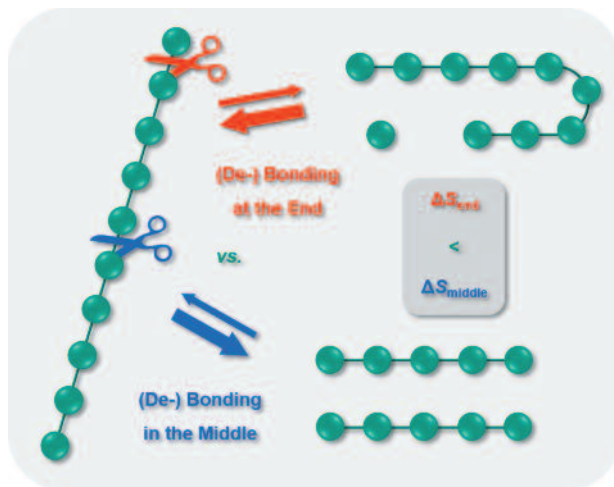


Where macromolecules cleave: entropic selectivity for chain scission



Reversible covalent and supramolecular bonding is increasingly being employed in applications such as self-healing and stimuli-responsive materials, complex macromolecular architectures, and protein mimics. Normally, dynamic ligation equilibria are tuned by modifying the ligating functional groups to alter their electronic properties and thus reaction enthalpy. However, researchers from the Karlsruhe Institute of Technology, the Australian National University and the Leibniz Institute for Polymer Research have demonstrated that the equilibria can be tuned by altering the molecular weight and chain stiffness of the linking groups without changing the actual bonding motifs, thus taking advantage of entropy instead of enthalpy. They showed that an important consequence of these entropic effects is a significant preference for cleavage of macromolecules in the middle of long chains, rather than at the ends (Pahnke K., Brandt J., Gryn'ova G., Lin C.Y., Altintas O., Schmidt F.G., Lederer A., Coote M.L., Barner-Kowollik C. *Angew. Chem. Int. Ed.* 2016, **55**, 1514–18). The results were predicted by model calculations and confirmed via experimental analysis of reversible covalent and supramolecular adducts. An important consequence of the work is the prediction of long-range chain-length effects on chemically controlled polymer–polymer reactions such as chain transfer, polymer degradation, and control agent addition.

Recyclable catalysts

Chemical industries rely heavily on catalytic processes to produce many fine and bulk chemicals efficiently and selectively. These industries are always looking for new means to modify current industrial catalytic processes to make them more sustainable. As homogenous transition metal catalysts become more widely used, strategies for developing immobilised catalysts that retain the high efficiency and selectivity of the homogeneous catalysts, while allowing easy catalyst–product separation, are highly desired. The Messerle research group at the University of New South Wales and Macquarie University has developed a new experimental method for synthesising immobilised rhodium catalysts on a range of carbon surfaces, including graphene, carbon black and glassy carbon, directly from the optimised homogeneous complex (Wong C.M., Walker D.B., Soeriyadi A.H., Gooding J.J., Messerle B.A. *Chem. Sci.* 2016, doi: 10.1039/c5sc03787e). The immobilised complexes showed comparable catalytic efficiency and selectivity to those of the parent homogeneous catalyst for the hydrosilylation of disubstituted acetylenes. These catalysts are the most efficient reported to date for the hydrosilylation of disubstituted acetylenes. The immobilised complexes further demonstrated an advantage over the homogeneous complex as the hybrid catalysts were highly recyclable, with no leaching of rhodium over 10 catalytic cycles. This research provides a new experimental approach to developing immobilised catalysts from industrially suited homogeneous catalysts, making product separation easier.

