

# Reactive Surfaces and Interfaces utilizing 2-Vinyl-4,4-Dimethylazlactone (VDMA): An Example of “Click” Chemistry

Jamie M. Messman,<sup>1</sup> S. Michael Kilbey, II,<sup>1,2</sup> Bradley S. Lokitz,<sup>3</sup> Juan Pablo Hinestrosa,<sup>4</sup> John F. Ankner<sup>3</sup>

<sup>1</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory,  
Oak Ridge, TN 37831 USA.

<sup>2</sup>Department of Chemistry, University of Tennessee,  
Knoxville, TN 37996 USA.

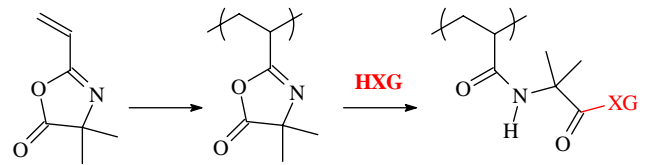
<sup>3</sup>Spallation Neutron Source, Oak Ridge National Laboratory,  
Oak Ridge, TN 37831 USA.

<sup>4</sup>Department of Chemical and Biomolecular Engineering, Clemson University,  
Clemson, SC 29634 USA

## ABSTRACT

Creating polymer-modified interfaces decorated with biologically-relevant materials – so-called “bio-interfaces” – with precise control over the nanoscale structure and properties is of increasing technological importance for a large number of advanced materials applications, including adaptive and/or lubricious biomaterial coatings, electro-actuators (synthetic muscles), biosensors with amplified response, coatings for stealth drug delivery, supports for enzymatic catalysts, protein or antibody arrays, and high affinity separation agents. The ability to design and decorate interfaces with biologically-relevant molecules and understand synthesis-structure-function relationships remains a significant challenge. The overarching objective of this research program is to investigate the polymerization and functionalization of a new class of polymeric materials that are capable of serving as a versatile platform from which bio-interfaces for specific applications can be created and evaluated.

Stimuli-responsive (co)polymers containing vinyl dimethyl azlactone (VDMA) have been prepared using free radical polymerization techniques (controlled and conventional). Subsequent immobilization of biomolecules (e.g., dansylcadaverine,  $N_{\alpha},N_{\alpha}$ -bis(carboxymethyl)-L-lysine hydrate) on PVDMA-containing surface scaffolds affords bio-interfaces. Reaction of nucleophiles with the azlactone moiety proceeds rapidly, quantitatively, and in the absence of byproducts, which are essential criteria governing the click-type nature of this procedure. The conversion of these materials into polyelectrolytes and bioconjugates can be monitored in real-time using infrared spectroscopy. Additionally, pVDMA polymers prepared using reversible addition fragmentation chain transfer (RAFT) polymerization are the basis for creating polymer brushes by a “grafting to” approach. We will describe how compositional differences and changes in molecular weight affect the solubility and responsiveness of pVDMA-based polymers and surface layers when functionalized with various biomolecules.



**G = modifying group**  
**X = O or NH**