

# STEP-GROWTH RADICAL-MEDIATED THIOL-ENE POLYMERIZATIONS IN WATER-BORNE SYSTEMS: EMULSIONS, SUSPENSIONS AND DISPERSIONS

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Key Words: Emulsion polymerization, water-borne polymerizations, thiol-ene 'click' chemistry.

Recent developments in radical-mediated thiol-ene polymerizations include the application of these reactions in emulsion, dispersion, and suspension systems.<sup>1-6</sup> These step-growth polymerizations have several significant advantages over traditional chain-growth (e.g., acrylic or styrenic) polymerizations. In particular, they allow for easy functionalization through simple stoichiometric adjustments of the monomers used in the polymerization; for example, adding a slight excess of thiol monomer produces colloidal polymer particles replete with thiol functionality. Furthermore, the subsequent use of thiol-ene (and thiol-yne) and other 'click' chemistries can lead to the facile production of biodegradable and bio-functionalized colloids.

Our early publications<sup>1-5</sup> showed that radical thiol-ene polymerizations can easily be performed in suspension, mini-emulsion, and dispersion polymerizations. In each of these cases, the initiator is oil (monomer) soluble, and thus particles grow either from the monomer droplets (in the cases of suspension or mini-emulsion systems), or from the precipitation of the growing polymer (in dispersion polymerizations). Very recently, we have shown that by using a water-soluble initiator, such as potassium persulfate (KPS), it is possible to perform thiol-ene polymerizations under conditions that essentially mimic those of traditional vinyl monomer emulsion polymerizations.<sup>6</sup> Furthermore, the formation of nanoparticles that may be uniform in size is possible.

In order to understand how reaction conditions effect particle size and polydispersity in these newly developed thiol-ene emulsion polymerizations, we have conducted a thorough study of these polymerizations using a wide range of initiator (KPS) and surfactant (sodium dodecyl sulfate, SDS) concentrations, with several different thiol-ene monomers (see Figure 1). Results from this study will be discussed, and conclusions regarding particle nucleation and growth mechanisms will be drawn.

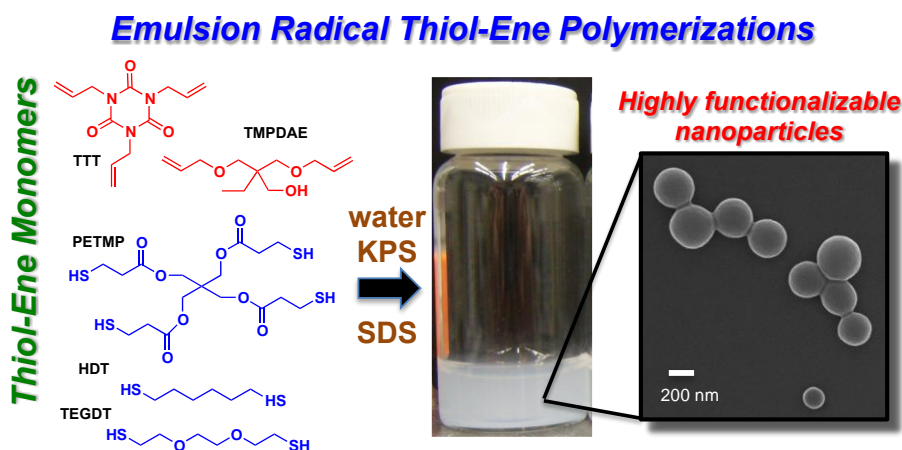


Figure 1. Outline of radical-mediated thiol-ene emulsion polymerizations.

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