Electronic Supplementary Information

Boosting the kinetics of PET Glycolysis

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A. Detailed Experimental Section

A.1 Materials

Table S1 presents a comprehensive list of the chemicals used in this study, along with their purities.

Table S1: Characteristics of chemicals used in this work.

Chemical	Abbreviation	CAS	M /$\mathrm{g\,mol^{-1}}$	Supplier	Type	Purity /w.-%
Poly(ethylene terephthalate)	PET	25038-59-9	$58{,}000^a$	Colorless single-use post-consumer bottles ("JA")		
Ethylene glycol	EG	107-21-1	62.07	Sigma-Aldrich	ReagentPlus	99
Zinc acetate	ZnAc$_2$	557-34-6	183.48	Sigma-Aldrich		99.99
γ-valerolactone	GVL	108-29-2	100.12	Sigma-Aldrich	ReagentPlus	99
Water	H$_2$O	7789-18-5	18.015	Deionized		
Acetone	-	67-64-1	58.08	VWR international	TECHNICAL	99
Bis(2-hydroxyethyl) terephthalate	BHET	959-26-2	254.238	Sigma-Aldrich		98.1
Methanol	-	67-56-1	32.04	VWR international	HiPerSolv	99.8

^{a} Mass average molecular weight determined by ASTM D 4603 standard test method in previous work[1]

The PET used in this study was sourced from colorless single-use post-consumer "JA" water bottles. To eliminate surface residues such as glue and ink, a minimal amount of acetone was used. Subsequently, the caps and labels were removed; further, the top and bottom part of the bottles were not used because of the enlarged wall thickness. The remaining material was manually cut into 5×5×0.2 mm pieces. Following this, the PET particles were shred into small particles using a grinder (Quadblade CH 580, Kenwood Ltd). These crushed PET particles underwent fractionation in a sieving tower. Unless otherwise stated, the experiments were carried out with a particle size fraction of $0.2 \leq d_p < 1$ mm.

A.2 Sample Preparation for PET Glycolysis kinetic investigations

The experiments were conducted in 20 ml glass vials, that served as batch reactors. About 0.65 g of PET was transferred to each glass vial. The relatively small PET particle size ($0.2 \leq d_p < 1$ mm), although not currently employed in industrial applications, was chosen

for its ability to enable homogeneous mixing of the reactants in our small glass vial reactor, as previously investigated.[2] Subsequently, a specific quantity of the $ZnAc_2$/EG catalyst solution was added. Additionally, pure EG and, when under investigation, GVL were transferred to the vial. For all experiments, the molar ratio of PET's repeating unit to $ZnAc_2$ ($\frac{n^0_{PETru}}{n_{ZnAc_2}}$) at the beginning of the reaction was set to 50 to accelerate the depolymerization accordingly. Moreover, the initial mass ratio of solvent to PET ($\frac{m^0_{EG}+m_{GVL}}{m^0_{PET}}$) was maintained at 6. This choice not only ensures a sufficient space-time yield of produced BHET per input material PET but also facilitates easier handling of the suspension due to lower viscosity. Finally, the overall liquid volume in each reaction vial resulted in approximately 3.5 ml. Afterwards, a small magnetic stirrer was added.

A.3 Set-Up and Procedure for PET Glycolysis kinetic investigations
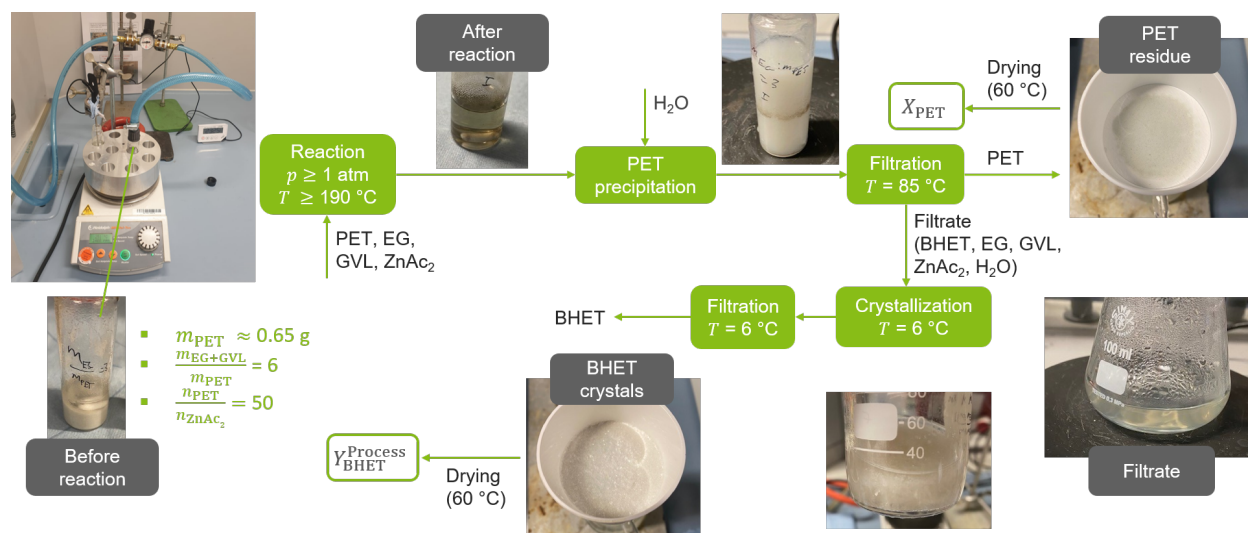
The experimental set-up is illustrated in Figure S1.

Figure S1: Experimental set-up of our lab scale process (adapted from[2,3]).

In order to conduct the depolymerization reactions, a magnetic hot plate stirrer (Heidolph MR Hei-Tec) was used. A cylindrical alumina heating block with perforations for holding the glass vials was positioned on the heating plate. Before initiating the reaction, the heating block was preheated to the desired temperature. As mentioned earlier, all the samples

including the catalyst were prepared at ambient conditions and put in the pre-heated aluminum block for the reaction. The time required for the samples to reach the desired reaction temperature was preliminary investigated. Figure S2 illustrates temperature profiles of thermal oil samples with a heat capacity comparable with that of EG in the heating block after transitioning from ambient conditions.
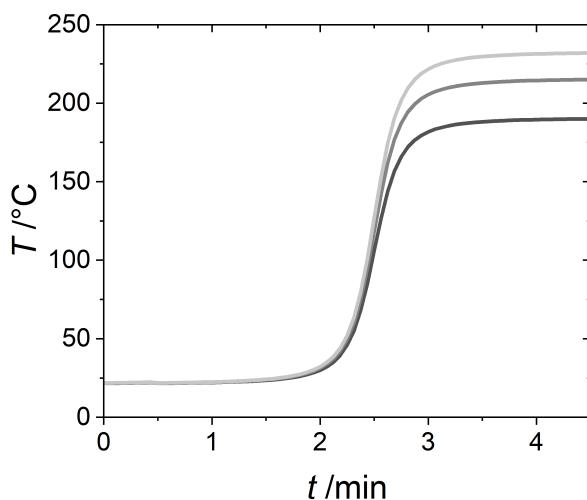

Figure S2: Temperature profiles of thermal oil samples while heating up from ambient temperature to 190 °C (dark grey), 215 °C (mid-grey) and 232 °C (dark grey) at 1 bar and a stirrer speed of 1400 rpm.

The sigmoidal temperature profiles indicate a time of 3 minutes to reach the intended reaction temperature. During the kinetic investigations, temperature monitoring of the suspensions was carried out using a thermometer (TFA Dostmann LT-101) with an accuracy of ± 0.5 K, placed in a reference vial containing the aforementioned thermal oil. For pressurized reactions, the glass vials were connected to an air pressure port, as illustrated in Figure S1. Following pressure adjustments, if necessary, the vials were placed inside the heating block for 3 minutes of pre-heating plus the specified reaction time. To mitigate the influence of the pre-heating on the reaction kinetic results, the experimental data points were assigned by a dead time of 3 minutes; this is reasonable since it is known from literature that the depolymerization of PET hardly takes place at temperatures lower than 170 °C.[3,4] Stirring at 1400 rpm was applied to ensure uniform mixing of the samples. Subsequently, the samples

were withdrawn and allowed to cool to 90 °C without external utilities. After removing the caps, the vials were filled with 14 ml of hot (90 °C) water, enabling an easier transfer and further treatment of these reaction mixtures. The suspensions were filtered using glass microfiber filters (grade GF/C-1.2 µm, Whatman) by applying vacuum. Thereby, the original reaction mixtures were separated into two different fractions. The solid residual fraction, primarily composed of unconverted PET, and the liquid filtrate fraction, consisting mainly of BHET, EG, water and $ZnAc_2$. The residue solid fraction was dried overnight in an oven at a temperature of 60 °C to determine the conversion of the initial PET substrate using Equation S1.

$$X_{PET} = \frac{m^0_{PET} - m_{PET}}{m^0_{PET}} \cdot 100 \tag{S1}$$

Here m^0_{PET} is the initial mass of PET and m_{PET} denotes the mass of incompletely depolymerized PET after a certain reaction time, obtained from weighing the filter paper with dried material.

The filtrate fraction was stored in the refrigerator at 6 °C overnight to induce crystallization of the BHET product. The resulting white crystalline BHET was subsequently filtered (MN GF-1-0.7 µm, Macherey-Nagel) under vacuum. The crystals were then dried overnight in an oven at a temperature of 60 °C. To calculate the process yield Equation S2 was applied.

$$Y^{process}_{BHET} = \frac{m_{BHET}/M_{BHET}}{m^0_{PET}/M_{PETru}} \cdot 100 \tag{S2}$$

In this equation, m_{BHET} represents the mass of crystallized and dried BHET, while M denotes the molecular weight. Therefore, the process yield quantifies the number of BHET molecules obtained as a solid product from the entire PET glycolysis process per mole of PET's repeating unit. Table 2 provides an overview of all the experimental kinetic series conducted in this work classified in the respective objectives mentioned in the introduction. Every experimental data point was measured twice. Based on that, a mean value and a standard deviation was calculated for the PET conversion X_{PET} and process yield $Y^{process}_{BHET}$.

A.4 Analytical Quantification of Glycolysis Products

Previous studies[2,3] already have demonstrated the feasibility of selectively isolating unconverted PET from the residual filtrate using the procedure described earlier. Additionally, it has been confirmed in these studies, that the crystallized solid in the obtained filtrate predominantly comprises the BHET monomer with minor quantities of the BHET dimer. Hence, this work streamlined the analysis of solid residues to exemplary samples. Differential Scanning Calorimetry (DSC) was employed for dried PET residue samples, while dried product samples were subject to High Performance Liquid Chromatography (HPLC).

DSC was employed to determine the melting temperature and enthalpy of samples. For this purpose, samples weighing 5-8 mg were placed into hermetically sealed aluminum pans. They were heated with a heating ramp of $5 \, \text{K} \, \text{min}^{-1}$ in a Q2000 DSC, which was equipped with a RCS90 cooling device by TA instruments (Eschborn, Germany). The sample cell underwent purging with a nitrogen flow of $50 \, \text{ml} \, \text{min}^{-1}$.

HPLC was employed to determine the composition of samples. Therefore, about $5 \, \text{mg}$ of the original samples were dissolved in $1 \, \text{ml}$ of GVL and analyzed in Agilent 1260 Infinity II HPLC. The HPLC was equipped with a C18 column (Agilent Poroshell 120 EC) and UV detector set at $248 \, \text{nm}$. An injection volume of $2 \, \mu\text{l}$ was utilized, and the column temperature was maintained at $30 \, °\text{C}$. The HPLC analysis was performed using a mixture of methanol/water as the mobile phase at a flow rate of $1 \, \text{ml} \, \text{min}^{-1}$. Initially, $5 \, \text{v.-\%}$ methanol was flushed for $1 \, \text{minute}$, followed by a continuous increase in methanol content over 13 minutes until reaching $100 \, \text{v.-\%}$. Finally, pure methanol was flushed for additional 6 minutes.

A.5 Measuring methods to access the GVL influence on reaction kinetics

Three experimental procedures were implemented to explore the hypothesis of enhanced kinetics attributed to GVL due to enhanced PET dissolution. Deviations from our con-

ventional procedure described in sections 2.2 and 2.3 or more detailed in A.2 and A.3 are explained below. PET particles with dimensions of 5×5×0.2 mm were utilized in all experiments. Additionally, a substantial GVL amount according to $\frac{m_{GVL}}{m_{EG}^0} = 0.946$ was chosen, along with $\frac{m_{EG}^0}{m_{PET}^0} = 6$, $T = 190\,°C$, $p = 1\,\text{bar}$, $\frac{n_{PETru}}{n_{ZnAc_2}} = 50$ and a stirrer speed of 1400 rpm. In the first procedure, samples were prepared and placed in the heating block following the conventional method described earlier. This involved preparing samples at ambient conditions, subjecting them to 3 minutes of pre-heating, and then proceeding with the required reaction time, resulting in a dead time of 3 minutes. In the second procedure, solvents EG, GVL, and ZnAc$_2$ were pre-heated for 3 minutes at the reaction temperature. PET was then added, initiating the reaction time, without any dead time. In the third procedure, PET was dissolved in GVL following Chen et al.[5]'s described procedure. The PET particles underwent a 1-hour swelling time at 120 °C in GVL. Afterwards, the suspensions were heated to the reaction temperature, during which PET completely dissolved. The pre-heated catalyst solution containing EG and ZnAc$_2$ was then added, and the reaction time started, with no dead time applied in these experiments. All subsequent process steps to determine PET conversion X_{PET}, serving as a measure for the influence of the three different procedures, were conducted as described earlier.

B. Detailed description of the kinetic model

As already shown in Figure 1, the reversible PET glycolysis reaction can be modeled as reaction of one mole of PET's repeating unit with one mole of EG giving one mole of BHET monomer. The moles n of the three reactants in the reaction mixture can be accessed from their initial state and the experimentally determined PET conversion over time (see Equation S1) by the following Equations S3, S4 and S5.

$$n_{PETru} = n_{PETru}^0 \cdot \left(1 - \frac{X_{PET}}{100}\right) \tag{S3}$$

$$n_{EG} = n_{EG}^0 - \frac{X_{PET}}{100} \cdot n_{PETru}^0 \tag{S4}$$

$$n_{BHET} = n_{BHET}^0 + \frac{X_{PET}}{100} \cdot n_{PETru}^0 \tag{S5}$$

The mole fraction x_i of the component i is determined by dividing the number of moles n_i by the total number of moles in the reaction system, as expressed in Equation S6.

$$x_i = \frac{n_i}{\sum_{j=1}^{N} n_j} \tag{S6}$$

Building on that, Equation S7 defines the K_x as equilibrium (eq) composition of the reaction mixture.

$$K_x = \frac{x_{BHET}^{eq}}{x_{PETru}^{eq} \cdot x_{EG}^{eq}} \tag{S7}$$

In terms of kinetic modeling, the change of the mole fractions of the reactants along the reaction coordinate can be described via Equation S8.

$$\frac{\mathrm{d}x_{PETru}}{\mathrm{d}t} = \frac{\mathrm{d}x_{EG}}{\mathrm{d}t} = -\frac{\mathrm{d}x_{BHET}}{\mathrm{d}t} = -k \cdot x_{PETru} \cdot x_{EG} + \frac{k}{K_x} \cdot x_{BHET} \tag{S8}$$

The set of differential equations was solved using Matlab™'s *ODE15s* solver, with the initial composition of the reactants serving as the initial condition. Simultaneously, using Matlab™'s internal function *lscurvefit* the kinetic constant k was fitted to the experimental data calculated by Equations S3, S4 and S5 and transferred to mole fractions by Equation S6. Additionally, the *nlparci* function generated the 95 % confidence interval for the k estimate.

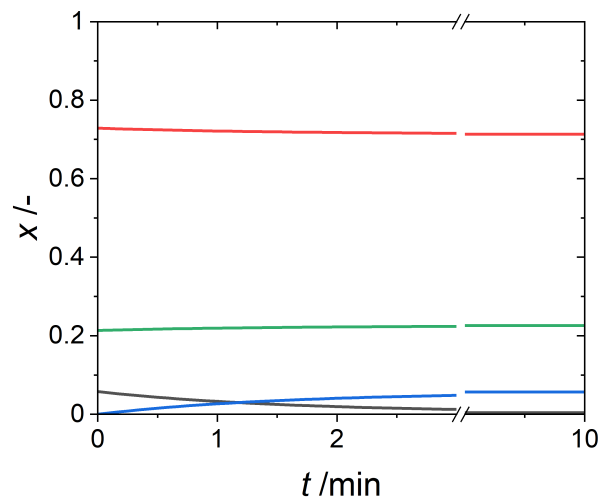# C. Validation of pseudo-first order reversible reaction approach

Figure S3: Mole fraction of EG (red), GVL (green), PETru (grey) and BHET (blue) over reaction time modeled via pseudo-first order reversible reaction approach with the kinetic constant k of 0.0138 s^{-1} and an equilibrium constant K_x of 19.37. Initial conditions were $n_{PET}^0 = 0.0034\,\text{mol}$, $n_{EG} = 0.0428\,\text{mol}$, $n_{BHET} = 0\,\text{mol}$ and $n_{GVL} = 0.0125\,\text{mol}$.
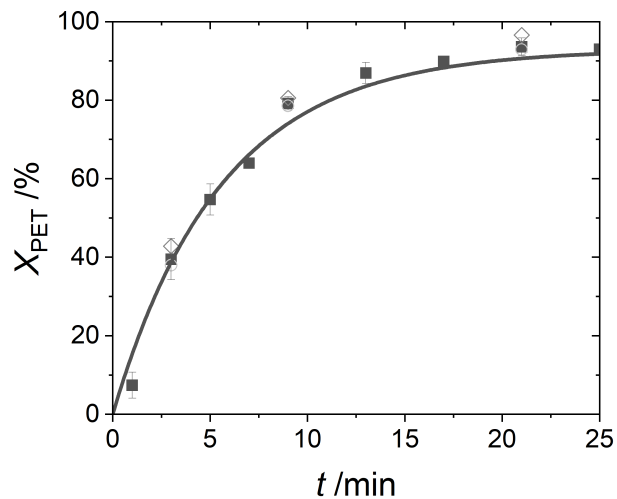
D. Pressure influence on reaction kinetics

Figure S4: PET conversion X_{PET} over reaction time t for different pressures: $p = 1\,\mathrm{bar}$ (squares full), $p = 2\,\mathrm{bar}$ (circles open) and $p = 3\,\mathrm{bar}$ (diamonds open) at $T = 190\,°\mathrm{C}$ with $\frac{m_{GVL}}{m_{EG}^0} = 0$, $\frac{m_{EG}^0 + m_{GVL}}{m_{PET}^0} = 6$, $\frac{n_{PETru}}{n_{ZnAc_2}} = 50$, $0.2 \leq d_p < 1\,\mathrm{mm}$ and a stirrer speed of $1400\,\mathrm{rpm}$ experimentally determined (symbols) and modeled for $T = 190\,°\mathrm{C}$ & $p = 1\,\mathrm{bar}$ (line) via pseudo-first order reversible reaction approach with the kinetic constant k of $0.0029\,\mathrm{s}^{-1}$ and an equilibrium constant K_x of 14.04.

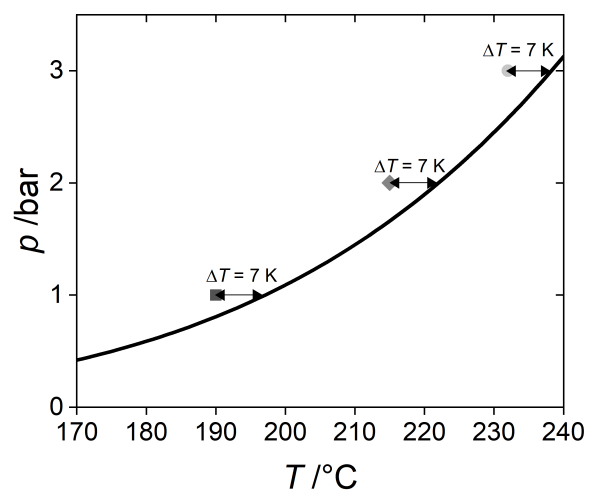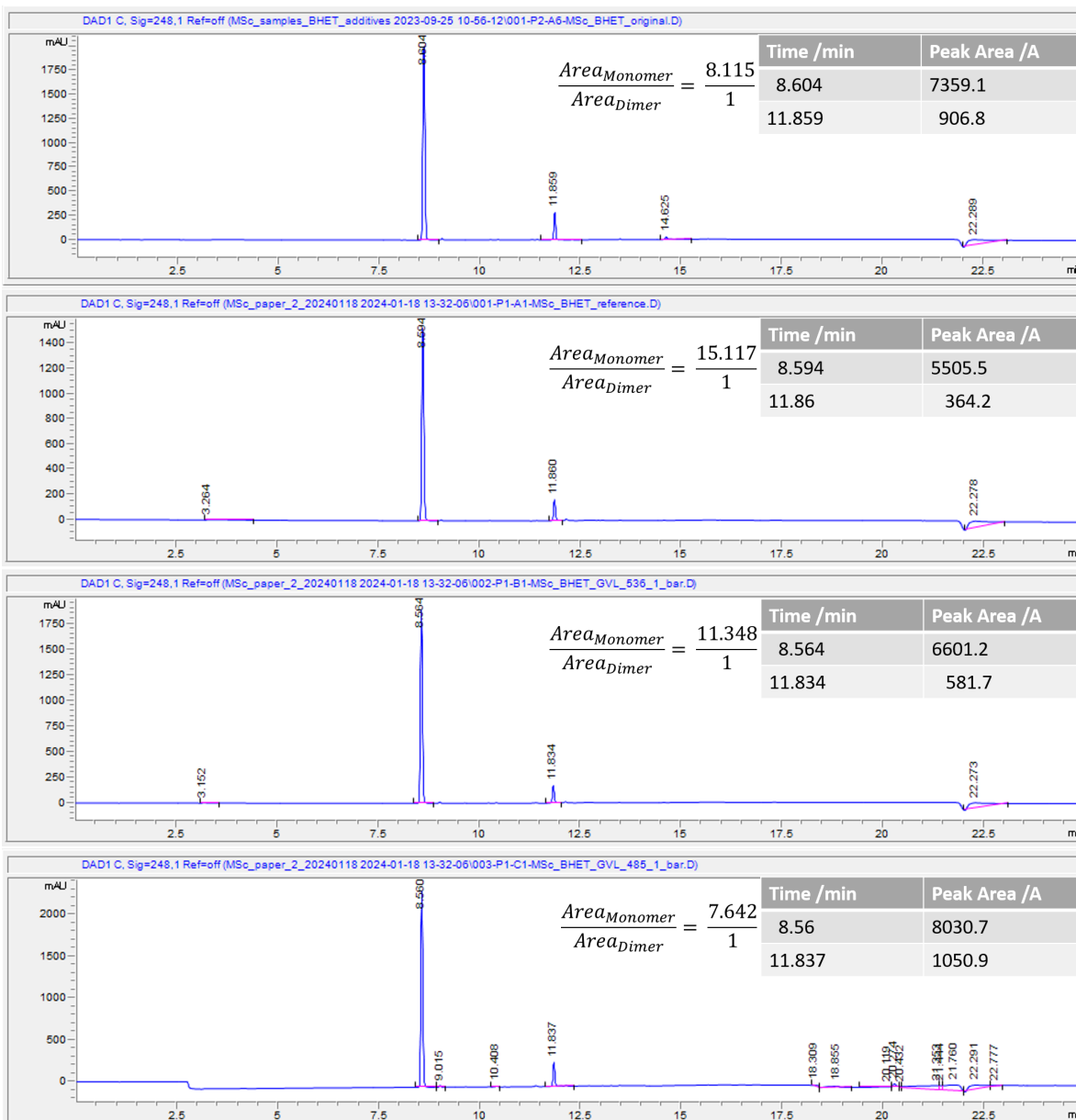# E. Temperature selection for pressurized reactions

Figure S5: Vapor pressure of EG as a function of temperature.[6] To prevent boiling of the solvent/reactant EG an uniform temperature difference of 7 K from the boiling curve was chosen. The so-chosen reaction conditions were 1 bar & 190 °C (dark grey square), 2 bar & 215 °C (mid-grey diamond) and 3 bar & 232 °C (light grey circle).

F. Analytical results

F.1 HPLC Results

DAD1 C, Sig=248,1 Ref=off (MSc_samples_BHET_additives 2023-09-25 10-56-12\001-P2-A6-MSc_BHET_original.D)

$$\frac{Area_{Monomer}}{Area_{Dimer}} = \frac{8.115}{1}$$

Time /min	Peak Area /A
8.604	7359.1
11.859	906.8

DAD1 C, Sig=248,1 Ref=off (MSc_paper_2_20240118 2024-01-18 13-32-06\001-P1-A1-MSc_BHET_reference.D)

$$\frac{Area_{Monomer}}{Area_{Dimer}} = \frac{15.117}{1}$$

Time /min	Peak Area /A
8.594	5505.5
11.86	364.2

DAD1 C, Sig=248,1 Ref=off (MSc_paper_2_20240118 2024-01-18 13-32-06\002-P1-B1-MSc_BHET_GVL_536_1_bar.D)

$$\frac{Area_{Monomer}}{Area_{Dimer}} = \frac{11.348}{1}$$

Time /min	Peak Area /A
8.564	6601.2
11.834	581.7

DAD1 C, Sig=248,1 Ref=off (MSc_paper_2_20240118 2024-01-18 13-32-06\003-P1-C1-MSc_BHET_GVL_485_1_bar.D)

$$\frac{Area_{Monomer}}{Area_{Dimer}} = \frac{7.642}{1}$$

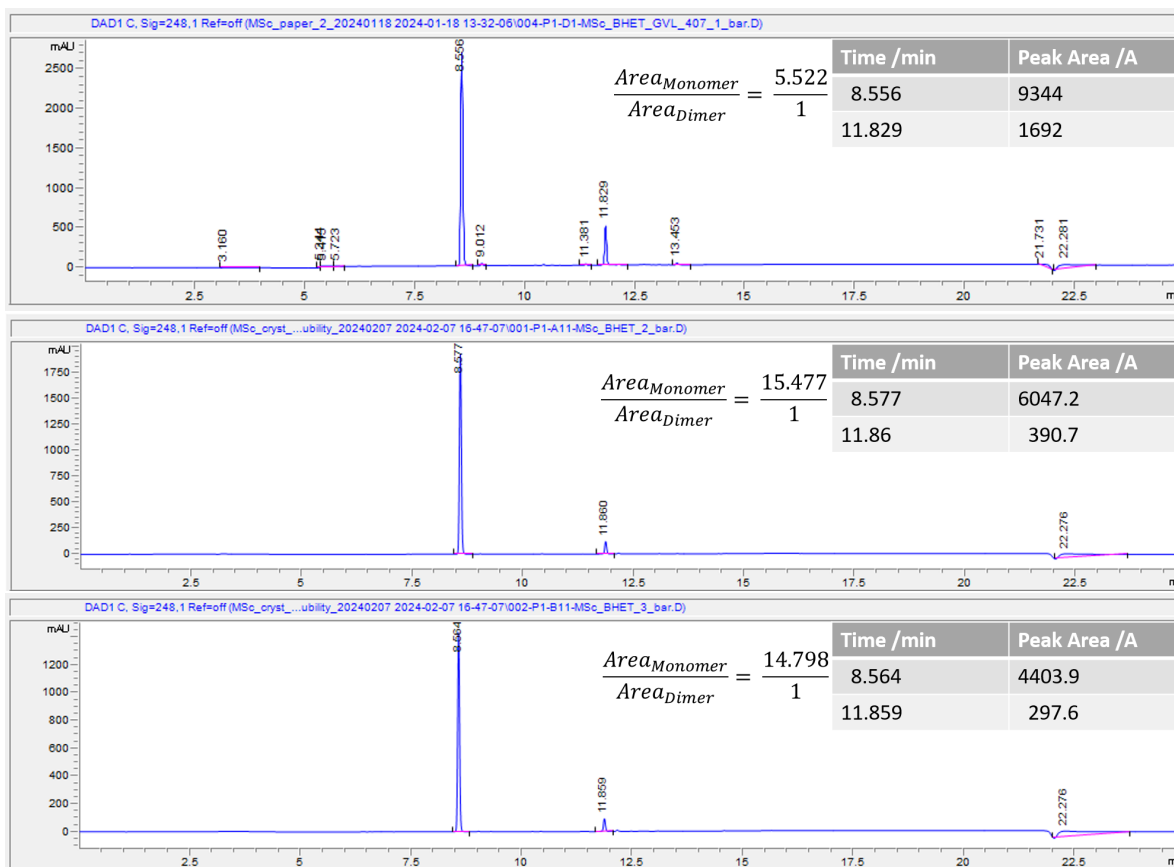| Time /min	Peak Area /A
8.56	8030.7
11.837	1050.9

Figure S7: Determined HPLC chromatograms of the bought BHET monomer by Sigma-Aldrich (top) and BHET produced by ourselves in the following experiments: reference (m_{GVL} / m_{EG}^0 = 0 & T = 190 °C & p = 1 bar); (m_{GVL} / m_{EG}^0 = 0.118 & T = 190 °C & p = 1 bar); (m_{GVL} / m_{EG}^0 = 0.236 & T = 190 °C & p = 1 bar); (m_{GVL} / m_{EG}^0 = 0.473 & T = 190 °C & p = 1 bar); (m_{GVL} / m_{EG}^0 = 0 & T = 215 °C & p = 2 bar); (m_{GVL} / m_{EG}^0 = 0 & T = 232 °C & p = 3 bar) (from top to bottom)
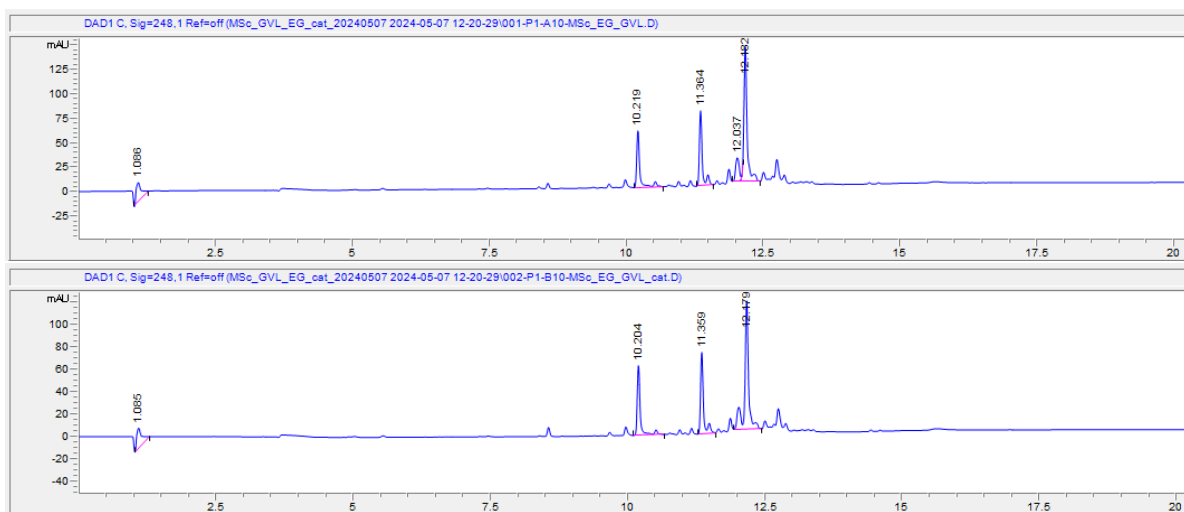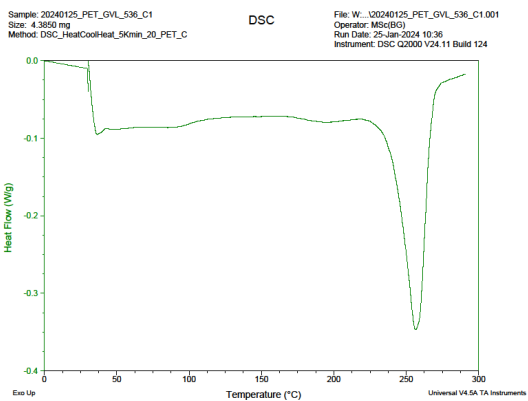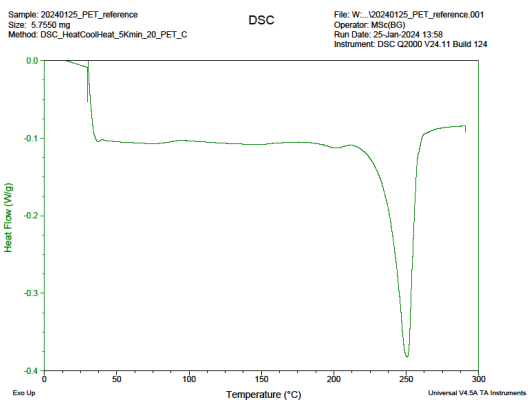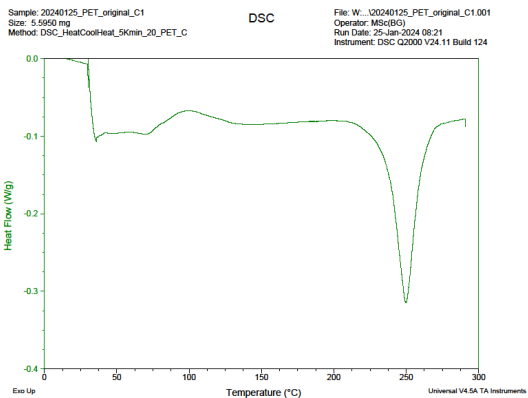
Figure S8: Determined HPLC chromatograms of retrieved filtrates after BHET filtration without ZnAc$_2$ catalysed reaction (top) with ZnAc$_2$ catalysed reaction (bottom) indicate no GVL reaction products due to a possible reaction between ZnAc$_2$ and GVL.
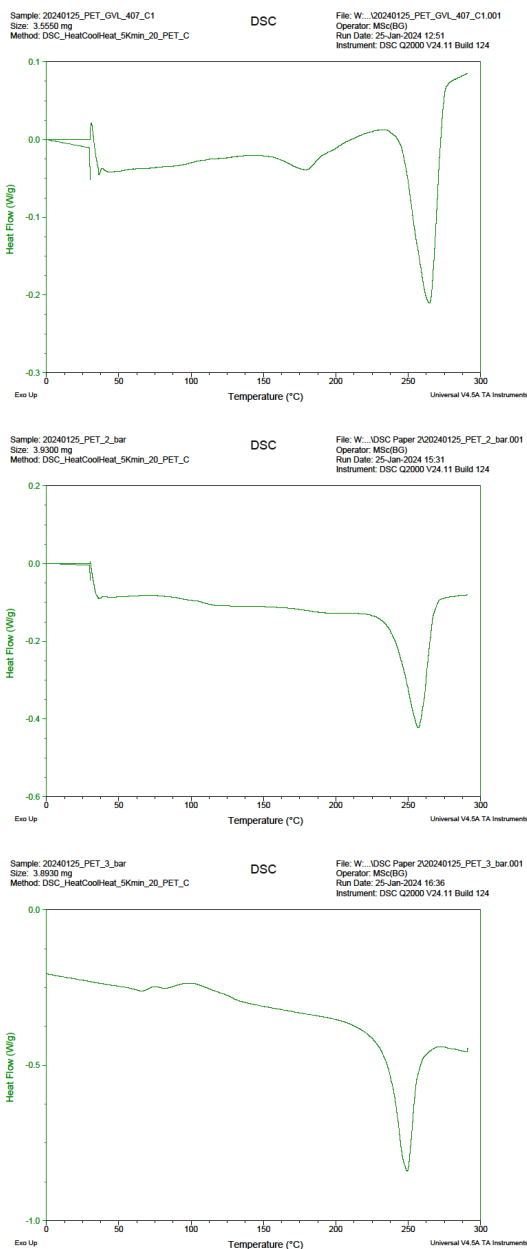
F.2 DSC Results
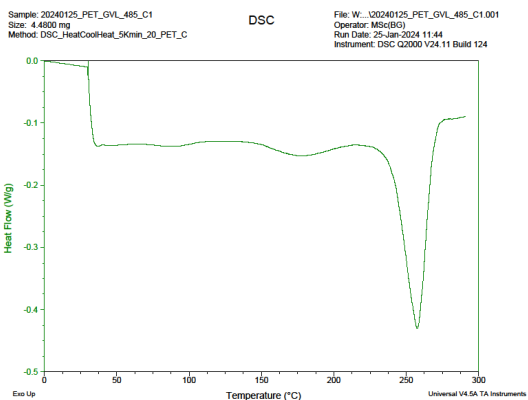
Figure S10: Determined DSC chromatograms of the PET starting material and PET residues from the following experiments: reference (m_{GVL} / $m_{EG}^0 = 0$ & $T = 190\,°C$ & $p = 1\,bar$); (m_{GVL} / $m_{EG}^0 = 0.118$ & $T = 190\,°C$ & $p = 1\,bar$); (m_{GVL} / $m_{EG}^0 = 0.236$ & $T = 190\,°C$ & $p = 1\,bar$); (m_{GVL} / $m_{EG}^0 = 0.473$ & $T = 190\,°C$ & $p = 1\,bar$); (m_{GVL} / $m_{EG}^0 = 0$ & $T = 215\,°C$ & $p = 2\,bar$); (m_{GVL} / $m_{EG}^0 = 0$ & $T = 232\,°C$ & $p = 3\,bar$) (from top to bottom)

G. Summarized experimental and modeling results of the kinetic series

Table S2: Experimental and modeling results of the kinetic series investigated in this work.

	Objective		Reference	GVL influence		
	Series	No.	1	2	3	4
Investigated parameters	$\frac{m_{GVL}}{m_{EG}^0}$	/g·g^{-1}	0	0.118	0.236	0.473
	$\frac{m_{EG}^0+m_{GVL}}{m_{PET}^0}$	/g·g^{-1}	6	6	6	6
	$\frac{m_{EG}^0}{m_{PET}^0}$	/g·g^{-1}	6	5.36	4.85	4.07
	p	/bar	1	1	1	1
	T	/°C	190	190	190	190
Experimental results	t^{eq}	/min	≈ 21	≈ 9	≈ 7	≈ 5
	X_{PET}^{eq}	/%	92.99	91.92	90.24	93.25
	K_x	/mol·mol^{-1}	14.04	12.98	11.35	19.37
	$Y_{BHET}^{process,eq}$	/%	79.98	72.52	61.28	54.73
	$x_{Monomer}^{product}$	/mol·mol^{-1}	0.9514	0.9398	0.9281	0.9214
Initial conditions	n_{PETru}^0	/mol	0.0035	0.0034	0.0034	0.0034
	n_{EG}^0	/mol	0.0650	0.0564	0.0510	0.0428
	n_{BHET}^0	/mol	0	0	0	0
	n_{GVL}	/mol	0	0.0041	0.0075	0.0125
Modeling results	k	/s^{-1}	0.0029	0.0055	0.0080	0.0138
	k lower limit	/s^{-1}	0.0027	0.0051	0.0076	0.0127
	k upper limit	/s^{-1}	0.0030	0.0059	0.0085	0.0149
	$\frac{k}{k_{ref}}$	/-	1	1.9028	2.7952	4.799
	$\frac{k}{k_{ref}}$ lower limit	/-	0.9492	1.7692	2.6327	4.4082
	$\frac{k}{k_{ref}}$ upper limit	/-	1.0508	2.0364	2.9575	5.1918

	Objective		Reference	Pressure and Temperature influence		Combined
	Series	No.	1	5	6	7
Investigated parameters	$\frac{m_{GVL}}{m_{EG}^0}$	/g·g^{-1}	0	0	0	0.118
	$\frac{m_{EG}^0 + m_{GVL}}{m_{PET}^0}$	/g·g^{-1}	6	6	6	6
	$\frac{m_{EG}^0}{m_{PET}^0}$	/g·g^{-1}	6	6	6	5.36
	p	/bar	1	2	3	3
	T	/°C	190	215	232	232
Experimental results	t^{eq}	/min	≈ 21	≈ 4	≈ 0.75	≈ 0.25
	X_{PET}^{eq}	/%	92.99	93.58	95.94	95.9
	K_x	/mol·mol^{-1}	14.04	15.43	24.97	26.71
	$Y_{BHET}^{process}$	/%	79.98	79.13	80.15	75.17
	$x_{Monomer}^{product}$	/mol·mol^{-1}	0.9514	0.9524	0.9503	n.a.
Initial conditions	n_{PETru}^0	/mol	0.0035	0.0035	0.0035	0.0034
	n_{EG}^0	/mol	0.0650	0.0650	0.0650	0.0564
	n_{BHET}^0	/mol	0	0	0	0
	n_{GVL}	/mol	0	0	0	0.0041
Modeling results	k	/s^{-1}	0.0029	0.0134	0.0705	0.1971
	k lower limit	/s^{-1}	0.0027	0.0125	0.0663	0.1820
	k upper limit	/s^{-1}	0.0030	0.0166	0.0747	0.2121
	$\frac{k}{k_{ref}}$	/-	1	4.6796	24.541	68.5908
	$\frac{k}{k_{ref}}$ lower limit	/-	0.9492	4.3615	23.0881	63.3616
	$\frac{k}{k_{ref}}$ upper limit	/-	1.0508	5.7694	25.9937	73.82

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