

Thermo-responsive Catalysts for PET Glycolysis: High-Throughput Design Towards Circular Recycling.

K. F. Batchelor¹, S. T. G. Street³, J. Sutton¹, S. J. Baker¹, O. Young¹, A. P. Dove^{2*}, and J. Wood^{1*}.

¹ School of Chemical Engineering, University of Birmingham, Edgbaston, Birmingham B15 2TT; ² School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT; ³ Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, United Kingdom.

*Corresponding author: j.wood@bham.ac.uk & a.dove@bham.ac.uk

Highlights

- HTE enabled rapid screening of organocatalyst–polymer systems for PET glycolysis.
- DBU–PVPhenol identified as a lead thermo-responsive catalyst showing UCST behaviour.
- Optimised conditions gave high BHET yield with improved sustainability metrics.
- Kinetic modelling showed a shrinking-core mechanism with distinct Ea. values.
- Thermo-response and reaction activity declined, revealing catalyst design challenges.

1. Introduction

Stimuli-responsive catalysts offer compelling opportunities for unconventional reactor design, enabling dynamic control over activity, phase behaviour, and separability within a single process [1]. Poly(ethylene terephthalate) (PET) glycolysis provides a challenging, industrially relevant platform to interrogate such systems, combining heterogeneous mass transfer, high-temperature operation, and evolving reaction media [2]. While organocatalysts offer metal-free, tuneable alternatives to conventional catalysts, their high solubility under reaction conditions limits integration into continuous or recyclable reactor concepts [3–5]. Thermo-responsive catalyst architectures that undergo reversible phase transitions represent a promising route to bridge homogeneous activity with heterogeneous operability. In this work, we design polymer-supported organocatalysts that exhibit Upper Critical Solution Temperature (UCST) behaviour via hydrogen-bond-driven self-assembly. A high-throughput experimentation (HTE) framework was employed to rapidly map catalyst structure–responsiveness–performance relationships, alongside reaction optimisation and kinetic analysis to probe reactor-relevant behaviour and scalability.

2. Methods

A bespoke HTE workflow (**Figure 1B**) was developed to screen 66 organobase–polymer combinations (**Figure 1A**) for coupled thermo-responsive phase behaviour and catalytic activity under glycolysis conditions. Lead systems were synthesised using scalable precipitation routes and characterised by spectroscopic and thermal methods. UCST behaviour and reversibility were quantified using turbidity and UV–Vis measurements across controlled thermal cycles. Catalytic performance was evaluated under inert conditions across a wide temperature and residence-time window, enabling systematic optimisation and acquisition of kinetic data for mechanistic and reactor-level interpretation.

3. Results and discussion

HTE screening rapidly identified a DBU-supported poly(4-vinylphenol) catalyst as a lead thermo-responsive system (**Figure 1C**), exhibiting sharp, reversible UCST-driven phase transitions alongside effective PET depolymerisation activity. Turbidity analysis revealed narrow transition windows (**Figure 1E**, over three cycles) and high reversibility, consistent with temperature-controlled hydrogen-bond association and dissociation (**Figure 1D**). Reaction optimisation identified operating regimes that balance conversion, sustainability metrics, and catalyst loading, while kinetic modelling revealed a shrinking-core mechanism with two distinct kinetic regimes (**Figure 1F**). These regimes are attributed to in situ changes in catalyst speciation arising from the formation of acidic by-products, directly linking catalytic activity to thermo-responsive behaviour under reaction conditions. This coupling between phase behaviour and kinetics highlights both the opportunities and constraints of deploying stimuli-

responsive organocatalysts in unconventional reactor concepts and provides design rules for improving catalyst robustness and process integration.

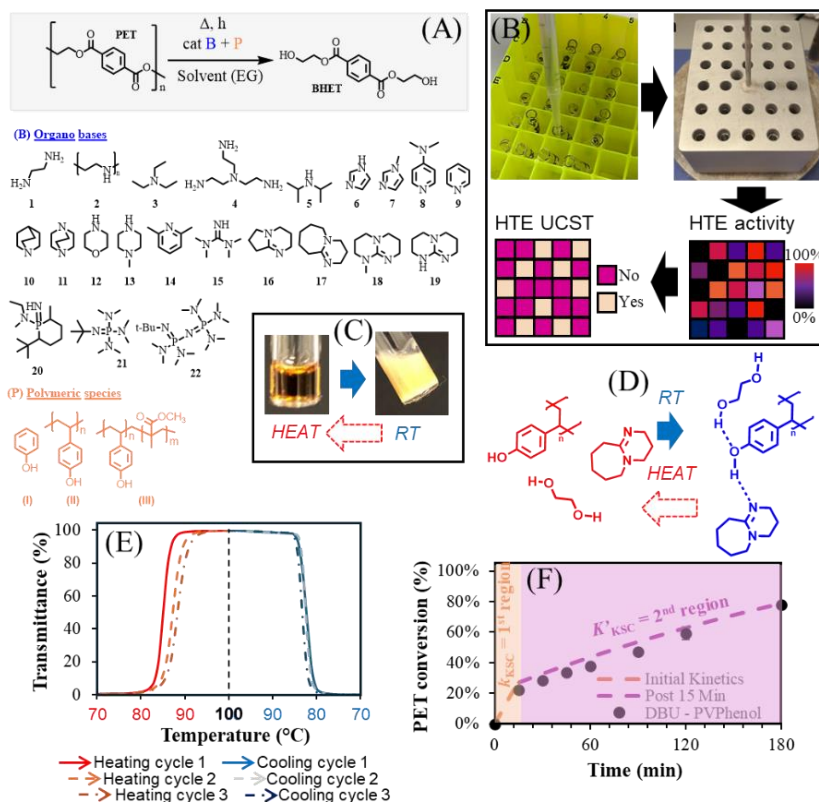


Figure 1. (A) Organo bases and polymers chosen for the HTE screen, (B) HTE methodology flow, (C) Observable UCST response, (D) proposed transition DBU-PVPhenol structures upon heating vs cooling, (E) Turbidity measurements showing temperature dependence, (F) PET Conversion vs time plots of glycolysis kinetic model.

4. Conclusions

High-throughput screening enabled the identification of DBU–poly(4-vinylphenol) as a recyclable, thermo-responsive organocatalysts for PET glycolysis, combining UCST-driven phase switching with effective depolymerisation activity. While reversible recovery could be achieved through temperature-controlled aggregation, catalyst responsiveness diminished in situ due to protonation by acidic by-products, leading to deactivation. These results position UCST-active organocatalysts as promising platforms for integrated catalytic–separation processes, while defining by-product tolerance as the critical design constraint for catalyst design.

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Keywords

“Poly(ethylene terephthalate)” “Glycolysis” “High throughput experimentation screening” “thermo-responsive” “shrinking core kinetics”