SUPPORTING INFORMATION

Optimisation for PET glycolysis applying recyclable heterogeneous organocatalysts

Zsuzsanna Fehér, Johanna Kiss, Péter Kisszékelyi, János Molnár, Péter Huszthy, Levente Kárpáti and József Kupai*

Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, P.O. Box 91, H-1521, Budapest, Hungary

kupai.jozsef@vbk.bme.hu

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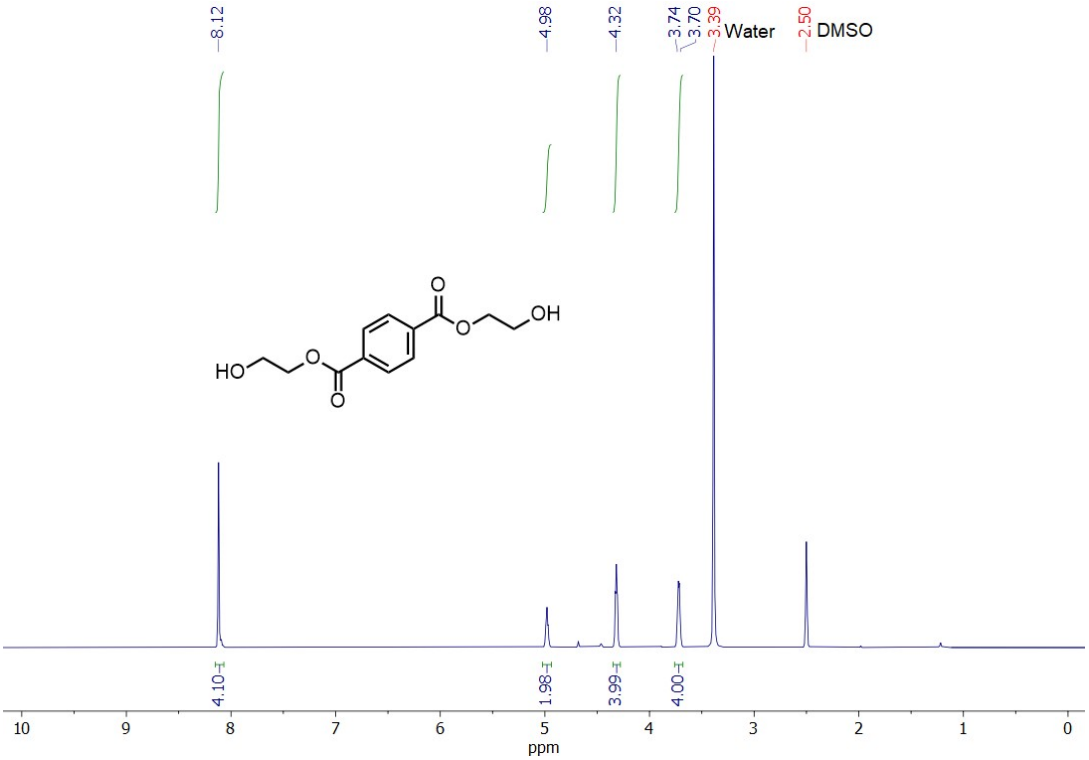


Figure S1. ^{1}H NMR spectrum of BHET in DMSO-d_6

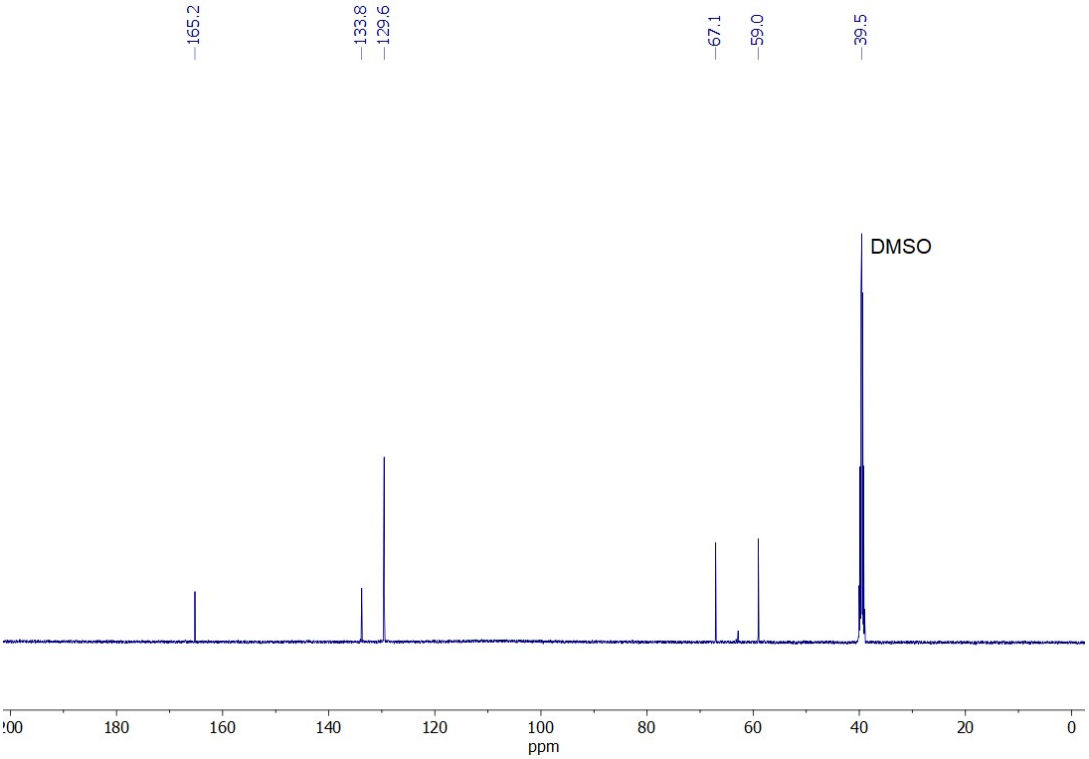


Figure S2. ^{13}C NMR spectrum of BHET in DMSO-d_6

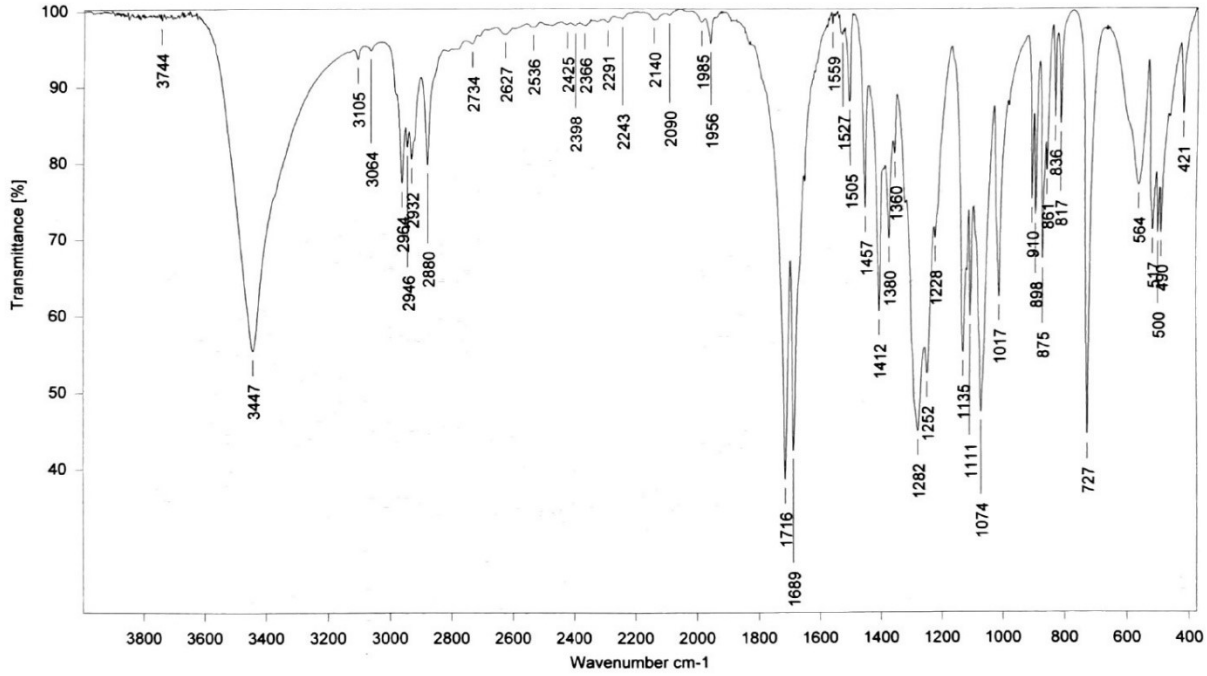


Figure S3. FTIR spectrum of BHET

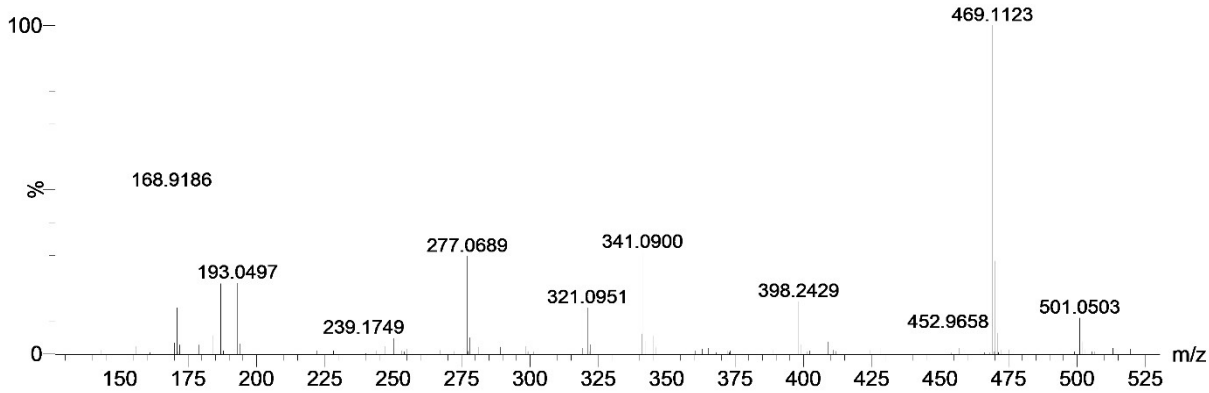


Figure S4. HRMS spectrum of BHET

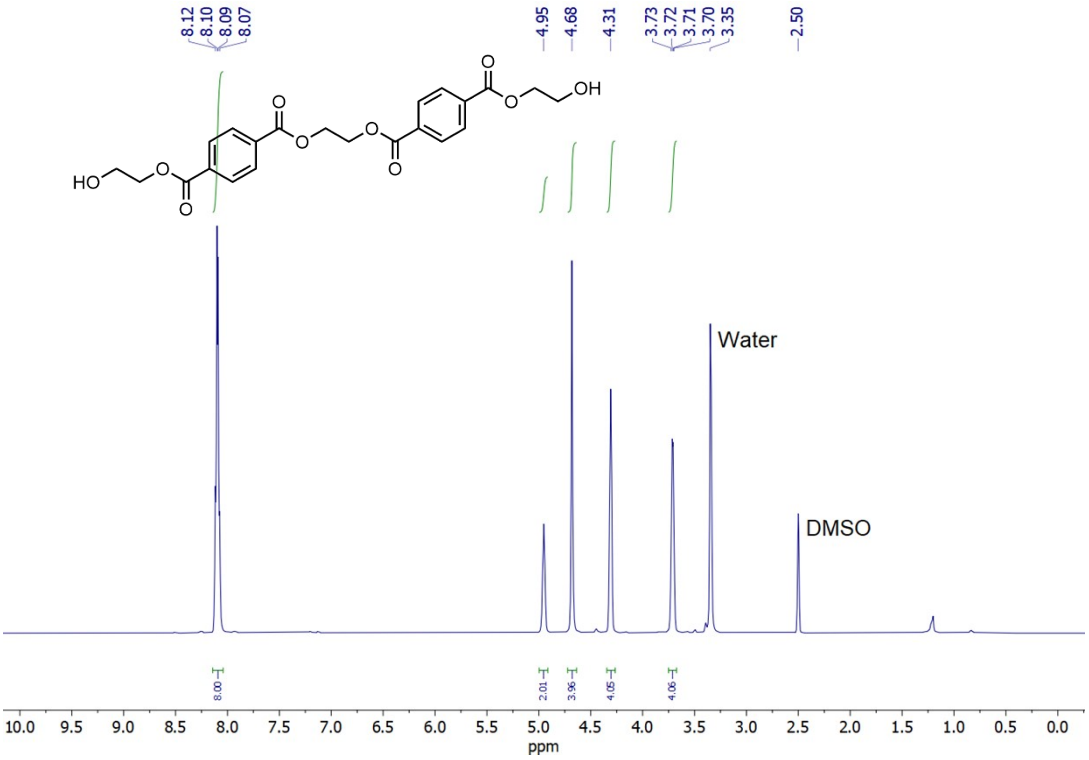


Figure S5. ^{1}H NMR spectrum of BHET dimer in DMSO-d_6

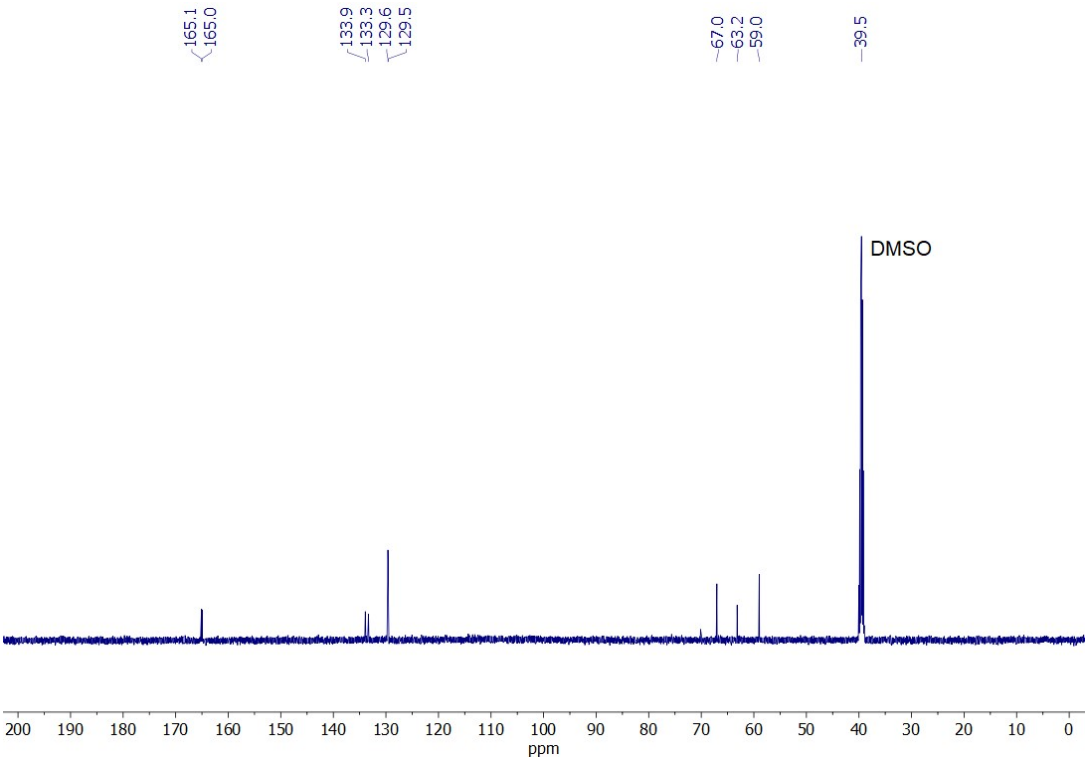


Figure S6. ^{13}C NMR spectrum of BHET dimer in DMSO-d_6

2 Characterisation and thermal stability of catalysts

Table S1. Properties of commercially available functionalized silica gels

Catalyst	Particle size (μm)	Specific surface area (m^2 g^{-1})	Molecular loading (mmol g^{-1})	Price (EUR g^{-1})
Si-TEA	40–63	480	1.29	26.93
Si-GUA	40–63	480	1.11	23.76
Si-THU	40–63	485	1.27	22.96
Si-GLY	40–63	494	1.11	20.43

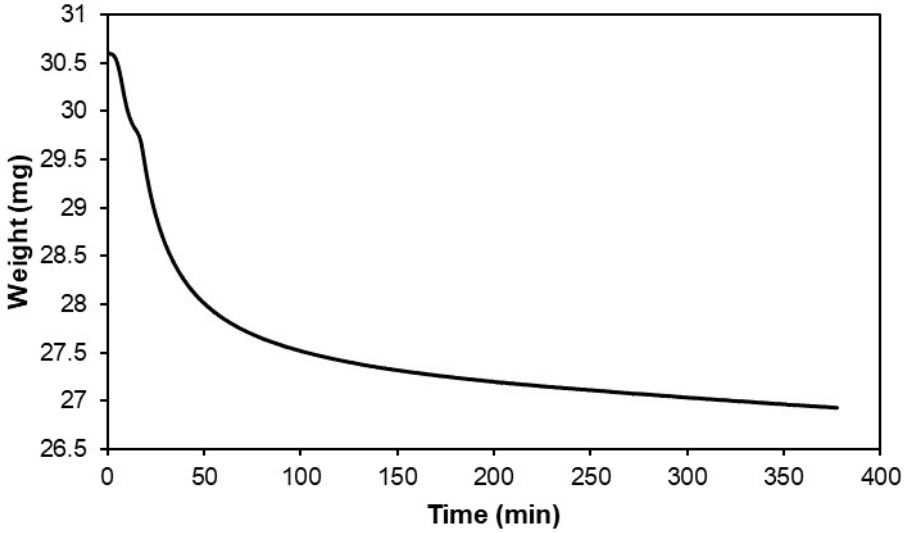


Figure S7. Mass decrease of Si-GUA measured by TG-DSC

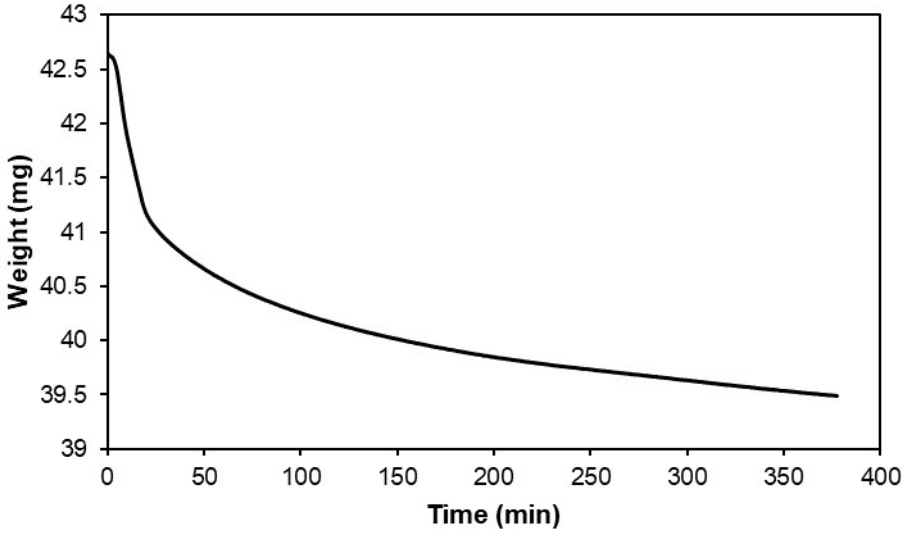


Figure S8. Mass decrease of Si-TBD measured by TG-DSC

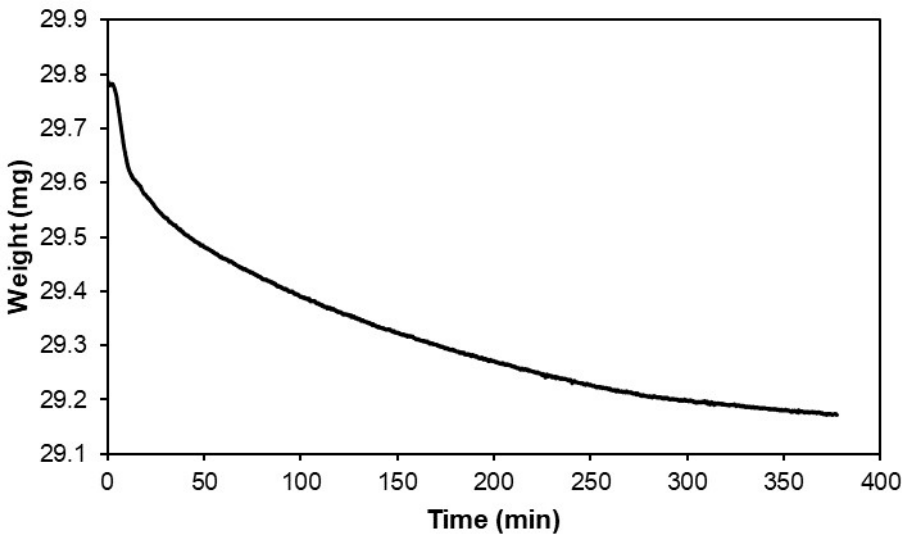


Figure S9. Mass decrease of Si-TEA measured by TG-DSC

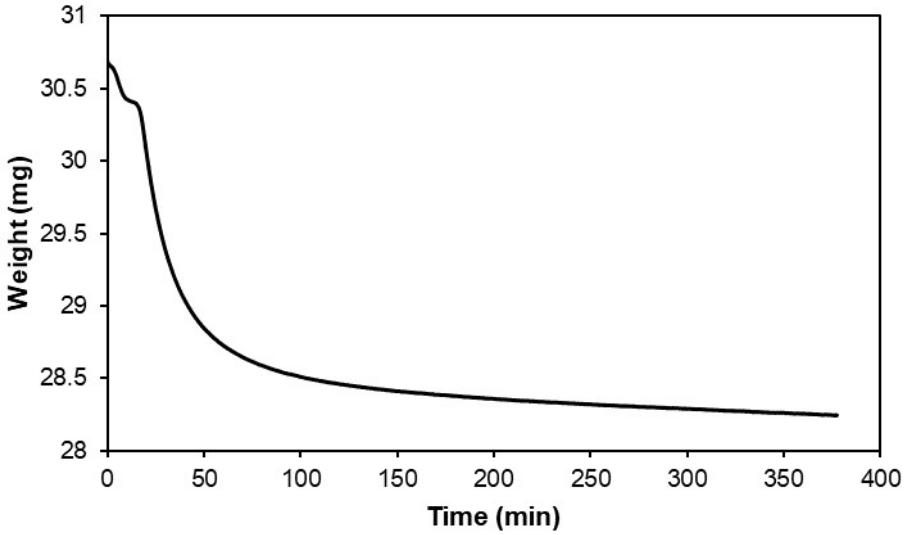


Figure S10. Mass decrease of Si-THU measured by TG-DSC

3 Monitoring of depolymerisation

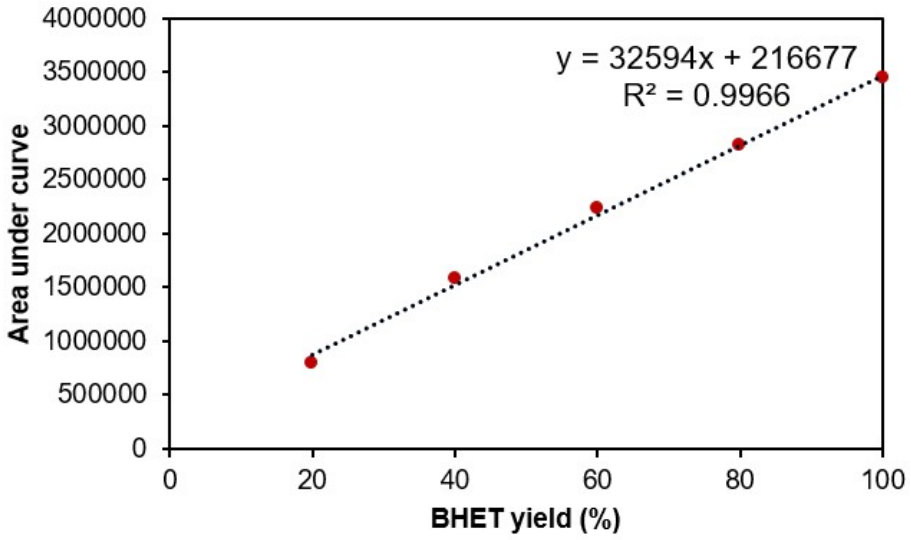


Figure S11. HPLC calibration curve for determining the non-isolated BHET yield

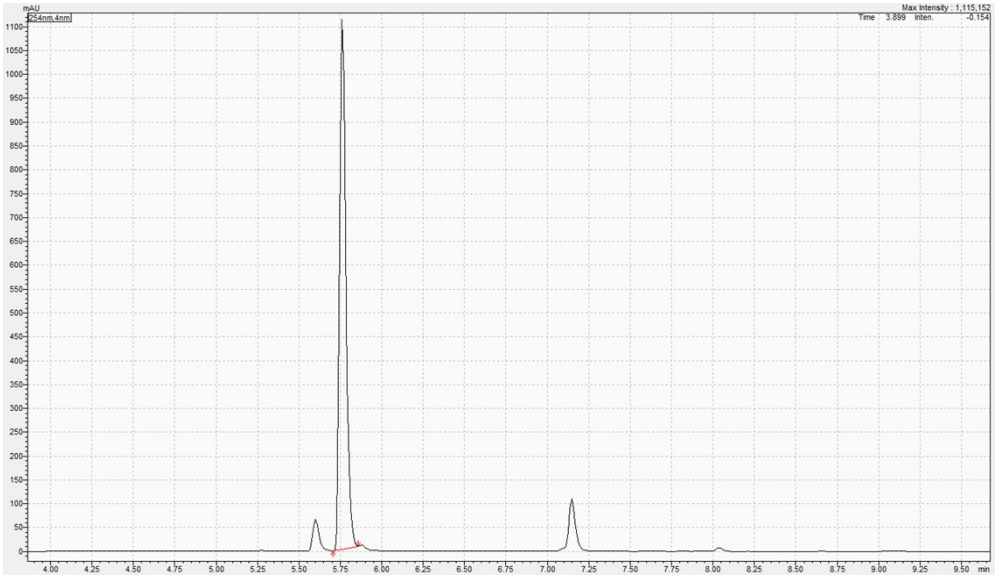
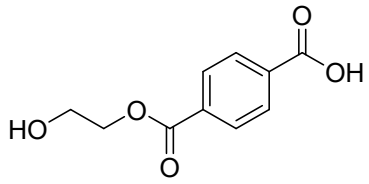
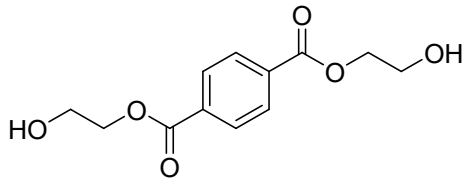
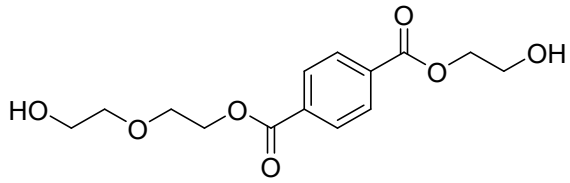
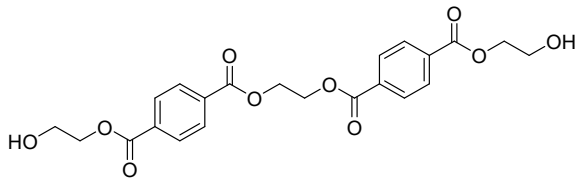
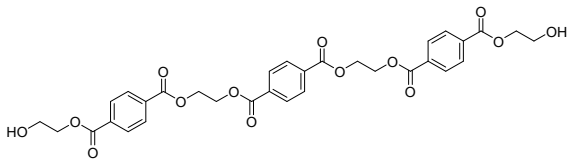


Figure S12. HPLC chromatogram of the 18-fold scaled-up PET glycolysis reaction

Table S2. Compounds detected by HPLC-MS in the 18-fold scaled-up PET glycolysis reaction

Detected compound	Retention time (min)	*m/z*
 MW: 210	5.60	209 ($-H^+$) 255 ($+HCOO^-$)
 MW: 254	5.76	209 ($-(CH_2-CH_2-OH)^+$) 255 ($+H^+$)
 MW: 298	5.88	299 ($+H^+$) 321 ($+Na^+$) 362 ($+MeCN+Na^+$)
 MW: 446	7.15	447 ($+H^+$) 429 ($-OH^-$) 491 ($+HCOO^-$) 469 ($+Na^+$)
 MW: 638	8.03	639 ($+H^+$) 621 ($-OH^-$) 683 ($+HCOO^-$)

4 Preliminary experiments for parameter investigation

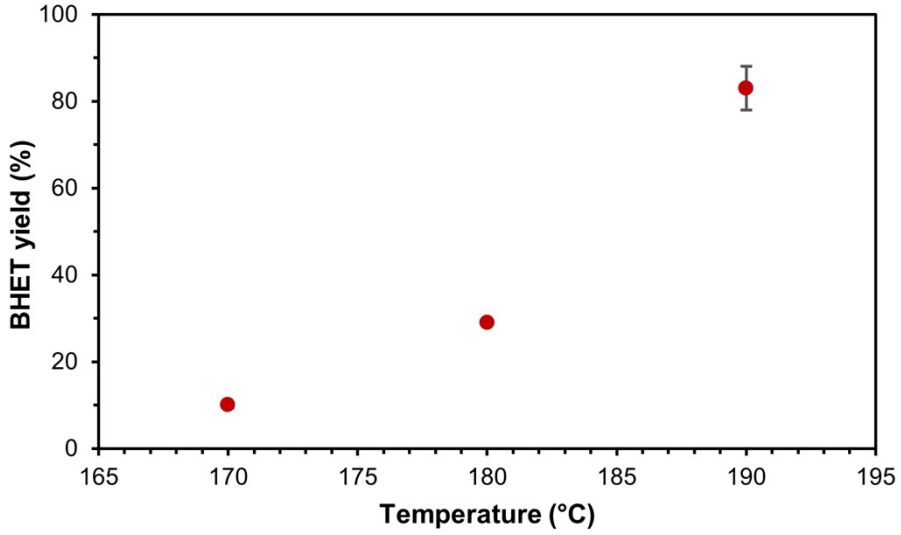


Figure S13. Effect of temperature on BHET yield
Reaction conditions: 10 mol% Si-TEA catalyst, EG/PET molar ratio: 16, 2 h

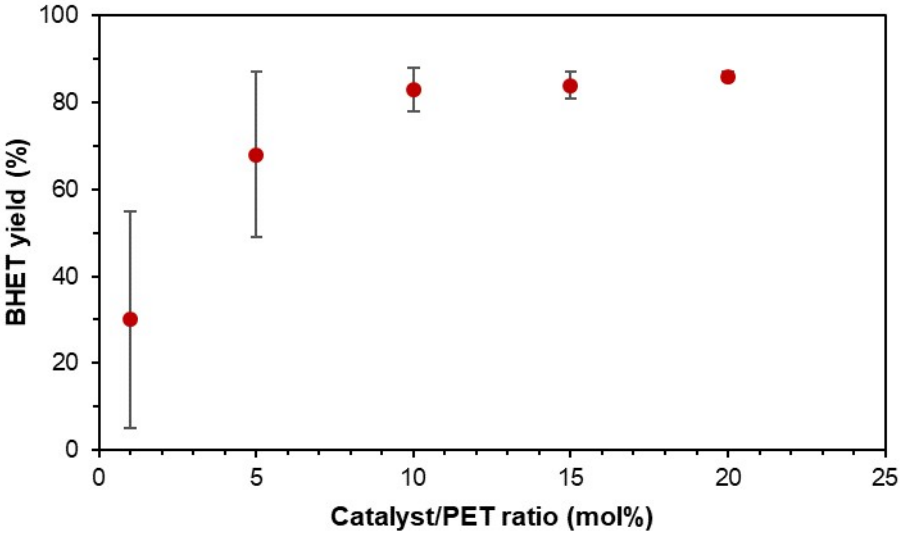


Figure S14. Effect of catalyst/PET ratio on BHET yield
Reaction conditions: 190 °C, Si-TEA catalyst, EG/PET molar ratio: 16, 2 h

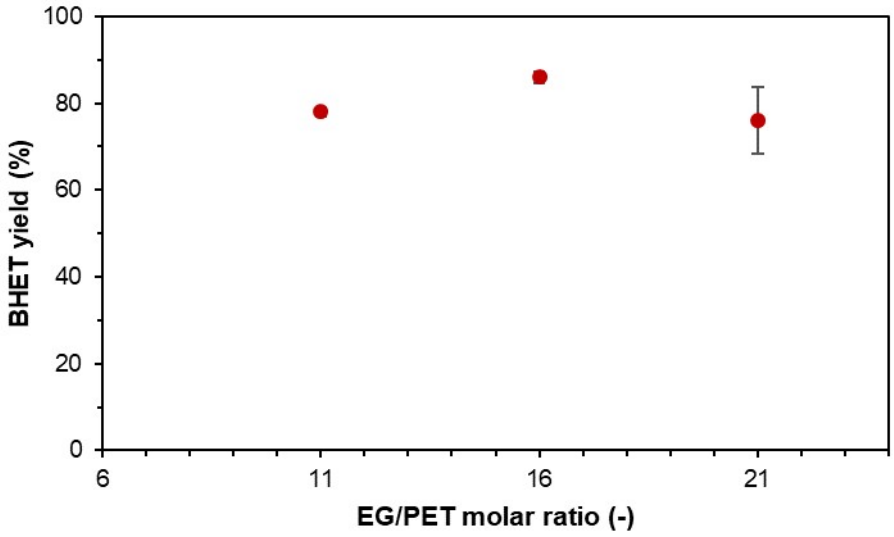


Figure S15. Effect of EG/PET molar ratio on BHET yield
Reaction conditions: 190 °C, 20 mol% Si-TEA, 2 h

5 Regression model based on experimental design

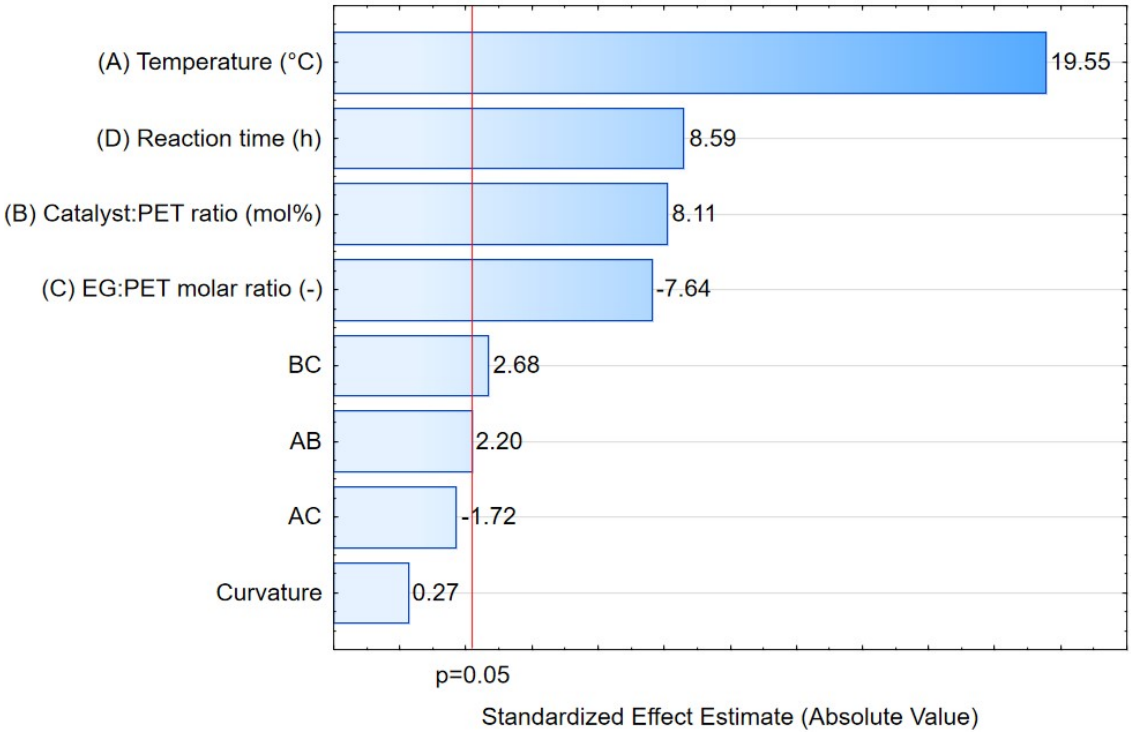


Figure S16. Pareto chart of standardised effects in the case of BHET yield as dependent variable

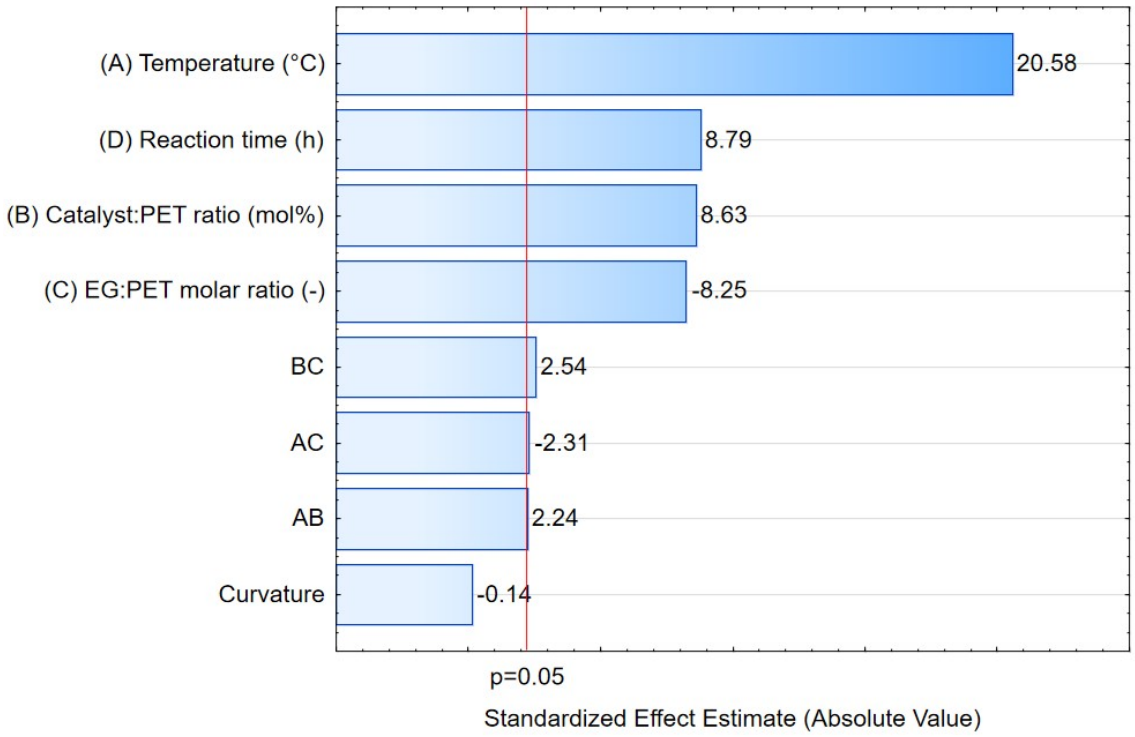


Figure S17. Pareto chart of standardised effects in the case of PET conversion as dependent variable

Table S3. Analysis of variance for the reduced linear regression model. Factors in red are statistically significant.

Factor	Sum of Squares	DF	Mean Square	F-value	p-value
Curvature	2.81	1	2.81	0.05	0.8270
(*A*) Temperature (°C)	14945.06	1	14945.06	264.38	<0.0001
(*B*) Catalyst:PET ratio (mol%)	2575.56	1	2575.56	45.56	<0.0001
(*C*) EG:PET molar ratio (-)	2280.06	1	2280.06	40.33	<0.0001
(*D*) Reaction time (h)	2889.06	1	2889.06	51.11	<0.0001
B by *C*	280.56	1	280.56	4.96	0.0442
Error	734.87	13	56.53		
Total Sum of Squares	23708.00	19			

DF: degree of freedom

5.1 Checking the constant error variance assumption

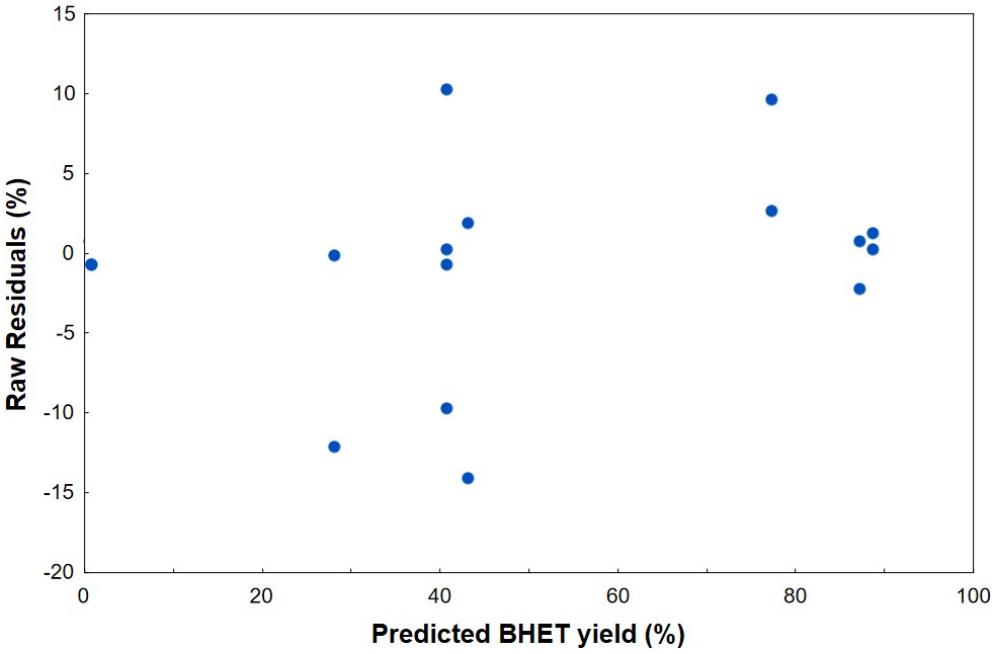


Figure S18. Predicted vs. residual values of BHET yield

Cochran's C test:

$$C = \frac{s_{max}^2}{\sum_i s_i^2} = \frac{128.0}{229.5} = 0.56 < 0.68 = G_{0.95}(1,8)$$

where s_i is the standard deviation of repeated experiments by group, and s_{max} is the highest of these values.

6 Optimisation of reaction conditions

Table S4. Calculated step intervals* and coded factor values* for factors *A*, *B*, *C*, and *D* at each optimisation experiment point

Optimisation experiment points	s_A	s_B	s_C	s_D	x_A	x_B	x_C	x_D
0	2.50	0.78	-0.24	0.05	0.00	0.00	0.00	0,00
1	2.50	0.75	-0.23	0.05	0.25	0.10	-0.10	0.11
2	2.50	0.73	-0.23	0.05	0.50	0.20	-0.19	0.22
3	2.50	0.71	-0.22	0.05	0.75	0.30	-0.28	0.33
4	2.50	0.68	-0.21	0.05	1.00	0.40	-0.37	0.44
5	2.50	0.66	-0.20	0.05	1.25	0.49	-0.45	0.55
6					1.50	0.57	-0.53	0.66

* Given to two decimal places to indicate monotonic growth of values

7 Catalyst recycling

Table S5. Catalyst mass decrease of Si-TEA and Si-TBD during catalyst recycling related to the initial catalyst mass in the first reaction cycle

	Si-TEA		Si-TBD	
Reaction cycle	Catalyst mass loss after reaction (%)	Catalyst mass remaining on filter (%)	Catalyst mass loss after reaction (%)	Catalyst mass remaining on filter (%)
1	6.9	3.8	12.4	3.7
2	11.9	1.8	6.9	1.7
3	5.5	6.9	5.9*	3.9
4	4.3	4.9	5.1*	2.6
5	3.7*	n.d.	4.5*	n.d.
Average	6.5	4.4	7.0	3.0
Std deviation	3.3	2.1	3.2	1.0
Sum	32.4	17.4	34.8	11.8

* In the labelled reactions, PET/insoluble oligomers were visually observed to remain on the filter, and therefore a certain previously observed catalyst loss (relative to the initial catalyst amount in the cycle) was assumed to calculate the estimated catalyst mass after reaction. This determines the decrease in catalyst mass during the reaction (but here in each case, the loss is relative to the initial catalyst amount in the first cycle, not the current cycle).

For Si-TEA, this assumed catalyst mass loss was 6.8% (observed in the 4th cycle), and for Si-TBD, it was 7.8% (observed in the 2nd cycle).

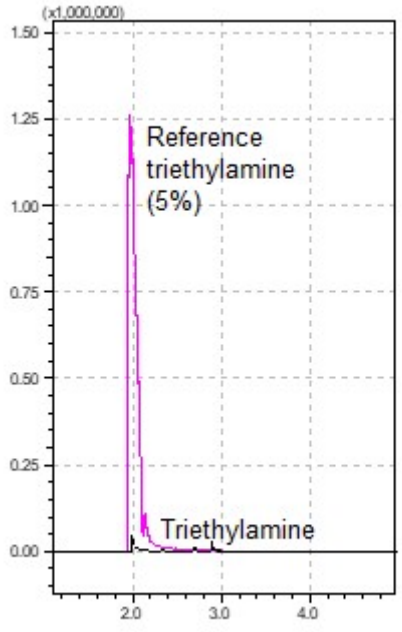


Fig. S19. HS-GC-MS chromatograms of reference triethylamine (5% of the TEA amount grafted on the silica gel) and PET glycolysis with Si-TEA (only TEA is depicted)

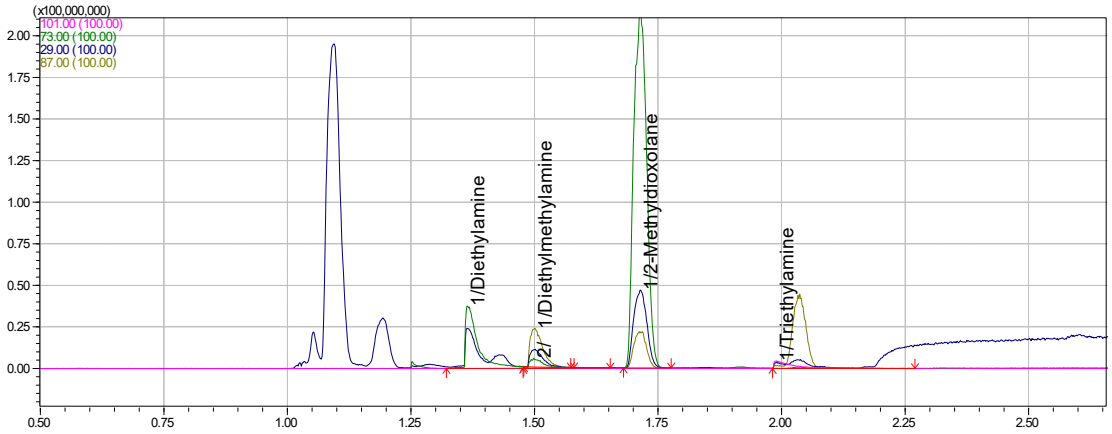


Fig. S20. HS-GC-MS chromatogram of PET glycolysis with Si-TEA

Table S6. Peak areas of detected compounds in PET glycolysis with Si-TEA (HS-GC-MS)

	m/z of fragment chosen for peak area calculation (approx. 20% intensity)	Area
Reference triethylamine (5%*)	101.00	8065745
Triethylamine	101.00	128593
Diethylmethylamine	73.00	432613
Diethylamine	29.00	677909
2-Methyldioxolane	87.00	865703

* 5% of the TEA amount grafted on the silica gel

8 Environmental energy impact

Calculation of environmental energy impact of Si-TEA and Si-TBD, and comparing them to other recyclable organocatalysts applied in PET glycolysis.

The cumulative BHET yields (for five reaction cycles) of Si-TEA and Si-TBD were applied in the calculations.

Environmental energy impact: $$\xi = \frac{E_{\text{factor}}}{\varepsilon} \quad (^{\circ}\text{C} \cdot \text{min})$$

Energy economy factor: $$\varepsilon = \frac{Y}{T \cdot t} \quad (^{\circ}\text{C}^{-1} \cdot \text{min}^{-1})$$

where Y is the yield (-), T is the temperature (°C), and t is the reaction time (min).

Environmental factor[a]: $$E_{\text{factor}} = \frac{\text{m}_{\text{waste}}}{\text{m}_{\text{product}}} = \frac{\left(0.1 \cdot \frac{\text{m}_{\text{solvent}}}{\text{m}_{\text{PET}}} + \frac{\text{m}_{\text{catalyst}}}{\text{m}_{\text{PET}}}\right) \cdot \text{m}_{\text{PET,0}}}{\text{yield} \cdot \frac{\text{MW}_{\text{BHET}}}{\text{MW}_{\text{PET,ru}}} \cdot \text{m}_{\text{PET,0}}} \quad (-)$$

where $m_{PET,0}$ is the initial mass of PET, $MW_{PET,ru}$ is the molecular weight of PET repeating unit (192.2), and MW_{BHET} is the molecular weight of the product BHET (254.2).

Since the following compared catalysts are all recyclable, the catalyst:PET ratio was not included in the calculations, as also applied in the work of Thielemans and co-workers.[1]

Table S7. Summary of results comparing Si-TEA and Si-TBD to other recyclable organocatalysts applied in PET glycolysis.

Ref.	Catalyst	Y (-)	T (°C)	t (min)	Solvent:PET ratio (-)	ε ($°C^{-1}$ min^{-1})	E (-)	ξ (°C min)
Ref. 2	TBD	0.78	190	210	5.0	1.955E-05	0.4875	24938
Ref. 3	TBD:MSA	0.91	180	120	6.5	4.213E-05	0.5440	12911
This work	Si-TEA	0.89	190	102	4.1	4.592E-05	0.3483	7585
	Si-TBD	0.88	190	102	4.1	4.541E-05	0.3523	7758

References

1 E. Barnard, J. J. R. Arias and W. Thielemans, *Green Chem.*, 2021, **23**, 3765–3789.

2 K. Fukushima, D. J. Coady, G. O. Jones, H. A. Almegren, A. M. Alabdulrahman, F. D. Alsewailem, H. W. Horn, J. E. Rice and J. L. Hedrick, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 1606–1611.

3 C. Jehanno, I. Flores, A. P. Dove, A. J. Müller, F. Ruipérez and H. Sardon, *Green Chem.*, 2018, **20**, 1205–1212.

4 R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273–1283.

[a] Thielemans and co-workers proposed a modification of the E factor, considering that it has been established that 90% of solvents are recycled in industrial processes.[4]