Hetero-Diels-Alder Chemistry for Nano-Structured Materials Design

James P. Blinco1,2, Michael Bruns3, Peter Gerstel1, Mathias Glassner1, Hartmut Glienemann4, Vanessa Trouillet3 and Christopher Barner-Kowollik1

1Preparative Macromolecular Chemistry, Institute für Technische Chemie und Polymerechemie, Karlsruhe Institute of Technology;
2Current Address: ARC Centre of Excellence for Free Radical Chemistry and Biotechnology, Queensland University of Technology;
3Institute for Applied Materials, Karlsruhe Institute of Technology; 4Institute of Functional Interfaces, Karlsruhe Institute of Technology

Introduction

Tuning the properties of surfaces and functional polymeric systems is a key focus in materials science. One of the major scientific challenges is to achieve well-defined properties and structural order on the surface of materials in an efficient and selective fashion. A range of efficient reactions, some of which adhere to the criteria defined for Click chemistries, (e.g. copper catalyzed Huisgen [2+3] cycloadditions, (hetero) Diels-Alder (HDA) cycloadditions, etc.), fulfill the criterion of reaching (ideally) quantitative conversions, making them particularly attractive reaction classes for orthogonal surface design. The development of such reactions for orthogonal design has been a recent focus of the Macroarc group; in particular the development of RAFT-HDA. As well as acting as an (ultra)rapid conjugation technique, the (H)DA reaction sequence also has the advantage of containing a cycloadduct linkage that is completely reversible (via a retro-Diels-Alder (rDA) reaction) at elevated temperatures. Below are two examples of how the (H)DA/rDA chemistry has been applied to the design of novel structured materials and surfaces.

Formation of Nanoporous Materials via Mild Retro-Diels-Alder Chemistry

In this example, it was possible to synthesize thermally cleavable P5-b-PEO block copolymers by RAFT-HDA click chemistry. The cleavage of P5-b-PEO can be carried out by heating to 90 °C in the solid state or in solution. UV-Vis analysis confirmed that the dithioester end group of the RAFT polymer is returned to the reformed homopolymer and that is reasonably stable under these conditions.

UV-Vis spectra of P5-b-PEO in toluene at 90 °C. Due to the rDA reaction the concentration of the dithioester-capped P5 increases with time.

SEC monitoring of the retro-HDA cleavage of P5-b-PEO in the solid state in water at 90 °C.

Comparison of XPS N 1s (Left), C 1s (middle) and Br 3d (right) spectra for substrates Si-Br (a), Si-CP (b) and Si-PBA (c). Peak heights have been normalized; the Br 3d intensity in (b) has been halved for a better visualization.

Dynamic Covalent Chemistry on Surfaces Employing Highly Reactive Cyclopentadienyl Moieties

Here, using a facile synthetic reaction, silicon substrates coated with a bromide-terminated silane were able to be transformed into highly reactive, cyclopentadiene covered analogues. The ability of these surfaces to undergo rapid cycloaddition reactions with various dienophile-capped polymers was then demonstrated.

High resolution XPS of the C 1s region (left) and water contact angle (right) of substrates cycling between poly(ethylene glycol) being attached or removed from the surface functionalized surface.

References and Acknowledgments

This work was supported by the Karlsruhe Institute of Technology via the Excellence Initiative of the German Federation of European Universities, the German Research Council, the Ministry of Science and Arts of the state of Baden-Württemberg and the Alexander von Humboldt Foundation (in the form of a research fellowship for JPB). a) "Formation of Nanoporous Materials via Mild Retro-Diels-Alder Chemistry" Glassner, M.; Blinco, J.; Barner-Kowollik, C. Polym. Chem., 2011, 2(1), 83-87. b) "Dynamic Covalent Chemistry on Surfaces Employing Highly Reactive Cyclopentadienyl Nitriles" Blinco, J.P.; Trouillet, V.; Bruns, M.; Gerstel, P.; Glienemann, H.; Barner-Kowollik, C. Adv. Mater. 2011 23(38), 4436-4439.