Electronic Supplementary Information for

Understanding the Important Variables to Optimize Glycolysis of Polyethylene Terephthalate with Lanthanide-Containing Ionic Liquids

Nancy G. Bush,[1] Caitlin H. Dinh,[1] Casandrah L. Catterton,[1] Megan E. Fieser[1,2]*

[1]Department of Chemistry, University of Southern California, Los Angeles, CA 90089

[2]Wrigley Institute for Environmental Studies, University of Southern California, Los Angeles, CA 90089

Email: fieser@usc.edu

1. General Considerations

Unless otherwise specified, all reactions were performed under open atmosphere. NMR solvents (DMSO-d_6) and all other solvents (ethylene glycol, deionized water) were used as received. Ionic liquids (ILs) were used as received from ROCO Global. Metal chloride salts and metal acetate salts were used as received from Blueline Corp., Sigma Aldrich and Alpha Aesar. The La/Ce metal chloride salt mixture is the chloride salt obtained from a La/Ce metal oxide mixture that was never separated in processing (for simplicity, a 1:1 ratio of La:Ce is assumed for mass calculations). NMR samples were analyzed on a Varian Mercury 400 Magnetic Resonance Spectrometer. EA samples were measured using a ThermoFisher Scientific Flash 2000 CHNS elemental analyzer. Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) analyses were carried out using an Agilent Cary 630 FTIR instrument. Differential scanning calorimetry data were collected using a Mettler-Toledo STARe System TGA/DSC3+ equipped with STARe software, a TA SDTA Sensor LF, XP1 Balance, and a sample robot.

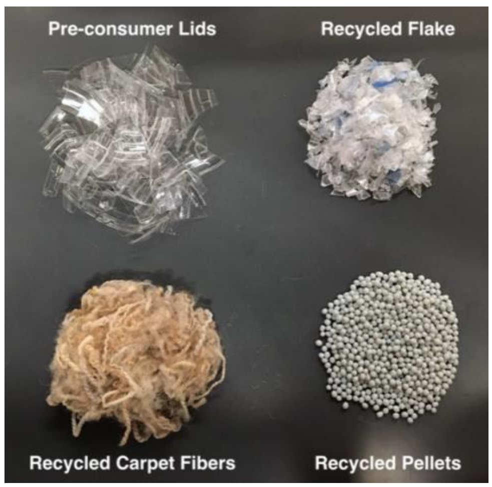

Fig. S1 Pre-consumer lids were the main PET plastic used in these studies unless otherwise stated and are EcoProducts cold drink lids containing 25% recycled content. Recycled PET materials were provided by Verdeco. Recycled pellets are from food grade PET plastics. Plastic bottle pieces were cut up from an Arrowhead water bottle.

1.1 General Procedures for PET Glycolysis Reactions

Lanthanide metal salt ($LaCl_3 \cdot 7H_2O$ 99%, $SmCl_3 \cdot 6H_2O$ 99.9%, $GdCl_3 \cdot 6H_2O$ 99.9%, $YCl_3 \cdot 6H_2O$ 99.99%, $TmCl_3 \cdot 6H_2O$ 99.9%, $Y(OAc)_3 \cdot 3H_2O$ 99.9%, $Gd(OAc)_3 \cdot 2.5H_2O$ 99.9%, $La(OAc)_3 \cdot 1.5H_2O$ 99.9%) and ionic liquid ([emim]OAc 98%, [bmim]OAc 98%, [bmim]Cl 99%, [B3DP]Cl >95%, [H3DP]Cl >95%) pairings were weighed in desired ratios (example of quantities shown in Tables S9a and S10a) in a 20 mL vial and stirred at 180 °C until homogeneous (only cases that became homogeneous were reported in this manuscript). Once homogeneous 3.00 grams of cut, 25% recycled material, pre-consumer PET lids were added to each vial followed by 12.00 grams of ethylene glycol (EG). The samples were then stirred at 180 °C for four hours (unless otherwise noted). Once cooled to a warm solution, each sample was vacuum filtrated with a medium glass filter frit. The PET remnants were excessively washed with cold deionized water (about 100mL) three times to wash away any bis(2-hydroxyethyl) terephthalate (BHET) and oligomers into the filtrate. The filtrate was then placed in the fridge for 24 hours to allow the BHET to crystallize. The residual PET was stored in 20 mL vials and dried under reduced pressure overnight at 110 ºC to calculate conversion.

Filtrate showed both long, white BHET crystals and cloudy, white oligomers. When pure BHET was present, the crystals were vacuum filtered using a medium filter frit. When pure oligomer was present, the sample was saved for future tests and the condition was noted. When both BHET and oligomer were present, the filtrate was filtered through a fine glass filter frit and washed. The cloudy oligomer was pipetted from the BHET and continued to be washed until the wash DI water was no longer cloudy. The BHET crystals were then placed in 20 mL vials and dried under reduced pressure overnight at 80-85 ºC. A representative ^1H NMR of the BHET product is shown in **Figure S2** as well as representative Fourier transform infrared spectroscopy (FT-IR) of PET, BHET, and oligomer and representative differential scanning calorimetry (DSC) of BHET. For quantitative analysis of the depolymerization of PET, the dried PET and BHET were weighed for each sample and percent conversion of PET, selectivity of BHET, and percent yield of BHET were calculated.

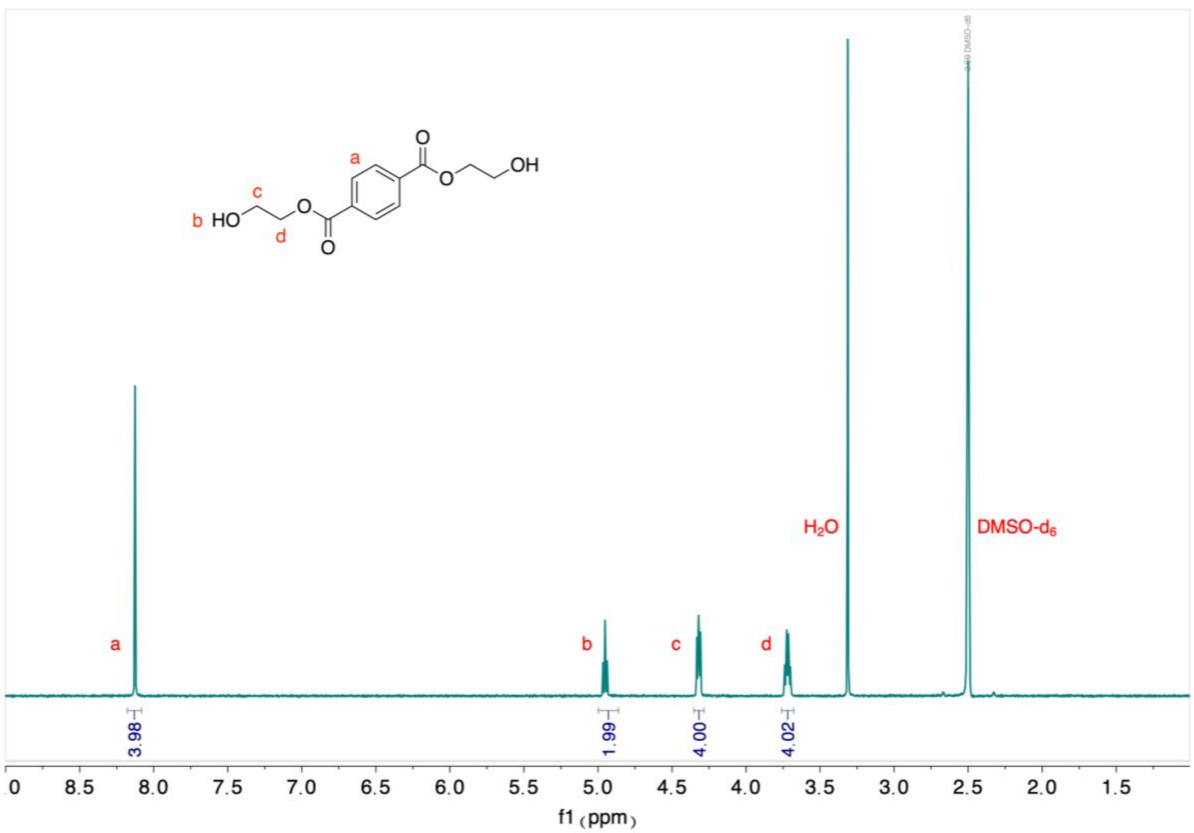

Fig. S2 ^1H NMR of BHET in DMSO-d_6.

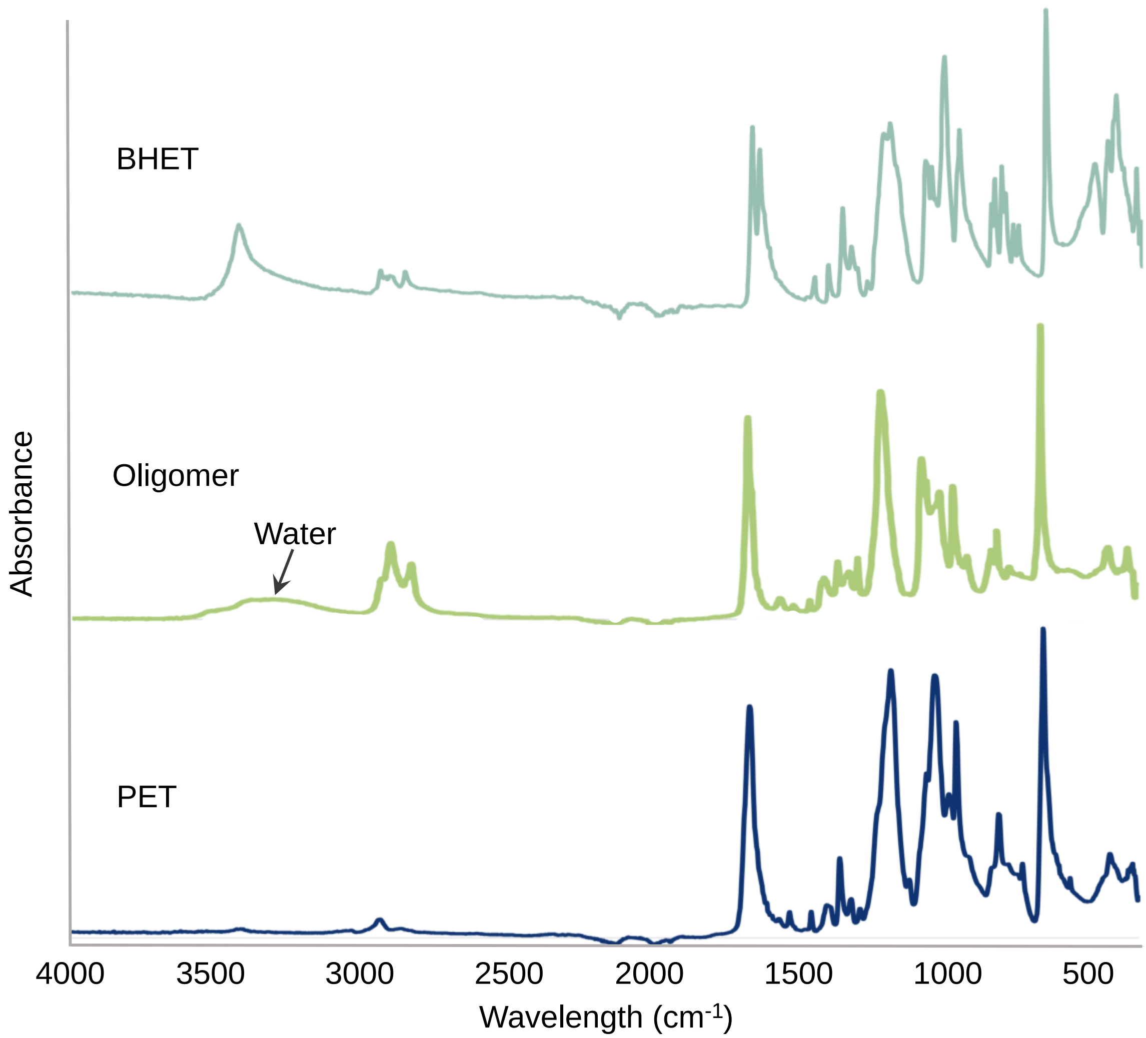

Fig. S3 ATR-IR of representative samples of PET, PET oligomer, and BHET.

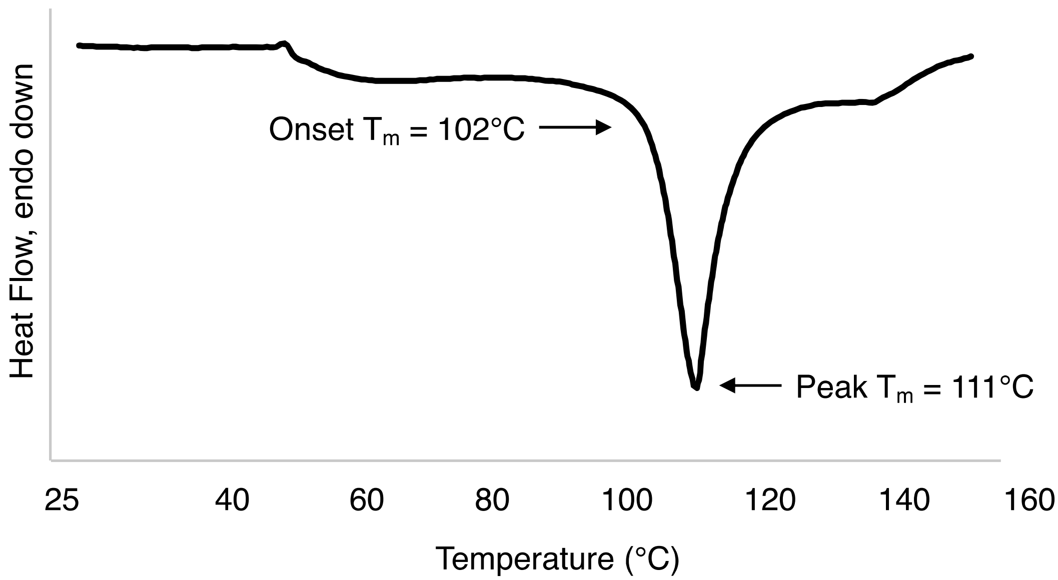

Fig. S4 Differential scanning calorimetry (DSC) of a representative sample of BHET, produced from glycolysis of PET.

1.2 Determining hydration on metal acetate salts

When using the acetate salts for La, Gd and Y, the hydration amount was not described on the commercial bottles. Therefore, NMR spectra and elemental analysis were used to approximate the amount of water in the metal salts. While these studies are not expected to be perfect, it allowed for a more realistic weight for proper stoichiometry.

2. Initial Screening

Initially, several ionic liquids with lanthanide metal chloride salts were tested. Metal salt:ionic liquid ratios of 1:2 and 1:6 were used, since lanthanide metals can handle a wide range of coordination numbers.

Table S1 Initial screening reactions with a metal salt: IL ratio of 1:2.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	$LaCl_3 \cdot 7H_2O$	[emim]OAc	21.8	12.2	56.1
2	$SmCl_3 \cdot 6H_2O$	[emim]OAc	80.6	47.7	59.2
3	$GdCl_3 \cdot 6H_2O$	[emim]OAc	96.9	21.5	22.2
4	$YCl_3 \cdot 6H_2O$	[emim]OAc	95.0	33.0	34.8
5	$TmCl_3 \cdot 6H_2O$	[emim]OAc	47.2	32.2	69.7
6	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	43.9	29.1	66.3
7	$SmCl_3 \cdot 6H_2O$	[bmim]OAc	68.4	2.2	3.2
8	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	55.9	36.2	64.7
9	$YCl_3 \cdot 6H_2O$	[bmim]OAc	54.8	25.3	46.1
10	$TmCl_3 \cdot 6H_2O$	[bmim]OAc	32.3	0.7	2.1
11	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	27.8	5.8	31.2
12	$SmCl_3 \cdot 6H_2O$	[bmim]Cl	26.7	-	-
13	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	11.5	-	-
14	$YCl_3 \cdot 6H_2O$	[bmim]Cl	7.9	-	-
15	$TmCl_3 \cdot 6H_2O$	[bmim]Cl	13.0	4.0	22.7
16	$LaCl_3 \cdot 7H_2O$	[B3DP]Cl	8.8	-	-
17	$SmCl_3 \cdot 6H_2O$	[B3DP]Cl	28.6	17.4	60.8
18	$GdCl_3 \cdot 6H_2O$	[B3DP]Cl	10.6	-	-
19	$YCl_3 \cdot 6H_2O$	[B3DP]Cl	25.6	12.6	49.1
20	$TmCl_3 \cdot 6H_2O$	[B3DP]Cl	14.1	-	-
21	$LaCl_3 \cdot 7H_2O$	[H3DP]Cl	42.7	19.6	45.9
22	$SmCl_3 \cdot 6H_2O$	[H3DP]Cl	56.8	42.9	75.5
23	$GdCl_3 \cdot 6H_2O$	[H3DP]Cl	42.0	19.7	46.8
24	$YCl_3 \cdot 6H_2O$	[H3DP]Cl	23.1	4.9	21.0
25	$TmCl_3 \cdot 6H_2O$	[H3DP]Cl	31.5	19.1	60.7

[a] Reaction conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:2), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

Table S2 Initial screening reactions with a metal salt: IL ratio of 1:6.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	$LaCl_3 \cdot 7H_2O$	[emim]OAc	97.1	26.2	27.0
2	$SmCl_3 \cdot 6H_2O$	[emim]OAc	72.1	13.5	18.7
3[b]	$GdCl_3 \cdot 6H_2O$	[emim]OAc	90.2	41.6	46.0
4[b]	$YCl_3 \cdot 6H_2O$	[emim]OAc	94.8	56.6	60.2
5	$TmCl_3 \cdot 6H_2O$	[emim]OAc	72.9	41.2	56.6
6	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	85.8	48.1	56.0
7	$SmCl_3 \cdot 6H_2O$	[bmim]OAc	73.3	58.3	66.0
8	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	91.7	58.9	64.3
9	$YCl_3 \cdot 6H_2O$	[bmim]OAc	80.8	33.7	41.7
10	$TmCl_3 \cdot 6H_2O$	[bmim]OAc	92.1	17.5	19.0
11	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	9.8	2.1	21.3
12	$SmCl_3 \cdot 6H_2O$	[bmim]Cl	19.5	6.2	31.8
13	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	20.2	-	-
14	$YCl_3 \cdot 6H_2O$	[bmim]Cl	14.4	2.7	18.8
15	$TmCl_3 \cdot 6H_2O$	[bmim]Cl	12.3	0.2	1.8
16	$LaCl_3 \cdot 7H_2O$	[B3DP]Cl	19.9	9.8	49.1
17	$SmCl_3 \cdot 6H_2O$	[B3DP]Cl	23.3	12.9	55.3
18	$GdCl_3 \cdot 6H_2O$	[B3DP]Cl	13.8	1.5	10.7
19	$YCl_3 \cdot 6H_2O$	[B3DP]Cl	18.3	7.8	42.4
20	$TmCl_3 \cdot 6H_2O$	[B3DP]Cl	29.5	12.7	43.0
21	$LaCl_3 \cdot 7H_2O$	[H3DP]Cl	7.9	-	-
22	$SmCl_3 \cdot 6H_2O$	[H3DP]Cl	18.3	-	-
23	$GdCl_3 \cdot 6H_2O$	[H3DP]Cl	11.9	-	-
24	$YCl_3 \cdot 6H_2O$	[H3DP]Cl	6.0	-	-
25	$TmCl_3 \cdot 6H_2O$	[H3DP]Cl	17.1	4.4	25.8

[a] Reaction conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:6), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

[b] Average of two experiments.

3. Cooperativity Studies

To establish that the combination of metal salt with ionic liquid is better than either component separately. Since the amount of metal salt and ionic liquid is varied based on the ratio (1:2 or 1:6), so these comparisons are separated into different tables. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

Table S3 Control reactions to determine cooperativity of metal salts with [emim]OAc with a 1:2 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[emim]OAc	25.8	5.5	21.3
2	$YCl_3 \cdot 6H_2O$	-	8.8	1.7	19.2
3	$GdCl_3 \cdot 6H_2O$	-	12.4	9.0	72.5
4	$LaCl_3 \cdot 7H_2O$	-	15.4	5.3	34.4
5[b]	$YCl_3 \cdot 6H_2O$	[emim]OAc	95.0	33.0	34.8
6[b]	$GdCl_3 \cdot 6H_2O$	[emim]OAc	96.9	21.5	22.2
7	$LaCl_3 \cdot 7H_2O$	[emim]OAc	21.8	12.2	56.1
8	$Y(OAc)_3 \cdot 3H_2O$	-	54.7	34.5	63.1
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	18.2	1.9	43.1
10	$La(OAc)_3 \cdot 1.5H_2O$	-	31.2	14.4	96.1
11	$Y(OAc)_3 \cdot 3H_2O$	[emim]OAc	20.7	-	-
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[emim]OAc	26.8	-	-
13	$La(OAc)_3 \cdot 1.5H_2O$	[emim]OAc	15.9	13.1	82.5

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:2), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

[b] Average values

Table S4 Control reactions to determine cooperativity of metal salts with [emim]OAc with a 1:6 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[emim]OAc	13.5	12.8	94.5
2	$YCl_3 \cdot 6H_2O$	-	10.6	3.2	30.5
3	$GdCl_3 \cdot 6H_2O$	-	15.0	5.2	34.5
4	$LaCl_3 \cdot 7H_2O$	-	11.6	-	-
5[b]	$YCl_3 \cdot 6H_2O$	[emim]OAc	94.8	56.6	60.2
6[b]	$GdCl_3 \cdot 6H_2O$	[emim]OAc	90.2	41.6	46.0
7	$LaCl_3 \cdot 7H_2O$	[emim]OAc	97.0	26.2	27.0
8	$Y(OAc)_3 \cdot 3H_2O$	-	15.9	7.0	44.0
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	25.3	10.1	39.9
10	$La(OAc)_3 \cdot 1.5H_2O$	-	19.8	11.3	57.2
11	$Y(OAc)_3 \cdot 3H_2O$	[emim]OAc	22.1	13.3	59.9
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[emim]OAc	36.6	20.0	54.5
13	$La(OAc)_3 \cdot 1.5H_2O$	[emim]OAc	13.0	4.6	34.9

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:6), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

[b] Average values

Table S5 Control reactions to determine cooperativity of metal salts with [bmim]Cl with a 1:2 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[bmim]Cl	2.7	-	-
2	$YCl_3 \cdot 6H_2O$	-	8.8	1.7	19.2
3	$GdCl_3 \cdot 6H_2O$	-	12.4	9.0	72.5
4	$LaCl_3 \cdot 7H_2O$	-	15.4	5.3	34.4
5	$YCl_3 \cdot 6H_2O$	[bmim]Cl	7.9	-	-
6	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	11.5	-	-
7	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	27.8	5.8	31.2
8	$Y(OAc)_3 \cdot 3H_2O$	-	54.7	34.5	63.1
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	18.2	1.9	43.1
10	$La(OAc)_3 \cdot 1.5H_2O$	-	31.2	14.4	96.1
11	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	18.0	9.7	53.8
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	22.3	12.1	54.2
13	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	22.3	15.3	68.5

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:2), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

Table S6 Control reactions to determine cooperativity of metal salts with [bmim]Cl with a 1:6 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[bmim]Cl	0.9	-	-
2	$YCl_3 \cdot 6H_2O$	-	10.6	3.2	30.5
3	$GdCl_3 \cdot 6H_2O$	-	15.0	5.2	34.5
4	$LaCl_3 \cdot 7H_2O$	-	11.6	-	-
5	$YCl_3 \cdot 6H_2O$	[bmim]Cl	14.4	2.7	18.8
6	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	20.2	-	-
7	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	9.8	2.1	21.3
8	$Y(OAc)_3 \cdot 3H_2O$	-	15.9	7.0	44.0
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	25.3	10.1	39.9
10	$La(OAc)_3 \cdot 1.5H_2O$	-	19.8	11.3	57.2
11	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	40.9	6.6	16.1
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	22.8	16.9	74.1
13	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	22.3	15.3	68.5

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:6), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

Table S7 Control reactions to determine cooperativity of metal salts with [bmim]OAc with a 1:2 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[bmim]OAc	26.6	14.6	54.9
2	$YCl_3 \cdot 6H_2O$	-	8.8	1.7	19.2
3	$GdCl_3 \cdot 6H_2O$	-	12.4	9.0	72.5
4	$LaCl_3 \cdot 7H_2O$	-	15.4	5.3	34.4
5	$YCl_3 \cdot 6H_2O$	[bmim]OAc	54.8	25.3	46.1
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	55.9	36.2	64.7
7	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	43.9	29.1	66.3
8	$Y(OAc)_3 \cdot 3H_2O$	-	54.7	34.5	63.1
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	18.2	1.9	43.1
10	$La(OAc)_3 \cdot 1.5H_2O$	-	31.2	14.4	96.1
11	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	23.7	57.6	76.5
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	35.7	16.4	45.9
13	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	20.5	16.9	82.6

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:2), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

Table S8 Control reactions to determine cooperativity of metal salts with [bmim]OAc with a 1:6 molar ratio.[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	-	[bmim]OAc	13.8	11.9	86.4
2	$YCl_3 \cdot 6H_2O$	-	10.6	3.2	30.5
3	$GdCl_3 \cdot 6H_2O$	-	15.0	5.2	34.5
4	$LaCl_3 \cdot 7H_2O$	-	11.6	-	-
5	$YCl_3 \cdot 6H_2O$	[bmim]OAc	80.8	33.7	41.7
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	91.7	58.9	64.3
7	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	85.8	48.1	56.0
8	$Y(OAc)_3 \cdot 3H_2O$	-	15.9	7.0	44.0
9	$Gd(OAc)_3 \cdot 2.5H_2O$	-	25.3	10.1	39.9
10	$La(OAc)_3 \cdot 1.5H_2O$	-	19.8	11.3	57.2
11	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	29.0	13.5	46.6
12	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	20.6	17.2	83.3
13	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	17.9	14.2	79.6

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:6), 1:4 PET:EG ratio, 180°C for 4 h, 3g PET.

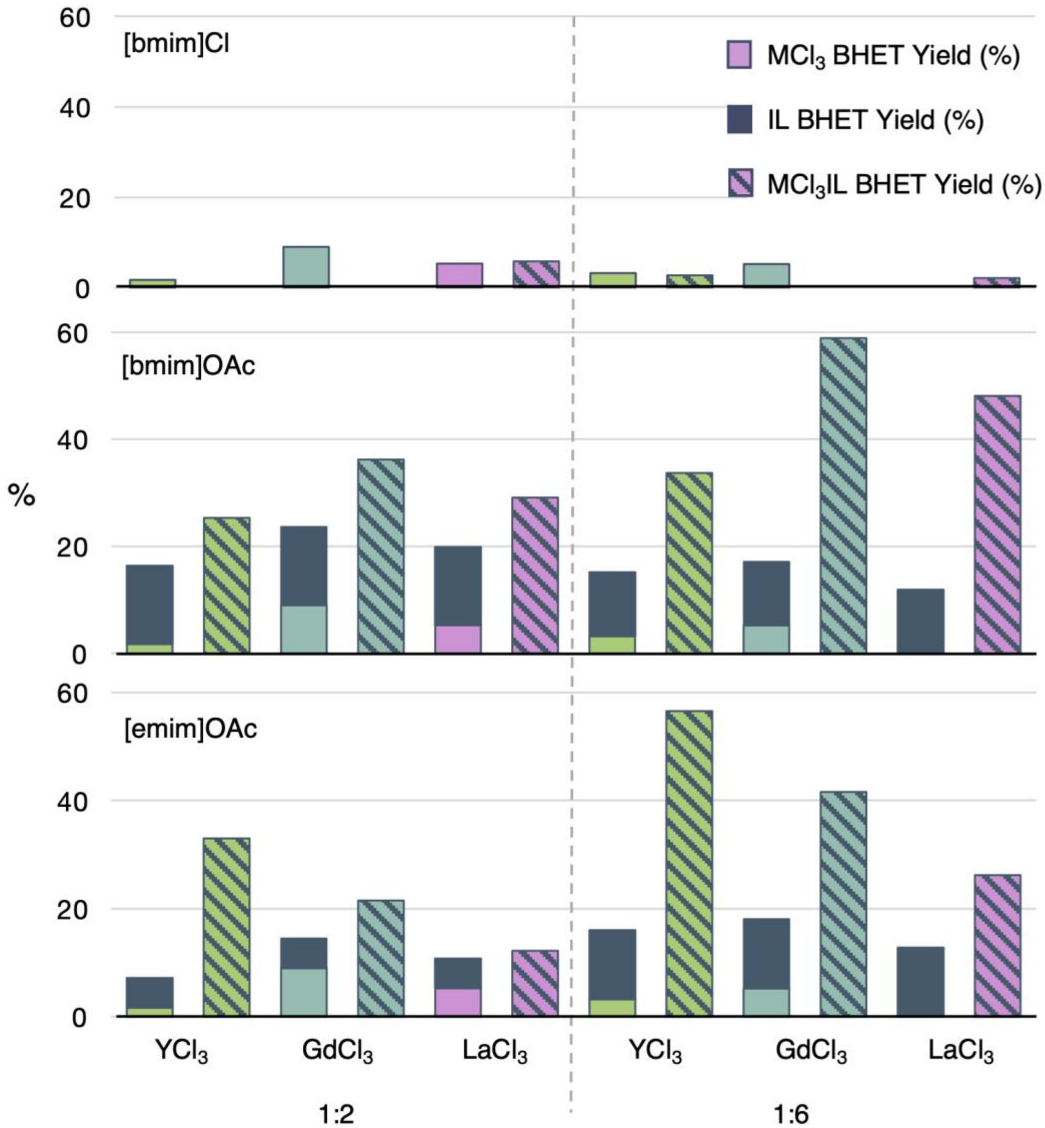

Fig. S5 BHET yield for Y, Gd and La hydrate salts and [emim]OAc, [bmim]OAc, and [bmim]Cl separately and mixed, to show cooperativity. All reactions were done with 3g of PET at 180ºC for 4 hrs with 5 wt% catalyst and a 1:4 PET:EG ratio.

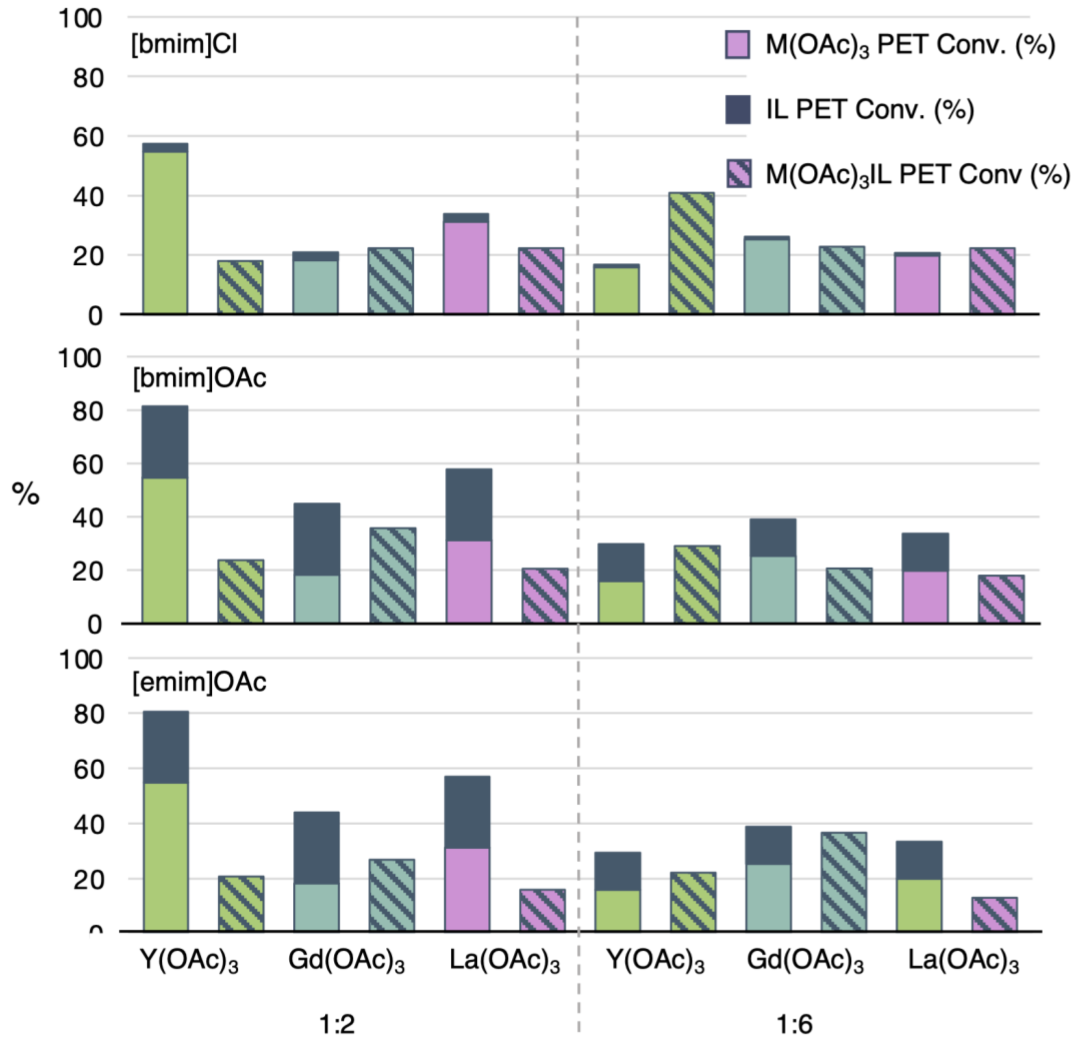

Fig. S6 PET conversion for Y, Gd and La hydrate salts and [emim]OAc, [bmim]OAc, and [bmim]Cl separately and mixed, to show cooperativity. All reactions were done with 3g of PET at 180ºC for 4 hrs with 5 wt% catalyst and a 1:4 PET:EG ratio.

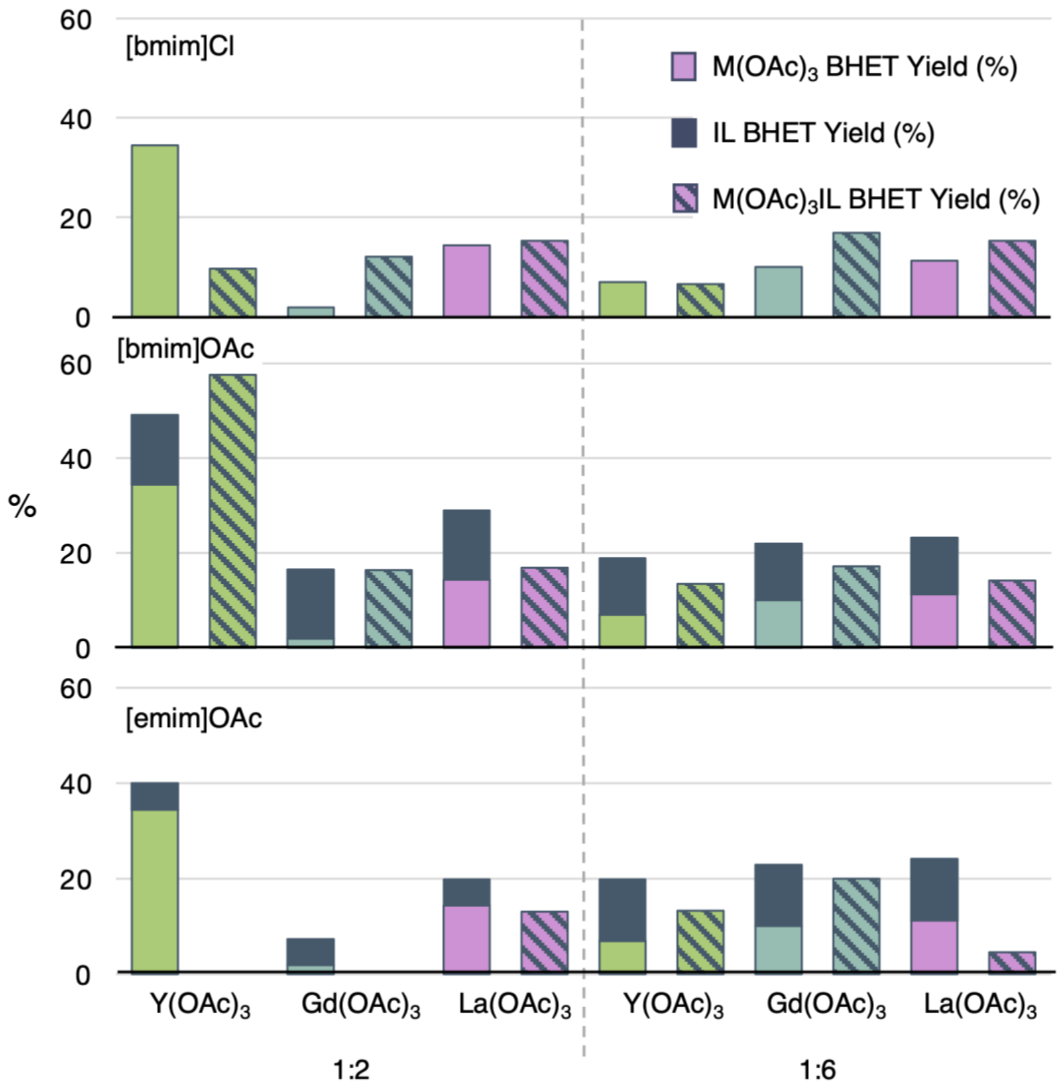

Fig. S7 BHET yield for Y, Gd and La hydrate salts and [emim]OAc, [bmim]OAc, and [bmim]Cl separately and mixed, to show cooperativity. All reactions were done with 3g of PET at 180ºC for 4 hrs with 5 wt% catalyst and a 1:4 PET:EG ratio.

4. Effects of Anion

To establish how the anions on both the metal salt and ionic liquids interact, various combinations with Y, Gd, and La chloride and acetate salts were made with [bmim]OAc and [bmim]Cl. Since the amount of metal salt and ionic liquid is varied based on the ratio (1:2 or 1:6), so these comparisons are separated into different tables. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

Table S9 Effects of Anion on metal salt:IL ratio of 1:2[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	$YCl_3 \cdot 6H_2O$	[bmim]Cl	7.9	-	-
2	$YCl_3 \cdot 6H_2O$	[bmim]OAc	54.8	25.3	46.1
3	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	18.0	9.70	53.8
4	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	23.7	19.3	81.4
5	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	11.5	-	-
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	55.9	36.2	64.7
7	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	22.3	12.1	54.2
8	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	35.7	16.4	45.9
9[f]	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	27.8	5.8	31.2
10[g]	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	43.9	29.1	66.3
11	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	22.3	15.3	68.5
12	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	20.5	16.9	82.6

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:2), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

Table S9a Molar Ratios of Anions for S9 Entries

Entry #	Metal Salt	Ionic Liquid	mmol of Salt	mmol of IL	mmol of Cl^-	mmol of OAc^-
1	$YCl_3 \cdot 6H_2O$	[bmim]Cl	0.29	0.36	1.58	0.00
2	$YCl_3 \cdot 6H_2O$	[bmim]OAc	0.28	0.33	0.83	0.67
3	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	0.27	0.36	0.71	0.82
4	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	0.27	0.33	0.00	1.45
5	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	0.25	0.33	1.41	0.00
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	0.24	0.31	0.71	0.62
7	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	0.24	0.33	0.66	0.73
8	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	0.23	0.31	0.00	1.32
9	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	0.33	0.39	1.78	0.00
10	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	0.32	0.36	0.97	0.71
11	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	0.26	0.35	0.69	0.78
12	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	0.25	0.32	0.00	1.40

Table S10 Effects of Anion on metal salt:IL ratio of 1:6[a]

Entry #	Metal Salt	Ionic Liquid	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	$YCl_3 \cdot 6H_2O$	[bmim]Cl	14.4	2.7	18.8
2	$YCl_3 \cdot 6H_2O$	[bmim]OAc	80.8	33.7	41.7
3	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	40.9	6.6	16.1
4	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	29.0	13.5	46.6
5	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	20.2	-	-
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	91.7	58.9	64.3
7	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	22.8	16.9	74.1
8	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	20.6	17.2	83.3
9	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	9.8	2.1	21.3
10	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	85.8	48.1	56.0
11	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	51.2	25.6	49.9
12	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	17.9	14.2	79.6

[a] Reaction Conditions: 5 wt% catalyst (metal salt:IL molar ratio, 1:6), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

Table S10a Molar Ratios of Anions for S10 Entries

Entry #	Metal Salt	Ionic Liquid	mmol of Salt	mmol of IL	mmol of Cl^-	mmol of OAc^-
1	$YCl_3 \cdot 6H_2O$	[bmim]Cl	0.15	0.59	4.00	0.00
2	$YCl_3 \cdot 6H_2O$	[bmim]OAc	0.15	0.53	0.44	3.19
3	$Y(OAc)_3 \cdot 3H_2O$	[bmim]Cl	0.15	0.58	3.50	0.45
4	$Y(OAc)_3 \cdot 3H_2O$	[bmim]OAc	0.14	0.53	0.00	3.59
5	$GdCl_3 \cdot 6H_2O$	[bmim]Cl	0.14	0.56	3.80	0.00
6	$GdCl_3 \cdot 6H_2O$	[bmim]OAc	0.13	0.51	0.39	3.07
7	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]Cl	0.14	0.56	3.37	0.41
8	$Gd(OAc)_3 \cdot 2.5H_2O$	[bmim]OAc	0.13	0.51	0.00	3.44
9	$LaCl_3 \cdot 7H_2O$	[bmim]Cl	0.17	0.61	4.20	0.00
10	$LaCl_3 \cdot 7H_2O$	[bmim]OAc	0.17	0.55	0.50	3.31
11	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]Cl	0.14	0.57	3.45	0.43
12	$La(OAc)_3 \cdot 1.5H_2O$	[bmim]OAc	0.14	0.52	0.00	3.53

5. Effects of Metal Salt/IL Ratio

To establish how the metal salt:ionic liquid ratio affects PET conversion, ratios of 1:0, 1:3, 1:4 and 1:5 were performed to compare with previous 1:2 and 1:6 results. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

Table S11 Effects of Metal Salt/IL Ratio on $GdCl_3 \cdot 6H_2O$/emimOAc on PET Conversion/BHET Yield[a]

Entry #	Catalyst Molar Ratio	PET Conv (%)	BHET Yield (%)	BHET Select. (%)
1	1:0	14.6	8.9	61.3
2[b]	1:2	96.9	21.5	22.2
3	1:3	41.3	9.7	23.6
4[b]	1:4	13.1	5.8	44.2
5	1:5	22.7	12.2	53.8
6[b]	1:6	90.2	41.6	46.0

[a] Reaction Conditions: 5 wt% catalyst ($GdCl_3 \cdot 6H_2O$:emimOAc), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.
[b] Average Values

Table S12 Effects of Metal Salt/IL Ratio on $GdCl_3 \cdot 6H_2O$/bmimOAc on PET Conversion/BHET Yield[a]

Entry #	Catalyst Molar Ratio	PET Conv (%)	BHET Yield (%)	BHET Select. (%)
1	1:0	14.6	8.9	61.3
2	1:2	91.7	58.9	64.3
3	1:3	68.5	-	-
4	1:4	28.1	13.2	46.8
5	1:5	84.3	37.9	45.0
6	1:6	90.8	57.3	52.0

[a] Reaction Conditions: 5 wt% catalyst ($GdCl_3 \cdot 6H_2O$:bmimOAc), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

Table S13 Effects of Metal Salt/IL Ratio on $YCl_3 \cdot 6H_2O$/emimOAc on PET Conversion/BHET Yield[a]

Entry #	Catalyst Molar Ratio	PET Conv (%)	BHET Yield (%)	BHET Select. (%)
1	1:0	24.1	6.2	25.6
2	1:2	95.0	33.0	34.8
3	1:3	97.5	15.6	16.0
4[b]	1:4	12.7	2.0	15.3
5	1:5	42.7	20.2	47.3
6	1:6	94.8	56.6	60.2

[a] Reaction Conditions: 5 wt% catalyst ($YCl_3 \cdot 6H_2O$:emimOAc), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.
[b] Average Values

Table S14 Effects of Metal Salt/IL Ratio on $YCl_3 \cdot 6H_2O$:bmimOAc on PET Conversion/BHET Yield[a]

Entry #	Catalyst Molar Ratio	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	1:0	24.1	6.2	25.6
2	1:2	98.8	47.6	48.2
3	1:3	51.6	28.3	54.7
4	1:4	51.6	9.4	18.2
5	1:5	56.5	26.0	46.2
6	1:6	80.8	33.7	41.7

[a] Reaction Conditions: 5 wt% catalyst ($YCl_3 \cdot 6H_2O$:bmimOAc), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET.

6. Effects of Temperature

To understand how temperature affects PET conversion and BHET yield, reactions were run from a range of 140°C to 190°C. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

Table S15 Effects of Temperature on 1:6 $GdCl_3 \cdot 6H_2O$/[emim]OAc[a]

Entry #	Temperature (°C)	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	140	7.3	-	-
2	150	18.6	-	-
3	160	22.7	-	-
4	170	65.3	23.5	36.0
5[b]	180	90.2	41.6	46.0
6[b]	190	89.0	64.9	73.0

[a] Reaction conditions: 5 wt% catalyst ($GdCl_3 \cdot 6H_2O$:emimOAc molar ratio, 1:6), 1:4 PET:EG ratio, 4 h, 3g PET.

[b] Average values.

7. Effects of EG:PET Ratio

We next sought to identify what ratio of EG:PET would lead to the best PET conversions and BHET yields. Since EG is critical for glycolysis, it is likely involved in the rate law. This suggests increases in EG concentration should increase the rate of glycolysis. However, increasing the EG volume also dilutes the catalyst, which would likely lead to a decrease rate in glycolysis. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

We first chose to keep the PET and catalyst scale the same, while increasing EG. This required the use of a 350 mL pressure vessel instead of a 20 mL vial. The metal salt and ionic liquid were still stirred until homogenous in a 20 mL but were then transferred via pipette into the pressure vessel. The above procedure was then followed, but in the larger vessels. In this case, a decrease in PET conversion was observed for all conditions, in comparison to reactions pursued in a 20 mL vial (**Table S16**). These results indicated that reaction vessel does make a difference in the glycolysis outcome. Nonetheless, results show that increasing EG volumes does increase the PET conversion to a point, at which the conversion starts to drop. Optimized ratios appear to be at a 15:1 EG:PET.

Table S16 Effects of EG:PET Ratio on 3g PET Samples[a]

Entry #	EG:PET Weight Ratio	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	4:1	47.2	10.7	22.7
2	8:1	57.9	18.0	31.1
3	10:1	60.1	18.1	30.1
4	15:1	67.3	20.5	30.5
5	20:1	58.8	17.0	28.9

[a] Reaction Conditions: 5 wt% catalyst ($GdCl_3·6H_2O$ /[emim]OAc molar ratio, 1:6), 180°C, 4 h.

In order to fit all conditions in a 20 mL vial, the PET scale had to be dropped to 1 g. While high PET conversions were obtained, they were too high for much direct comparison. We do note that the highest BHET yield under these conditions was also found to be with the 15:1 EG:PET.

Table S17 Effects of EG:PET Ratio on 1g PET Samples[a]

Entry #	EG:PET Weight Ratio	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	4:1	92.7	12.2	13.1
2	8:1	97.8	13.4	13.7
3	10:1	>99.9	17.1	17.1
4	15:1	>99.9	21.5	21.5
5	20:1	>99.9	17.0	17.0

[a] Reaction Conditions: 5 wt% catalyst ($GdCl_3·6H_2O$/[emim]OAc molar ratio, 1:6), 180°C, 4 h.

8. Effects of PET Material

Since PET material shape, size and purity can impact the activity of catalysts, we sought to identify the activity of the $GdCl_3 \cdot 6H_2O$/[emim]OAc (1:6) catalyst towards different PET products. As shown below, the surface area had a large effect on the PET conversion, with thicker items showing lower conversion than fibers that have a high surface area. Some conditions listed are identical to reactions conducted above. They are included in these tables for proper comparisons of the different variables studied in this section.

Table S19 Effects of PET Material[a]

Entry #	PET Material	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1	Pellets	64.7	40.3	62.3
2	Flakes	74.7	15.3	20.4
3	Bottle	68.6	19.9	29.0
4	Lids	90.2	41.6	46.0
5[b]	Carpet fiber	99.1	54.1	54.5

[a] Reaction Conditions: 5 wt% catalyst ($GdCl_3 \cdot 6H_2O$:emimOAc molar ratio, 1:6), 1:4 PET:EG ratio, 180°C, 4 h, 3g PET. [b] Reactions with carpet fibers were run at half the scale and at a 1:8 PET:EG ratio to allow the material to fit into the same reaction vessel and aide solubility of the high volume fibers.

9. Sustainability of the Metal Salt Choice

Table S20 Sustainability of the Metal Salt Choice[a]

Entry #	Metal Salt	PET Material	PET Conv. (%)	BHET Yield (%)	BHET Select. (%)
1[b]	$GdCl_3·6H_2O$	Lids	64.7	40.3	62.3
2	$LaCl_3·7H_2O$	Pellets	67.1	23.5	35.0
3	$LaCl_3·7H_2O$	Flakes	74	58.6	79.2
4	$LaCl_3·7H_2O$	Bottle	23.2	17.3	74.6
5	$LaCl_3·7H_2O$	Lids	87.5	30.0	34.3
6	$LaCl_3·7H_2O$	Carpet Fibers[d]	90.8	0.81	0.89
7	$CeCl_3·7H_2O$	Pellets	66.6	0.00	0.00
8	$CeCl_3·7H_2O$	Flakes	49.9	39.3	78.7
9	$CeCl_3·7H_2O$	Bottle	65.7	50.8	77.3
10	$CeCl_3·7H_2O$	Lids	51.0	7.60	14.9
11	$CeCl_3·7H_2O$	Carpet Fibers[d]	39.2	29.8	76.0
12[c]	$LnCl_3·7H_2O$ Ln= La/Ce	Pellets	51.8	24.0	46.3
13[c]	$LnCl_3·7H_2O$ Ln= La/Ce	Flakes	34.1	0.00	0.00
14[c]	$LnCl_3·7H_2O$ Ln= La/Ce	Bottle	57.2	44.1	77.1
15[c]	$LnCl_3·7H_2O$ Ln= La/Ce	Lids	70.4	50.8	72.1
16[c]	$LnCl_3·7H_2O$ Ln= La/Ce	Carpet Fibers[d]	63.5	46.3	72.9

[a] Reaction Conditions: 5 wt% catalyst (MCl_3:emimOAc molar ratio, 1:6), 1:4 PET:EG ratio, 190°C, 4 h, 3g PET. [b] Same as Table S15. Entry 6. [c] unseparated La/Ce mixture [d] Reactions with carpet fibers were run at half the scale and at a 1:8 PET:EG ratio to allow the material to fit into the same reaction vessel and aide solubility of the high volume fibers.