

## Electronic Supplementary Information

for

### **Ionic Liquid [Bmim][Lac]-Catalyzed Melt Polycondensation for Bisphenol A-based Polycarbonate Synthesis**

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## Materials and Methods

### Materials

Unless otherwise stated, all chemicals are used without further purification. Bisphenol A ( $\geq 98\%$ ) and diphenyl carbonate ( $\geq 99\%$ ) were purchased from Beijing innochem Co., Ltd., and 1-butyl-3-methylimidazole lactate ( $\geq 98\%$ ), 1-butyl-3-methylimidazole acetate ( $\geq 95\%$ ), 1-butyl-3-methylimidazole trifluoromethanesulfonate ( $\geq 95\%$ ), 1-butyl-3-methylimidazole hexafluorophosphate ( $\geq 99\%$ ), 1-butyl-3-methylimidazole tetrafluoroborate ( $\geq 99\%$ ), tetramethylammonium hydroxide (25 wt.% in H<sub>2</sub>O, solution) and sodium hydroxide ( $\geq 98\%$ ) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., and lanthanum acetylacetonate ( $\geq 98\%$ ) was purchased from Shanghai yuanye Bio-Technology Co., Ltd., and the commercial product PC (CH60-0-L) was obtained from Sinopec&Sabic Tianjin Petrochemical Company Ltd.

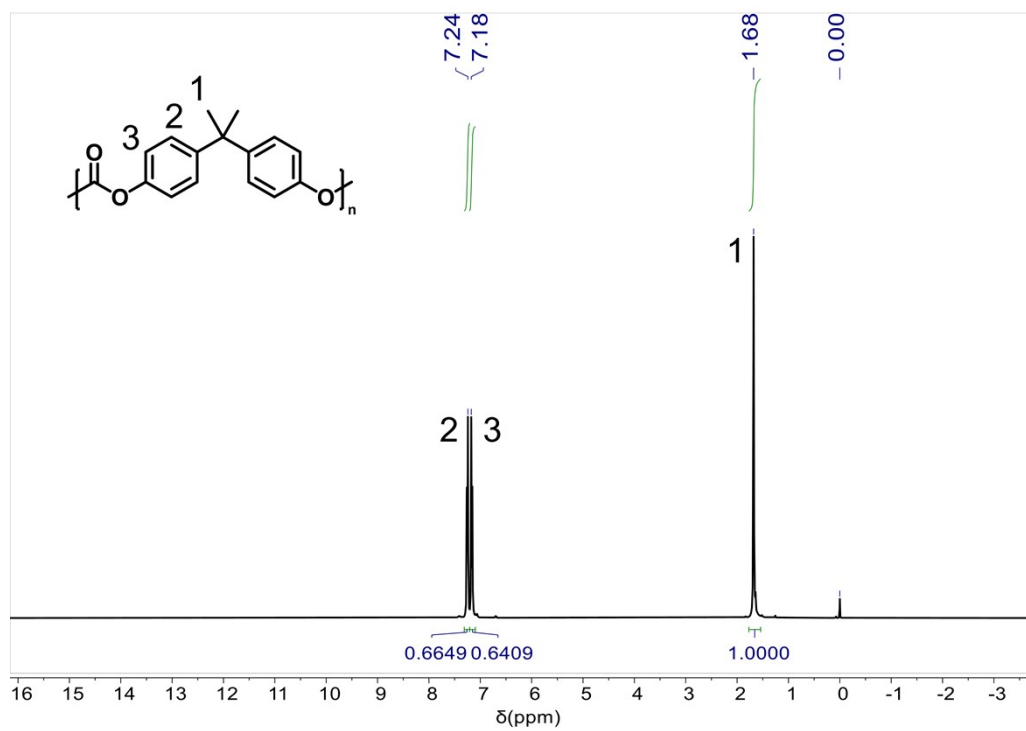
### Methods

<sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz for <sup>1</sup>H NMR and 101 MHz for <sup>13</sup>C NMR) at room temperature in chloroform-d (purchased from Innochem), and chemical shift values were referenced to chloroform-d as internal standard at 7.26 ppm or TMS as internal standard at 0 ppm for <sup>1</sup>H NMR and against chloroform-d at 77.16 ppm for <sup>13</sup>C NMR. When using DMSO-d<sub>6</sub> (purchased from Innochem) as a solvent, chemical shift values were referenced to DMSO-d<sub>6</sub> as internal standard at 2.50 ppm for <sup>1</sup>H NMR and at 39.52 ppm for <sup>13</sup>C NMR. Gel permeation chromatography (GPC) analyses were carried out at 40 °C and a flow rate of 1.0 mL/min, with THF as the eluent on an Agilent PL-GPC 50 instrument coupled with a refractive index (RI) detector with respect to polystyrene (PS) standards. The columns included a PLgel guard 5 $\mu$ m 50  $\times$  7.5 mm column, a PLgel mixed-B 300  $\times$  7.5 mm column, and a PLgel mixed-C 300  $\times$  7.5mm column. Samples for GPC analysis were filtered through 0.22  $\mu$ m PTFE filters. Differential scanning calorimetry (DSC) was performed on a TA Q2000 differential scanning calorimeter. Heating and cooling rates were set at 10 °C/min. Thermograms were recorded and analyzed with the TA Universal Analysis software. Data of glass transition temperature ( $T_g$ ) was recorded from the second heating scan. Thermal gravimetric analysis (TGA) was conducted on a Q600-SDT thermogravimetric analyzer (TA Co. Ltd.) at a heating rate of 10 °C/min under a nitrogen flow of 100 mL/min. Decomposition onset temperature ( $T_{d,5\%}$ ) was defined at 5% mass loss. Tensile stress/strain testing was performed by an Instron 5969 universal testing system. Samples were made by solution casting

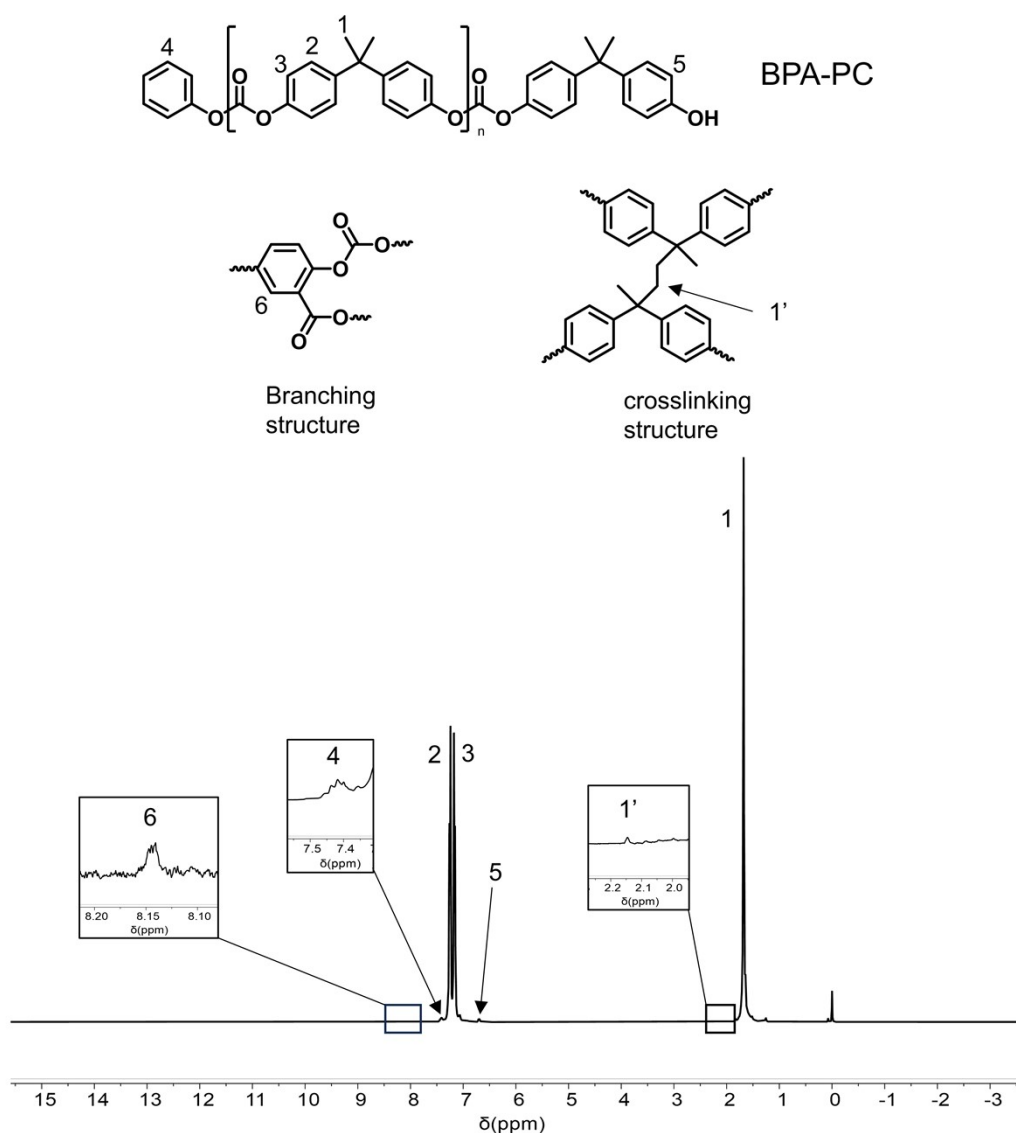
in a steel mold ( $40 \times 40 \times 0.1 \text{ mm}^3$ ) and were stretched at a strain rate of 10 mm/min at ambient temperature until break. The measurements were performed 3 times for the test, and the average values with standard error were calculated. The rheological tests were performed using a DHR-2 rheometer (TA Instruments) with a nitrogen flow to prevent degradation. Experiments on the time dependence of shear viscosity (in a 250 °C melt) were conducted at a shear rate of  $1.0 \text{ s}^{-1}$  in a flow-through mode over 30 minutes.

## **General Polymerization**

BPA-PC was synthesized via melt polycondensation using a miniature reactor. The reaction comprised two stages: transesterification and polycondensation. First, the monomers were added to the reactor in a specific ratio, followed by the ionic liquid catalyst in its designated proportion. After the apparatus was assembled and its airtightness verified, the internal atmosphere was purged and replaced with inert nitrogen gas. Subsequently, the first stage (transesterification) was initiated by heating the mixture to 240 °C for 3 hours. During this stage, the by-product phenol was substantially distilled off and collected in a cold trap. Following this, the system proceeded to the polycondensation stage. The pressure was gradually reduced to 500 Pa, and the reaction temperature was increased to 280 °C. The reaction was maintained under these conditions for approximately 1.5 hours before terminating by stopping the stirring and heating. For post-processing, dichloromethane was added to the reactor to thoroughly dissolve the polymer. The solution was then dripped into a large volume of ethanol to precipitate the product. Finally, the obtained polymer was dried in a vacuum oven at 120 °C for 24 hours and stored in a desiccator for subsequent testing.



**Figure S1.** <sup>1</sup>H NMR spectrum of BPA-PC(400 MHz, CDCl<sub>3</sub>).



$$n_{\text{-OH}} = \frac{17 \times 2 \times I(5) \cdot \frac{I(3)}{I(4) + I(5)}}{(254 \times \frac{I(3)}{I(4) + I(5)} + 107 \frac{2 \times I(4)}{I(4) + I(5)} + 241 \frac{2 \times I(5)}{I(4) + I(5)}) \cdot I(3)} \times 10^6$$

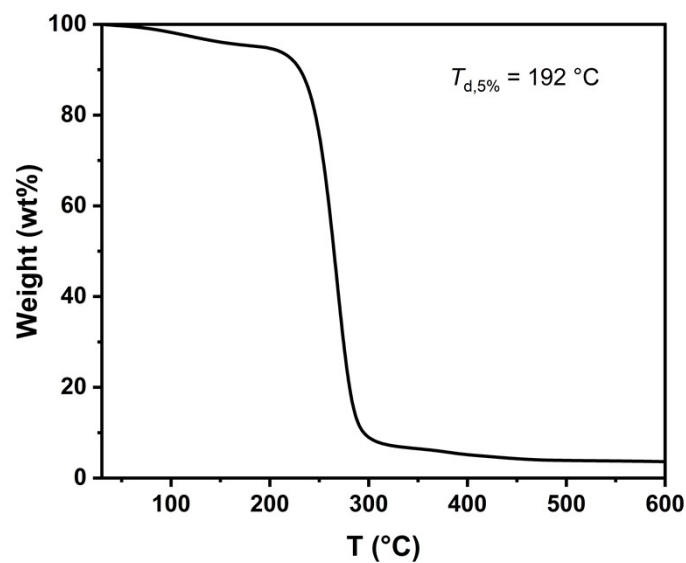
$$n_{\text{Ph}}/n_{\text{-OH}} = \frac{I(4)}{I(5)}$$

$$n_{\text{branching}} = \frac{I(6) \times 4}{I(3)} \times 10^6$$

$$n_{\text{crosslinking}} = \frac{I(1')}{I(3)} \times 10^6$$

**Figure S2.** Branching, crosslinking structures, and  $^1\text{H}$  NMR spectrum of BPA-PC(400 MHz,  $\text{CDCl}_3$ ).

The formulas for calculating the end groups, branching, and cross-linking structures of BPA-PC are as shown above.



**Figure S3.** TGA curve of [Bmim][Lac].

**Table S1.** Results of the optimal condition screening.

Run <sup>a</sup>	$T_1$ (°C)	$T_2$ (°C)	$t_1$ (h)	$t_2$ (h)	$M_{n,GPC}$ (kDa)	$M_{w,GPC}$ (kDa)	PDI
1	220	280	3	1.5	23.5	43.6	1.86
2	230	280	3	1.5	30.6	58.4	1.90
3	240	280	3	1.5	35.4	69.6	1.97
4	250	280	3	1.5	32.4	62.8	1.94
5	260	280	3	1.5	26.8	52.9	1.97
6	240	260	3	1.5	18.7	32.3	1.73
7	240	270	3	1.5	22.6	40.7	1.80
8	240	280	3	1.5	35.4	69.6	1.97
9	240	290	3	1.5	21.7	38.3	1.77
10	240	300	3	1.5	17.6	31.2	1.77
11	240	280	2	1.5	24.7	49.2	1.99
12	240	280	2.5	1.5	26.9	55.7	2.07
13	240	280	3	1.5	35.4	69.6	1.97
14	240	280	3.5	1.5	33.4	66.8	2.00
15	240	280	4	1.5	24.5	45.8	1.87
16	240	280	3	0.5	25.8	47.7	1.84
17	240	280	3	1	29.1	56.6	1.94
18	240	280	3	1.5	35.4	69.6	1.97
19	240	280	3	2	28.9	57.5	1.99
20	240	280	3	2.5	22.6	47.9	2.11

<sup>a</sup> Catalyst: [Bmim][Lac], DPC: BPA: Cat.= 10600:10000:0.01

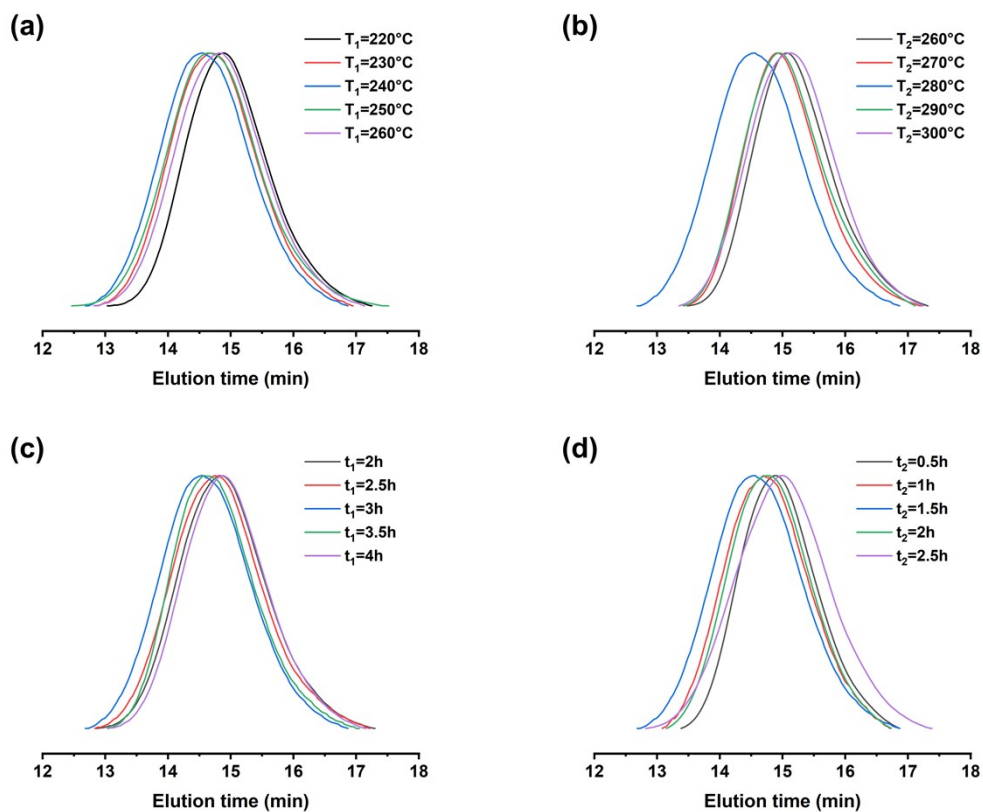


Figure S4. GPC traces of results in Table S1.

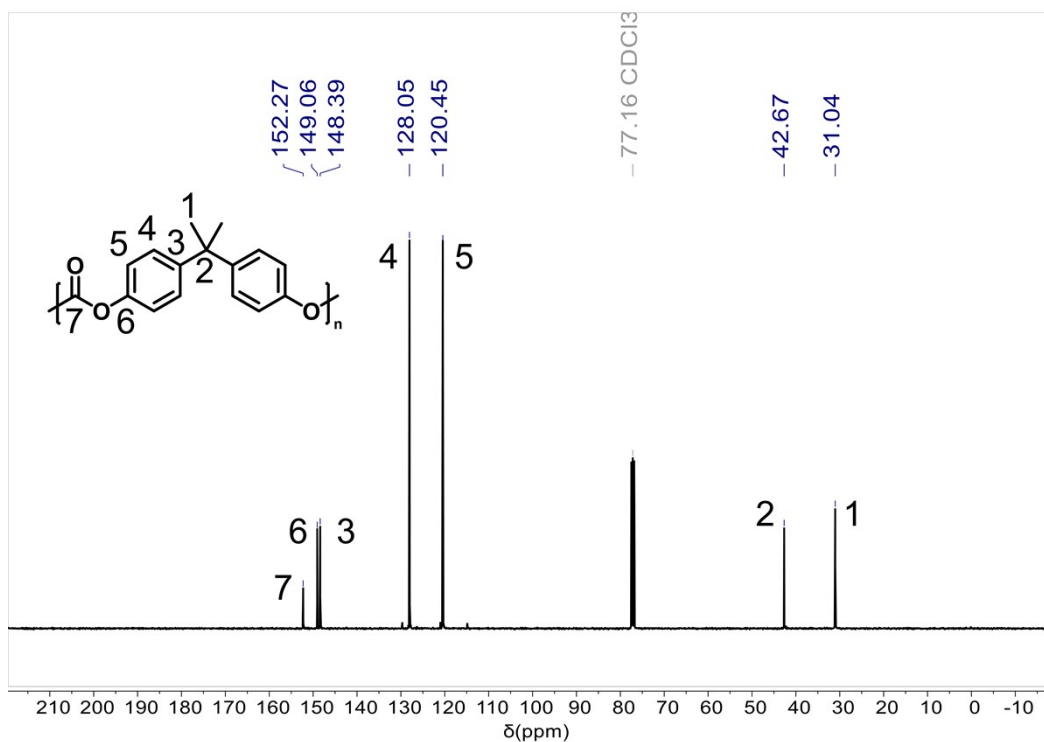
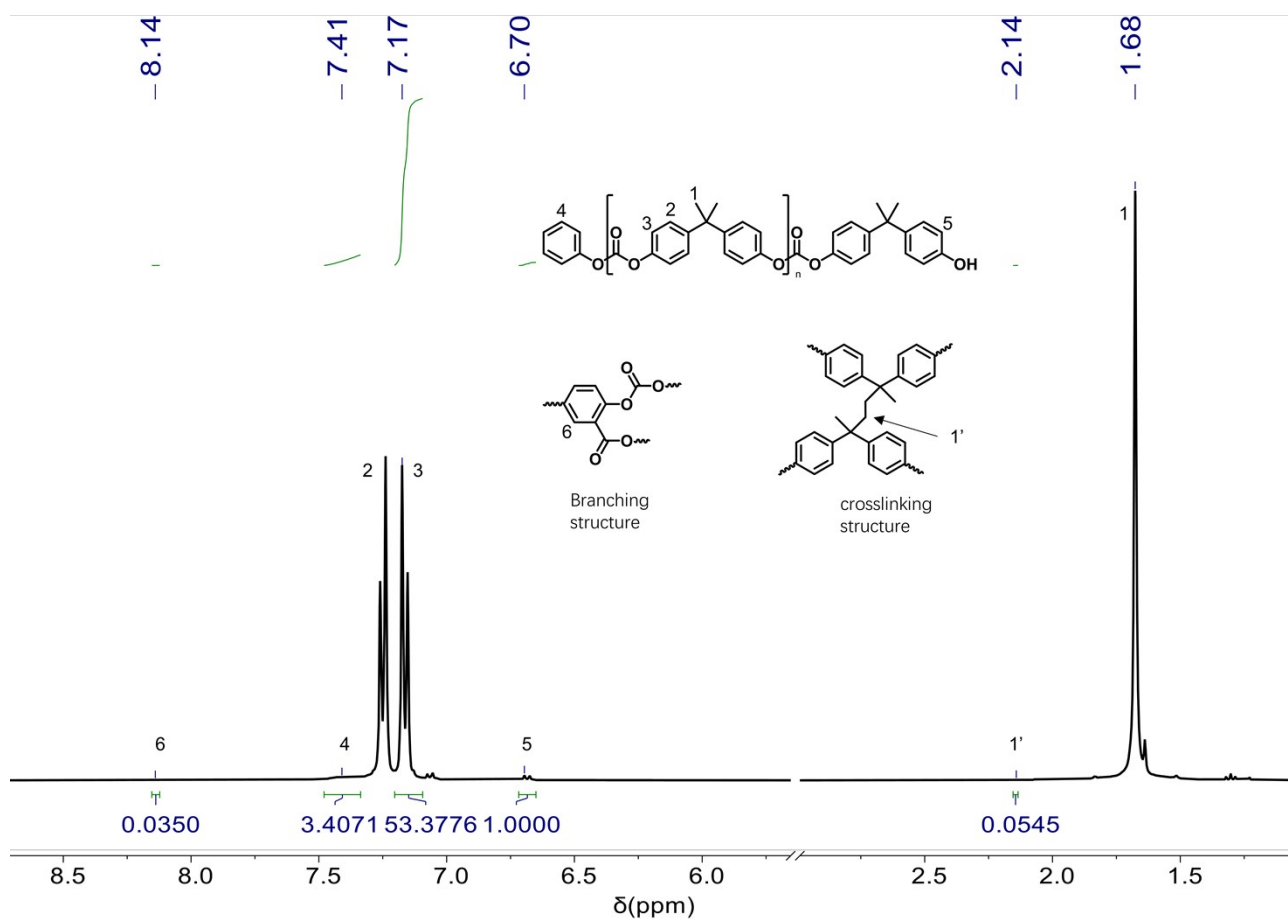
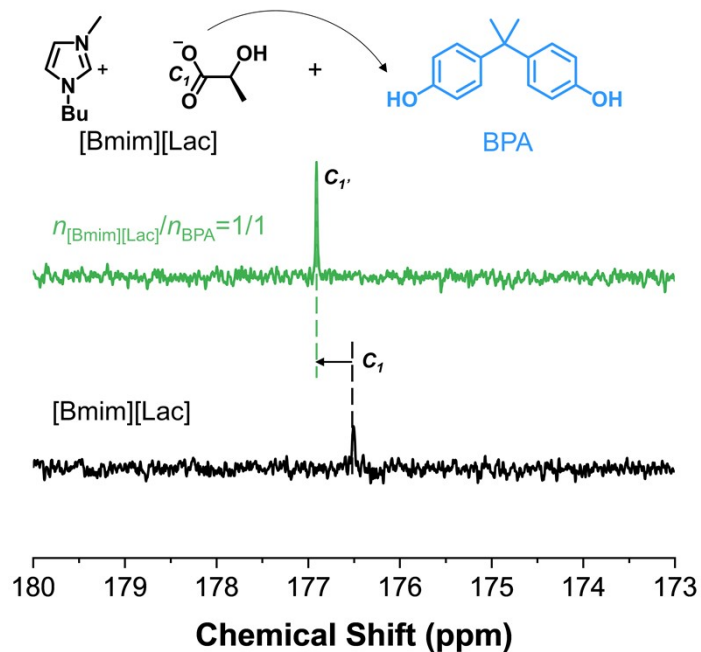


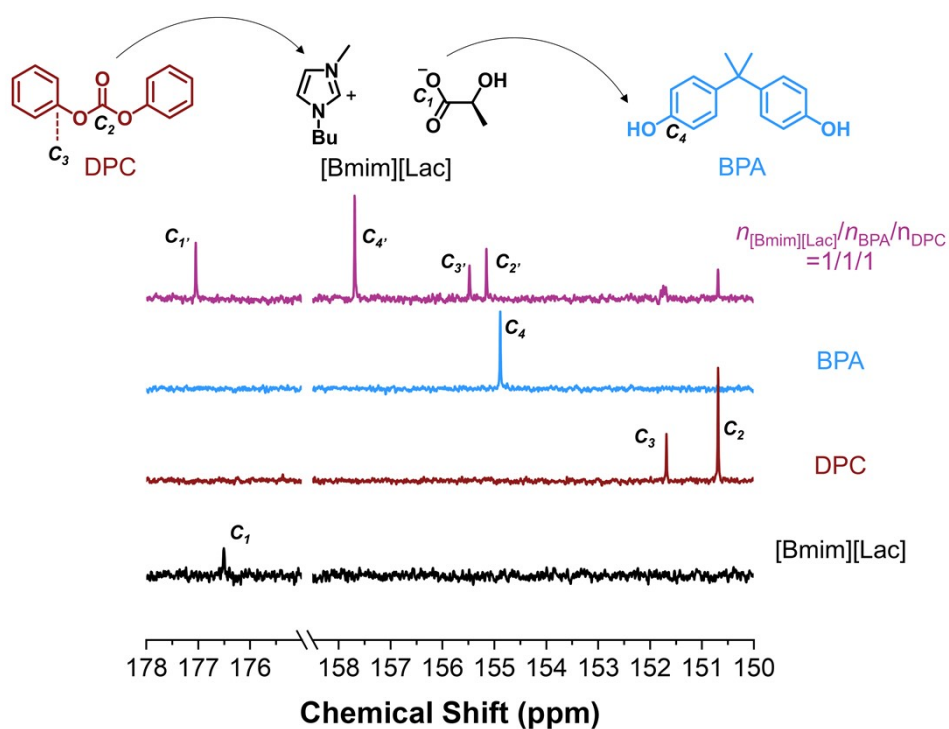
Figure S5.  $^{13}\text{C}$  NMR spectrum of BPA-PC(100 MHz,  $\text{CDCl}_3$ ).



**Figure S6.**  $^1\text{H}$  NMR spectrum and analysis of CH60-0-L (400 MHz,  $\text{CDCl}_3$ ).



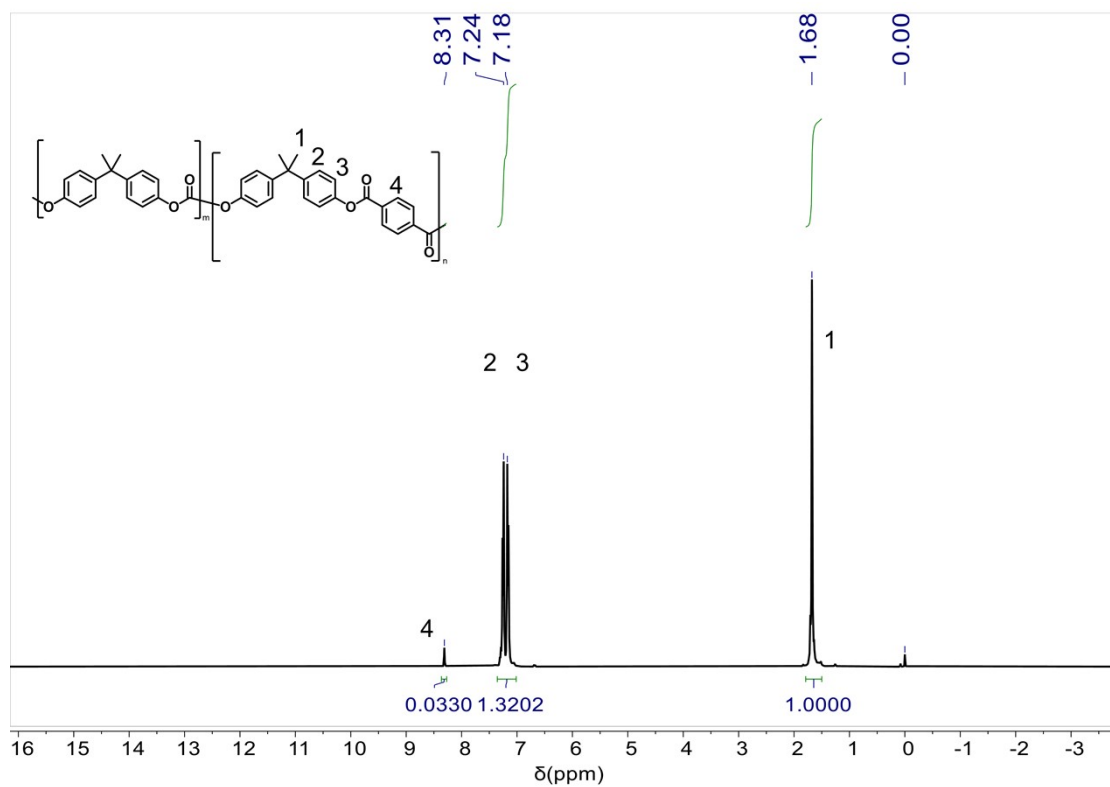
**Figure S7.** Synergistic nucleophilic-electrophilic mechanism: Activation of BPA mediated by lactate anion in  $^{13}\text{C}$  NMR spectra. (DMSO- $d_6$ , 100 MHz)



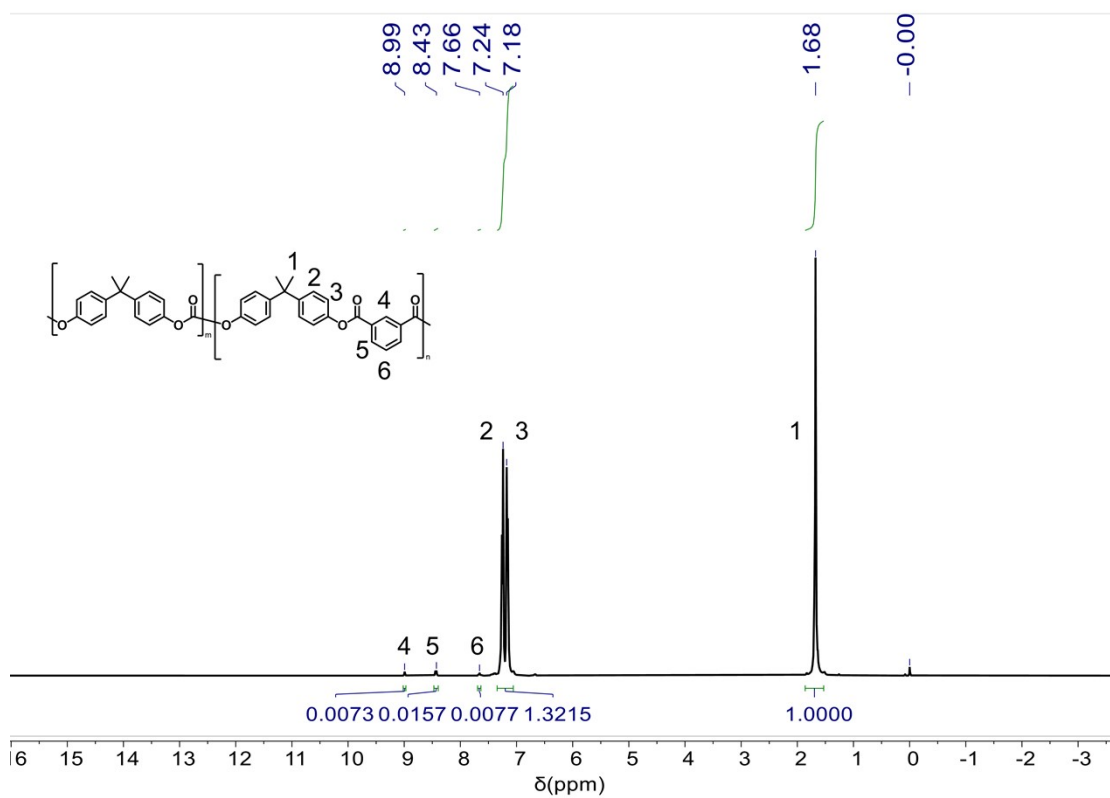
**Figure S8.** Synergistic nucleophilic-electrophilic mechanism: Activation of BPA and DPC mediated by [Bmim][Lac] in  $^{13}\text{C}$  NMR spectra. (DMSO- $d_6$ , 100 MHz)

**Table S2.** Detailed conditions for copolymerization reactions.

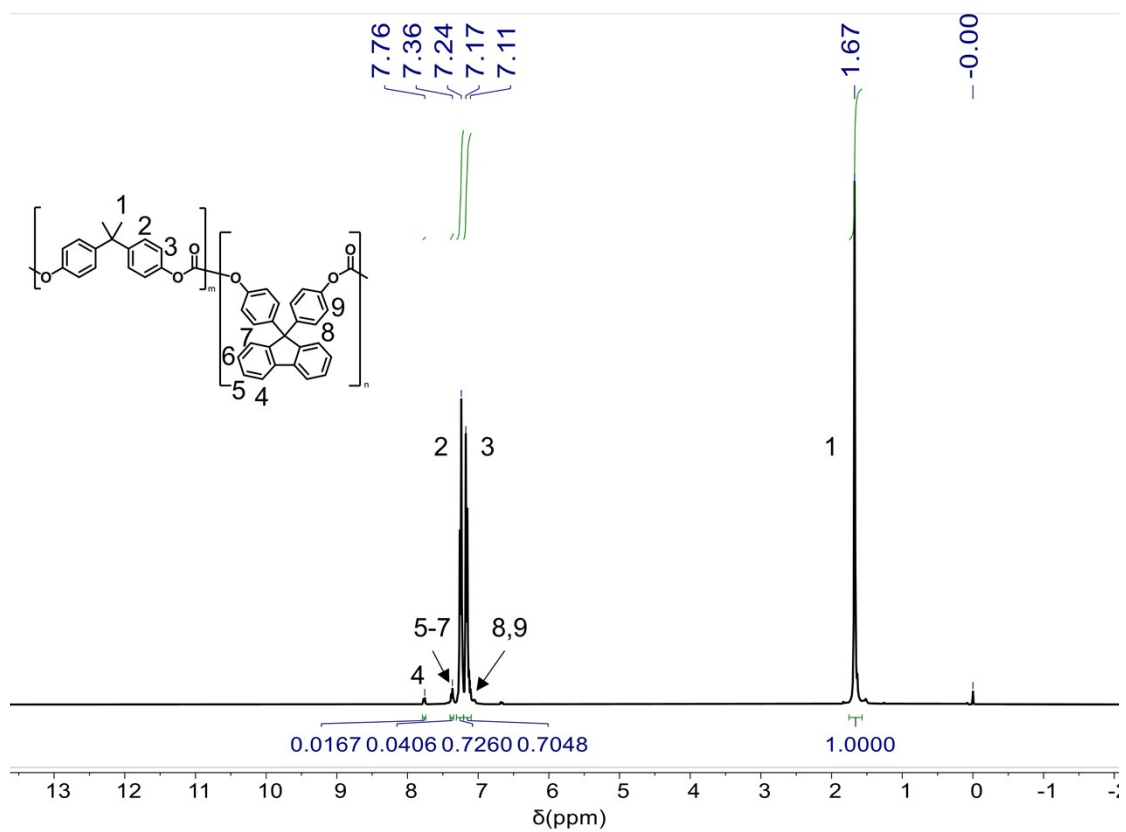
Run	Sample	Diols: Cat.	$T_1$ ( $^{\circ}\text{C}$ )	$T_2$ ( $^{\circ}\text{C}$ )	$t_1$ (h)	$t_2$ (h)
1	PC <sub>T3</sub>	1000000:1	240	280	4	1.5
2	PC <sub>T5</sub>	1000000:1	240	280	3	1.5
3	PC <sub>T10</sub>	1000000:1	240	280	2	1.5
4	PC <sub>I3</sub>	1000000:1	240	280	4	1.5
5	PC <sub>I5</sub>	100000:1	240	280	4	1.5
6	PC <sub>I10</sub>	10000:1	240	280	4	1.5
7	PC <sub>BHPF</sub>	10000:1	240	280	3	1.5
8	PC <sub>PP</sub>	100000:1	260	280	3	1.5
9	PC <sub>BHPF-La</sub>	10000:1	240	280	3	1.5
10	PC <sub>PP-La</sub>	100000:1	260	280	3	1.5



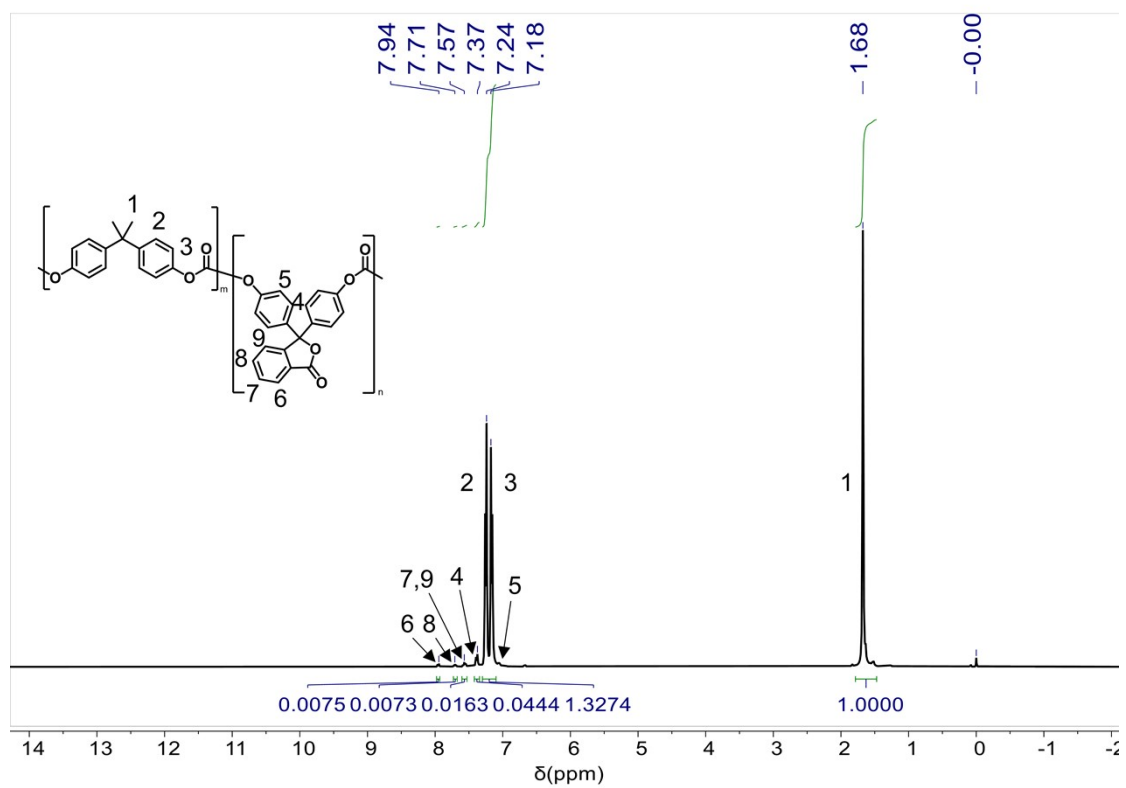
**Figure S9.**  $^1H$  NMR spectrum of  $PC_{T5}$  (400 MHz,  $CDCl_3$ ).



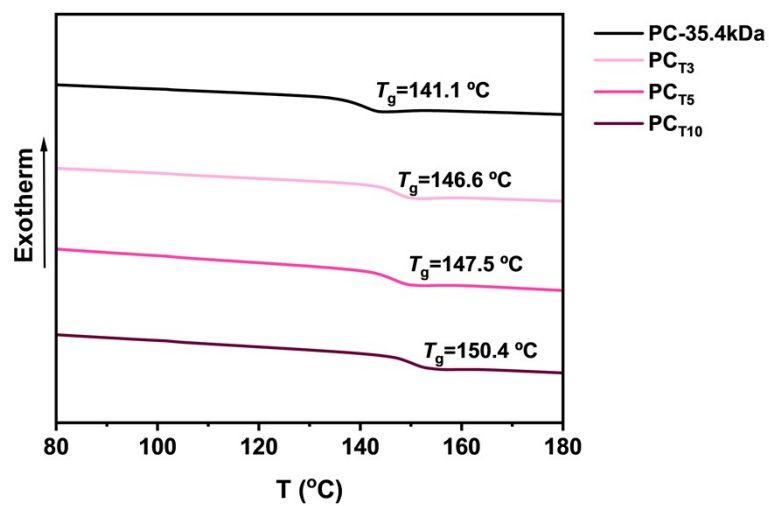
**Figure S10.**  $^1H$  NMR spectrum of  $PC_{I5}$  (400 MHz,  $CDCl_3$ ).



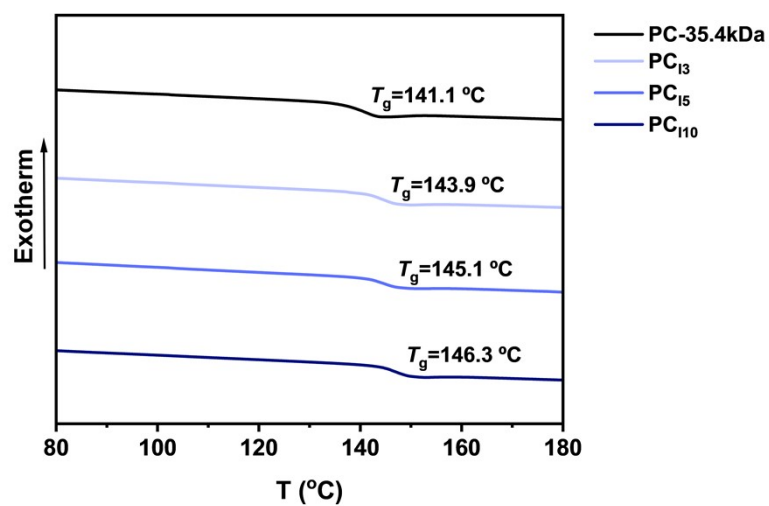
**Figure S11.** <sup>1</sup>H NMR spectrum of PC<sub>BHPF5</sub>(400 MHz, CDCl<sub>3</sub>).



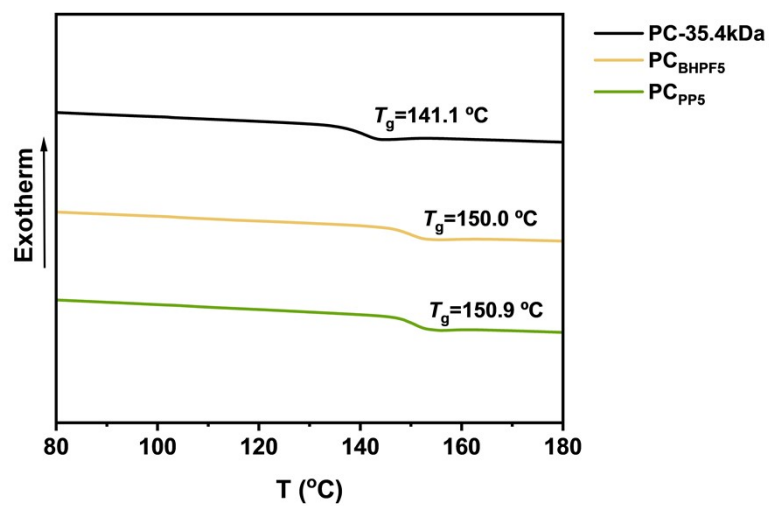
**Figure S12.** <sup>1</sup>H NMR spectrum of PC<sub>PP5</sub>(400 MHz, CDCl<sub>3</sub>).



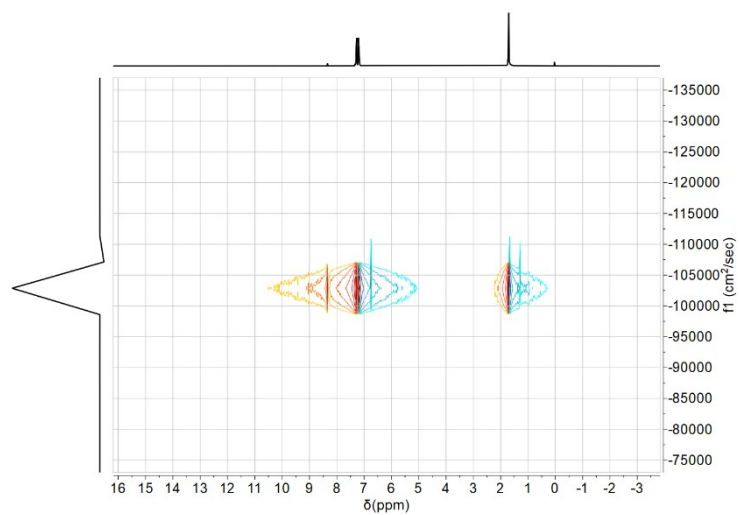
**Figure S13.** DSC curves of PC-35.4kDa and PCs with DPT linkage content from 3%, 5% to 10%.



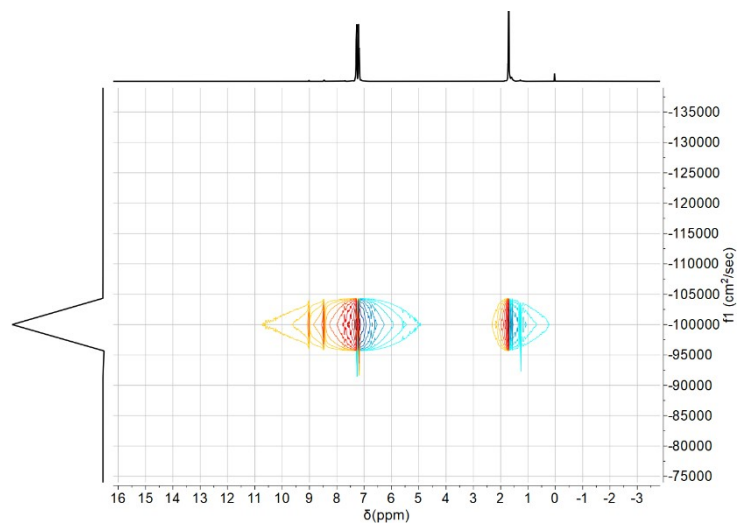
**Figure S14.** DSC curves of PC-35.4kDa and PCs with DPI linkage content from 3%, 5%, to 10%.



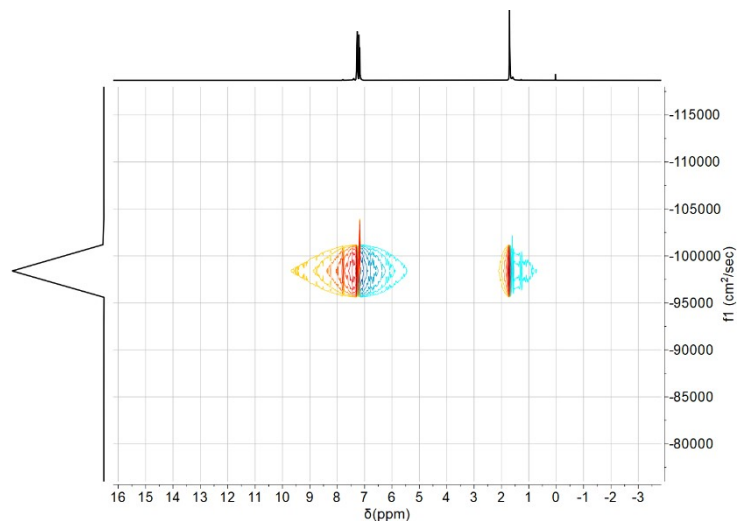
**Figure S15.** DSC curves of PC-35.4kDa and PCs with BHPF and PP linkage content 5%.



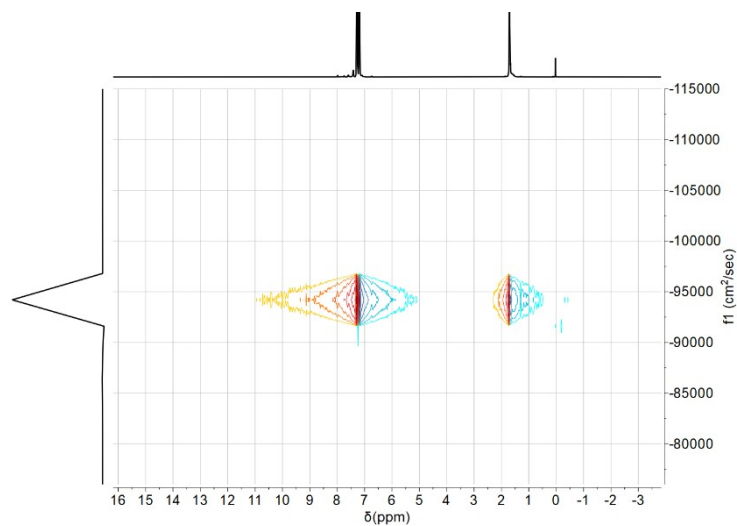
**Figure S16.** DOSY NMR spectrum of PC<sub>T5</sub>(400 MHz, CDCl<sub>3</sub>).



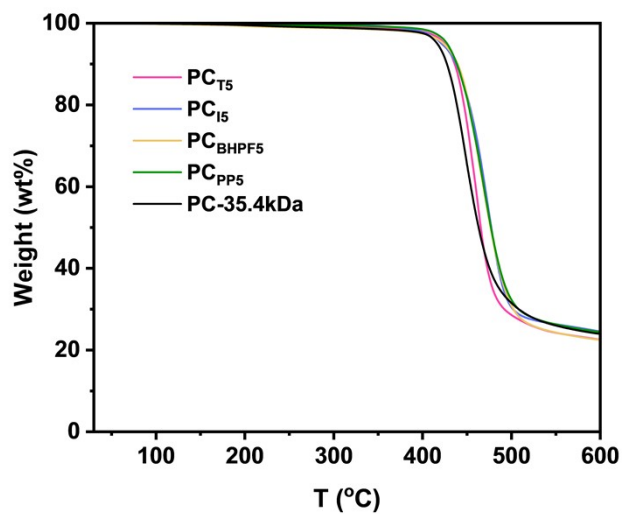
**Figure S17.** DOSY NMR spectrum of PC<sub>I5</sub>(400 MHz, CDCl<sub>3</sub>).



**Figure S18.** DOSY NMR spectrum of PC<sub>BHPF5</sub>(400 MHz, CDCl<sub>3</sub>).



**Figure S19.** DOSY NMR spectrum of PC<sub>PP5</sub>(400 MHz, CDCl<sub>3</sub>).



**Figure S20.** TGA curves of PC-35.4kDa and PCs with a 5% M3-linkage content.

**Table S3.**  $T_{d,5\%}$  of copolycarbonates.

Run	Sample	$T_{d,5\%}$ (°C) <sup>a</sup>
1	PC <sub>T5</sub>	425
2	PC <sub>I5</sub>	424
3	PC <sub>BHPF5</sub>	424
4	PC <sub>PP5</sub>	428
5	PC-35.4kDa	417

<sup>a</sup>  $T_{d,5\%}$  represents the temperature at 5% weight loss of the sample.