

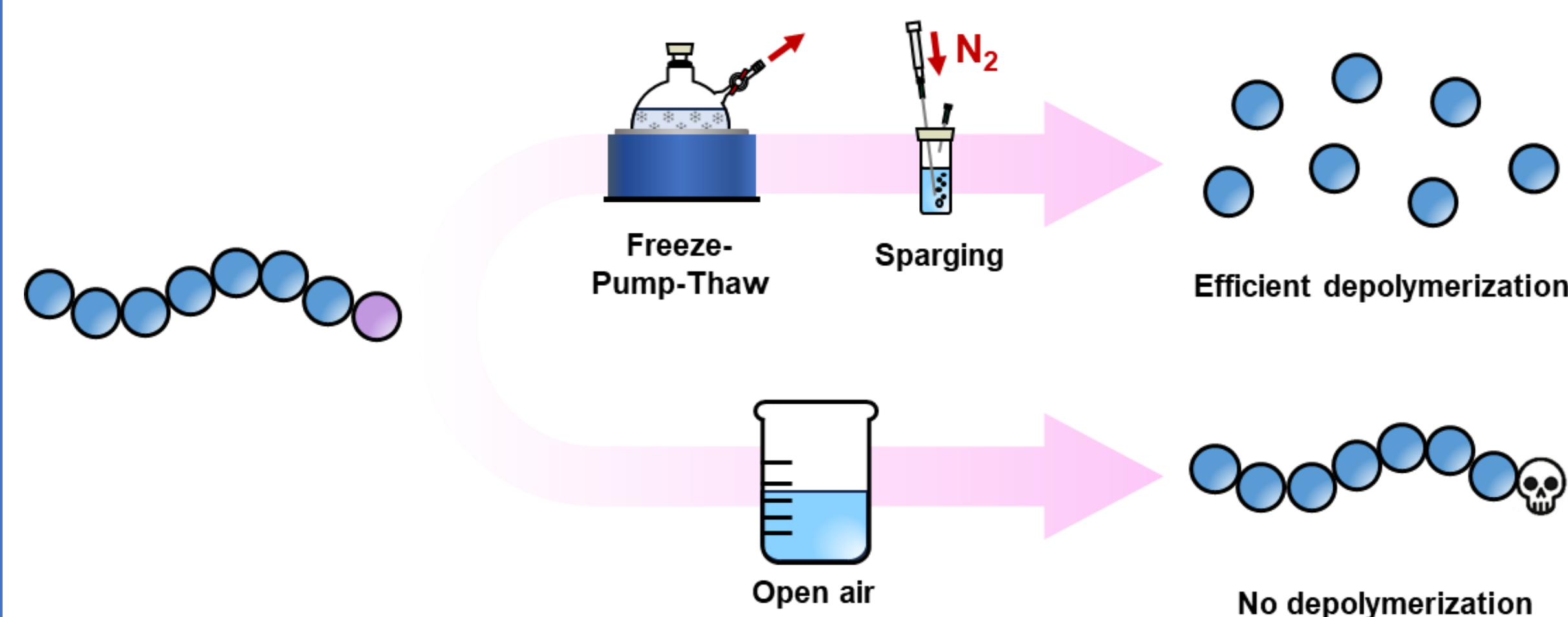
Open-Air Chemical Recycling: Fully Oxygen Tolerant ATRP Depolymerization

Stella Afroditi Mountaki¹, Richard Whitfield¹, Evelina Liarou², Nghia P. Truong¹, Athina Anastasaki¹

¹Laboratory of Polymeric Materials, Department of Materials, ETH Zurich, Zurich 8093, Switzerland

²Department of Chemistry, University of Warwick, Library Road, Coventry, UK

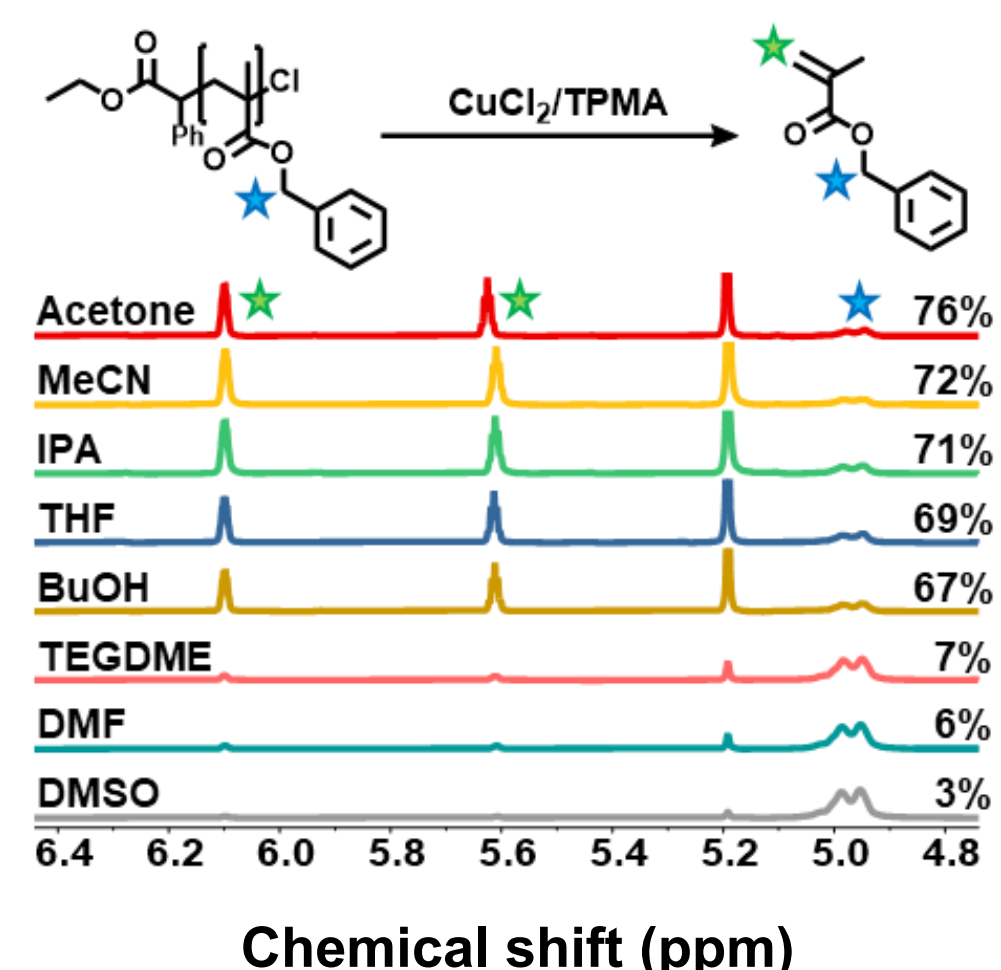
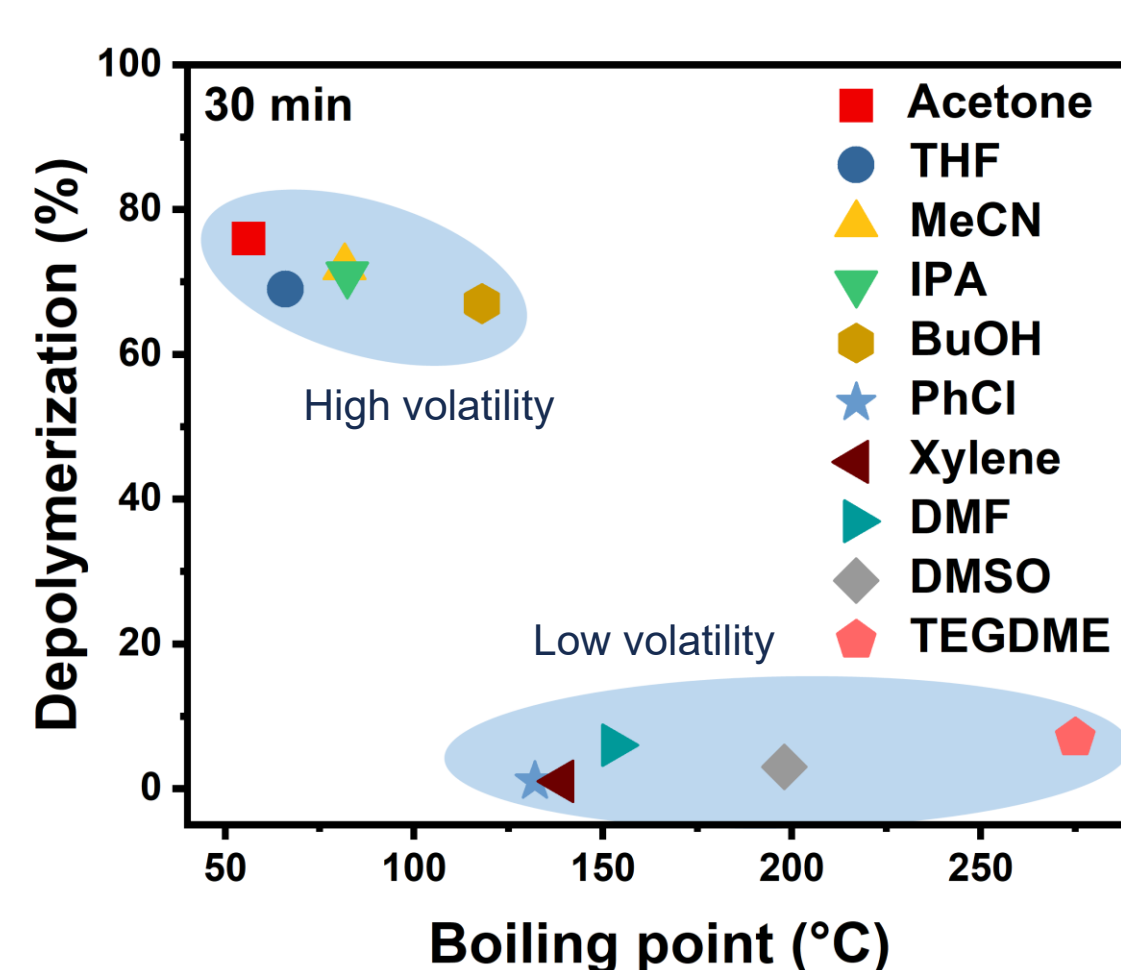
Introduction



While oxygen-tolerant strategies have been overwhelmingly developed for controlled radical polymerizations, the low radical concentrations typically required for high monomer recovery render oxygen-tolerant solution depolymerizations particularly challenging. Here, we present open-air ATRP depolymerization methods achieving over 90% monomer recovery. By using low-boiling co-solvents or external radical sources to remove dissolved oxygen, we enable efficient, oxygen-tolerant depolymerization. These approaches offer a practical and versatile route to chemically recycle ATRP-derived polymers.

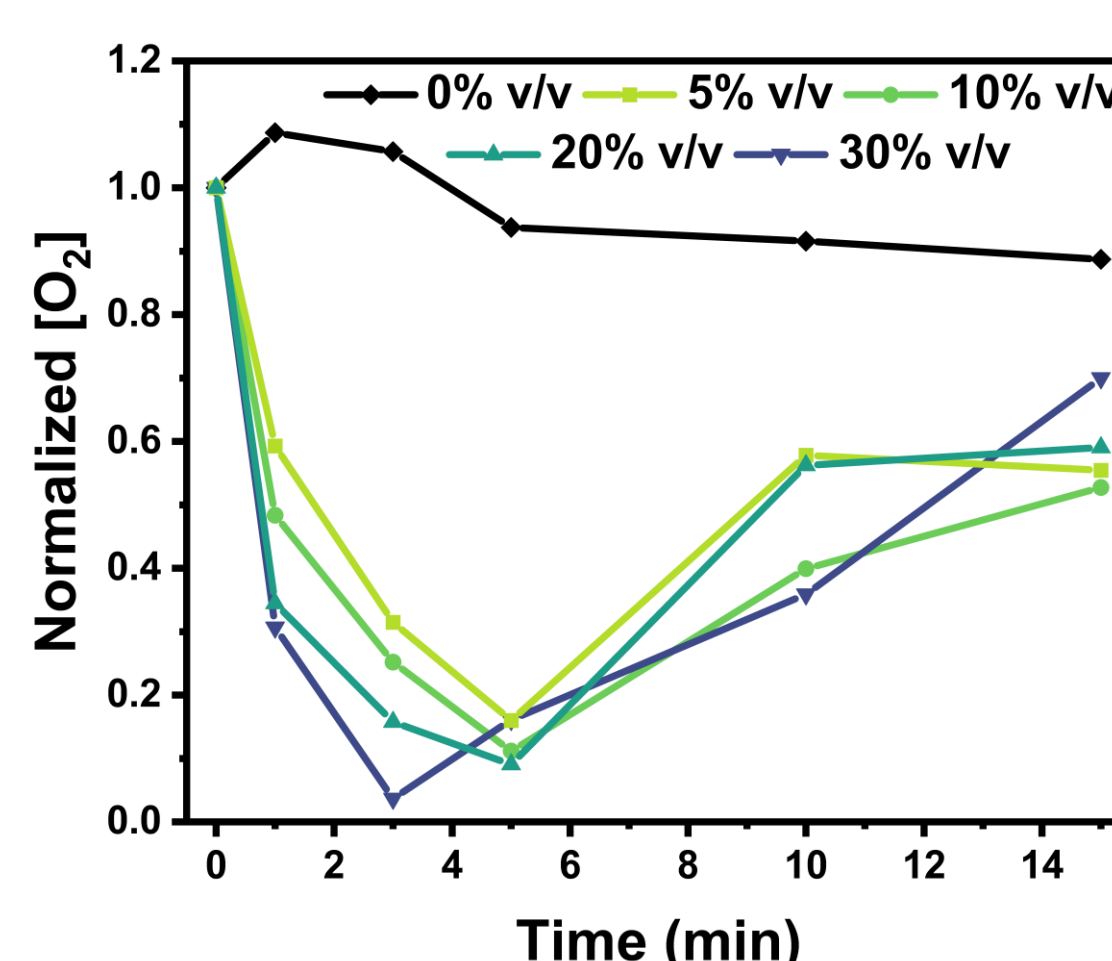
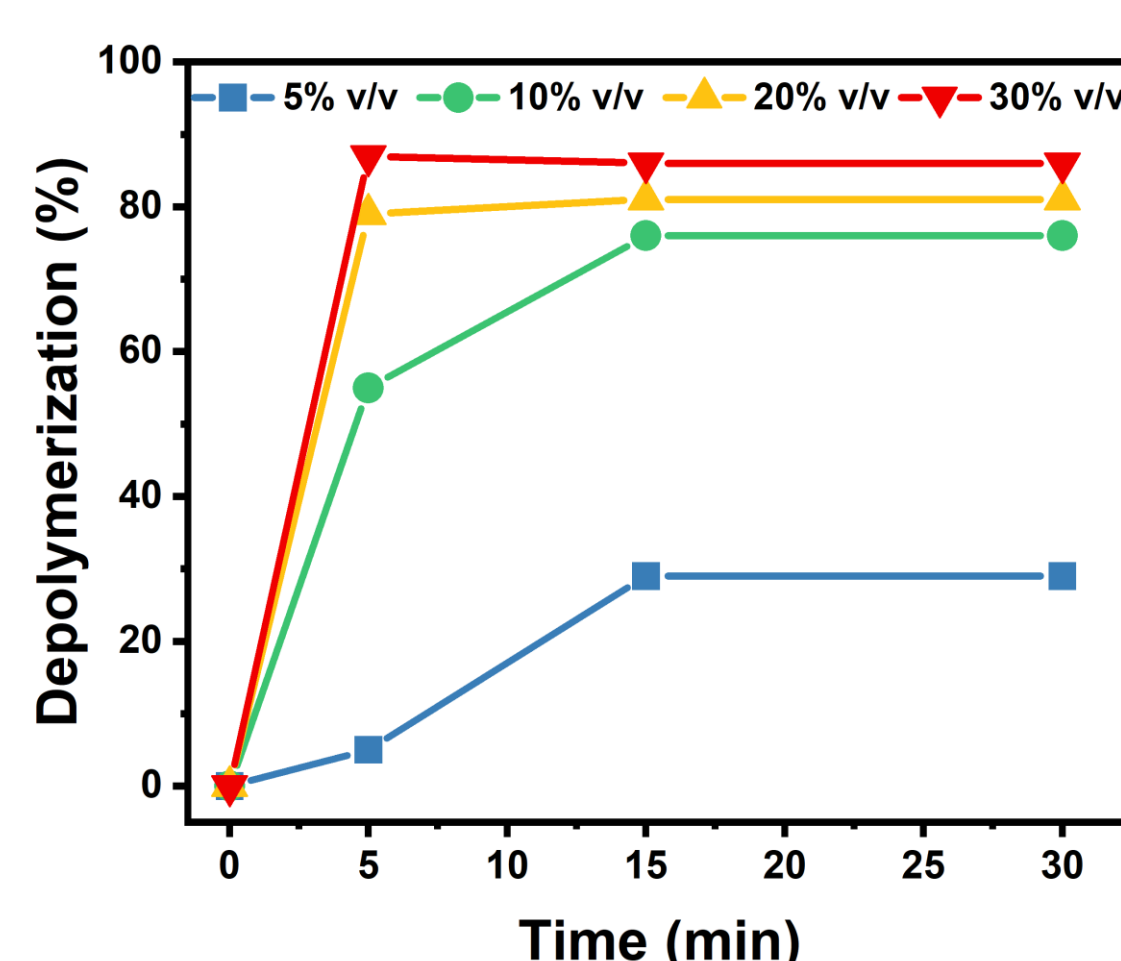
A. Low-boiling point co-solvent

Co-solvent type



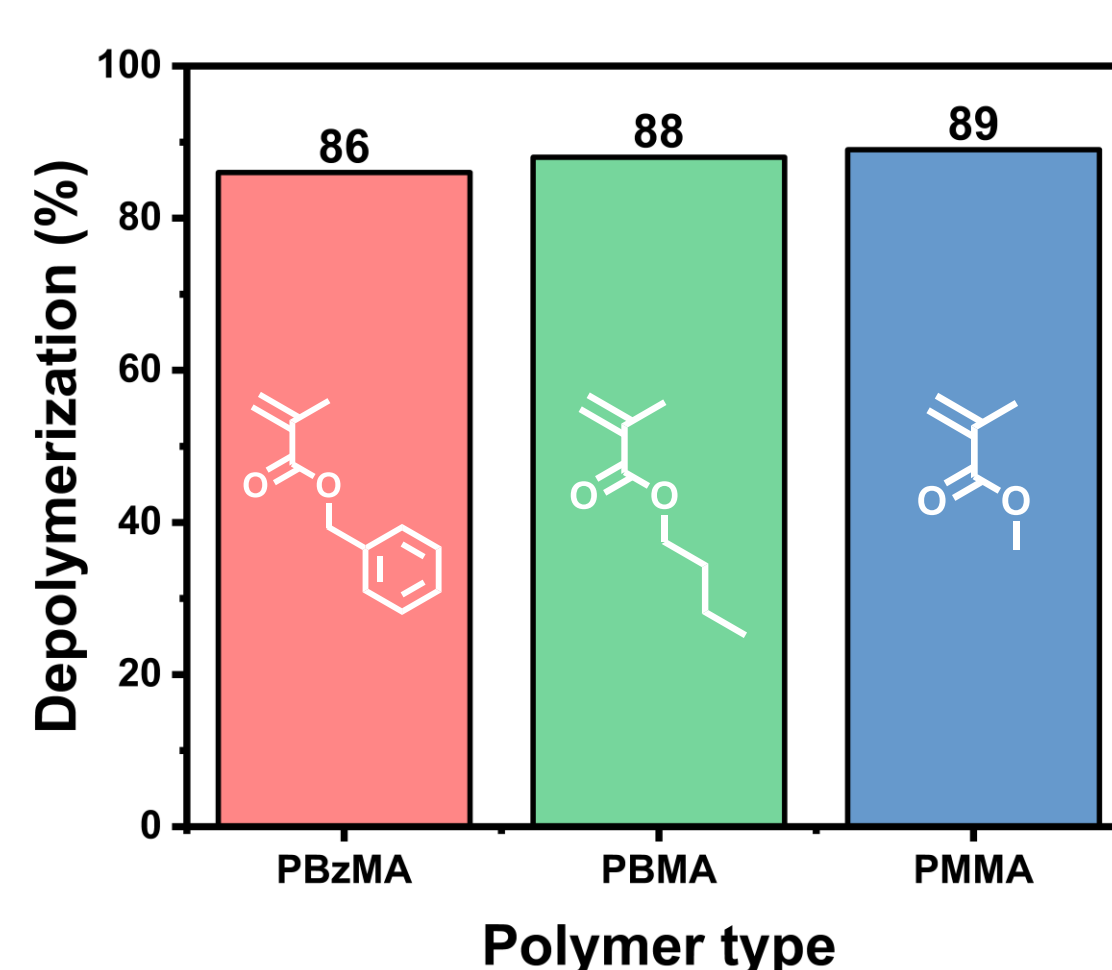
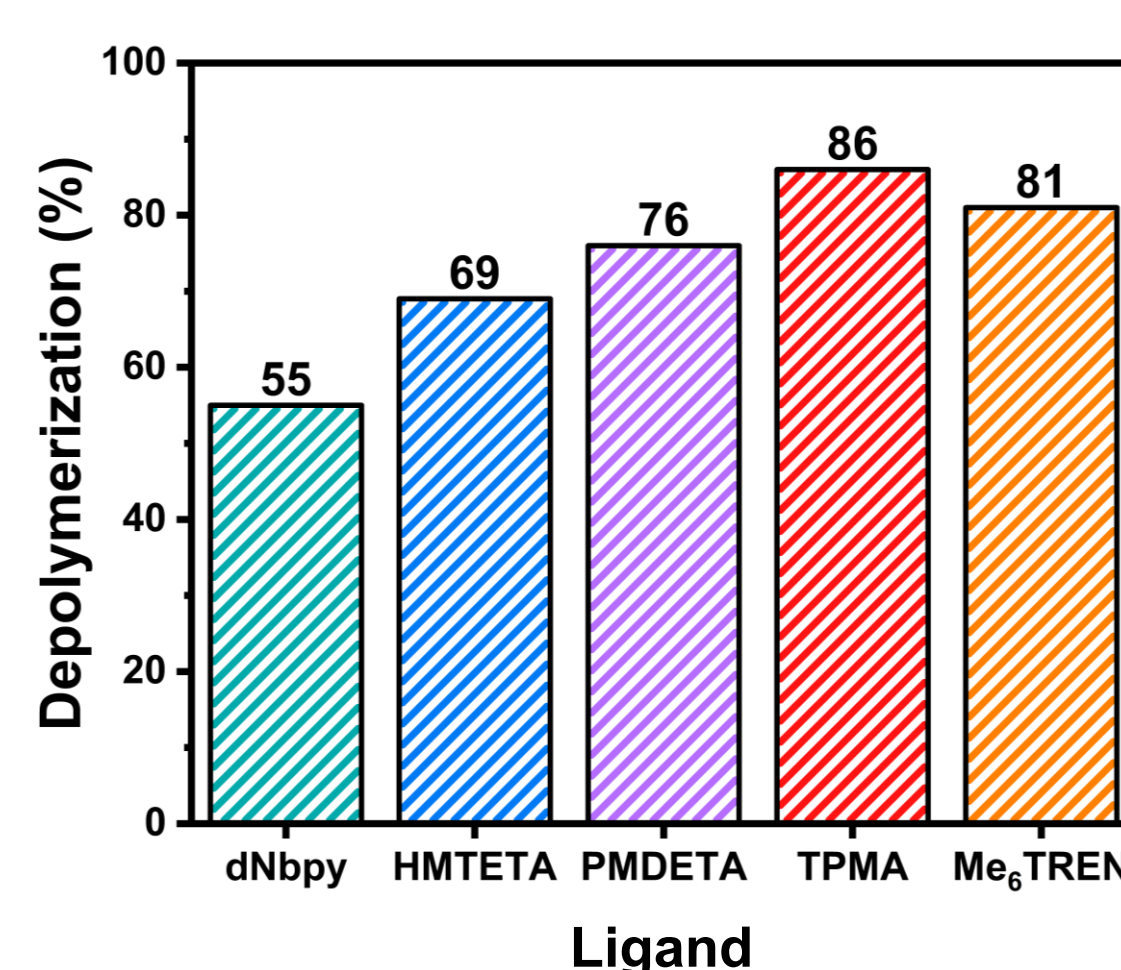
Efficient open-air depolymerization with volatile co-solvents

Co-solvent content



Higher acetone content – higher depolymerization conversion

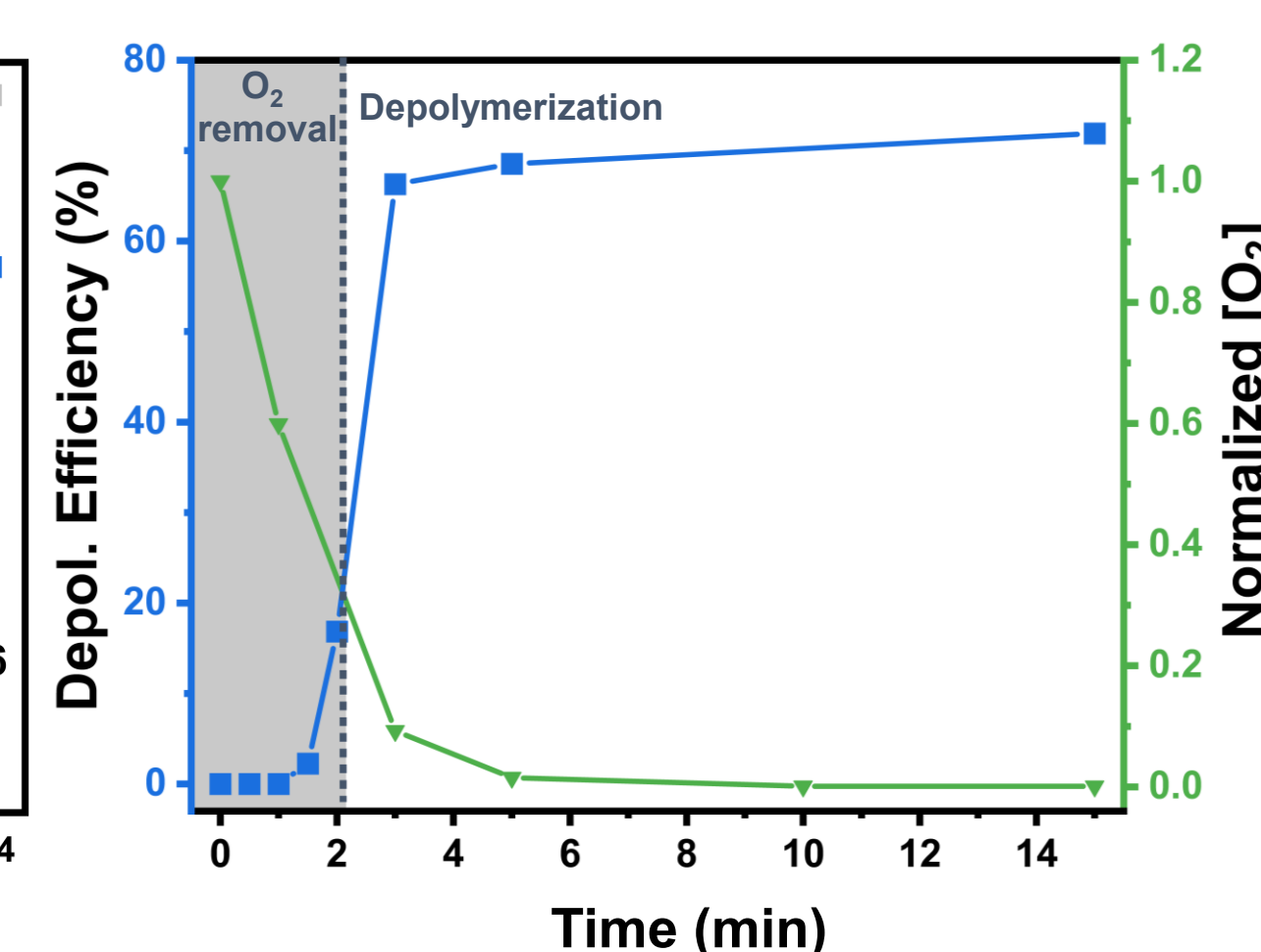
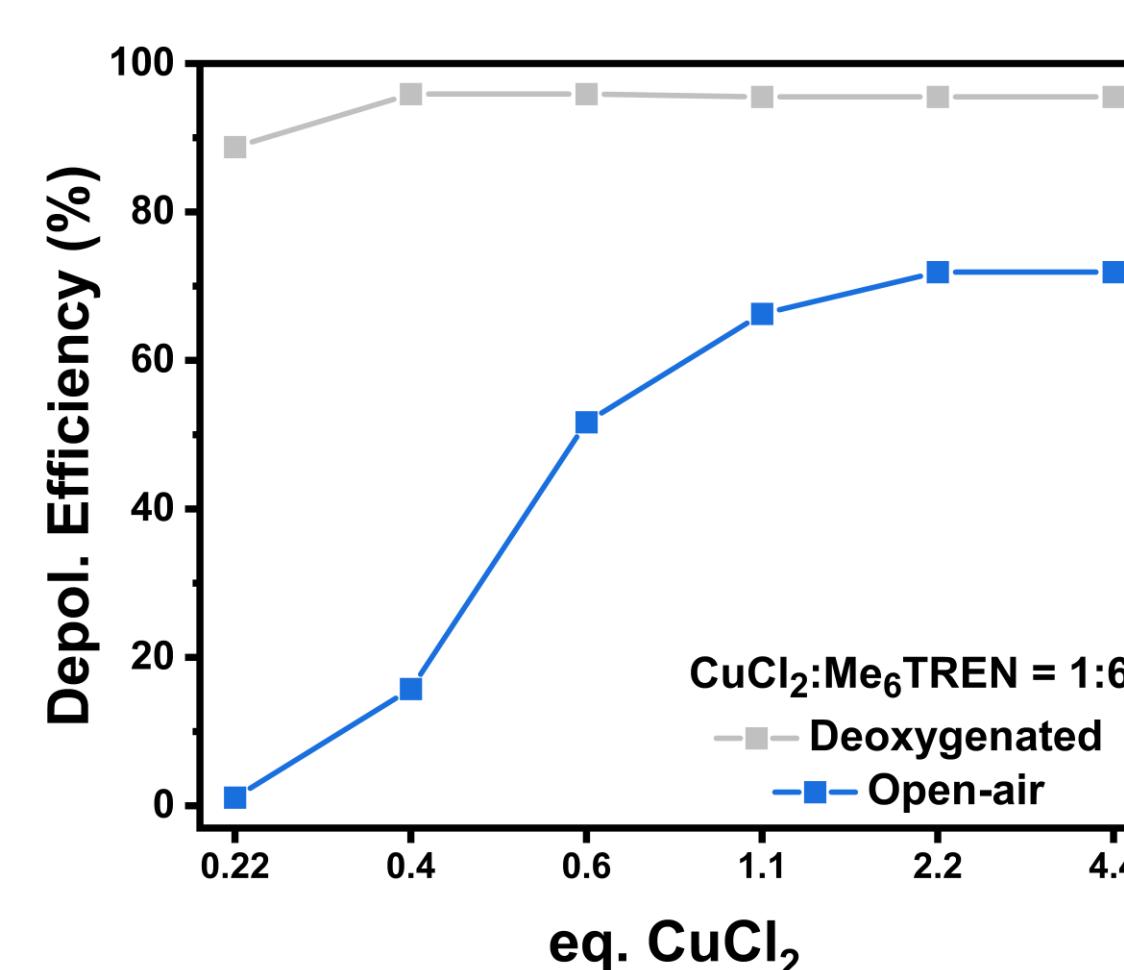
Expanding the scope



Compatible with various ligands and polymethacrylates

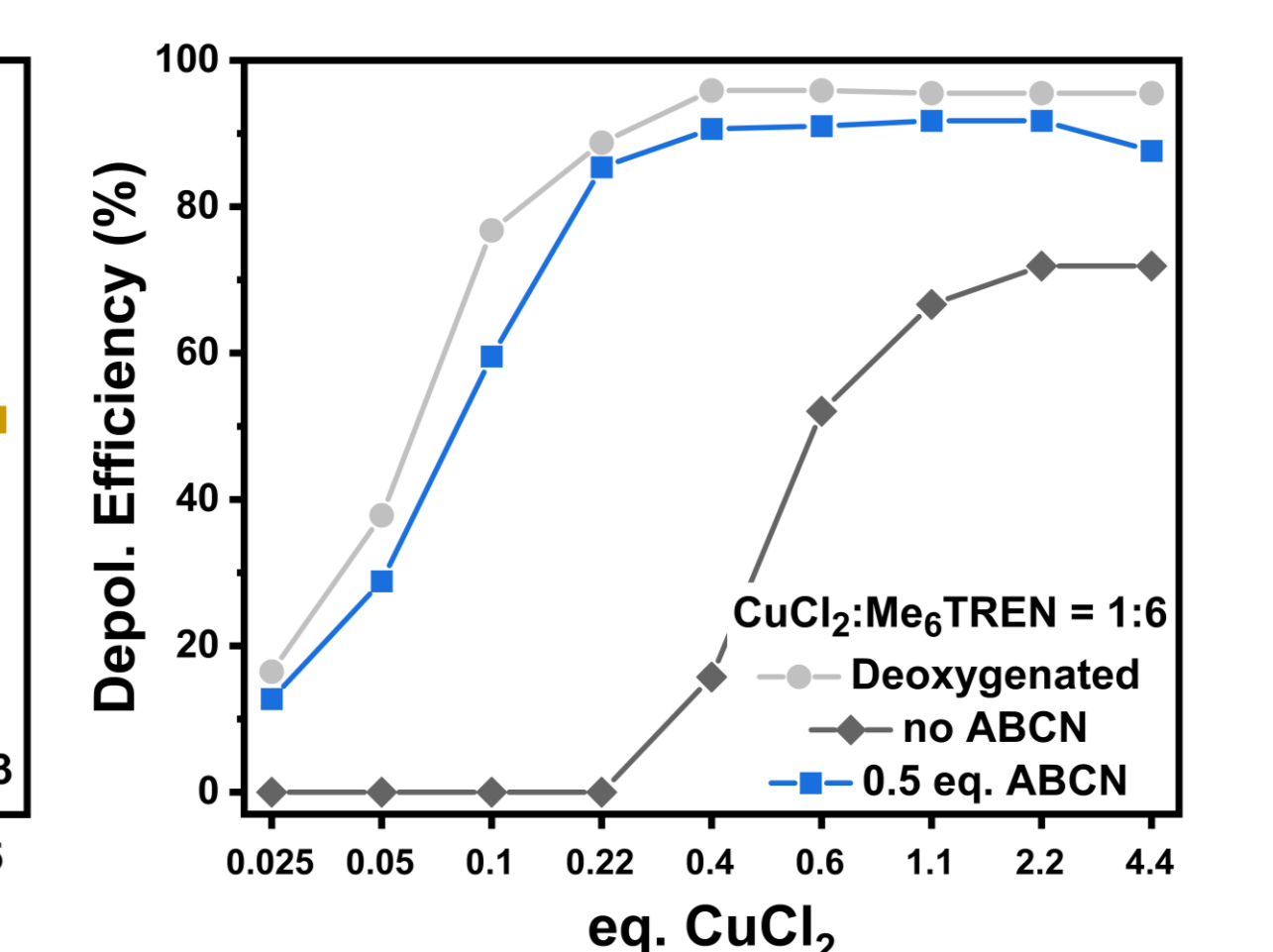
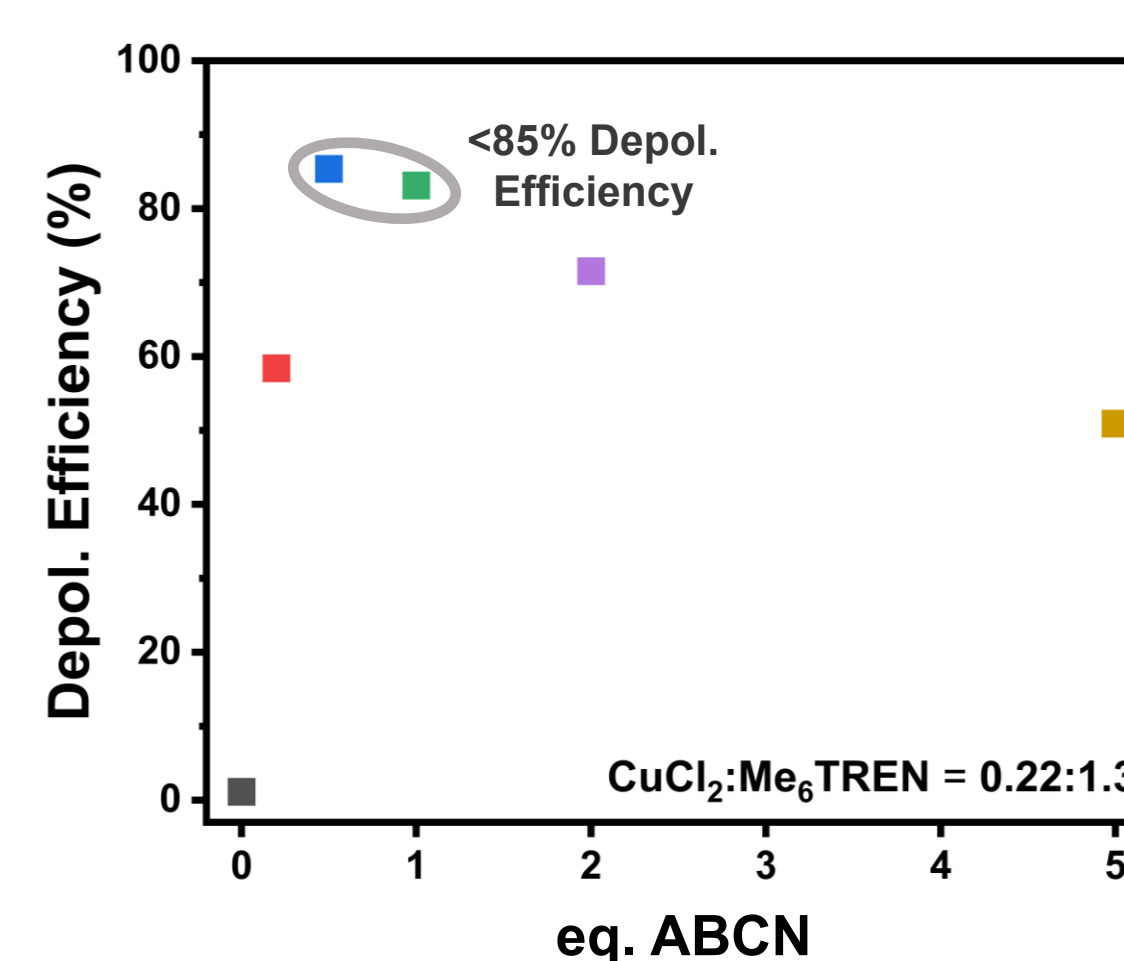
B. Chemical methods

Effect of catalyst concentration



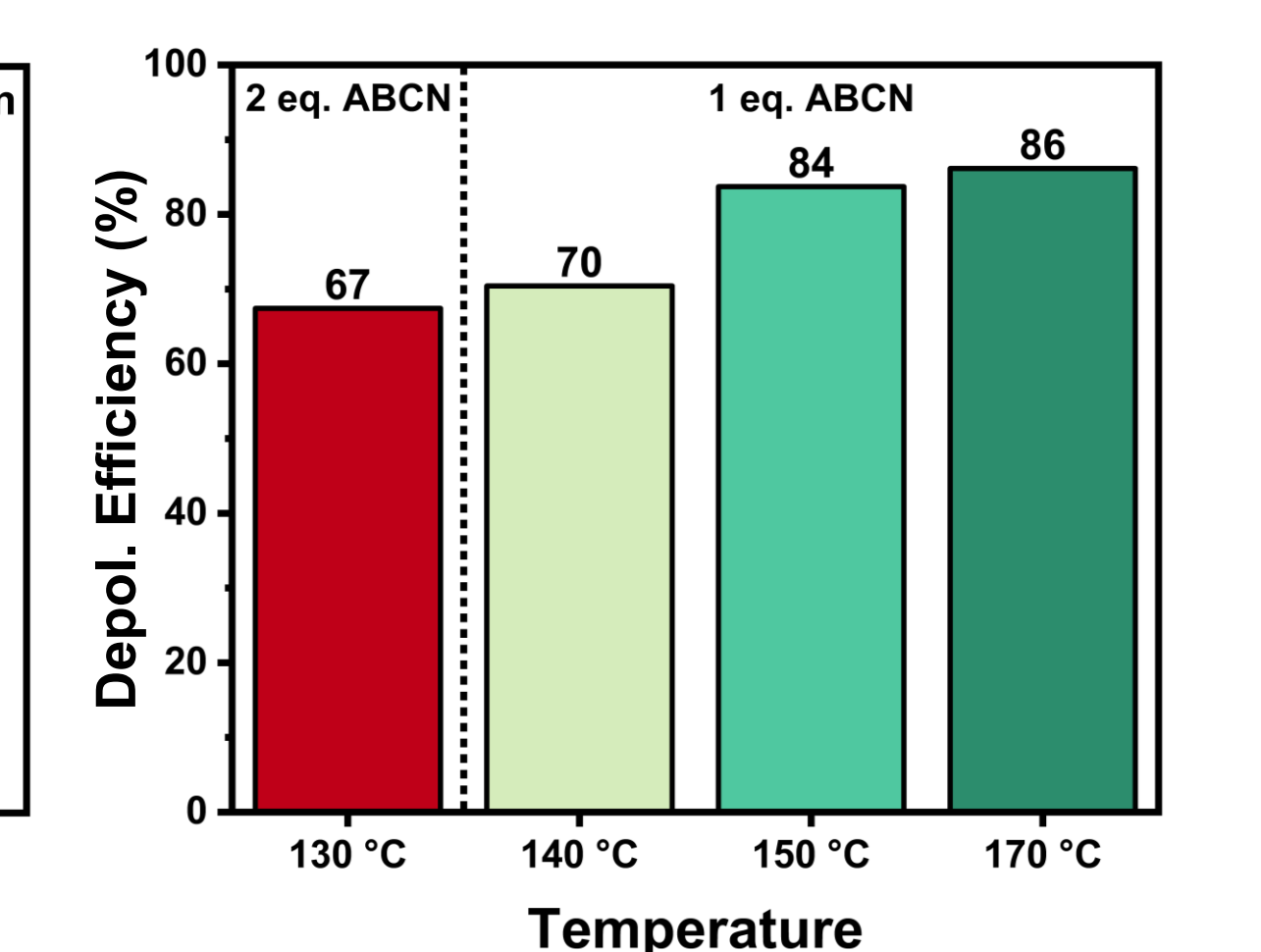
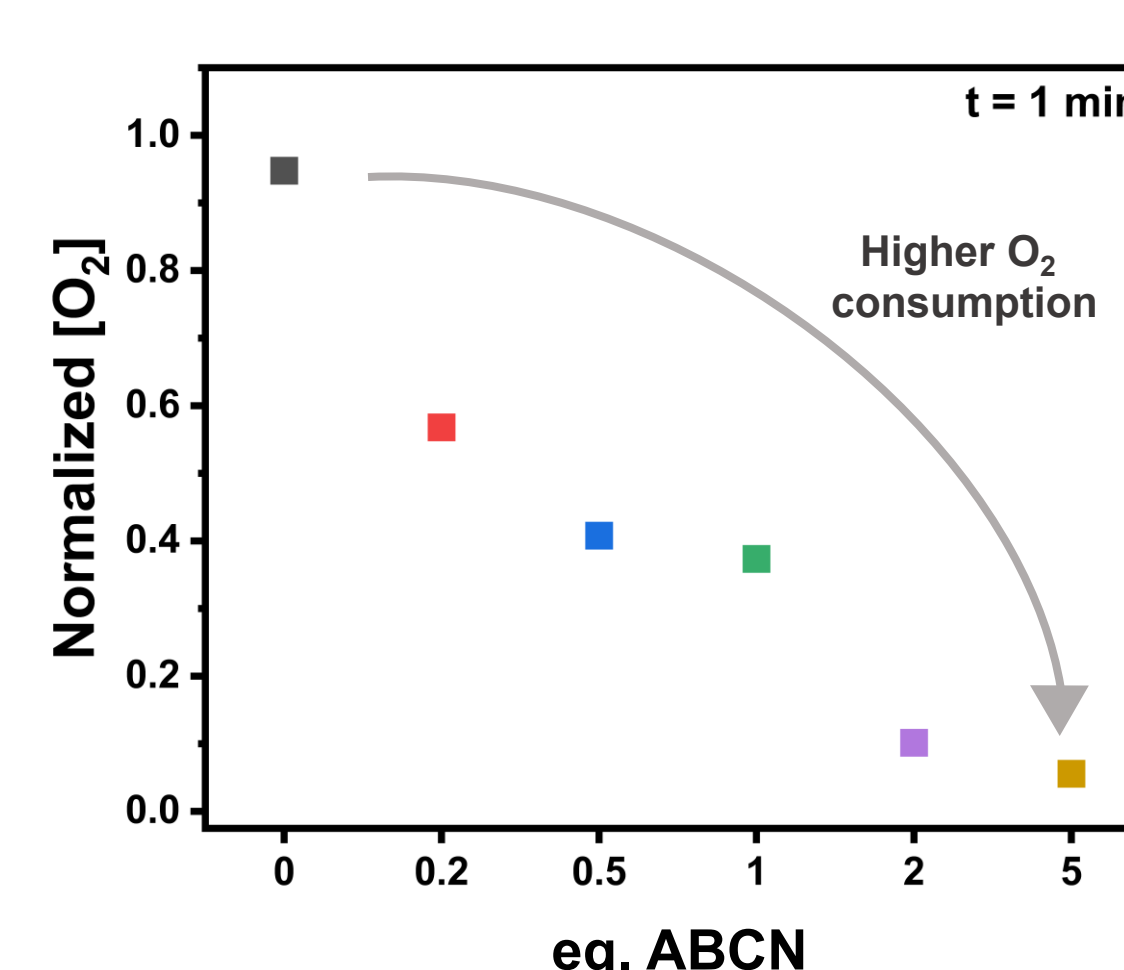
High catalyst concentration – fast O₂ consumption

Addition of radical initiator



Efficiency comparable to deoxygenated

Synergistic effect



Lower depolymerization temperatures achievable

Conclusions

- ✓ Open-vessel
- ✓ *In situ* oxygen removal
- ✓ High depolymerization efficiency (>90%)
- ✓ Versatile approaches
- ✓ Easy optimization
- ✓ Lower reaction temperatures feasible

References

- S.A. Mountaki, R. Whitfield, E. Liarou, N. P. Truong, A. Anastasaki, *J. Am. Chem. Soc.* **2024**, 146 (28), 18848-18854.
- S.A. Mountaki, R. Whitfield, A. Anastasaki, *Macromol. Rapid Commun.* **2025**, 2401067.

Acknowledgements

ETH zürich

