Multiple hydrogen bonds promote the nonmetallic degradation process of PET with amino acid IL catalyst

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Design Expert software version 8.0.6 was used to evaluate the influence of different reaction conditions (reaction time, temperature and mass ratio of EG/PET, respectively) on the yield of BHET. Box–Behnken design with three-level-three-factor was applied. The coded and uncoded independent variables and levels used in the experimental design are shown in Table S1. There is a total of 17 three-level-three-factor Box–Behnken design experiments and responses as shown in Table S2.

Table S1. Coded and uncoded levels of variables for Box–Behnken design

Variable	Symbol	Coded factor levels		
		-1	0	1
Reaction temperature (°C)	A	170	180	190
Reaction time (min)	B	60	90	120
mass ratio of EG/PET	C	3:1	4:1	5:1

Table S2. Experimental design and results

Standard	Run	Factor 1 A:Temperature	Factor2 B:Time	Factor 3 C:EG/PET	Response Yield
5	1	-1	0	-1	61.6
12	2	0	1	1	74.7
15	3	0	0	0	64.0

2	4	1	-1	0	74.2
16	5	0	0	0	71.8
17	6	0	0	0	63.6
6	7	1	0	-1	71.6
9	8	0	-1	-1	57.0
14	9	0	0	0	61.6
4	10	1	1	0	75.6
11	11	0	-1	1	52.4
8	12	1	0	1	76.9
1	13	-1	-1	0	50.3
3	14	-1	1	0	59.7
13	15	0	0	0	67.8
7	16	-1	0	1	38.7
10	17	0	1	-1	72.7

The model used in RSM is generally a quadratic equation for predicting response as a function of independent variables. Due to the high conversion of PET and yield of BHET, [Bmim]Pro was chosen as catalyst to study the interaction of independent variables. The results show that the quadratic equation has a good fitting effect on BHET yield and the fitting results is shown in the equation (S1).

$$\text{Yield}=0.67+0.17A+0.059B-0.011C-0.031AB+0.033AC+8.023e^{-3}BC-0.072A^2-0.03B^2-9.027\,e^{-3}C^2 \quad \text{(S1)}$$

Analysis of variance (ANOVA) was studied to determine the signification of fit between mathematical model and experimental data. The results are depicted in Table S4. When the p-value is lower than 0.05, it means the model terms are significant. The p-value of BHET yield model is 0.0004 < 0.05. Meanwhile, the lack of fit test for the model are not dignificant and the value is 0.441 > 0.05. Hence, the model is suitable for fitting experimental data. By setting other parameters as constants, we can get a smooth surface of the influence of two independent parameters on BHET yield. The interaction effects of two independent parameters can be expressed in terms of smooth surface. The interaction effect between temperature and time on the BHET yield is shown in Figure S1a. With the increment of reaction temperature and time, the BHET yield generally show a rising trend. The researchers believe that by increasing the temperature, the swelling efficiency of PET can be increased which speed up the reaction process. Meanwhile, the reaction temperature would also affect the reaction equilibrium. When keeping reaction time as a constant, BHET yield are increased with the temperature and mass ratio of EG/PET as shown in Figure S1b. This result could be explained by the results above that the increasing in temperature and mass ratio of EG/PET are benefits to dissolve the PET into EG. The two figures depict that mass ratio of EG/PET has little effect on the BHET yield when compared with temperature. The interaction of EG/PET with reaction time are decipted in Figure S1c. These two figures shows that the mass ratio of EG/PET have a less significant influence on the response surface of BHET yield, compared with the reaction time. The results above are consistent with the AVONA results. In the PETdegradation reaction, the order of the influence of independent factors on the reaction is: Temperature > Time > EG/PET.

To get the maximum BHET yield, the optimization of independent parameters in this work were carried out. The parameters including temperature, time and mass ratio of EG/PET were set within the range which have been shown in Table S1. According to the suggesttion by the software for glycolysis reaction, the optimum operating conditions for glycolysis temperature, time, and mass ratio of EG/PET were 190 ^{o}C, 89 min and 5, respectively. Under the optimum reaction conditions, the actual PET conversion was 100% which is consistent with theoretical one. In the meanwhile, the actual value of BHET yield 77.46% which is very close to the theoratical value. In conclusion, the response surface model can accurately predict the response value.

Table S3. Comparison of response by theoretical and actual

	Temperature (^{o}C)	Time (min)	EG/PET	Conversion (%)	Yield (%)	Error of Yield (%)
Theoratical value	190	89	5	100	75.3	2.84
Actual value				100	77.5	

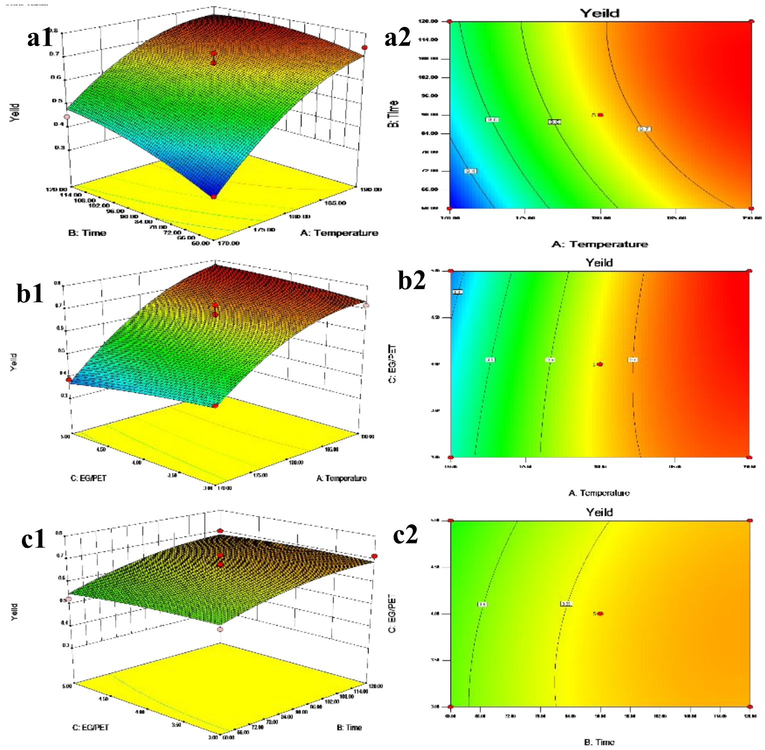

Figure S1. Response surface and contour plots for effects of different factors on BHET yield (A: Reaction temperature and time at mass ratio of EG/PET 4; B: Reaction temperature and EG/PET mass ratio at 90 min; C: Reaction time and EG/PET mass ratio at 180 ^{o}C.)

Table S4. ANOVA for quadratic model

	Source	Sum of Squares	DF	Mean Square	F Value	p-value Prob > F	Significant
Yield of BHET	Model	0.300	9	0.033	20.600	0.0003	Yes
	A-Temperature	0.240	1	0.24	145.470	< 0.0001	Yes
	B-Time	0.028	1	0.028	17.080	0.004	Yes
	C-EG/PET	9.259E-4	1	9.259E-4	0.570	0.474	No
	AB	3.798E-3	1	3.798E-3	2.350	0.169	No
	AC	4.343E-3	1	4.343E-3	2.690	0.145	No
	BC	2.575E-4	1	2.575E-4	0.160	0.702	No
	A^2	0.022	1	0.022	13.580	0.0078	Yes
	B^2	3.752E-3	1	3.752E-3	2.320	0.172	No
	C^2	3.430E-4	1	3.430E-4	0.210	0.659	No
	Residual	0.011	7	1.617E-3			
	Lack of Fit	5.156E-3	3	1.719E-3	1.120	0.441	No
	Pure Error	6.164E-3	4	1.541E-3			

Cor Total	0.310	16

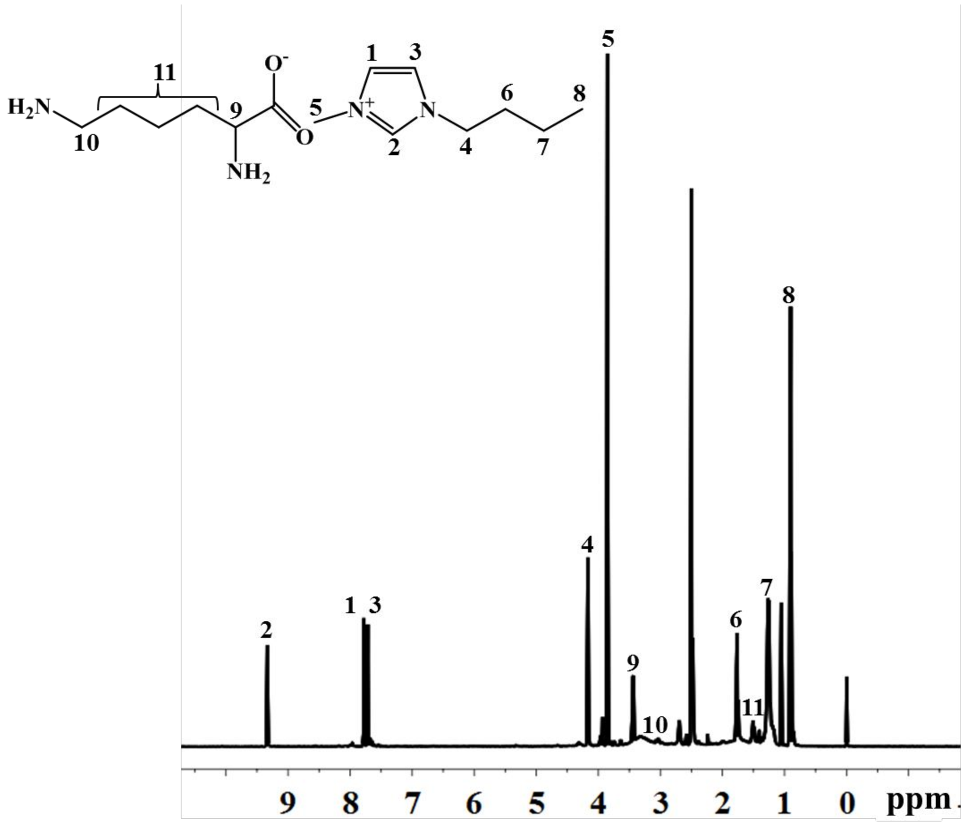

Figure S2. ^{1}H NMR of BMIMLys

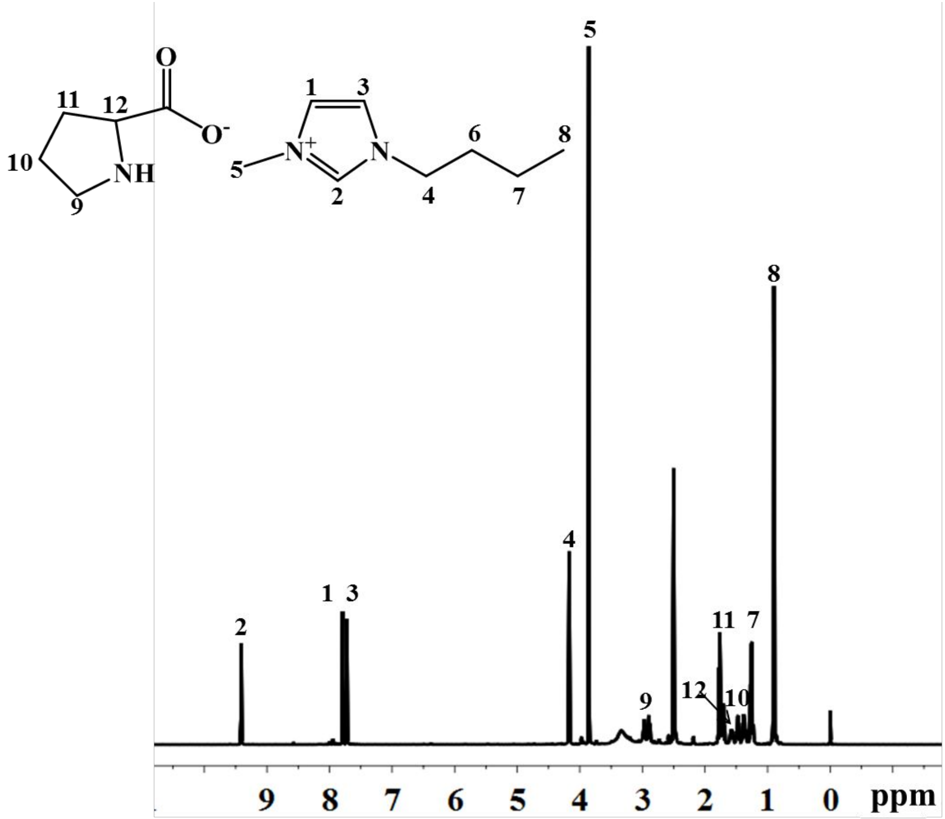

Figure S3. ^{1}H NMR of BMIMPro

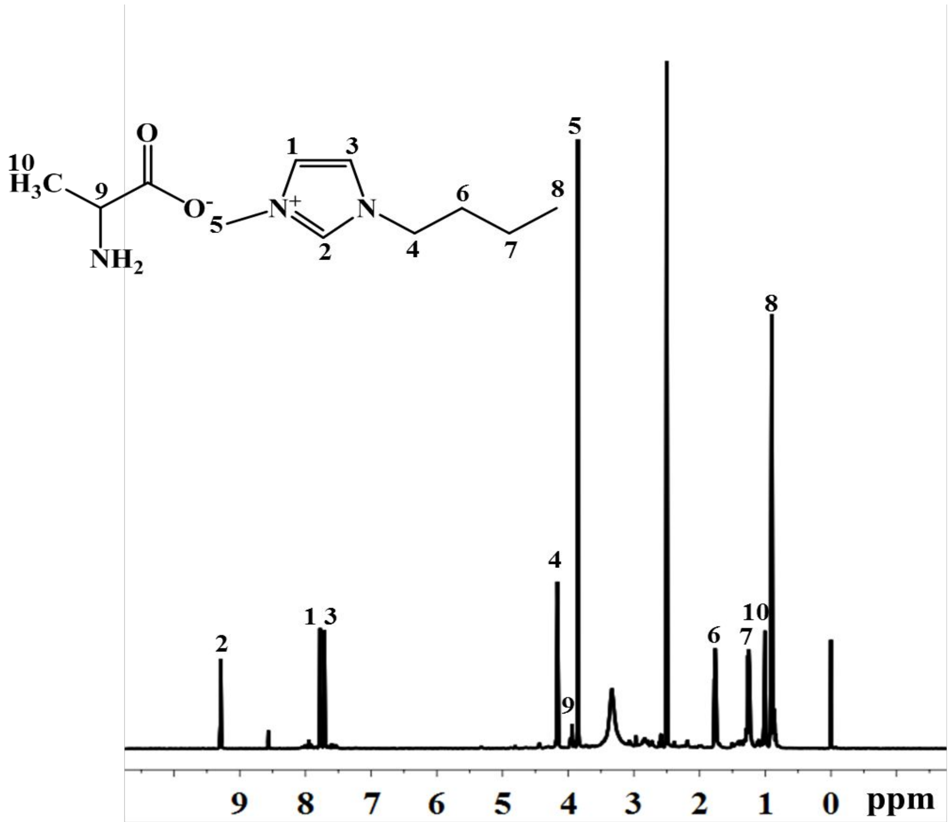

Figure S4. ^{1}H NMR of BMIMAla

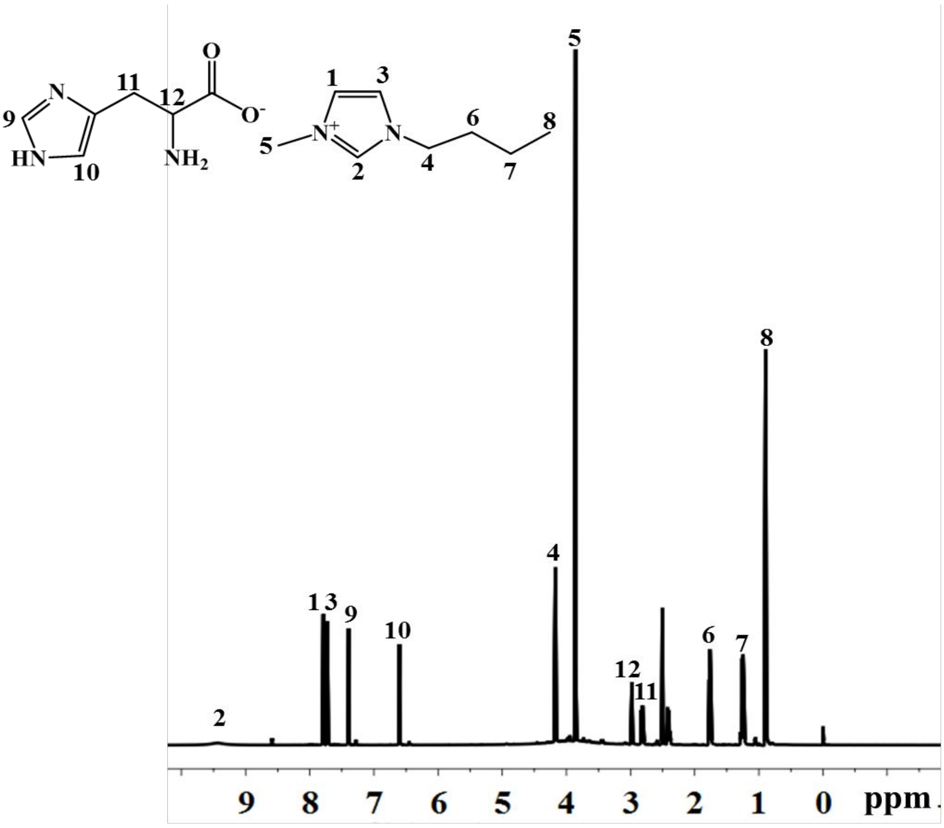

Figure S5. ^{1}H NMR of BMIMHis

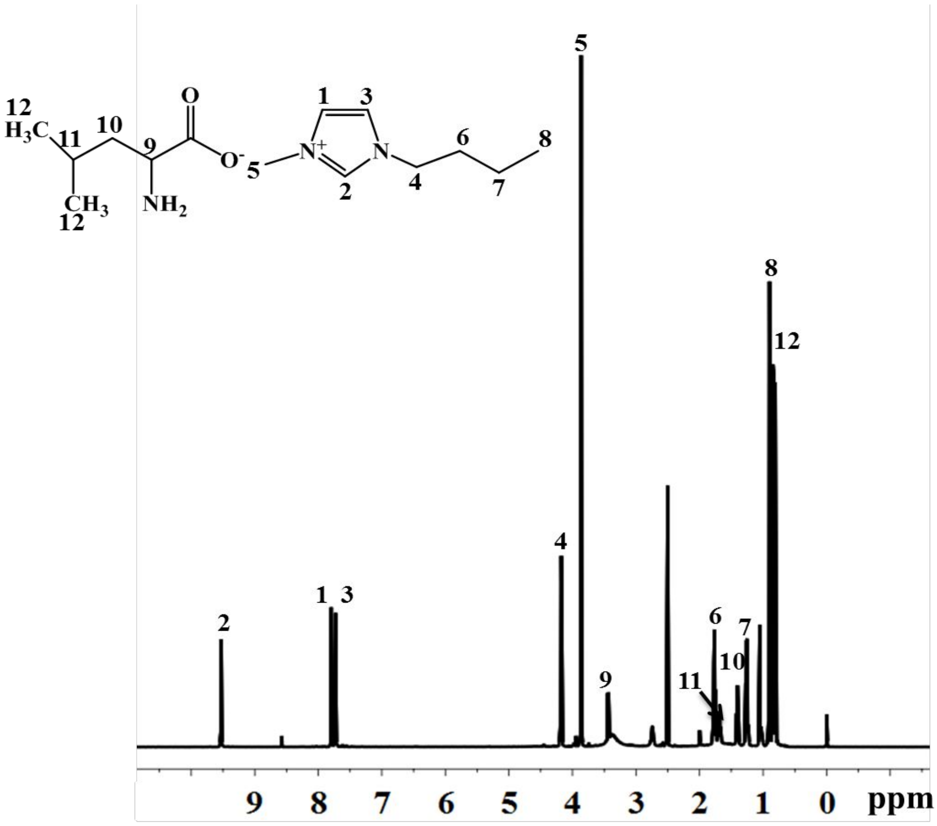

Figure S6. ^{1}H NMR of BMIMLeu

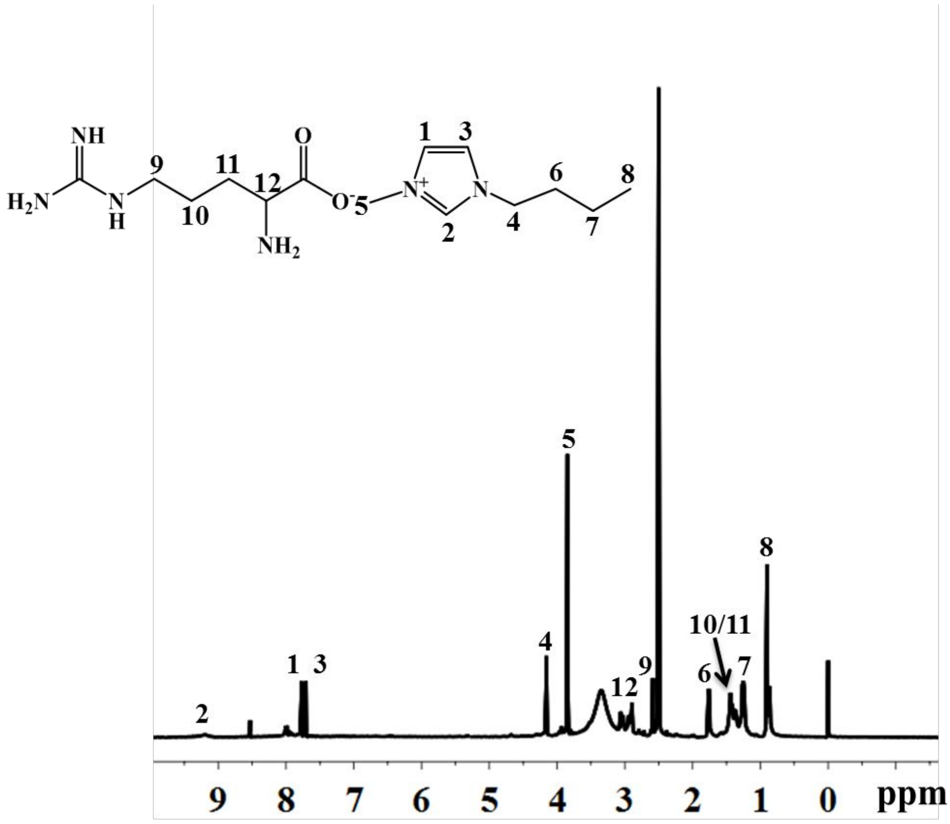

Figure S7. ^{1}H NMR of BMIMArg