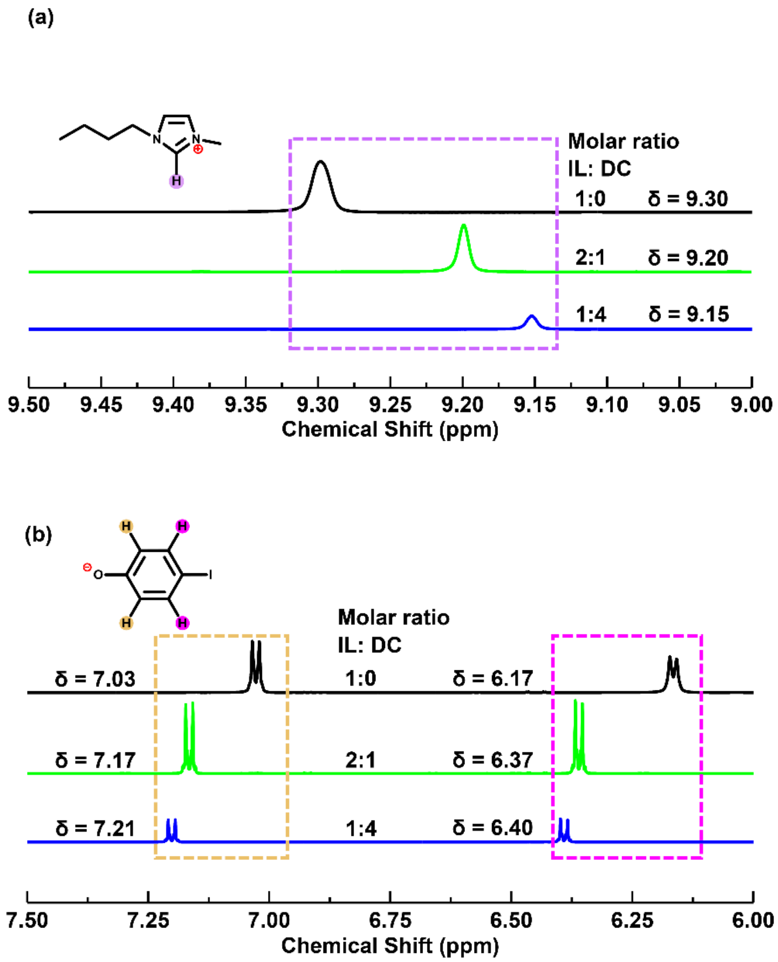


Fig. S8 Shift in ^{1}H NMR of [Bmim][4-I-Phen] (a) C-2 hydrogen of [Bmim] cation and (b) proton of [4-I-Phen] anion after blending with different amount DC dissolved in DMSO-d_6.

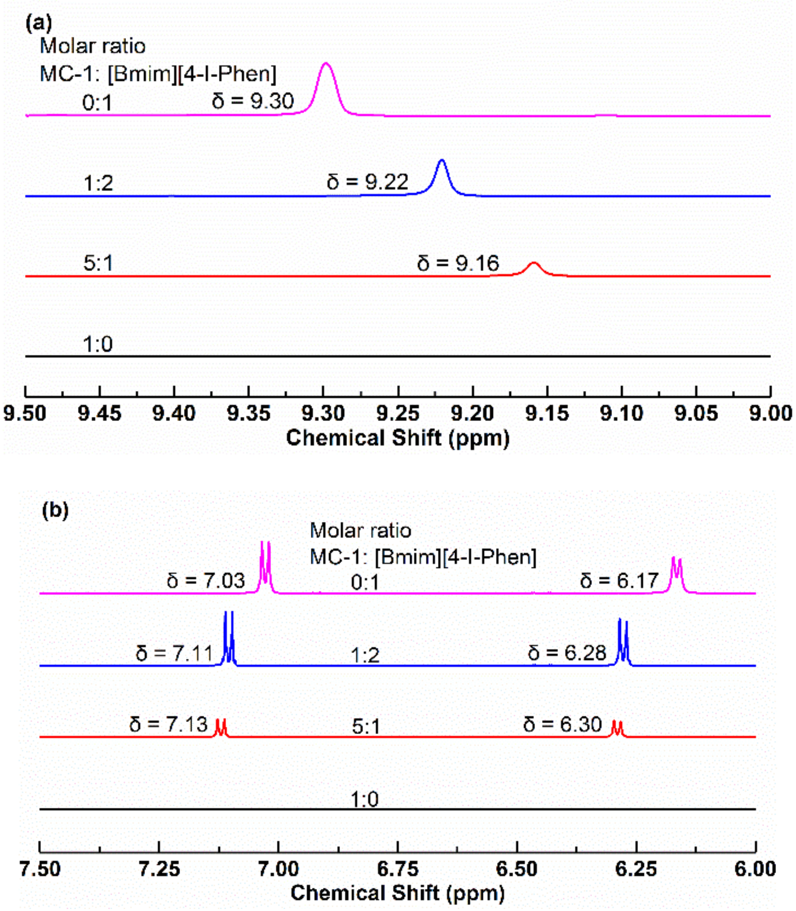
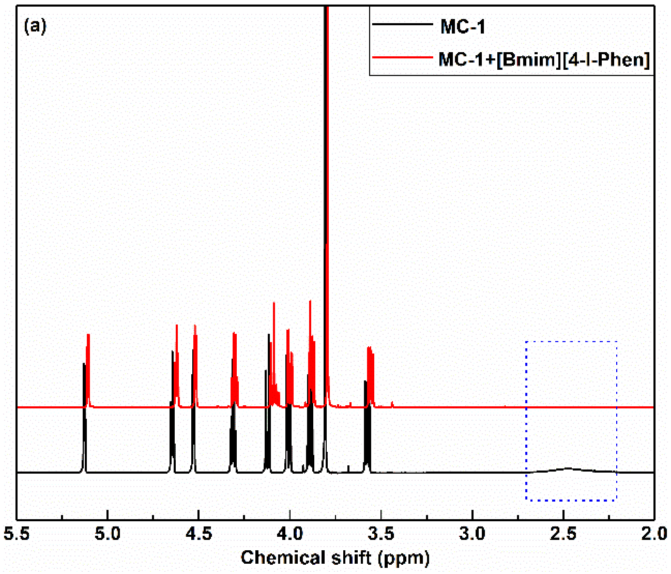


Fig. S9 Shift in ^{1}H NMR of [Bmim][4-I-Phen] (a) C-2 hydrogen of [Bmim] cation and (b) proton of [4-I-Phen] anion after blending with different amount MC-1 dissolved in DMSO-d_6.



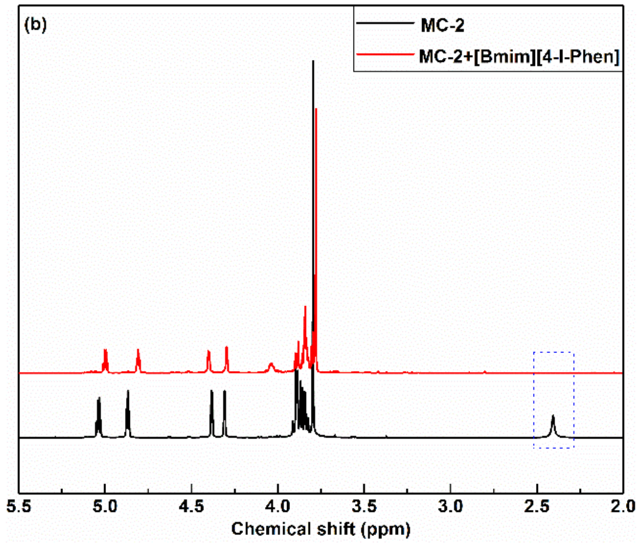


Fig. S10 Shift in ^{1}H NMR of (a) pure MC-1 and MC-1 after blending with [Bmim][4-I-Phen]; (b) pure MC-2 and MC-2 after blending with [Bmim][4-I-Phen] dissolved in $CDCl_3$.

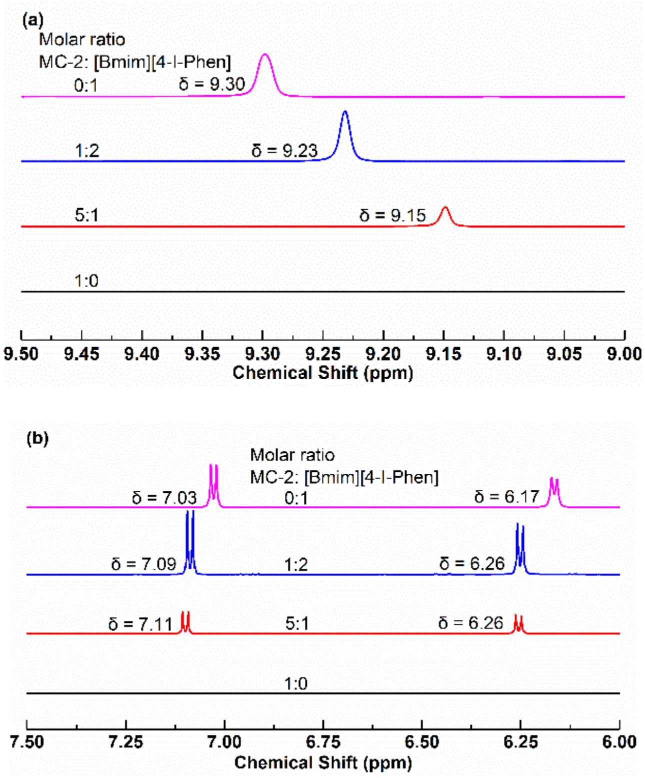


Fig. S11 hift in ^{1}H NMR of [Bmim][4-I-Phen] (a) C-2 hydrogen of [Bmim] cation and (b) proton of [4-I-Phen] anion after blending with different amount MC-2 dissolved in DMSO-d_6.

Table S3. ESI-MS analysis results of PIC oligomers obtained at 160 ºC

n	Structure A		Structure B		Structure C		Structure D	
	Measd	Calcd	Measd	Calcd	Measd	Calcd	Measd	Calcd
0	227.0496	227.1671	285.0577	285.2031	-	-	-	-
1	399.0842	399.3025	457.0791	457.3386	341.0752	341.2664	-	-
2	571.1193	571.4379	629.1181	629.4740	513.1255	513.4018	-	-
3	743.1571	743.5733	801.1417	801.6094	685.4172	685.5372	-	-
4	915.1963	915.7087	973.1827	973.7448	857.1833	857.6727	871.2456	871.6992
5	1087.2082	1087.8442	1145.2217	1145.8802	-	-	1043.7112	1043.8347
6	1259.1949	1259.97957	1317.2271	1318.0157	-	-	-	-
7	1431.2872	1432.1150	1489.2090	1490.1511	-	-	-	-

Table S4. MALDI-TOF-MS analysis results of PIC oligomers obtained at 180 ºC

n	Structure E		Structure F		Structure G		Structure H		Structure I		Structure J	
	Measd	Calcd	Measd	Calcd	Measd	Calcd	Measd	Calcd	Measd	Calcd	Measd	Calcd
3	885.164	885.251	899.127	899.267	943.170	943.257	-	-	-	-	-	-
4	1057.215	1057.288	1071.215	1071.304	1115.167	1115.294	973.082	973.207	999.157	999.283	1013.212	1013.299
5	1229.228	1229.326	1243.215	1243.341	1287.280	1287.331	1145.079	1145.244	1171.203	1171.320	1185.217	1185.336
6	1401.266	1401.363	1415.280	1415.378	1459.209	1459.368	1317.127	1317.282	1343.220	1343.357	-	-
7	1573.222	1573.400	1587.237	1587.416	1631.206	1631.405	1489.228	1489.319	-	-	-	-
8	1745.222	1745.437	-	-	-	-	1661.233	1661.356	-	-	-	-

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