



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

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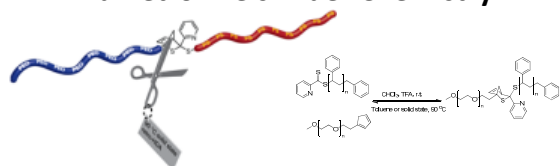
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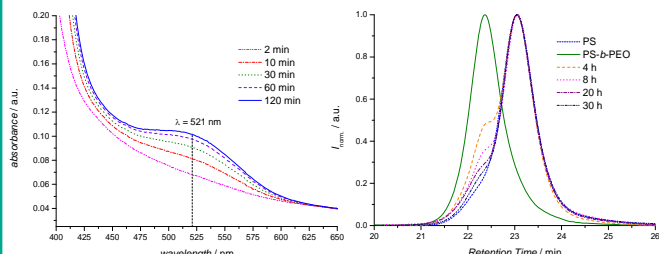
Introduction

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^a



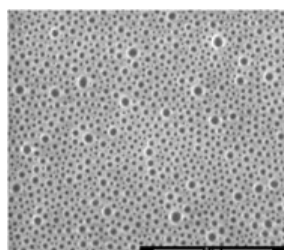
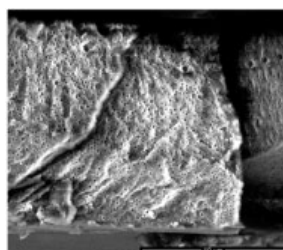
In this example, it was possible to synthesize thermally cleavable PS-b-PEO block copolymers by RAFT-HDA click chemistry. The cleavage of PS-b-PEO can be carried out by heating to 90 °C in the solid state or in solution. UV-Vis analysis confirmed that the dithioester end-group of the RAFT polymer is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



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

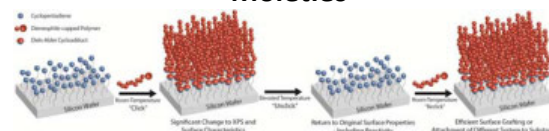
SEC monitoring of the retro-HDA cleavage of PS-b-PEO in the solid state in water at 90 °C.

Nanoporous PS films were easily prepared by removal of the PEO block by applying a simple heating and washing procedure. The method described here enables an easy preparation of nanoporous films bearing a reactive functional group from block copolymer precursors which are accessible in various molecular weight compositions via the combination of RAFT polymerization and HDA cycloaddition.

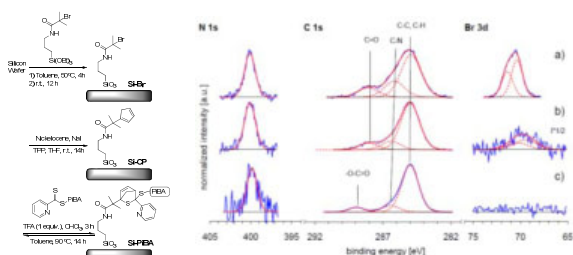


SEM images of PS-b-PEO after heating to 90 °C in the solid state and then washing with water.

Dynamic Covalent Chemistry on Surfaces Employing Highly Reactive Cyclopentadienyl Moieties^b

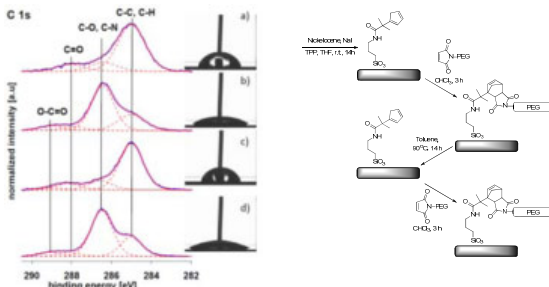


Here, using a facile synthetic reaction, silicon substrates coated with a bromide-terminated silane were able to be transformed into highly reactive, cyclopentadiene covered analogues. The ability of these surfaces to undergo rapid cycloaddition reactions with various dienophile-capped polymers was then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



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

It was found that mild heating of the substrates evoked the rDA reaction to occur, reforming the reactive cyclopentadiene surface. The exposed surface exhibited no evidence of decrease in reactivity, with a second round of grafting yielding similar densities to the original experiments. Thus, an efficiently switchable surface was generated.



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

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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 Moieties" Blinco, J.P.; Trouillet, V.; Bruns, M.; Gerstel, P.; Gliemann, H.; Barner-Kowollik, C. *Adv. Mater.* 2011 23(38), 4435-4439.