

## EFFICIENT AVENUES TOWARDS THE FUNCTIONALIZATION OF UNSATURATED POLYMERS

Hatice Mutlu<sup>a,b,\*</sup> Christopher Barner-Kowollik<sup>a,b,c,\*</sup>

<sup>a</sup>Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstraße 18, 76128 Karlsruhe, Germany.

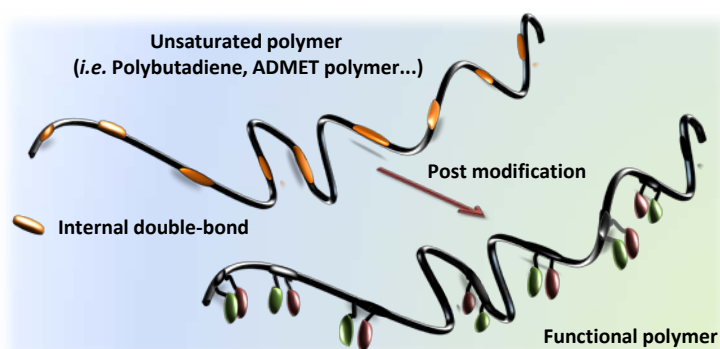
<sup>b</sup>Soft Matter Synthesis Laboratory, Institut für Biologische Grenzflächen, Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. E-Mail: hatice.mutlu@kit.edu and christopher.barner-kowollik@kit.edu

<sup>c</sup>School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), 2 George Street, QLD 4000, Brisbane, Australia, E-mail: christopher.barnerkowollik@qut.edu.au

### ABSTRACT

Inserting variable functional groups into a polymer backbone offers the possibility to carefully adjust the material properties of the polymer for tailored applications.<sup>1</sup> However, the well-known reversible deactivation radical polymerization methods do not allow for the incorporation of all functional groups.<sup>2,3</sup> Moreover, only few methods for the modification of unsaturated polymers have been developed so far. Herein, new strategies for the synthesis of post-functionalized polymers are explored and a new, catalyst-free post-polymerization modification method for unsaturated polymers is introduced. The method rests on a metal-free, novel electrophilic cascade reaction – employing inexpensive and commercially available reagents – to decorate alkene functionalities within a lateral polymer chain with pendent bromine and alkoxyether motifs.<sup>4,5</sup> Critically, the introduced pendent bromine groups serve as an intermediate to afford other chemical functionalities, thus opening vast possibilities for post-polymer functionalization. Further, an alternative facile and atom-economical method is introduced for the synthesis of  $\beta$ -acetamido sulfide derivatives based on unsaturated polymers. Thus, a metal-free direct difunctionalization of the alkene functionality of the polymer backbone with thiols and nitriles was successfully adopted.

By employing the above mentioned methods, we demonstrate that it is possible for unsaturated polymers to be readily functionalized, allowing for the adaptation of the materials properties of the polymers.



**Fig. 1:** Efficient avenues towards the functionalization of unsaturated polymers

### References:

<sup>1</sup>Hawker, C. J.; Wooley, K. L. *Science* **2005**, *309*, 1200.

<sup>2</sup>Gauthier, M. A.; Gibson, M. I.; Klok, H. A. *Angew. Chem. Int. Ed.* **2009**, *48*, 48.

<sup>3</sup>Guenay, K. A.; Theato, P.; Klok, H. A. *J. Polym. Sci. Part A Polym. Chem.* **2013**, *51*, 1.

<sup>4</sup>Geiselhart, C. M.; Offenloch, J. T.; Mutlu, H.; Barner-Kowollik, C. *ACS Macro Lett.* **2016**, *5*, 1146.

<sup>5</sup>Offenloch, J. T.; Willenbacher, J.; Tzvetkova, P.; Heiler, C.; Mutlu, H.; Barner-Kowollik, C. *Chem Commun.* **2016**, submitted.