

## Supplemental Information to:

### Efficient synthesis of bio-derived polycarbonates from dimethyl carbonate and isosorbide: regulating *exo*-OH and *endo*-OH reactivity by ionic liquids

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## 1. Materials

Dimethyl Isosorbide (IS, 98%) was received from Alfa Aesar. Dimethyl carbonate (DMC, 99%, anhydrous), tetrabutylphosphonium bromide ( $[P_{4444}]Br$ , 98%), tetrabutylammonium bromide ( $[N_{4444}]Br$ , 99%), 1-methylimidazole (99%), bromoethane (99%), n-butyl bromide (99%), 1-bromooctane (98%), and 1-bromodecane (98%) were purchased from Aladdin biochemical technology Co., Ltd., (Shanghai, China). Additionally, isosorbide was recrystallized with acetone. The others were used as received without further purification.

## 2. Characterizations

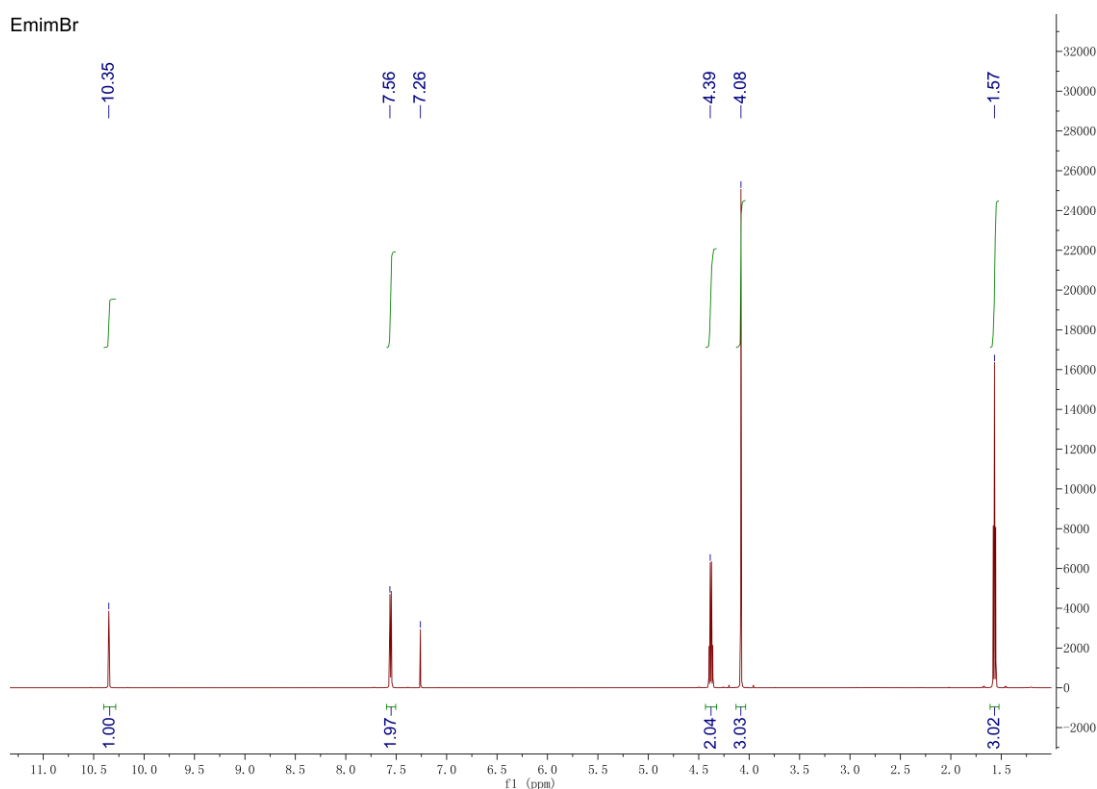
The molecular weights of all PIC samples were measured employing an Agilent PL-GPC 50 gel permeation chromatography (GPC) and polystyrene was adopted to establish the standard curve with dimethylformamide (DMF) as the mobile phase. The selectivities of PIC intermediates were measured on a SHIMADZU LC-20AT HPLC with an InertSustain C18 chromatographic column and a differential refraction detector (RID) using methanol and  $H_2O$  as a mobile phase.<sup>1</sup> The  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on a Bruker AVANCE III HD 600 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal reference using deuterated chloroform ( $CDCl_3$ ) or dimethylsulfoxide ( $DMSO-d_6$ ) as the solvent. Mass spectra data were collected on a Bruker micrQTOF-Q II mass spectrometer. An elemental analyzer (elementar vario EL cube) was used for measuring element content. The Br anion contents of ILs were measured using the  $AgNO_3$  titration method with a Mettler Toledo EasyPlus automated titrator. Water contents of ILs were determined by a Mettler Toledo V10S Karl-Fischer titrator. The thermogravimetric analysis (TGA) curves were recorded on a Setaram Labsys Evo thermal gravimetric 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 and a nitrogen flow rate of 50 mL/min.

### 3. Characterization of ILs

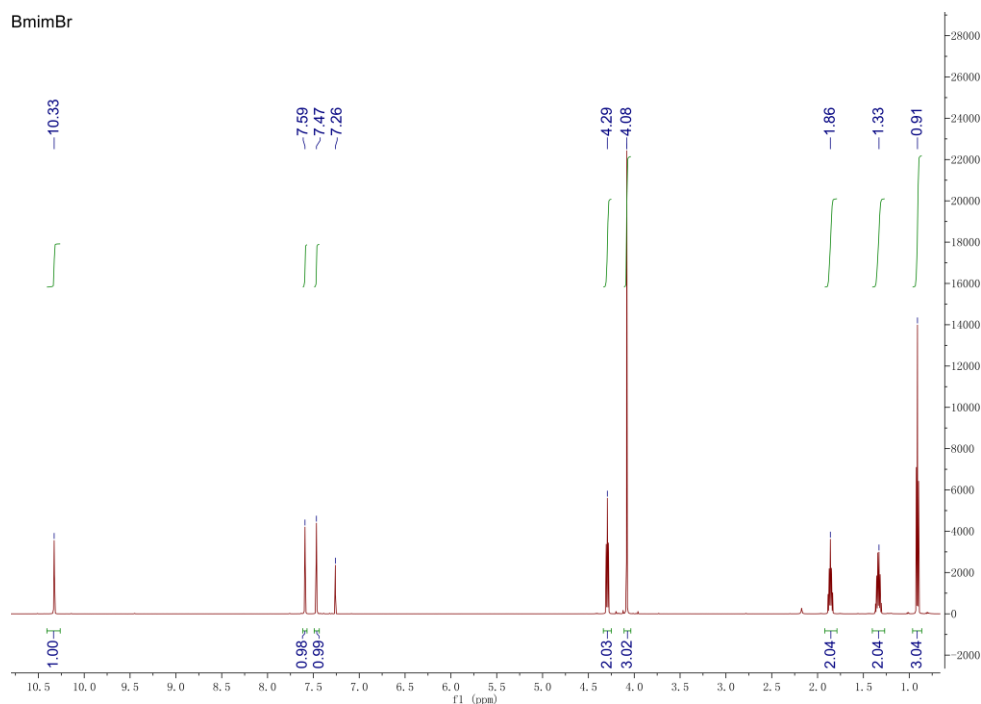
#### 1-ethyl-3-methylimidazolium bromide ([Emim]Br)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.35 (s, 1H), 7.56 (m, 2H), 4.39 (m, 2H), 4.08 (s, 3H), 1.57 (t, 3H); MS (ESI):  $m/z$ : 110.17 [Emim], 301.20 [Emim] $_2$ Br; elemental analysis calcd (%) for  $\text{C}_6\text{H}_{11}\text{N}_2\text{Br}$ : C 37.72, H 5.80, N 14.66, Br 41.82; found: C 37.80, H 5.75, N 14.72, Br 41.31. Purity (Based on Br anion) = found (%) Br  $\times$  100% / calcd (%) Br = 98.78%. Water content: 0.12 wt%.



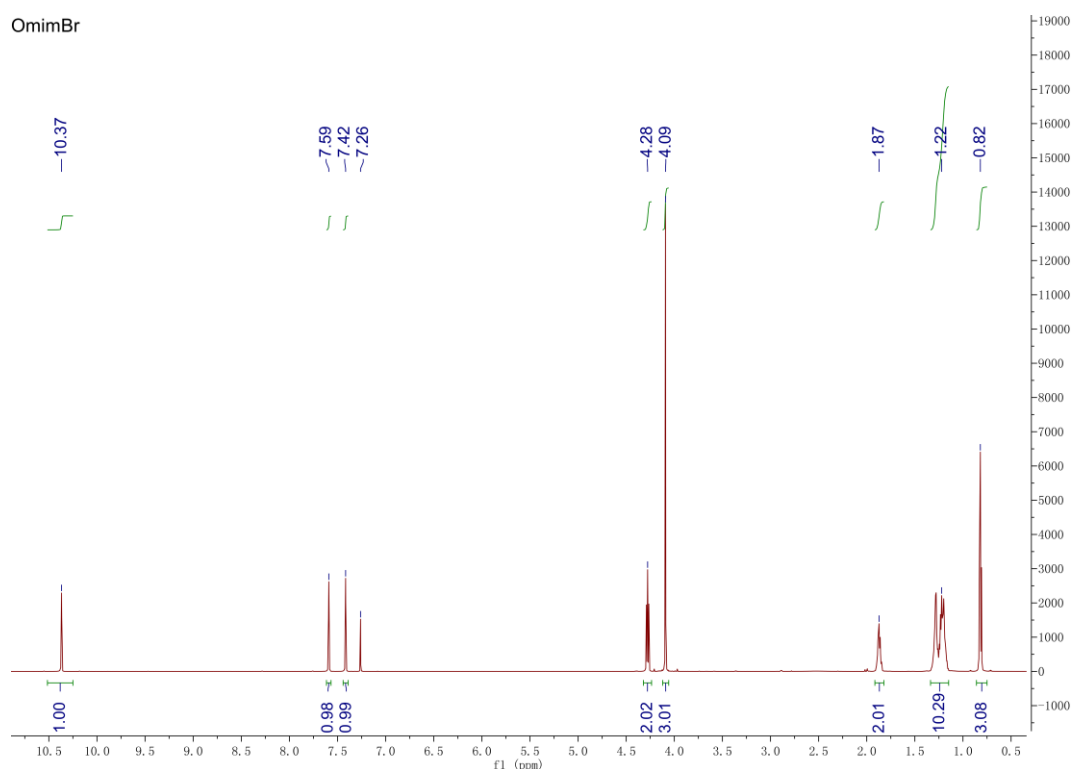
### 1-butyl-3-methylimidazolium bromide ([Bmim]Br)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.33 (s, 1H), 7.59 (t, 1H), 7.47 (t, 1H), 4.29 (t, 2H), 4.08 (s, 3H), 1.86 (m, 2H), 1.33 (m, 2H), 0.91 (t, 3H); MS (ESI):  $m/z$ : 139.18 [Bmim], 357.19 [Bmim] $_2$ Br; elemental analysis calcd (%) for  $\text{C}_8\text{H}_{15}\text{N}_2\text{Br}$ : C 43.85, H 6.90, N 12.78, Br 36.47; found: C 43.78, H 6.94, N 12.83, Br 35.85. Purity (Based on Br anion) = found (%) Br  $\times$  100% / calcd (%) Br = 98.30%. Water content: 0.13 wt%.



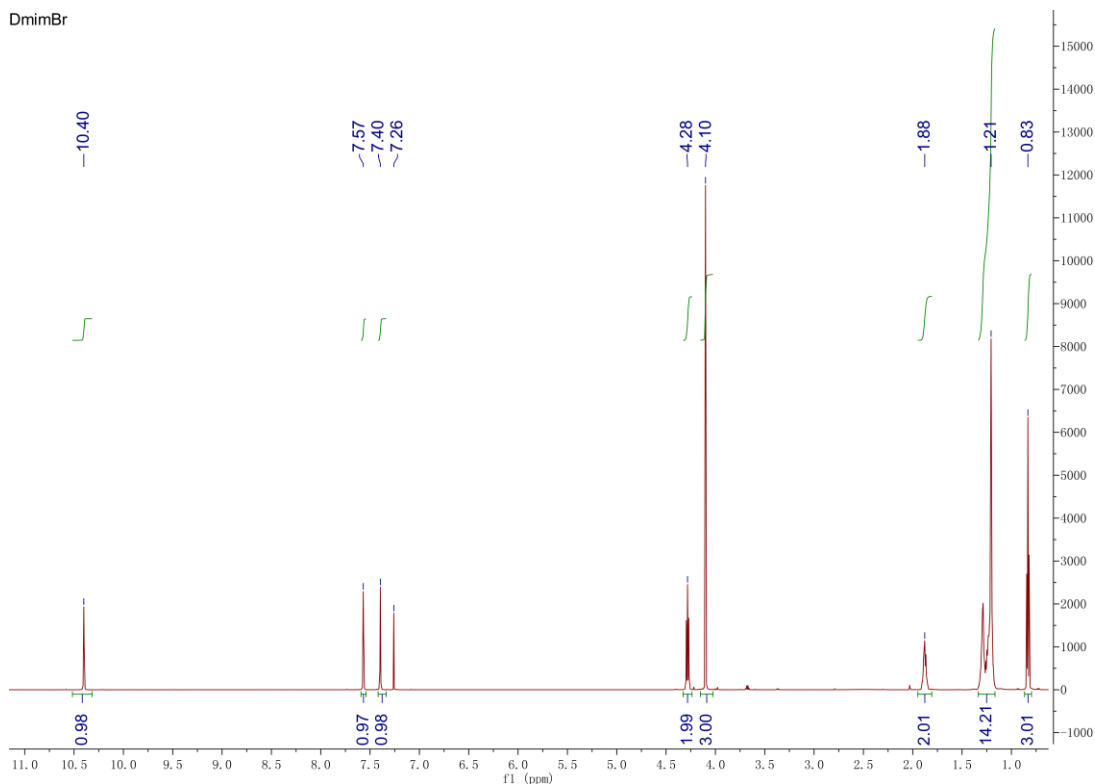
### 1-octyl-3-methylimidazolium bromide ([Omim]Br)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.37 (s, 1H), 7.59 (t, 1H), 7.42 (t, 1H), 4.28 (t, 2H), 4.09 (s, 3H), 1.87 (m, 2H), 1.22 (m, 10H), 0.82 (t, 3H); MS (ESI):  $m/z$ : 195.19 [Omim], 469.35 [Omim] $_2$ Br; elemental analysis calcd (%) for  $\text{C}_{12}\text{H}_{23}\text{N}_2\text{Br}$ : C 52.37, H 8.42, N 10.18, Br 29.03; found: C 52.41, H 8.46, N 10.13, Br 28.66. Purity (Based on Br anion) = found (%) Br  $\times$  100% / calcd (%) Br = 98.73%. Water content: 0.08 wt%.



### 1-decyl-3-methylimidazolium bromide ([Dmim]Br)

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.40 (s, 1H), 7.57 (t, 1H), 7.40 (t, 1H), 4.28 (t, 2H), 4.10 (s, 3H), 1.88 (m, 2H), 1.21 (m, 14H), 0.83 (t, 3H); MS (ESI):  $m/z$ : 223.26 [Dmim], 529.29 [Dmim] $_2$ Br; elemental analysis calcd (%) for  $\text{C}_{14}\text{H}_{27}\text{N}_2\text{Br}$ : C 55.44, H 8.97, N 9.24, Br 26.35; found: C 55.51, H 8.90, N 9.29, Br 25.78. Purity (Based on Br anion) = found (%) Br  $\times$  100% / calcd (%) Br = 97.84%. Water content: 0.09 wt%.



#### tetrabutylphosphonium bromide ([P<sub>4444</sub>]<sup>+</sup>Br<sup>-</sup>)

Water content: 0.04 wt%.

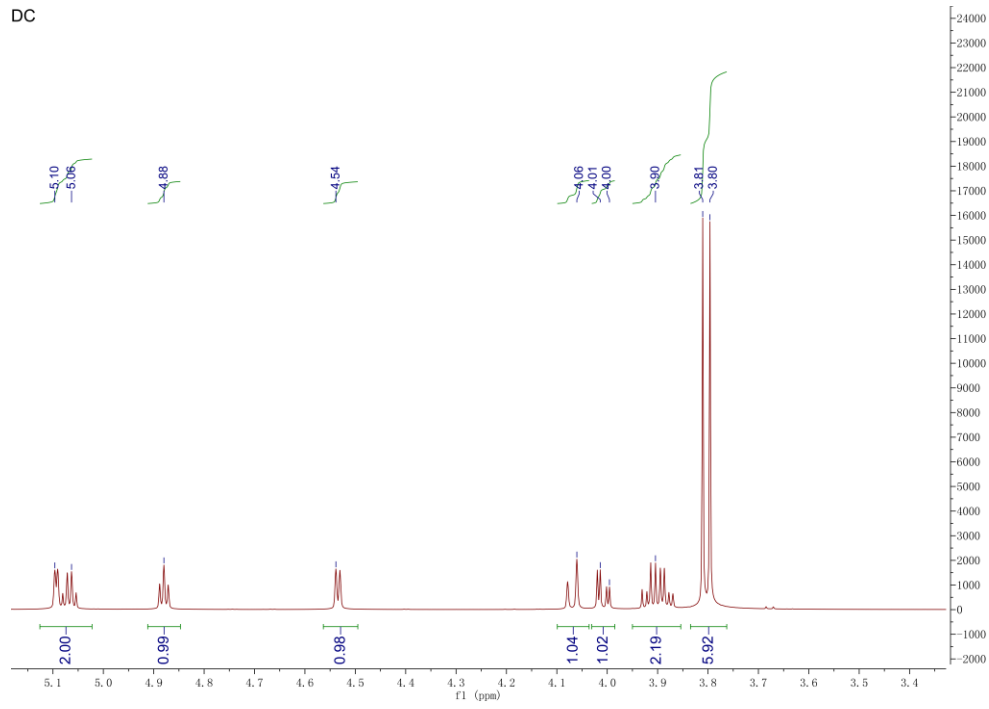
#### tetrabutylammonium bromide ([N<sub>4444</sub>]<sup>+</sup>Br<sup>-</sup>)

Water content: 0.08 wt%.

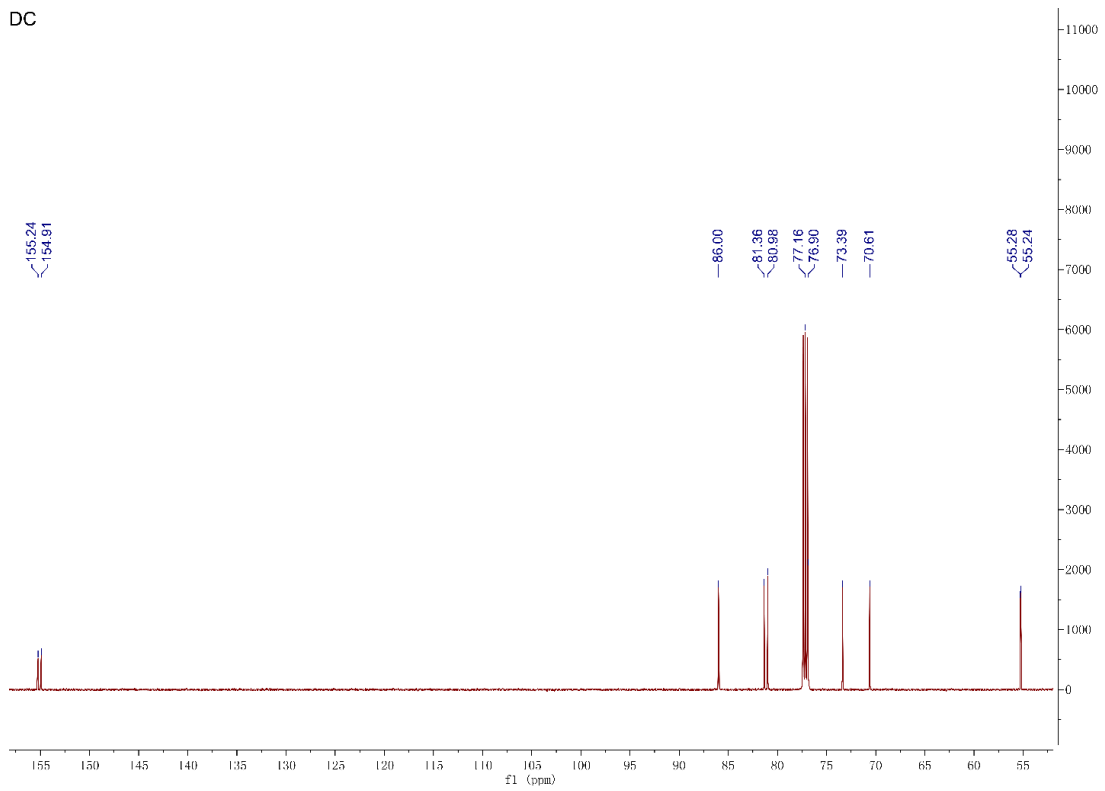
### 4. Characterization of carboxymethyl products

**DC:** C<sub>10</sub>H<sub>14</sub>O<sub>8</sub>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.10 (m, 2 H), 4.88 (t, 1H), 4.54 (d, 1H), 4.06 (d, 1H), 4.01 (m, 1H), 3.90 (m, 2H), 3.81 (s, 3H), 3.80 ppm (s, 3H); <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>): 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: 285.06 [DC+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>10</sub>H<sub>14</sub>O<sub>8</sub>: C 45.81, H 5.38, O 48.81; found: C 45.78, H 5.37, O 48.82.

DC

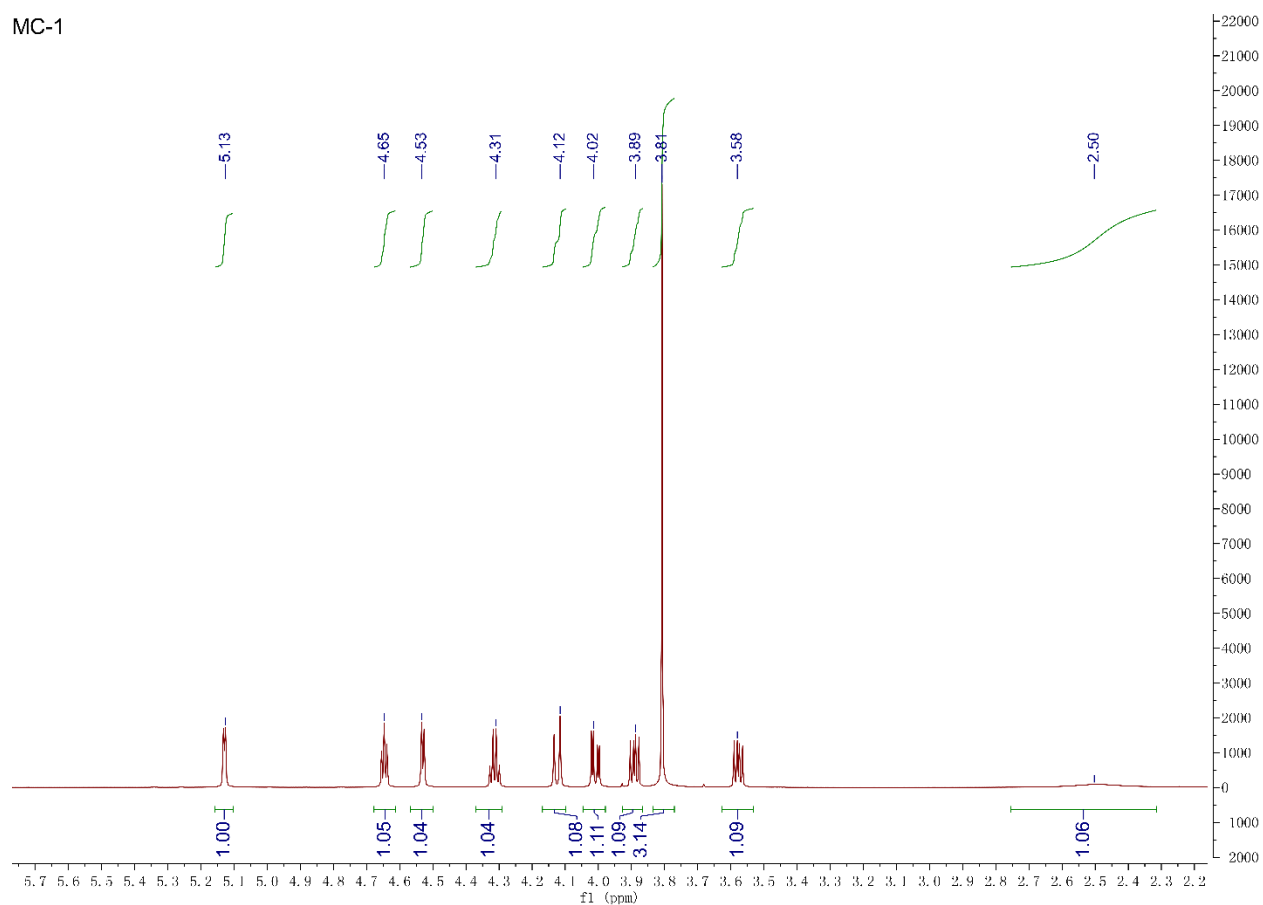


DC



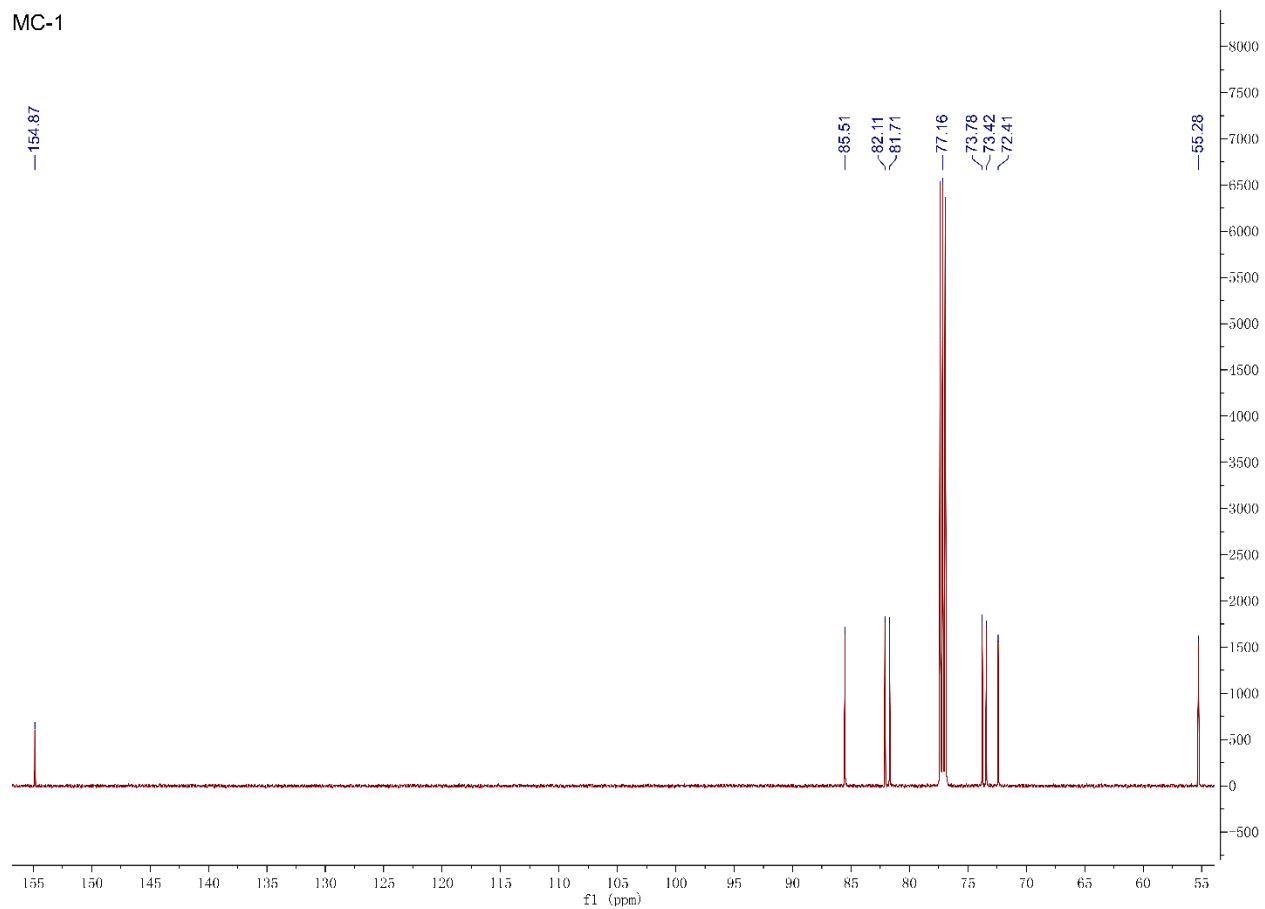
**MC-1:** C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.13 (d, 1 H), 4.65 (t, 1 H), 4.53 (d, 1H), 4.31 (m, 1H), 4.02 (dd, 1H), 3.89 (m, 1H), 3.81 (s, 3H), 3.58 (m, 1 H), 2.50 ppm (s, 1H); <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>): δ 154.87, 85.51, 82.11, 81.71, 73.78, 73.42, 72.41, 55.28 ppm; MS (ESI): m/z: 227.06 [MC-1+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>: C 47.06, H 5.92, O 47.02; found: C 47.08, H 5.88, O 46.98.

MC-1

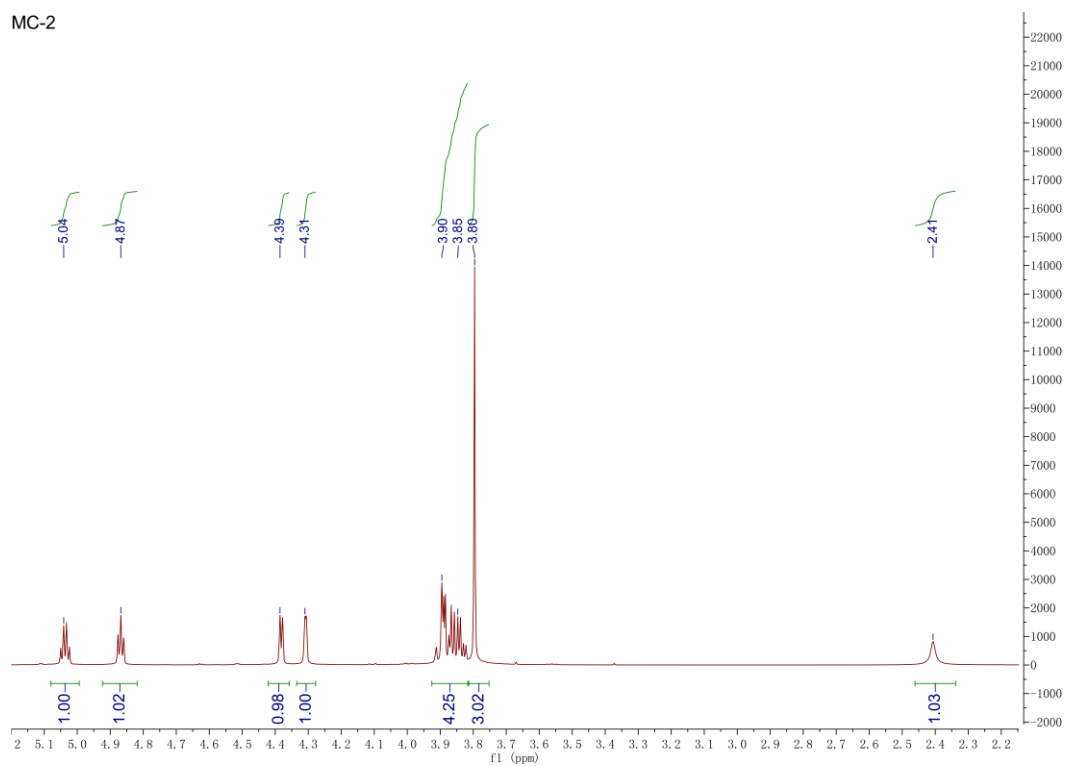




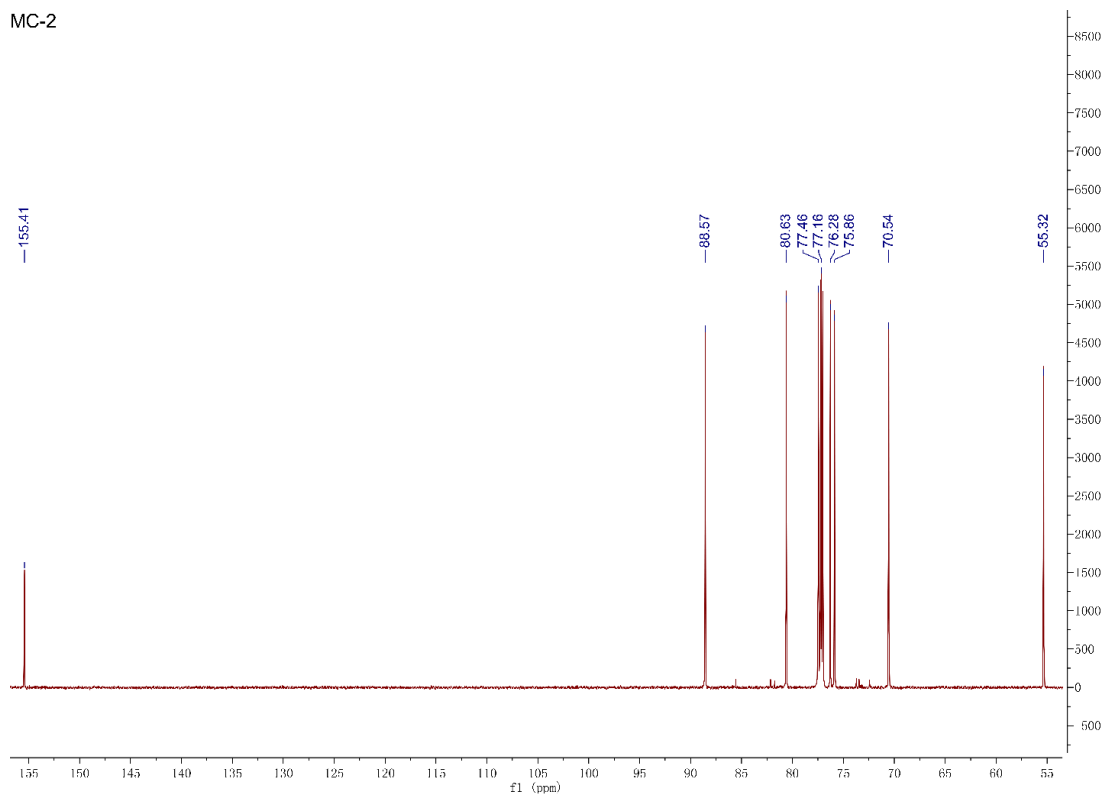
MC-1



**MC-2:** C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>; <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): δ 5.04 (m, 1H), 4.87 (t, 1H), 4.39 (d, 1H), 4.31 (d, 1H), 3.90 (m, 4H), 3.80 (s, 3H), 2.41 ppm (s, 1H); <sup>13</sup>C NMR (600 MHz, CDCl<sub>3</sub>): 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-2+Na]<sup>+</sup>; elemental analysis calcd (%) for C<sub>8</sub>H<sub>12</sub>O<sub>6</sub>: C 47.06, H 5.92, O 47.02; found: C 47.08, H 5.85, O 47.03.

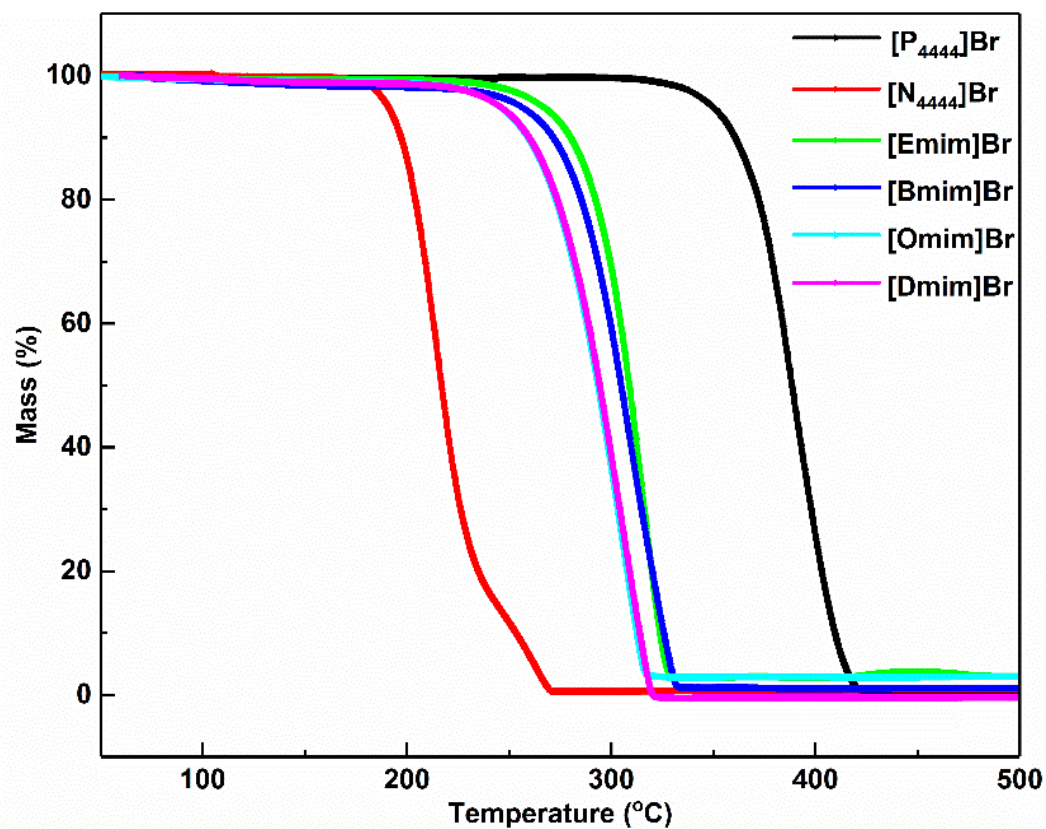


MC-2



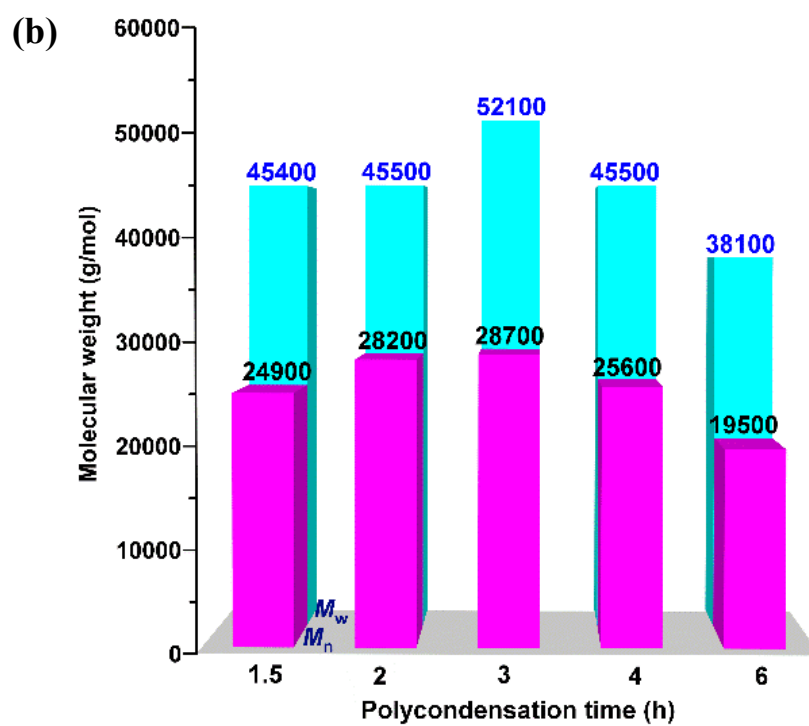
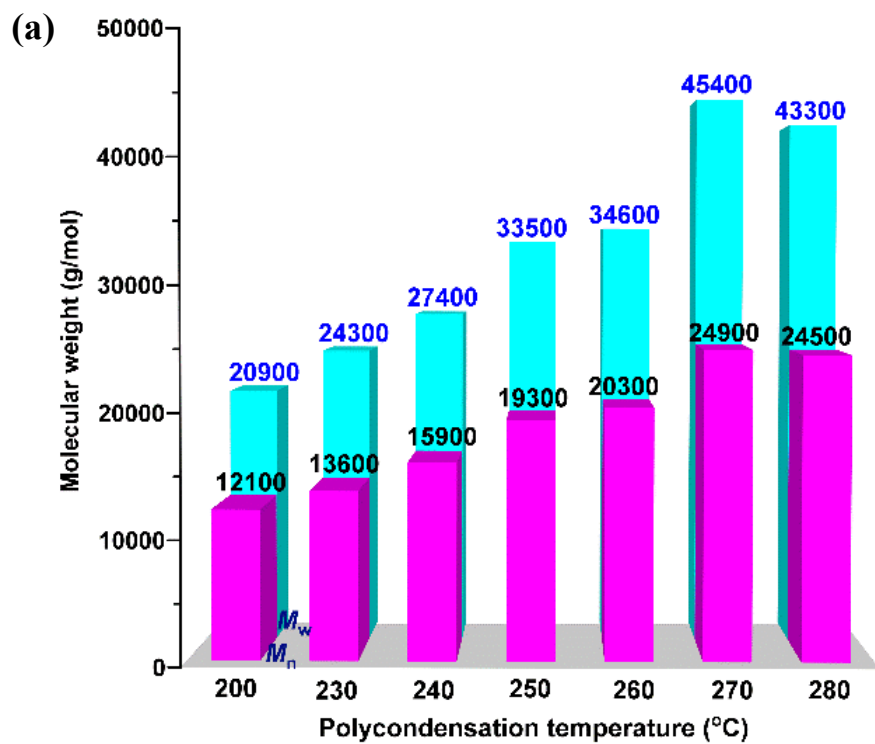
The standard curves of PIC intermediates were determined using isosorbide 5-mononitrate as the internal standard. Subsequently, the selectivities of PIC intermediates could be calculated using HPLC analysis.

## 5. The thermability of IL catalysts



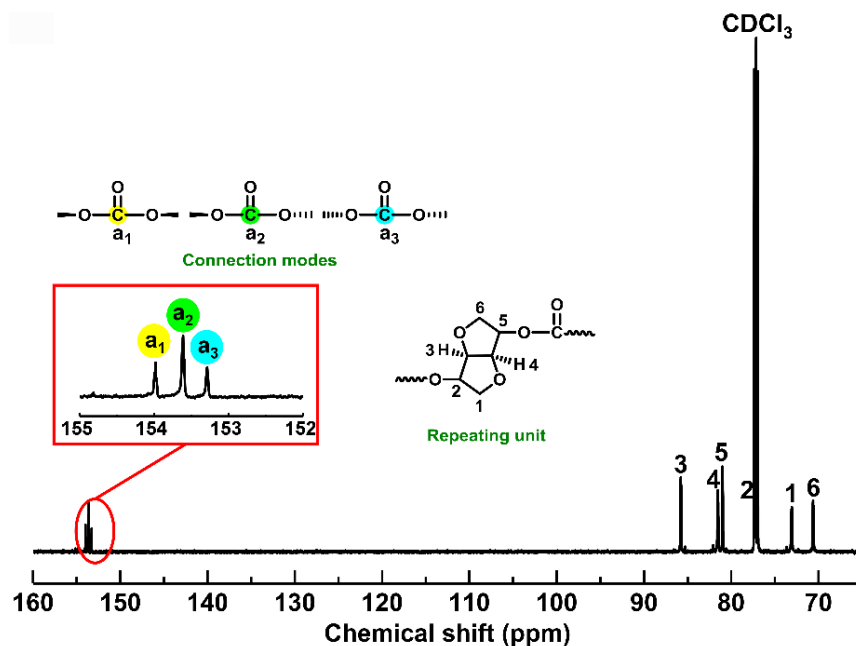
**Fig. S1** The thermostability of selected bromide-based IL catalysts.

## 6. Influence of reaction parameters on PIC molecular weight



**Fig. S2** Influence of (a) polycondensation temperature and (b) polycondensation time on PIC molecular weight.

## 7. The $^{13}\text{C}$ NMR analysis of PIC



**Fig. S3.** Typical chemical structure of PIC identified through the spectra of  $^{13}\text{C}$  NMR catalyzed by [Emim]Br.

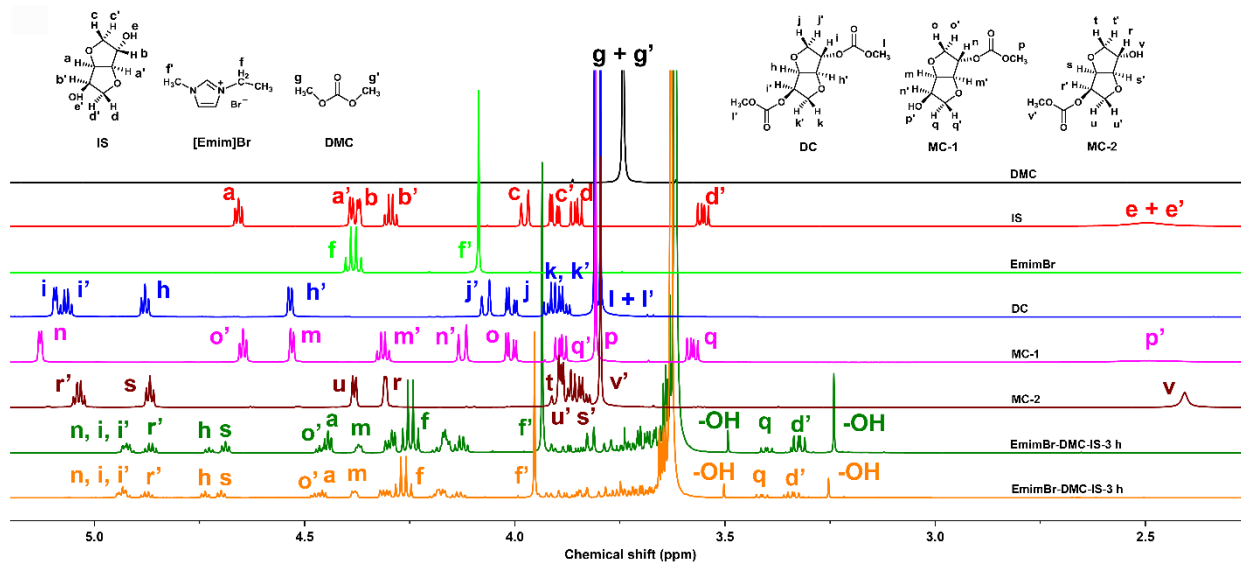
## 8. The correlation of thermal behaviors with the molecular weight

**Table S1.** The correlation of thermal behaviors with molecular weight.

Entry	PT ( $^{\circ}\text{C}$ )	$T_{d-5\%}$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$M_w$ (kg/mol)
1	200	317	138	20.9
2	230	322	141	24.3
3	240	325	146	27.4
4	250	329	150	33.5
5	260	330	150	34.6
6	270	336	156	45.4
7	280	334	155	43.3

PT represents polycondensation temperature.

## 9. In-situ <sup>1</sup>H NMR of transesterification products with the reaction progressed



**Fig. S4** Chemical shift of proton of transesterification products with the reaction progressed.

## 10. GPC charts of PICs

### (1) Influence of cation structure of IL

#### MW Averages

Mp: 5966

Mn: 4227

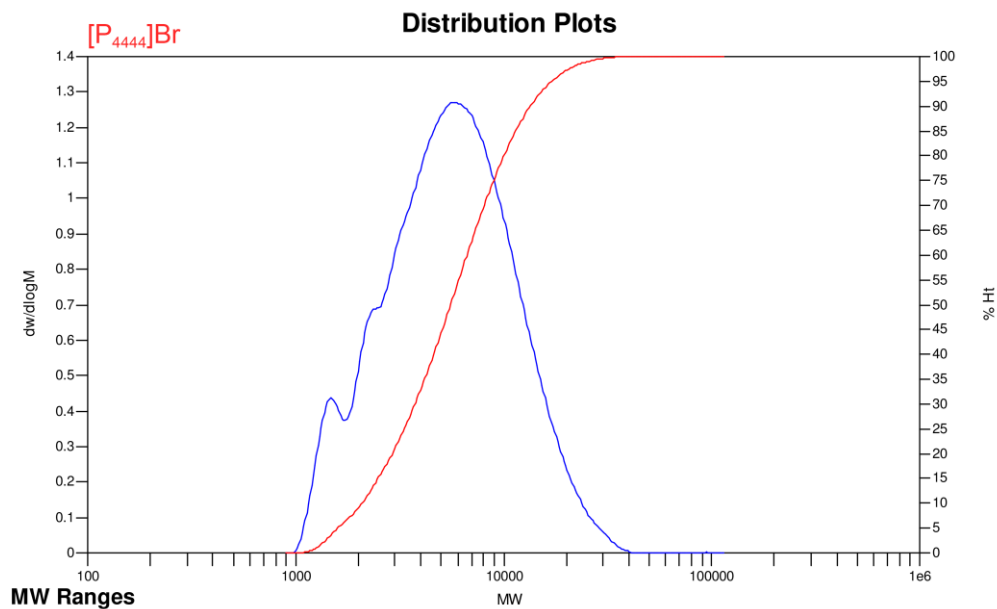
Mv: 6382

Mw: 6846

Mz: 10604

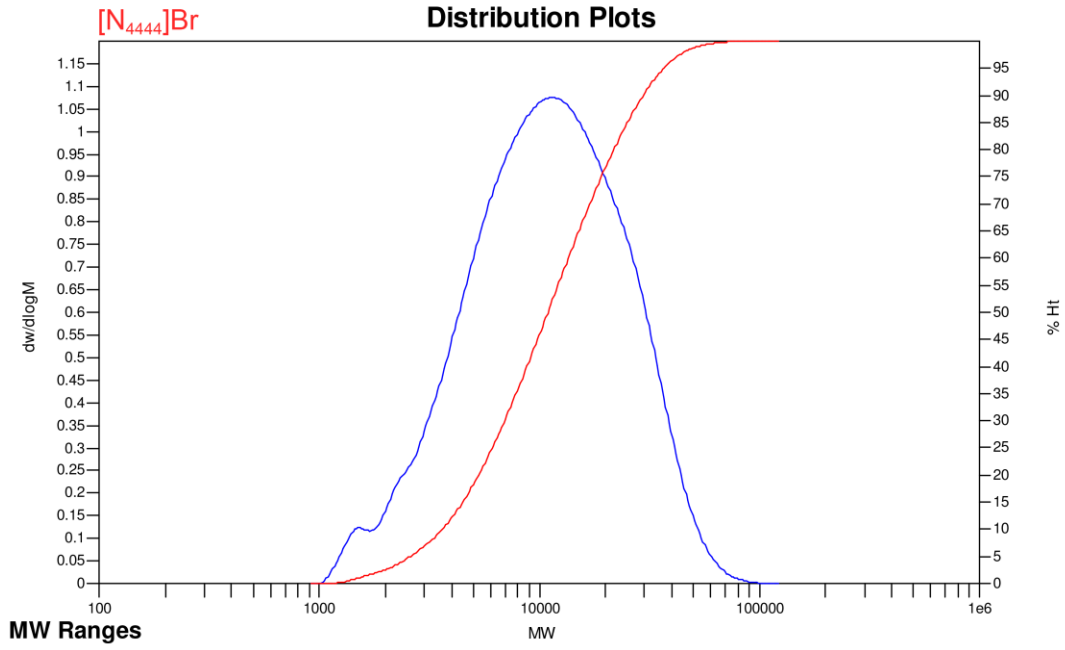
Mz+1: 15584

PD: 1.6196



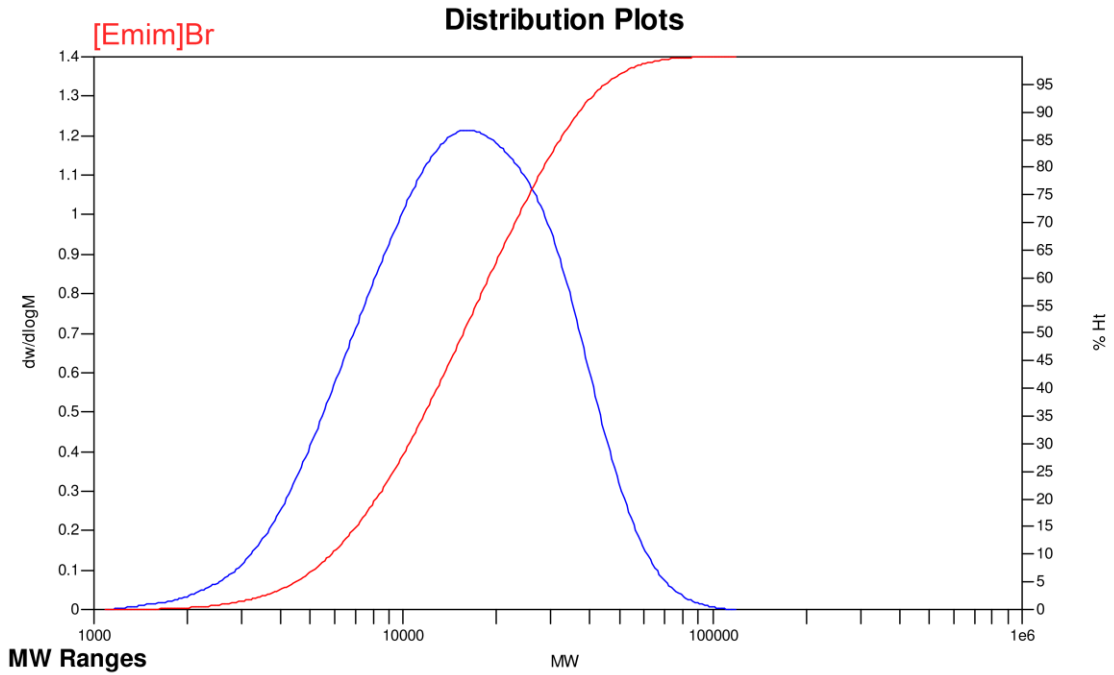
**MW Averages**

Mp: 11479      Mn: 7501      Mv: 12961      Mw: 14090  
Mz: 22834      Mz+1: 31879      PD: 1.8784



**MW Averages**

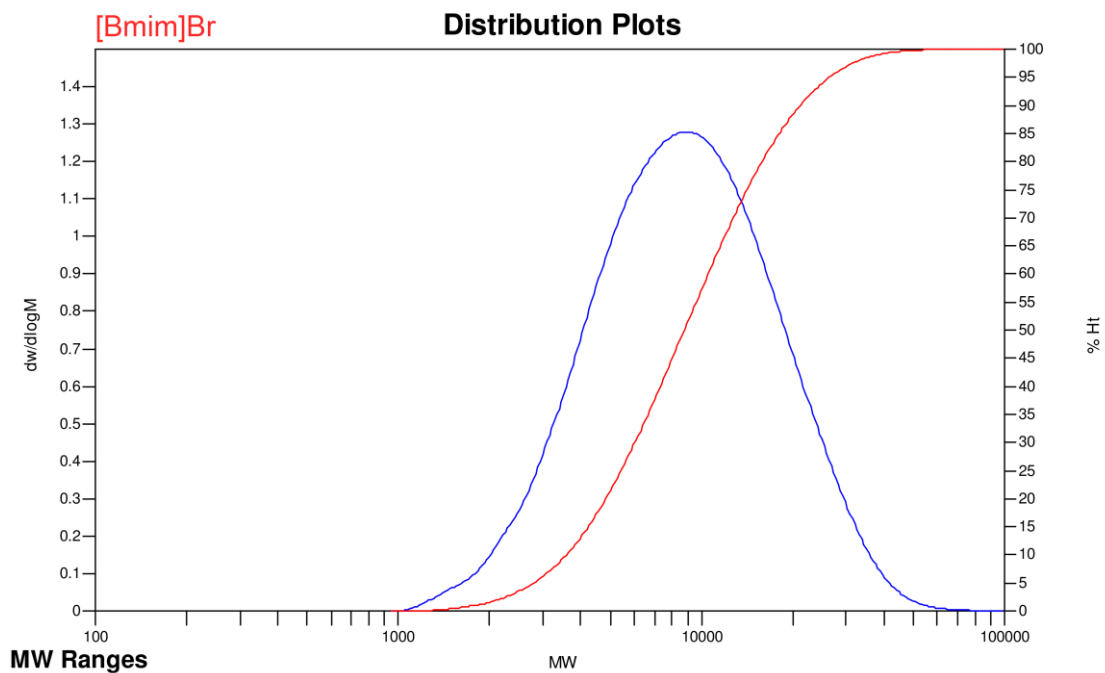
Mp: 16350      Mn: 11476      Mv: 17651      Mw: 18860  
Mz: 27921      Mz+1: 37351      PD: 1.6434





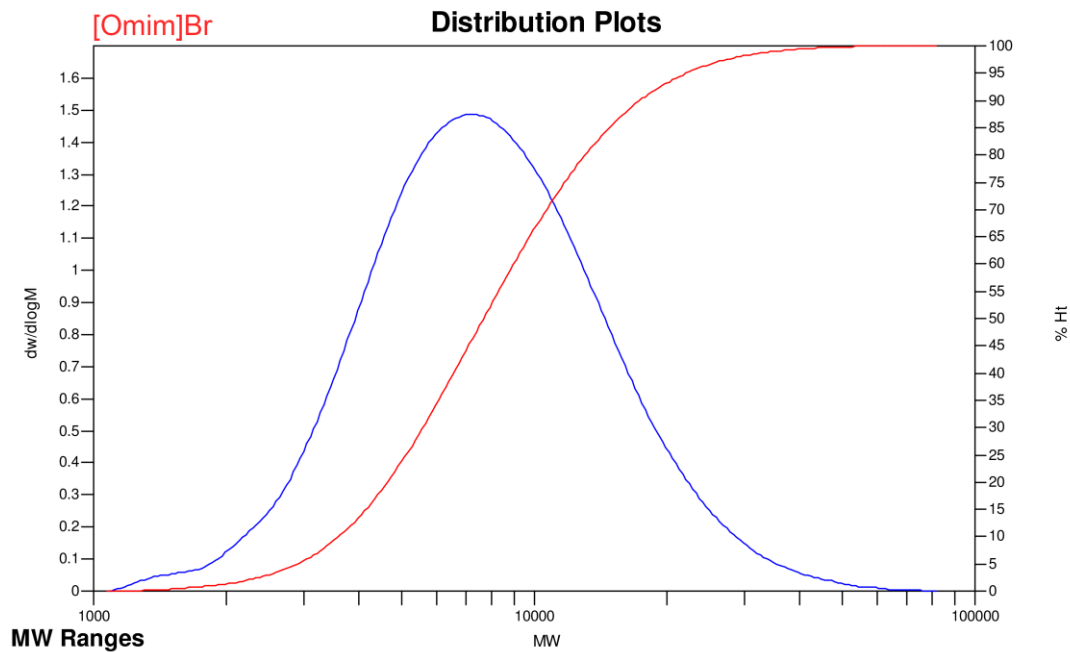
**MW Averages**

Mp: 8961                      Mn: 6843                      Mv: 10135                      Mw: 10827  
Mz: 16336                      Mz+1: 22916                      PD: 1.5822



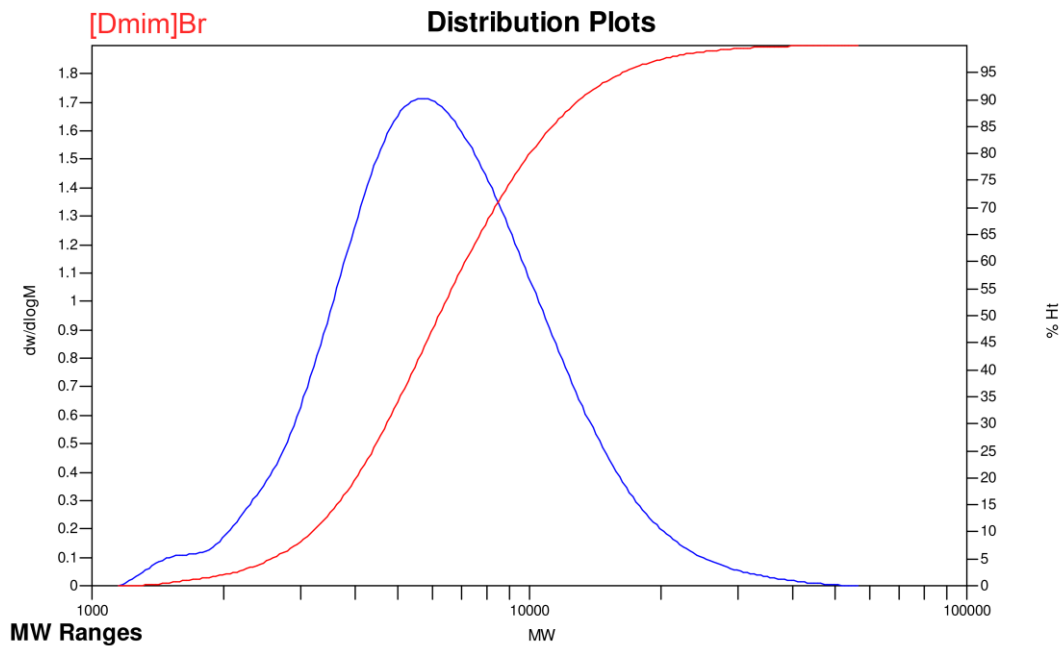
**MW Averages**

Mp: 7120                      Mn: 6400                      Mv: 8845                      Mw: 9387  
Mz: 14042                      Mz+1: 20835                      PD: 1.4667



**MW Averages**

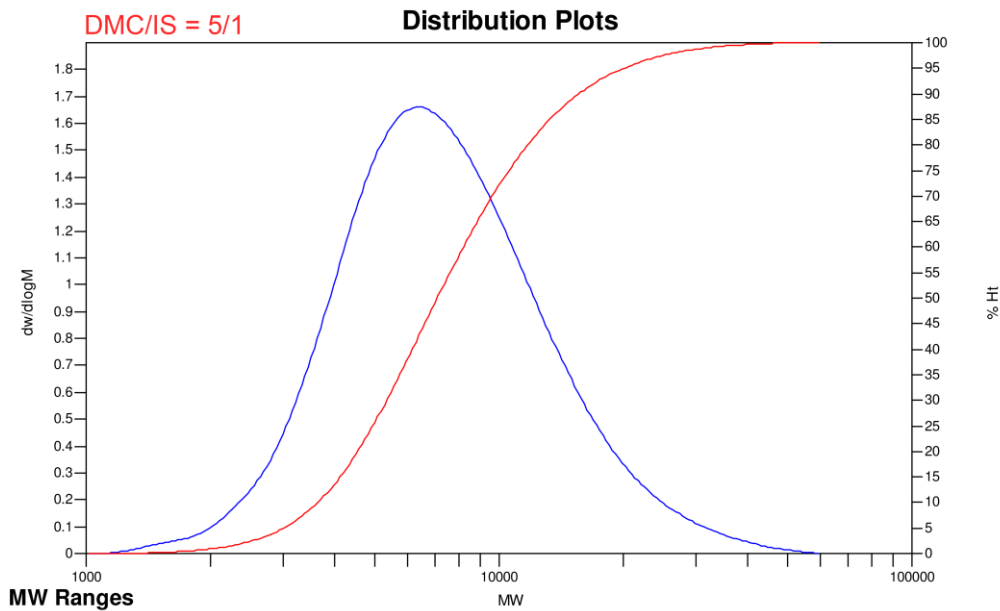
Mp: 5657                      Mn: 5385                      Mv: 7028                      Mw: 7387  
Mz: 10441                      Mz+1: 15030                      PD: 1.3718



**(2) Influence of reaction parameters catalyzed by [Emim]Br**

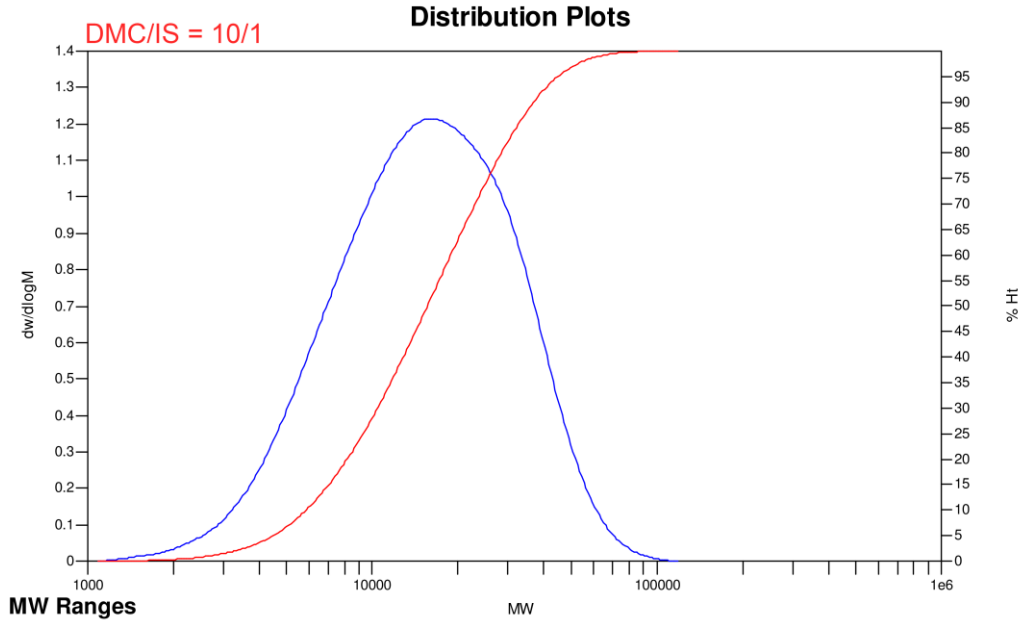
**MW Averages**

Mp: 6403                      Mn: 6196                      Mv: 8182                      Mw: 8634  
Mz: 12550                      Mz+1: 18302                      PD: 1.3935



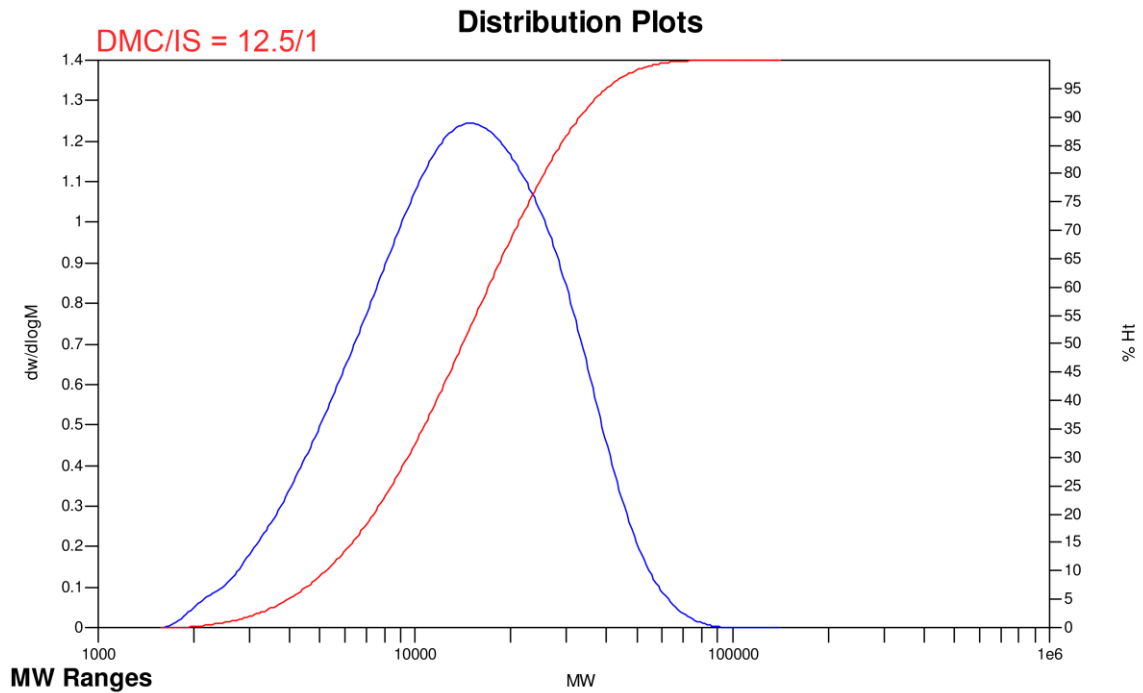
**MW Averages**

Mp: 16350      Mn: 11476      Mv: 17651      Mw: 18860  
Mz: 27921      Mz+1: 37351      PD: 1.6434



**MW Averages**

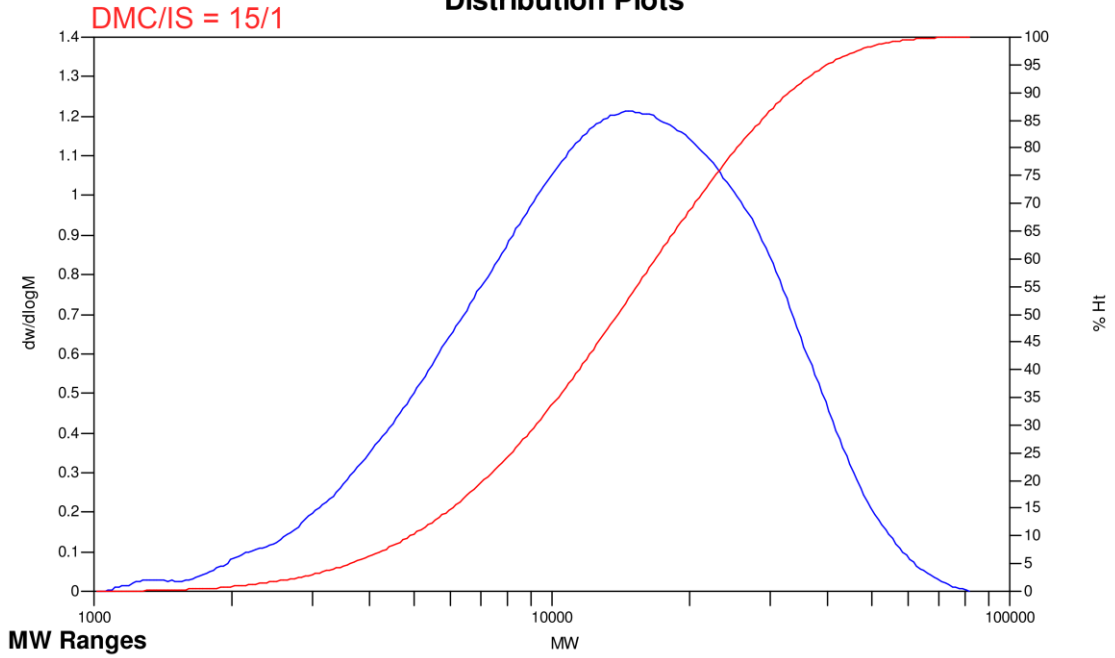
Mp: 14966      Mn: 10429      Mv: 15847      Mw: 16908  
Mz: 24772      Mz+1: 32731      PD: 1.6212



**MW Averages**

Mp: 14704                      Mn: 9834                      Mv: 15616                      Mw: 16705  
Mz: 24620                      Mz+1: 32207                      PD: 1.6987

**Distribution Plots**

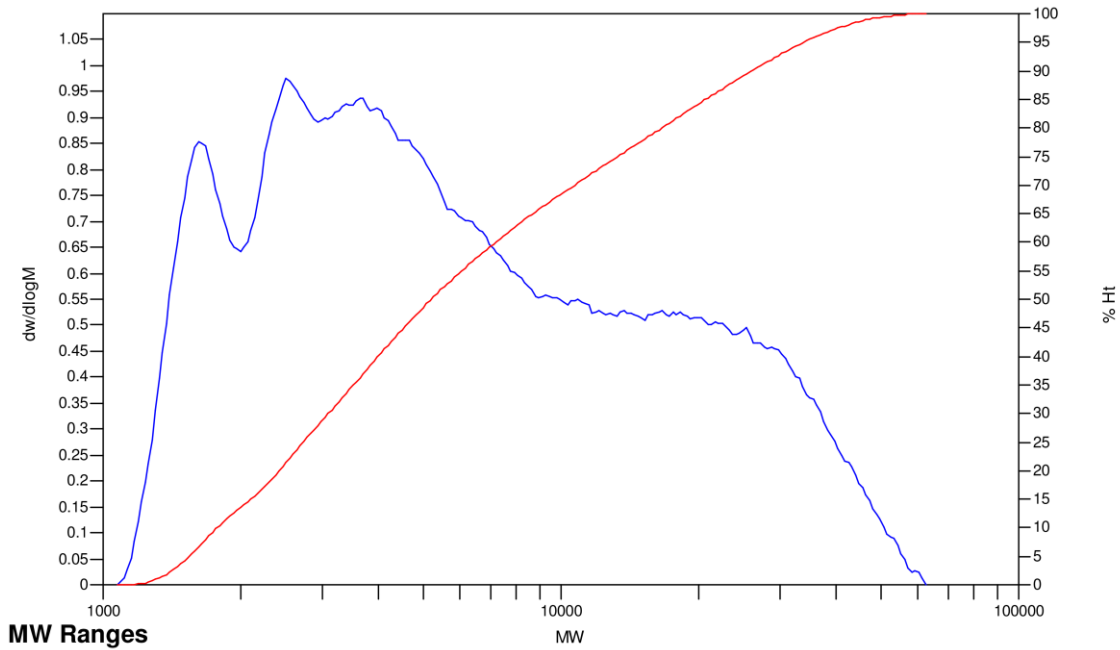


**MW Ranges**

**MW Averages**

Mp: 2507                      Mn: 4048                      Mv: 8544                      Mw: 9854  
Mz: 21208                      Mz+1: 30568                      PD: 2.4343

**Transesterification time 3.5 h Distribution Plots**

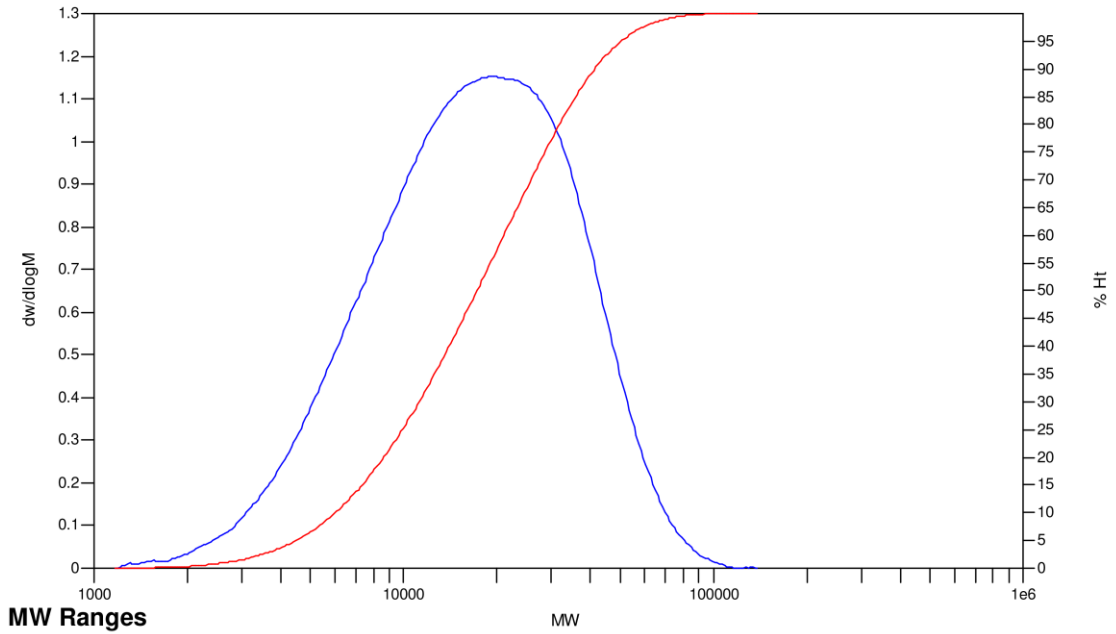


**MW Ranges**

**MW Averages**

Mp: 18836                      Mn: 12109                      Mv: 19464                      Mw: 20883  
Mz: 31389                      Mz+1: 41912                      PD: 1.7246

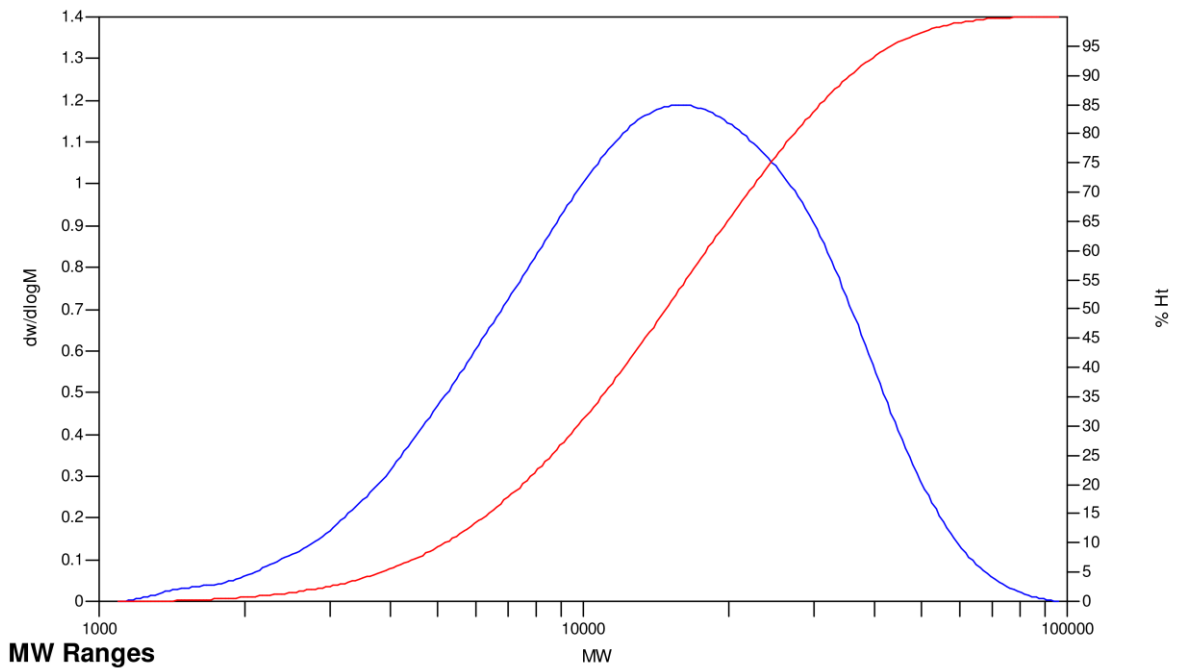
**Transesterification time 6 h      Distribution Plots**



**MW Averages**

Mp: 16064                      Mn: 10429                      Mv: 16718                      Mw: 17921  
Mz: 26759                      Mz+1: 35389                      PD: 1.7184

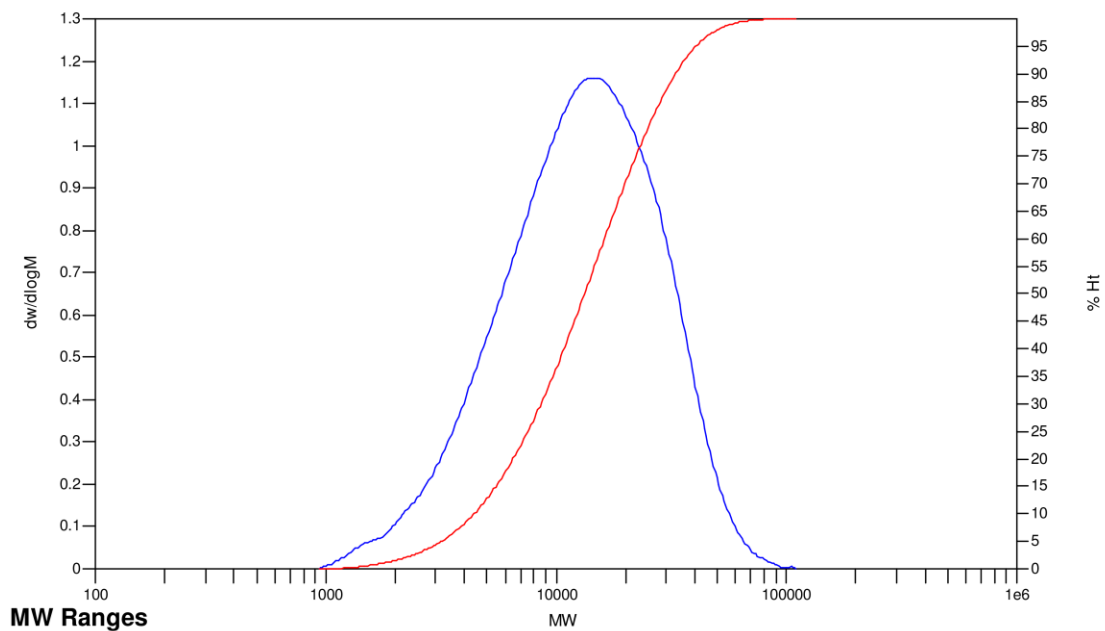
**Transesterification time 8 h      Distribution Plots**



**MW Averages**

Mp: 14704                      Mn: 9005                      Mv: 15146                      Mw: 16337  
Mz: 25317                      Mz+1: 34655                      PD: 1.8142

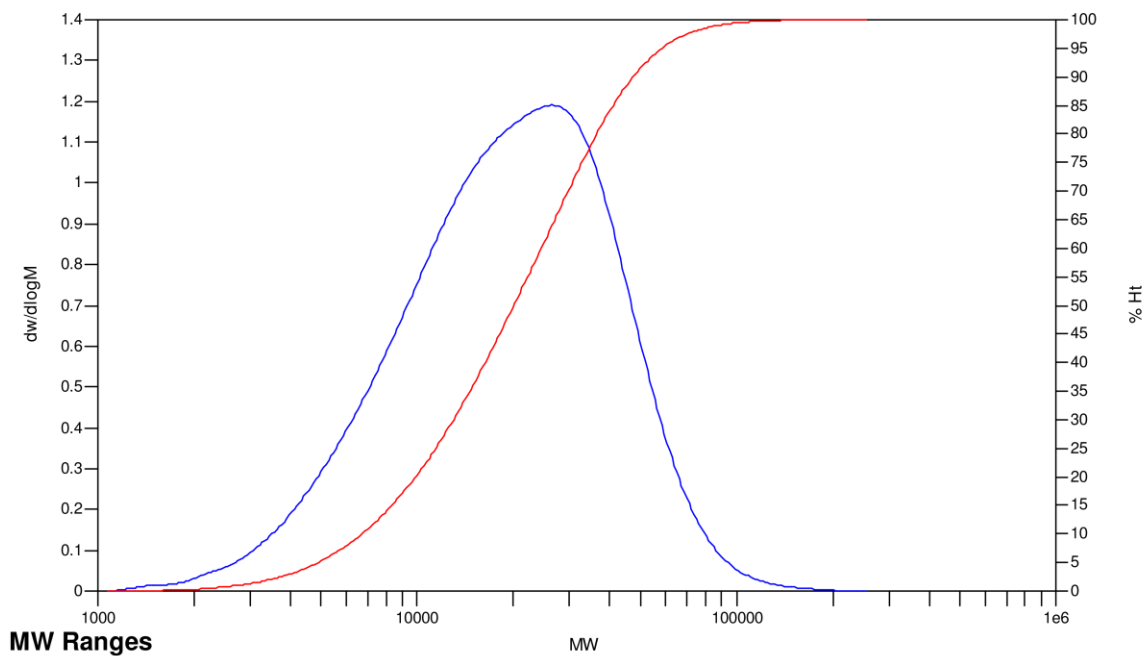
**Tranesertification time 10 h Distribution Plots**



**MW Averages**

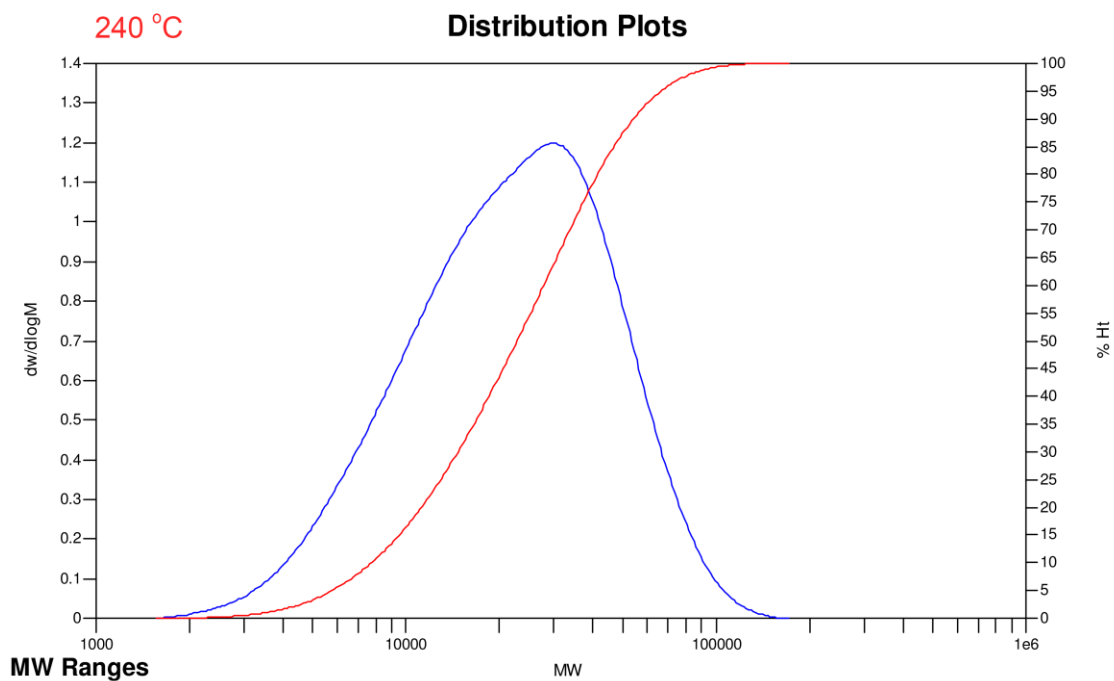
Mp: 26359                      Mn: 13639                      Mv: 22573                      Mw: 24306  
Mz: 37808                      Mz+1: 54426                      PD: 1.7821

**230 °C Distribution Plots**



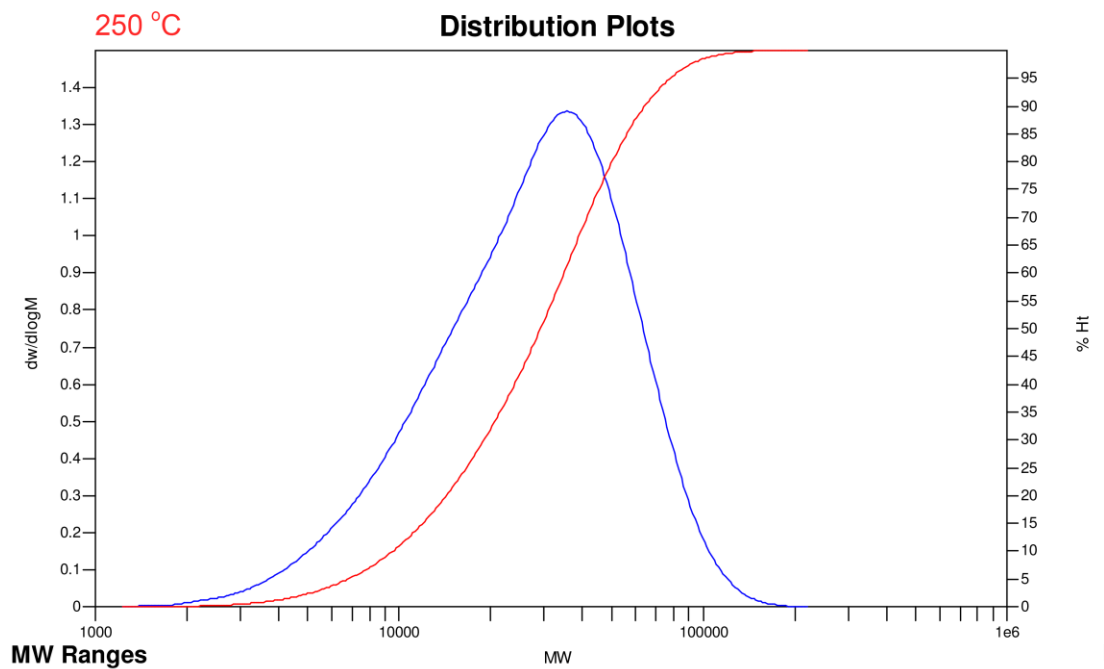
**MW Averages**

Mp: 29834      Mn: 15868      Mv: 25561      Mw: 27438  
Mz: 41377      Mz+1: 55468      PD: 1.7291



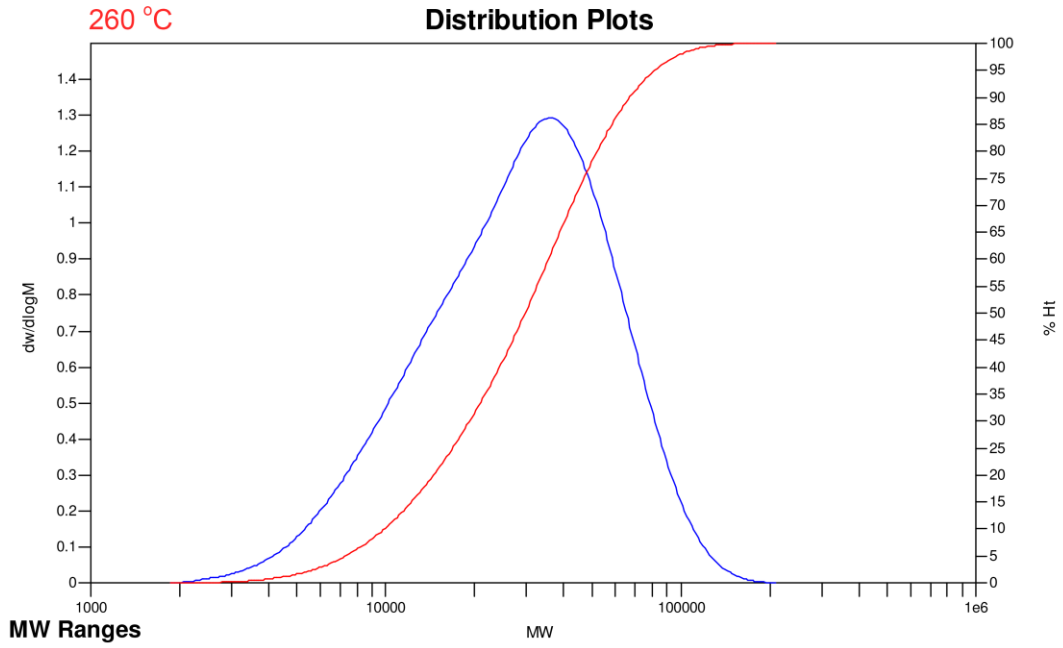
**MW Averages**

Mp: 35606      Mn: 19315      Mv: 31393      Mw: 33532  
Mz: 48811      Mz+1: 63878      PD: 1.7361



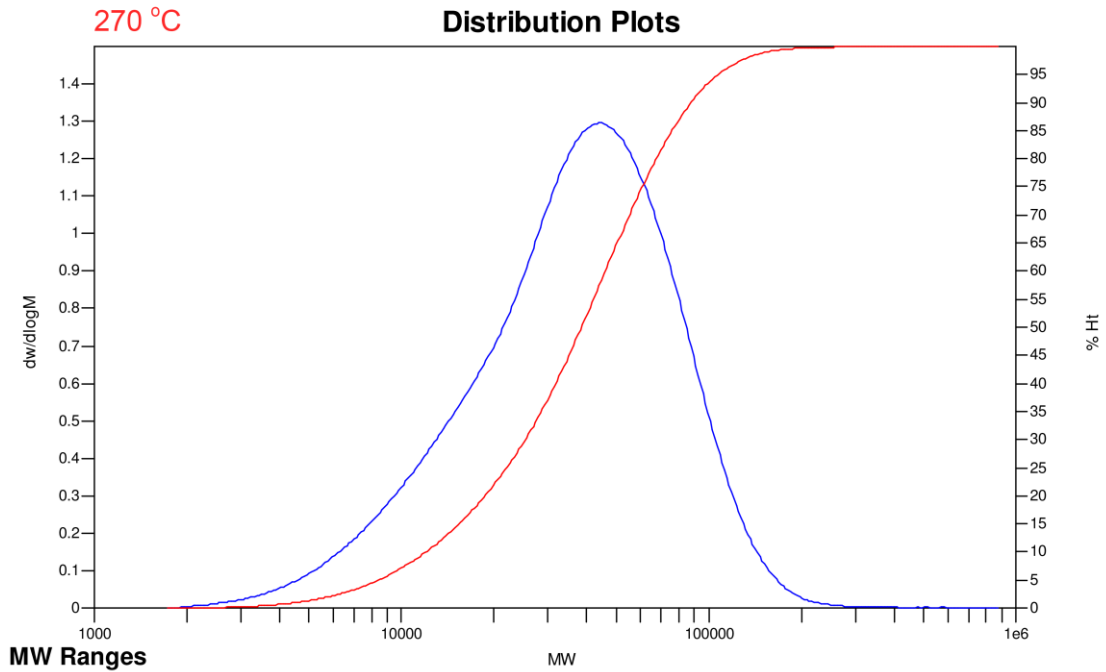
**MW Averages**

Mp: 36242      Mn: 20297      Mv: 32366      Mw: 34606  
Mz: 50839      Mz+1: 66890      PD: 1.7050



**MW Averages**

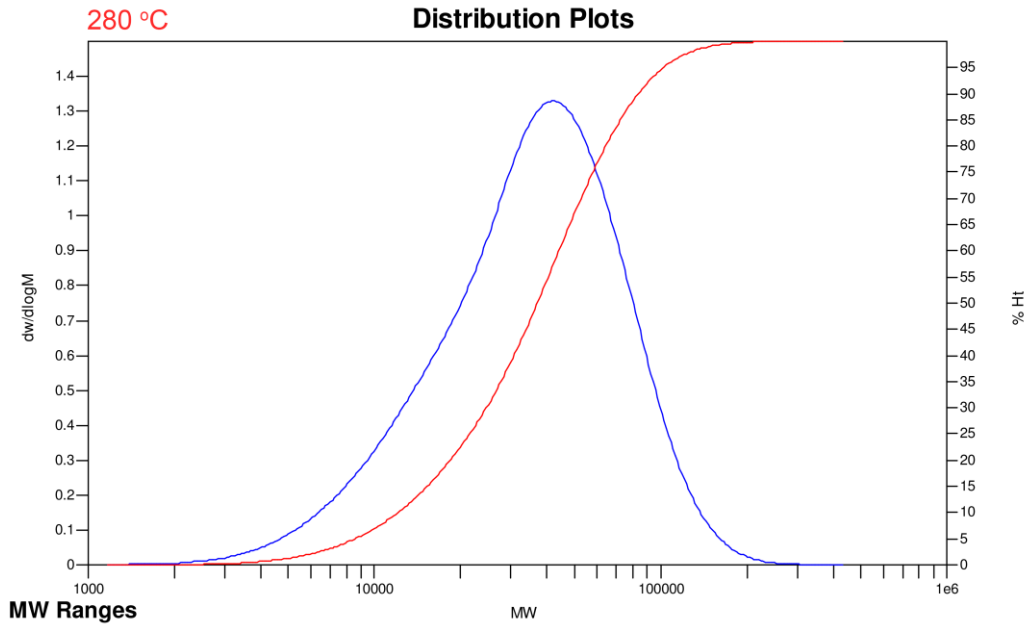
Mp: 44026      Mn: 24918      Mv: 42192      Mw: 45389  
Mz: 71218      Mz+1: 118543      PD: 1.8215





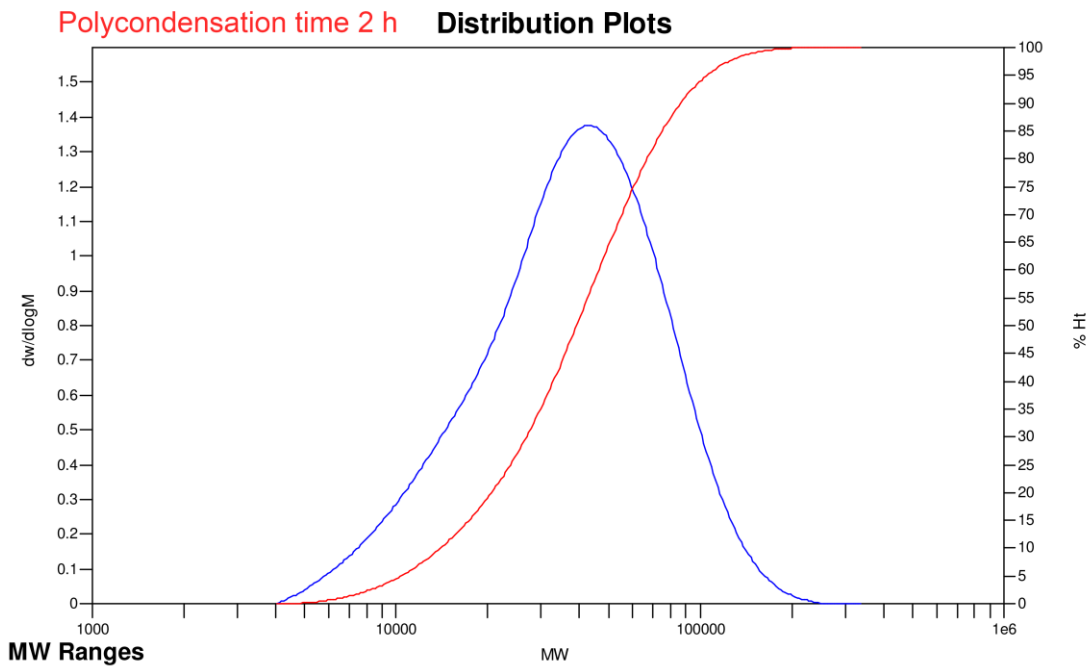
**MW Averages**

Mp: 41751      Mn: 24475      Mv: 40446      Mw: 43323  
Mz: 64649      Mz+1: 88026      PD: 1.7701



**MW Averages**

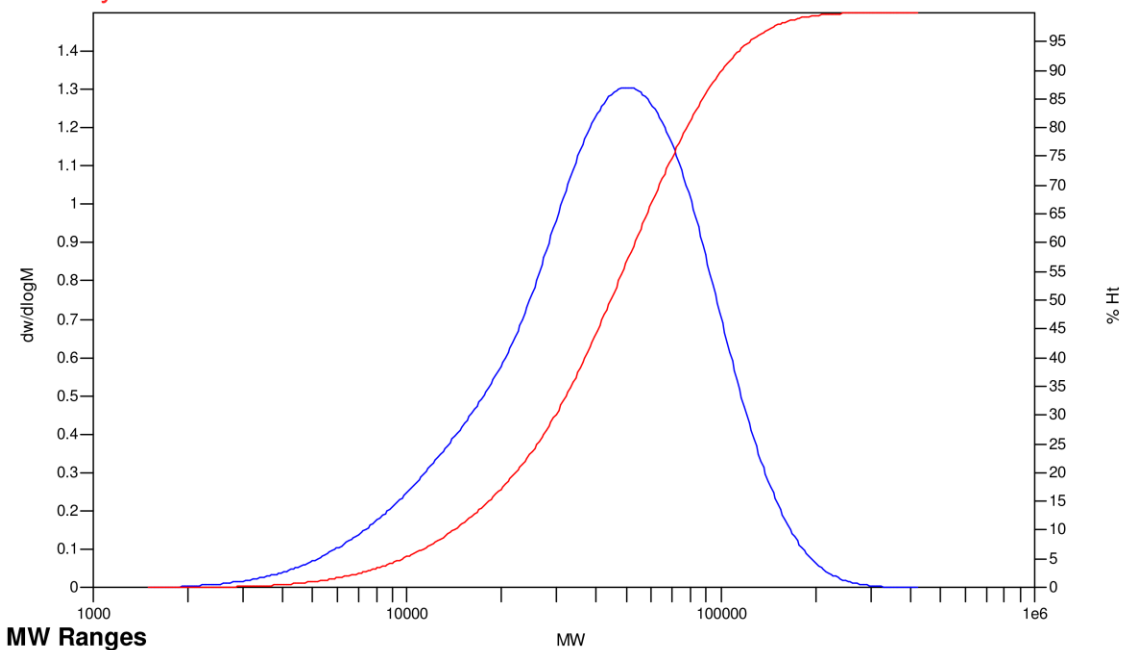
Mp: 43254      Mn: 28216      Mv: 42802      Mw: 45534  
Mz: 65664      Mz+1: 86849      PD: 1.6138



**MW Averages**

Mp: 49829      Mn: 28736      Mv: 48641      Mw: 52138  
Mz: 77666      Mz+1: 104392      PD: 1.8144

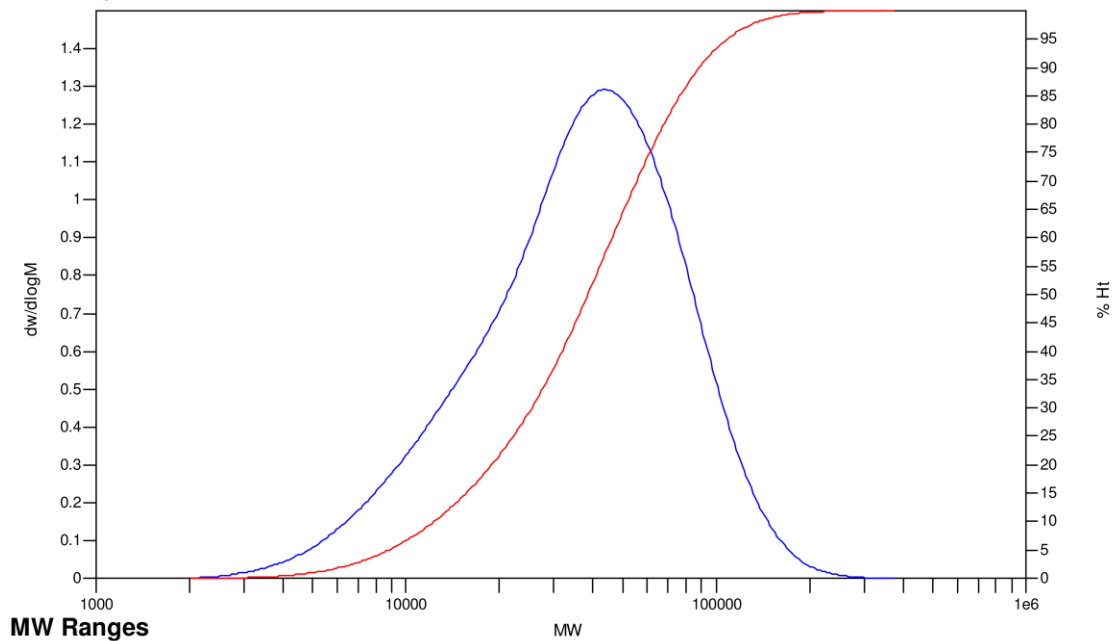
**Polycondensation time 3 h      Distribution Plots**



**MW Averages**

Mp: 44026      Mn: 25590      Mv: 42381      Mw: 45477  
Mz: 68479      Mz+1: 93355      PD: 1.7771

**Polycondensation time 4 h      Distribution Plots**



### MW Averages

Mp: 36242

Mn: 19498

Mv: 35098

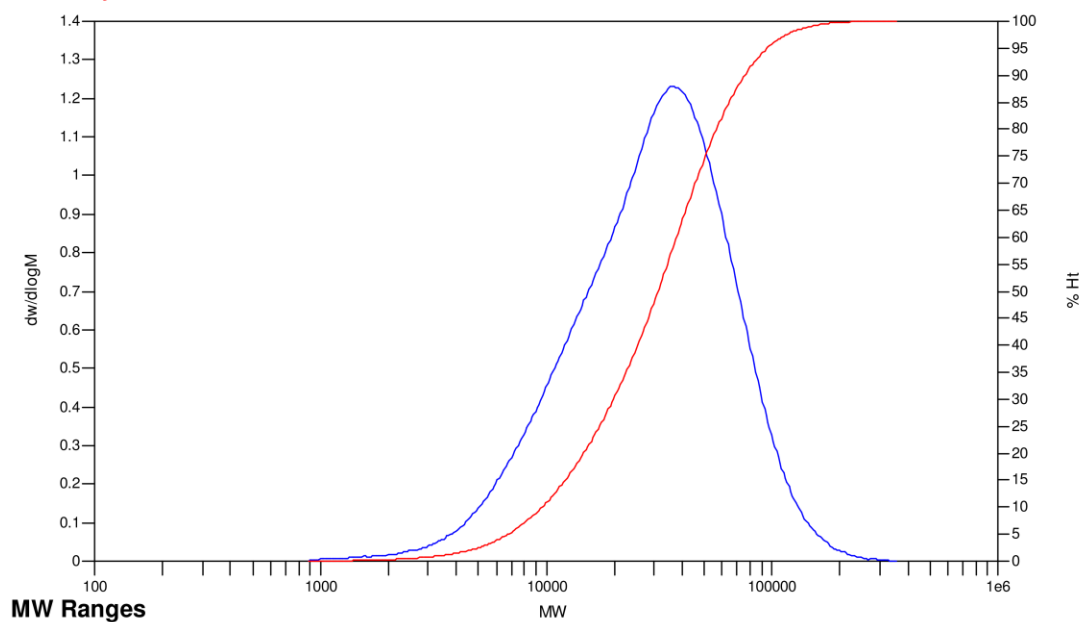
Mw: 38050

Mz: 61360

Mz+1: 89980

PD: 1.9515

### Polycondensation time 6 h Distribution Plots



### References

- (1) Qian, W.; Tan, X.; Su, Q.; Cheng, W.; Xu, F.; Dong, L.; Zhang, S. *ChemSusChem* **2019**, *12*, 1169.