Basicity Driven Regeneration in Homogeneous ARGET ATRP of Styrene

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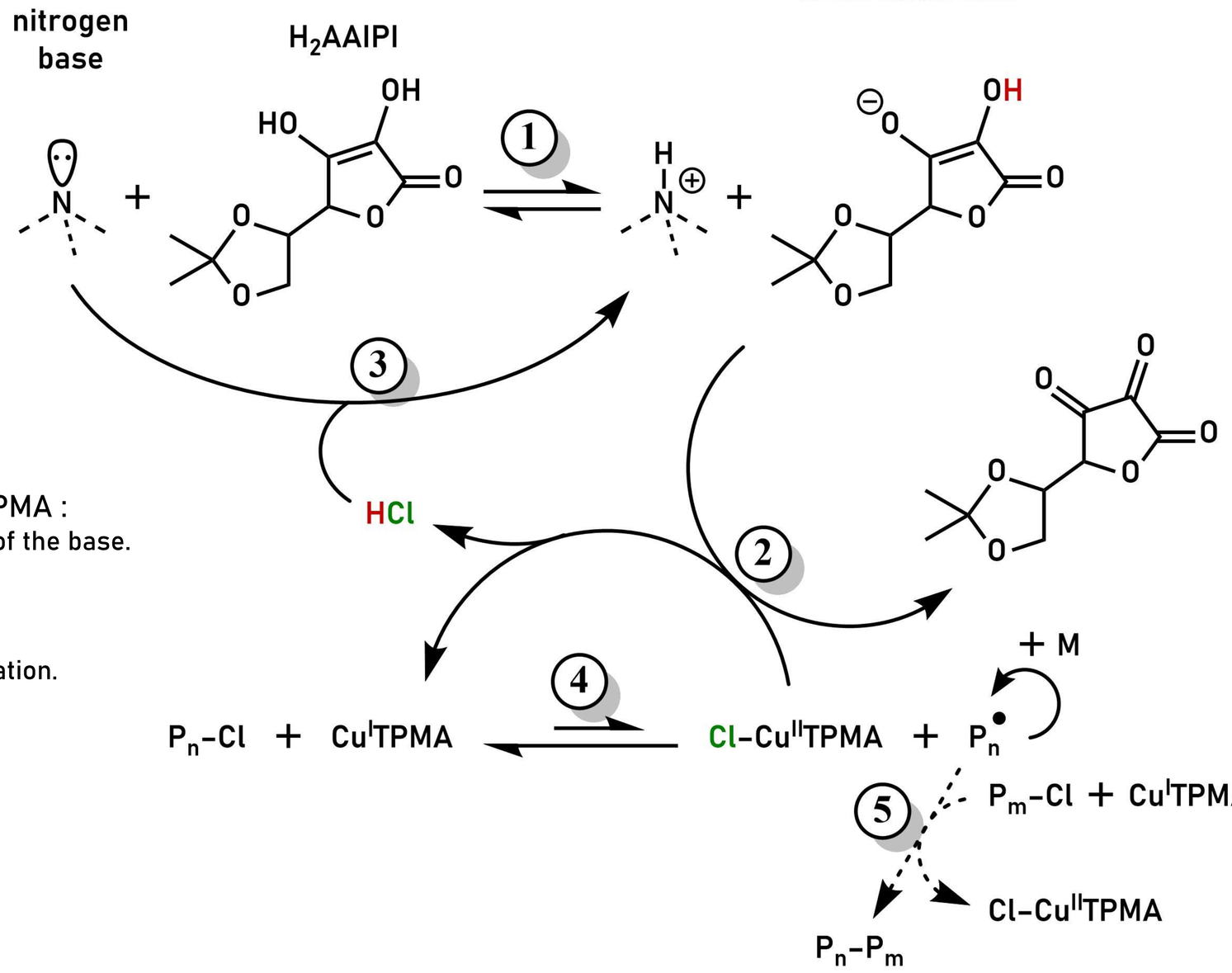
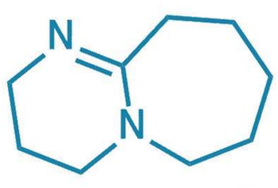
Activators Regenerated by Electron Transfer Atom Transfer Radical Polymerization (ARGET ATRP) employs non-radical reducing agents (such as ascorbic acid, H_2AA). H_2AA is hardly soluble in apolar media, and it exhibits a reduction towards Cu(II) two-orders of magnitude slower than that of ascorbate (HAA^-).[1] Thus, especially when dealing with hydrophobic monomers such as styrene, a low polymerization rate could be observed because of the lower efficiency of H_2AA.
To enhance HAA^- generation we recently proposed the use of sodium carbonate.[2] Nevertheless, the mixture was heterogeneous making scale-up and modeling of the system challenging. To overcome this problem, a more lipophilic ascorbic acid derivative (5,6-isopropylidene ascorbic acid, H_2AAIPI) was employed in place of H_2AA, together with nitrogen bases of varying basicity.



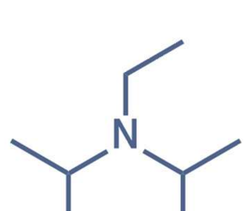
Proposed mechanism for basicity driven regeneration of $Cu^{I}TPMA$:

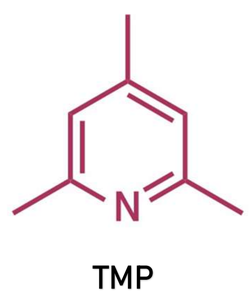
(1) Ascorbic acid deprotonation is driven by the pK_a and concentration of the base.
(2) Reduction of Cl–Cu^{II}TPMA is much faster with the ascorbate anion.
(3) Generation of HCl during reduction of Cl–Cu^{II}TPMA.
(4) Equilibrium between radical and halogenated polystyrenes.
(5) Termination between two radicals increases Cl–Cu^{II}TPMA concentration.

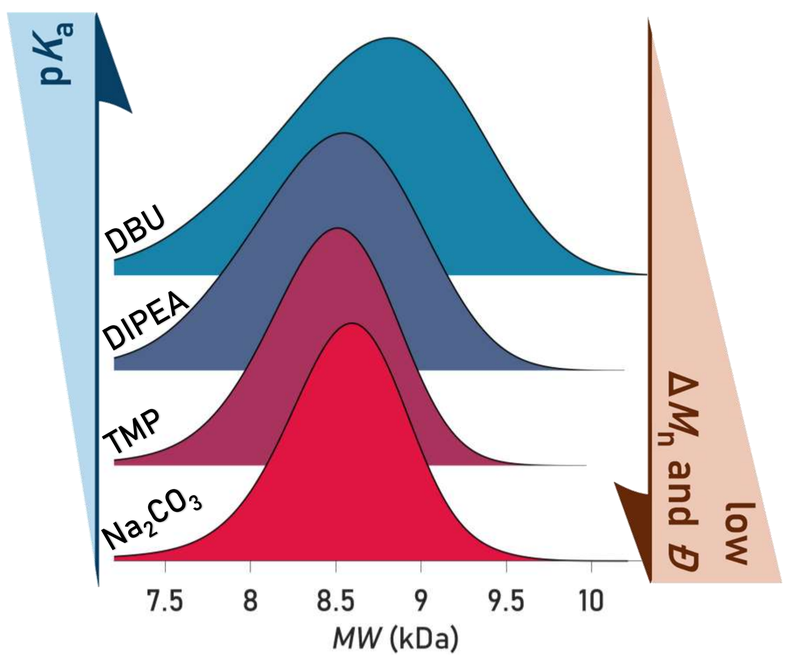
To validate the proposed mechanism, we decided to:



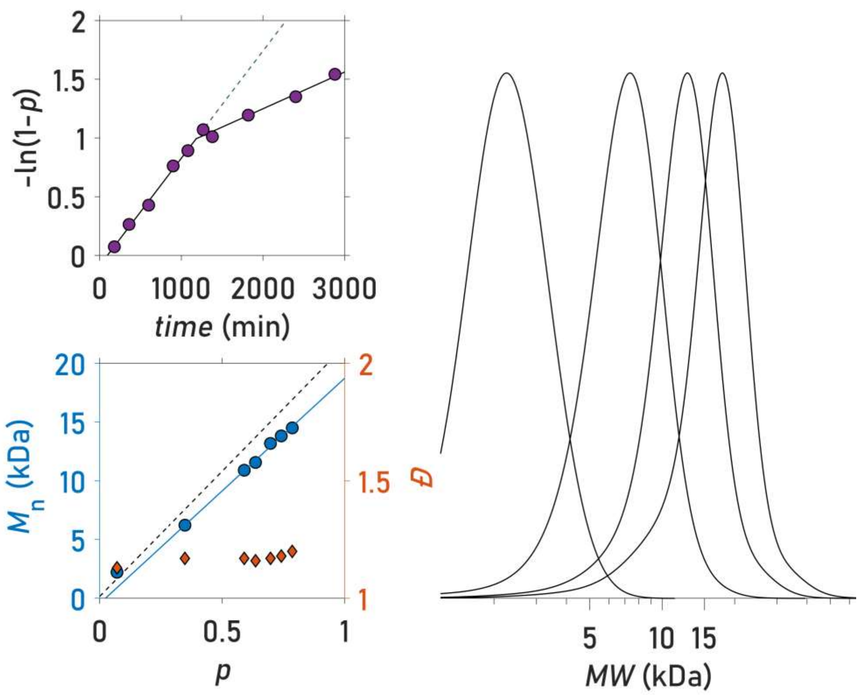
A) Test different bases and show how pK_a influences [P•]





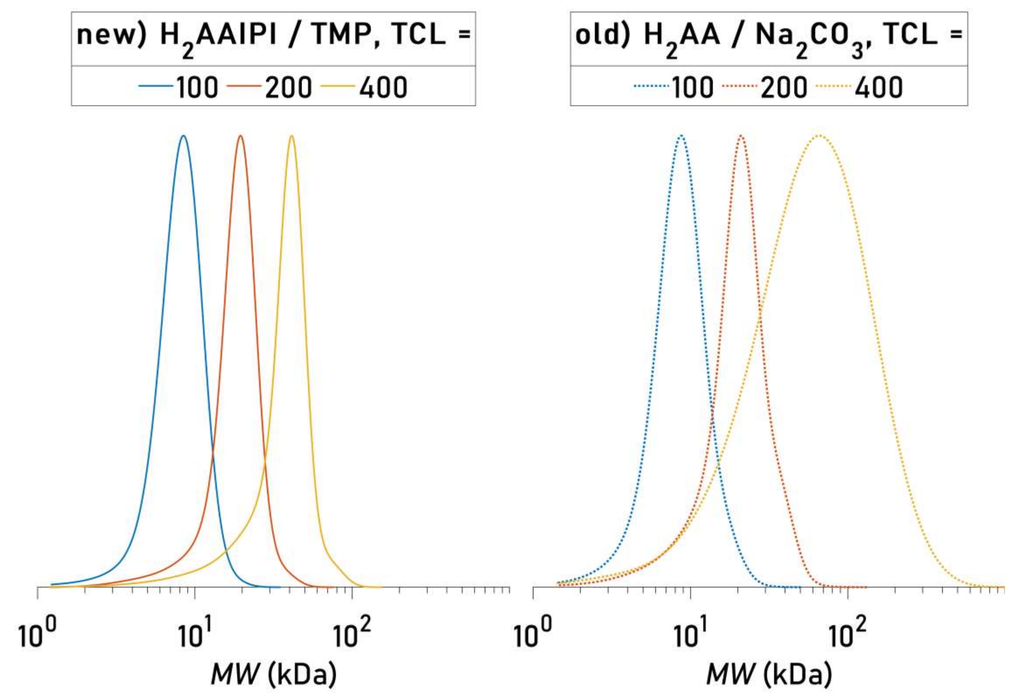


B) Assess the kinetics of the ARGET ATRP with TMP

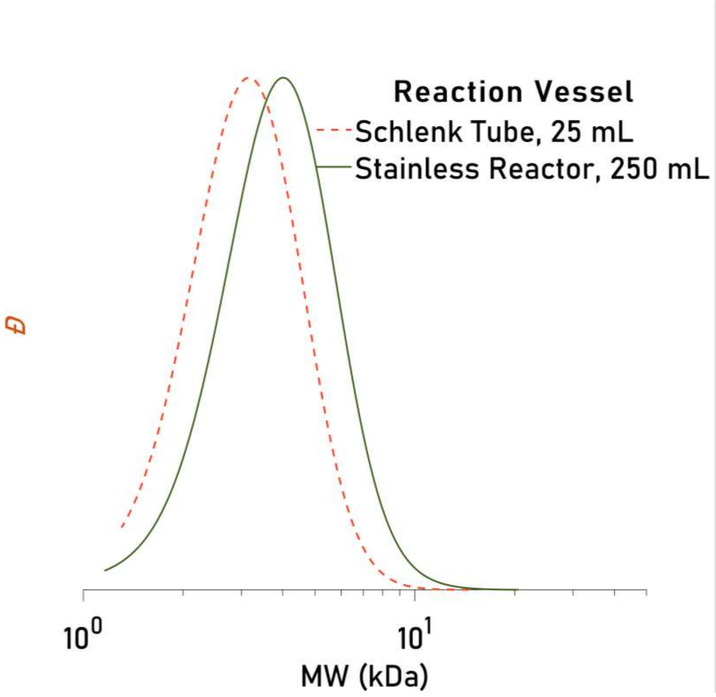


Then, we showed:

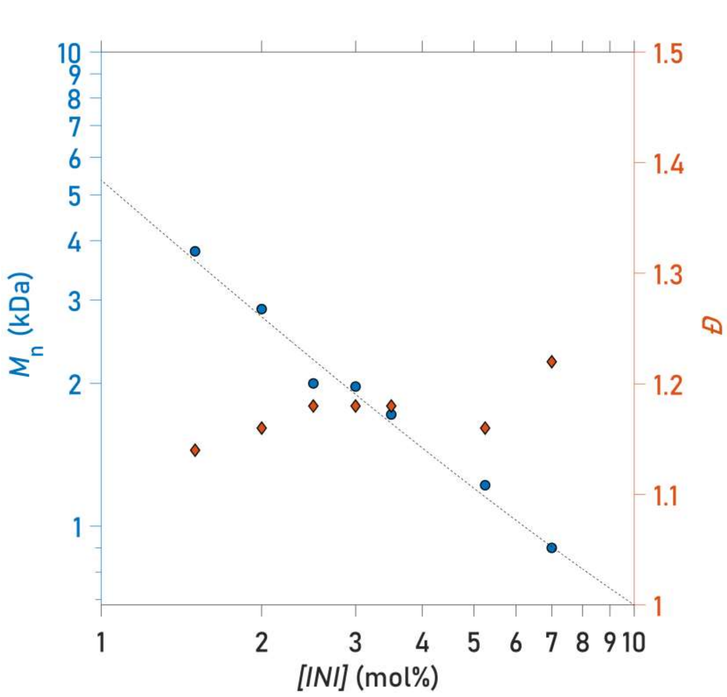
How advantageous is homogeneity



By also achieving scalable synthesis



Down to oligomeric lenghts



References:
[1] Shen, J. et al.; Scientific Reports 2021, 11:7417; [2] Borsari, M. et al.; European Polymer Journal, 2021, 157, 110675.