

Two-Stage Reactive Polymer Systems

Devatha P Nair¹, Neil B Cramer¹, John C Gaipa¹, Emily M. Matherly¹, Mathew K Mcbride², Robert R. McCleod³, Robin Shandas⁴, Christopher N Bowman^{1,5}

¹ Dept. of Chemical and Biological Engg, Uni. Of Colorado, Boulder, CO

² Dept. of Chemical and Biological Engg, Auburn University, Auburn, Al

³ Dept. of Electrical Engg, Uni. Of Colorado, Boulder, CO

⁴ Dept. of Bioengineering, Uni. Of Colorado, Denver, CO

⁵ Dept. of Restorative Dentistry, Uni. Of Colorado, Denver, CO

The advent of various photopolymerization mechanisms used in tandem with traditional polymerization mechanisms has enabled the optimization of polymer networks which allow for their properties to be tailored for highly specific applications that range from soft lithographic substrates to high performance parts on aircrafts.¹⁻³ From an applications perspective, however it would be highly advantageous to have one stage of the polymerization process occur through a self-limiting polymerization reaction that can form a stable polymer network with desirable physical attributes, which also simultaneously maintains the ability, upon stimulus, to react further and achieve a second and final set of material properties. The thiol-acrylate “click” Michael addition reaction has been a platform for biomaterial applications ranging from tissue scaffolds to drug delivery applications.⁴⁻⁷ It is known that the stoichiometry of thiol-acrylate Michael addition networks must be 1:1 to form optimized networks. In this work we exploit the ability to vary the stoichiometry of thiol and acrylate functional groups to enable greater versatility of these systems, particularly a desirable two stage curing reaction.

Two-Stage Reactive Polymer Systems

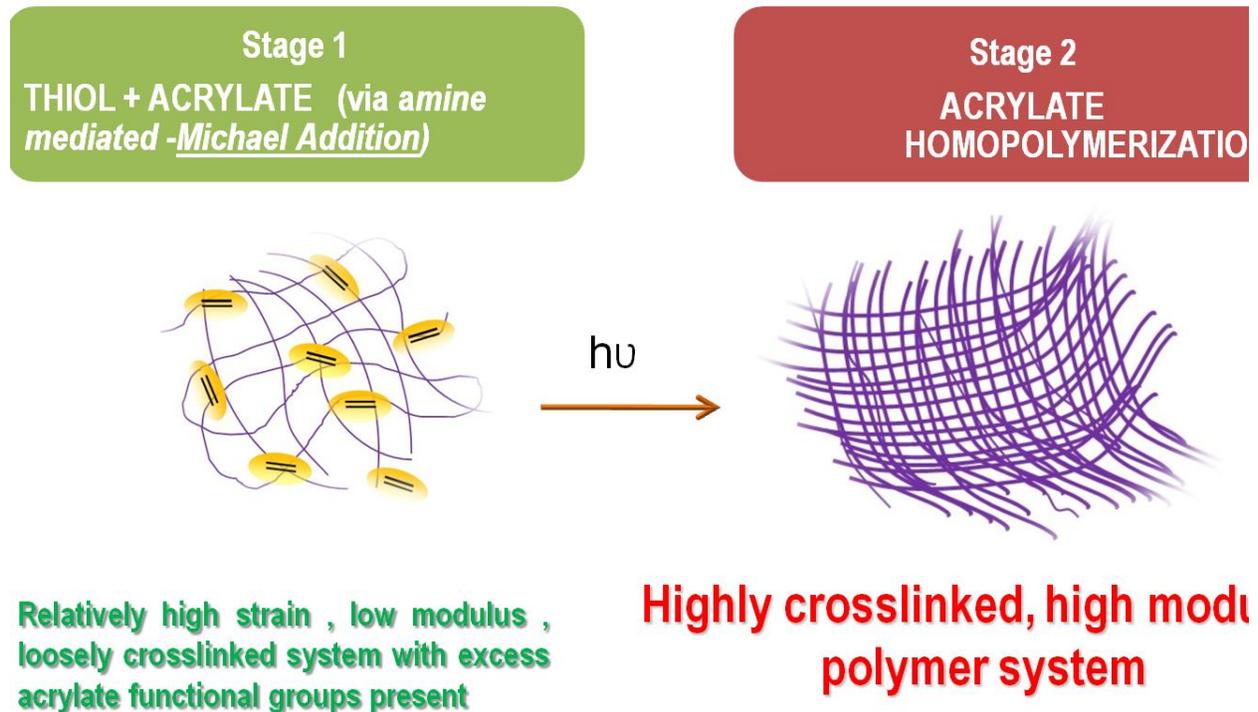


Figure 1. Thiol-acrylate two-stage reactive polymer systems methodology.

A thiol-acrylate network formed by a Michael addition reaction from an initial monomer mixture with a stoichiometric excess of acrylate groups leads to an initial polymer network with residual acrylate functional groups. The residual acrylate functional groups can subsequently be photopolymerized in a second polymerization reaction. The ensuing dual-cure system exhibits a first polymerization reaction that is a base catalyzed, self-limiting reaction to form an initial polymer network and a second polymerization reaction, orthogonal to the first reaction that is photoinitiated to form the final polymer network. The acrylates homopolymerize via a free radically initiated chain growth polymerization mechanism with initiation and termination steps similar to the thiol-ene mechanism. Such a system enables the achievement of two distinct and largely independent sets of material properties as might be necessary for multiple stages in the life-cycle of certain applications

In this study we demonstrate that by varying the stoichiometry within the initial monomers we choose, two-stage reactive polymeric systems with a wide range of moduli and glass transition temperatures at the end of both the first and second stages of cure were achieved. Further, we can optimize and characterize the polymer formulation for three different applications - shape memory polymers, impression materials and optical materials.

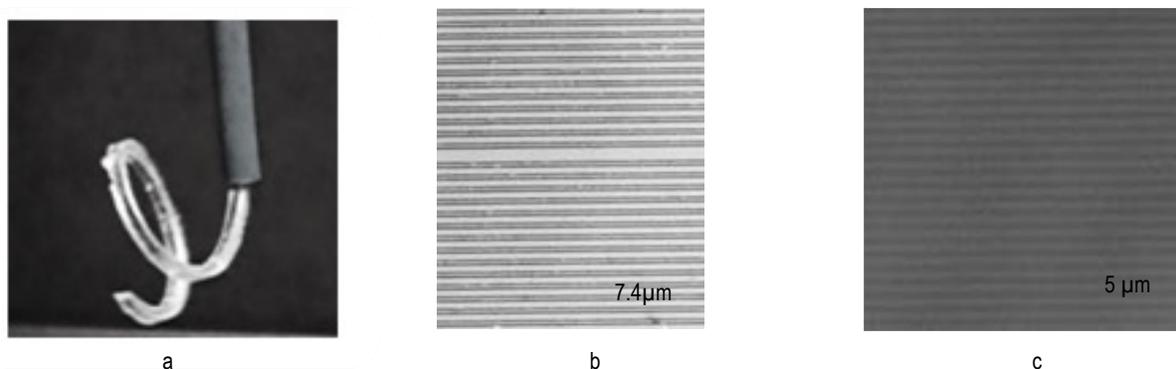


Figure 2. A shape memory polymer coil (a), a micron scale lithography pattern (b) and a diffraction grating pattern indicating a refractive index gradient (c) made from a two-stage reactive polymer system

References

- [1]. A. R. Kannurpatti, K. J. Anderson, J. W. Anseth, C. N. Bowman, *J. Polym. Sci. Part B*, 1997, **35**, 2297
- [2]. P.T. Mather, X Luo, I.A. Rousseau, *Ann. Rev. Mater. Research*. 2009, **39**, 445
- [3]. C. Liu, H. Qin, P.T Mather, *J. Mater. Chem.* 2007, **17**, 1543
- [4]. A. E. Rydholm, C. N. Bowman and K. S. Anseth, Degradable thiol-acrylate photopolymers: polymerization and degradation behavior of an in situ forming biomaterial. *Biomaterials*, **26** (2005), pp. 4495-4506.
- [5]. D.L. Elbert, A.B. Pratt, M.P. Lutolf, S. Halstenberg and J.A. Hubbell. Protein delivery from materials formed by self-selective conjugate addition reactions. *Journal of Controlled Release*, **76** (2004), pp.11-25.
- [6]. J. W. Chan, H. Wei, H. Zhou and C.E. Hoyle, The effects of primary amine catalyzed thio-acrylate Michael reaction on the kinetics, mechanical and physical properties of thio-acrylate network. *European Polymer Journal*, **45** 9 (2009), pp.2717-2725.
- [7]. D.P.Nair, N.B. Cramer, J.C.Gaipa, M.K.McBride, E.M. Matherly, R.M. McLeod, R. Shandas and C.N. Bowman, *Adv Funct Mater* 2012, doi: 10.1002/adfm.201102742.