ChemISTry Colloquia

Making and Unmaking Vinyl Polymers via Radical Polymerizations

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Controlled radical polymerization (CRP) is widely used to prepare a broad range of polymeric materials for diverse applications in various fields [1,2]. One of the most important properties of CRP polymers is the ability to maintain high livingness throughout the polymerization. In the first part of the talk, an acid-triggered radical polymerization will be demonstrated which leads to the next generation of complex multiblock copolymers with controlled sequence, dispersity, and end-group fidelity [3,4]. Although high end-group fidelity is crucial to facilitate the synthesis of well-defined block copolymers, it has rarely been exploited to reverse controlled radical polymerization and regenerate the starting materials. In the second part of the talk, I will first show how, under thermodynamically favoured conditions [5,6], it is possible to depolymerize linear, bulky, cross-linked, and functional polymethacrylates made by reversible addition–fragmentation chain-transfer (RAFT) polymerization [7]. Notably, the depolymerization product can be utilized to either reconstruct the linear polymer or create an entirely new insoluble gel that can also be subjected to depolymerization. A solvent-free chemical recycling methodology that efficiently operates for both ATRP and RAFT-synthesized materials will also be presented [8]. However, both depolymerization reactions are uncontrolled in nature (i.e., rapid monomerization of activated chains), thus providing no handle over the molecular weight and limiting further applications. To address this, a controlled depolymerization strategy is developed that enables a linear decrease in molecular weight over time [9]. Such gradual unzipping of polymer chains is not only useful for recycling purposes but also enables the structural characterization of various copolymers (i.e., AB diblock vs. BA diblock vs statistical vs gradient) by facilitating the sequential release of monomers from the chain-end. At the end, I will discuss how we can potentially utilize the obtained knowledge to switch from “designer polymers” to commercially available materials containing undisclosed impurities.

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[2] N. P. Truong, G. R. Jones, K. G. E. Bradford, D. Konkolewicz, A. Anastasaki, *Nat. Rev. Chem.* **2021**, *5*, 859–869.
[3] M.-N. Antonopoulou, R. Whitfield, N. P. Truong, D. Wyers, S. Harrisson, T. Junkers, A. Anastasaki, *Nat. Chem.* **2022**, *14*, 304–312.
[4] M.-N. Antonopoulou, G. R. Jones, A. A. Kroeger, Z. Pei, M. L. Coote, N. P. Truong, A. Anastasaki, *Nat. Synth.* **2024**, *3*, 347–356.
[5] G. R. Jones, H. S. Wang, K. Parkatzidis, R. Whitfield, N. P. Truong, A. Anastasaki, *J. Am. Chem. Soc.* **2023**, *145*, 9898–9915.
[6] V. Lohmann, G. R. Jones, N. P. Truong, A. Anastasaki *Chem. Sci.* **2024**, *15*, 832–853.
[7] H. S. Wang, N. P. Truong, Z. Pei, M. L. Coote, A. Anastasaki, *J. Am. Chem. Soc.* **2022**, *144*, 4678–4684.
[8] R. Whitfield, G. R. Jones, N. P. Truong, L. E. Manring, A. Anastasaki, *Angew. Chem. Int. Ed.* **2023**, *62*, e202309116.
[9] H. S. Wang, K. Parkatzidis, T. Junkers, N. P. Truong, A. Anastasaki, *Chem* **2024**, *10*, 388–401.

Athina Anastasaki was born and raised in Athens, Greece, and obtained her B.S. in Chemistry at the University of Athens. She then commenced her PhD studies at the University of Warwick under the supervision of Prof. Dave Haddleton. In early 2015, she accepted a Monash–Warwick research fellow position between the Pharmaceutical Department at Monash University and the University of Warwick, jointly supervised by Professor Thomas Davis and Professor Dave Haddleton. She then received an Elings Fellowship, followed by a Global Marie Curie Fellowship, to conduct research alongside Professor Craig Hawker at the University of California, Santa Barbara. Since January 2019, she is an Assistant Professor at ETH and her group focuses on polymer synthesis, depolymerization and self-assembly predominantly in the area of controlled and free radical polymerizations. Athina currently serves as an Associate Editor in the RSC journal *Polymer Chemistry*.