Designing Thermally Stable Organocatalysts for Poly(ethylene terephthalate) Synthesis: Toward a One-Pot, Closed-Loop Chemical Recycling System for PET

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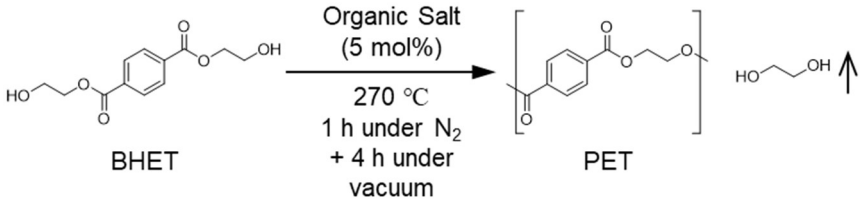
Keywords: Organocatalysts; Organic salts; Polymer synthesis; Chemical recycling; Polyesters

Organocatalysis provides robust methodology to provide 'greener' routes to polymer synthesis. However, the application towards the synthesis of aromatic polymers *via* step-growth polymerization is an area that justifies more investigation, as a consequence of the poor thermal stability of many organic catalysts and the high reaction temperatures commonly required.

In this study, thermally stable organic salts consisting of an organic base and an organic acid were explored to understand key elements required for the bulk synthesis of polyethylene terephthalate (PET) at 270 °C.[1] The ΔpK_a values of the salts played an important role in the thermal stability such that the salts with higher ΔpK_a values showed higher stability because of the strong acid-base interactions. The 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) salts with high ΔpK_a values ($\geq$ 16.9) showed the best catalytic activity among the investigated salts both in terms of low amounts of side reaction and discoloration. The thermal and chemical stability of the salts also affected the polymer properties. Dimerization side reactions that lead to defects in the polymer backbone were found to occur more readily in salts containing strong acids as components, particularly as the ΔpK_a between the acid-base components decreased. The discoloration of the PET sample was also correlated to the thermal stability of the organic salt catalyst, with a lower stability generally leading to enhanced discoloration likely due to decomposition of base components. Polymerization-depolymerization cycles were also investigated with the TBD:*p*-toluenesulfonic acid (TSA) salt and the feasibility of simple, closed-loop recycling of PET with the system was established.



1) Shu Kaiho, Ali Al Rida Hmayed, Kayla R. Delle Chiaie, Joshua C. Worch, and Andrew P. Dove, *Macromolecules* **2022**, *55*, 10628-10639.