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

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Recent developments in radical-mediated thiol-ene polymerizations include the application of these reactions in emulsion, dispersion, and suspension systems. 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 facile production of biodegradable and bio-functionalized colloids.

Our early publications 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. 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- and 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.