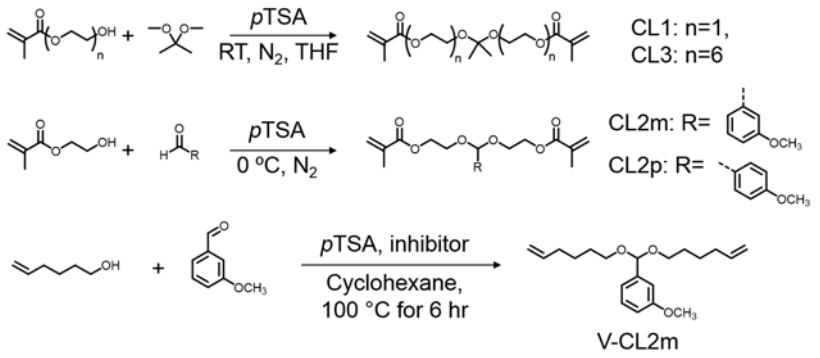
Degradation Kinetics of Acid-Sensitive Hydrogels

*Soeun Kim, Olga Linker, Kim Garth, and Kenneth R. Carter**
Department of Polymer Science and Engineering, Conte Center for Polymer Research, University of Massachusetts- Amherst, Governors Drive, Amherst, Massachusetts 01003, United States
*The correspondence should be addressed. E-mail: krcarter@polysci.umass.edu



We are developing new approaches for in-the-field protection from highly nucleophilic nerve chemical warfare agents (CWAs), exploring the use of reactive catalytic compounds embedded in a thin protective layer. Upon CWA challenge, the latter actively reacts with the toxin, neutralizes the threat and then self-exfoliates, removing the compromised layer and exposing fresh protective under-layers. This process mimics the function of natural living skin where blistering and peeling occurs when overcome by dangerous external factors. The artificial exfoliation requires specially designed stimuli responsive materials. The stimuli in this case are the highly acidic byproducts formed during the neutralization of highly nucleophilic CWAs. We are developing layers that when exposed to CWAs, first neutralize the threat as it diffuses into the layer and concurrently the acidic byproducts of the neutralization initiate reactions that destabilize the contaminated regions of the matrix leading to exfoliation of the compromised areas and re-exposing fresh uncontaminated protective layers.

Dimethacrylate or divinyl-functionalized acetal-based crosslinkers were synthesized as building elements of acid-sensitive crosslinked hydrogels. Each crosslinker was prepared under catalytic acidic conditions with different functional groups installed at the acetal position. The hydrophilicity of the crosslinkers was tuned to control acidic-hydrolysis rate. We report the synthesis of hydroxyethyl dimethacrylate-functionalized dimethyl ketal (CL1), *meta*- or *para*-methoxybenzaldehyde based acetals (CL2m and CL2p), poly(ethylene glycol) dimethacrylate-functionalized dimethyl ketal-based crosslinker (CL3), and divinyl-functionalized *meta*-methoxybenzaldehyde-based acetal crosslinker (V-CL2m). An examination of acetal hydrolysis kinetics of the monomers was performed in aqueous buffer solutions using ^{1}H NMR (proton nuclear magnetic resonance) and UV-Vis (ultraviolet-visible) spectroscopy at various pH ranges. The hydrolysis rates were strongly dependent on the structure of the acetal. Network films containing CL2m were prepared by thermally initiated polymerization with either hydroxyethylmethacrylate (HEMA) or methylmethacrylate (MMA). A study of the hydrolysis kinetics of these crosslinked films was performed using GC-MS (gas chromatography and mass spectroscopy) to understand the effect of monomer hydrophilicity, crosslinking density, and polymerization mechanism at different pHs. The crosslinked films composed of the hydrophilic monomer, HEMA, show faster hydrolysis than those containing more hydrophobic monomers (e.g. MMA). The hydrolysis rate decreases as the crosslinking density increases. In the case of thiol-ene networks formed by reacting pentaerythritol tetrakis(3-mercaptopropionate) and V-CL2m, each repeating unit is composed of an acid-degradable acetal-moiety. Hydrolysis of the thio-ene network films results in depolymerization into two lower molecular weight components, pentaerythritol tetrakis(3-(6-hydroxyhexylthio)propanoate) and *meta*-methoxybenzaldehyde. This work is supported by the Chemical and Biological Technologies Department of the Defense Threat Reduction Agency (DTRA-CB) via grant BA12PHM123 in the "Dynamic Multifunctional Materials for a Second Skin D[MS]2" program. *(last edited June 6, 2015)*