



Suspension thiol-ene photopolymerization: Effect of stabilizing agents on particle size and stability



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ABSTRACT

The impact of several surfactant species employed in the suspension photopolymerization of water-borne thiol-ene polymer microspheres is reported. The focus of analysis was on how different surfactant species and the surfactant concentrations affected particle size and particle size distributions. Surfactants used included sodium dodecyl sulfate (SDS), sodium dodecylbenzene sulfonate (SDBS), dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB), Tween 20, Tween 40, Tween 60, Tween 80, Lutensol XL 70, Lutensol XP 70, Pluronic PE 6400, and Pluronic F108 Pastille. Using stabilizing agents or surfactants is necessary to prevent extensive aggregation and agglomeration of crosslinked thiol-ene polymer. All surfactants used in this study for particle stabilization and development produced spherical thiol-ene polymer particles. The chemical structure and concentration of the surfactants influenced the final particle size and size distribution of particles obtained. In general, it was found that smaller particles are obtained with higher concentrations of stabilizing agent, especially for ionic surfactants.

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1. Introduction

The development of colloidal polymer particles with an assortment of shapes, sizes, and chemical properties has been greatly enhanced with advancements in material synthesis and characterization [1,2]. Furthermore, such particles allow for the incorporation of diverse chemical and mechanical functionality into a variety of devices and applications including pharmaceutical materials, biomedical scaffolds, cosmetics, drug delivery, infrastructure, chromatographic separation, and encapsulation of pigments or therapeutic agents. Water-borne polymer colloids with diameters ranging from nanometers to hundreds of microns [3–7] are often synthesized using direct polymerization of monomers because these approaches offer high yields, are relatively inexpensive to make in terms of materials and equipment, and are environmental compatible with reduced use of organic solvents [1,8]. These reactions can be accomplished through a variety of heterogeneous polymerization methods in a two-phase reaction system [3,9]. Classical heterogeneous polymerizations include emulsion, suspension, miniemulsion, microemulsion, and

dispersion polymerization [4,10–13]. The mechanism of particle synthesis plays a vital role in obtaining specific sizes and chemical properties for various applications [3,4,9].

In all methods of heterogeneous polymerization the stabilization of monomer droplets and/or polymer particles is a particularly important factor, and often determines the many outcomes of the reaction and product. During particle growth, there must be a balance between the phenomena of droplet comminution and coalescence as well as the attractive and repulsive forces associated with the polymer particles. The use of emulsifying agents or surfactants [14–20] can aid in developing equipose between these colloidal events while influencing particle growth and final particle size. Surfactants and polymeric materials often manipulate surface tension, surface charge, and surface viscosity as well as properties relating to aggregation state, sedimentation, and rheological properties [1,21–29]. As such, stabilizing materials allow for efficient tailoring of polymer particle properties. Furthermore, during particle synthesis, it is necessary to examine both the type of heterogeneous polymerization and type of stabilizing agent that can optimize particle growth and stability [3,13,14,17,30–32].

We have recently demonstrated that spherical, crosslinked polymer particles can be made using thiol-ene chemistry in a water-borne photopolymerization [33]. We found that the polymerizations exhibited characteristics that follow a suspension

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mechanism for particle development and growth. Others have developed a microfluidic approach for the suspension polymerization that resulted in larger thiol-ene/yne-based polymer beads [34]. In a suspension polymerization, the dispersed phase typically consists of monomer species and organic soluble initiators, and is added to an aqueous continuous phase that may include water and stabilizing compounds such as surfactants or emulsifiers. Thiol-ene polymerization follows a step-growth mechanism and thus offers an innovative approach to particle development in water-borne systems [35–39]. This method of polymer growth is a stark contrast to the chain-growth mechanism of polymer particle development encountered in traditional heterogeneous polymerizations that involve acrylic and styrenic monomers [35,40,41].

Given the significant influence that surfactants play in heterogeneous polymerizations it is important to evaluate surfactant influences on our newly developed suspension thiol-ene photopolymerizations. Our previously published work [33] on thiol-ene suspension polymerizations used only sodium dodecyl sulfate (SDS) as a surfactant. Because of the wide range of surfactants available, and the potential for them to alter particle formation and stability, and potentially polymerization mechanism (suspension vs. emulsion vs. dispersion), it is important to evaluate such stabilizing agents and determine if any significant changes occur. Thus, in this paper we demonstrate the effect of surfactant type and concentration on the final particle size and size distributions of thiol-ene polymer particles. Key parameters that are examined include the variation of surfactant concentration and the variation of surfactant species (anionic, cationic, and nonionic surfactants) and structural analogs. It is found that stabilizing agents are necessary to prevent extensive aggregation or agglomeration of the product particles during water-borne thiol-ene photopolymerizations [13,14,33].

2. Materials and methods

2.1. Materials

The photoinitiator 1-hydroxycyclohexyl phenyl ketone as well as monomers 1,3,5-triallyl-1,3,5-triazine-2,4,6(1H,3H,5H)-trione (TTT) and pentaerythritol tetrakis (3-mercaptopropionate) (PETMP) were obtained from Sigma Aldrich. Toluene was purchased from Fisher Scientific. Anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (SDBS) were obtained from J.T. Baker and Sigma Aldrich, respectively. Cationic surfactants dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB), and hexadecyltrimethylammonium bromide (HTAB) were purchased from Sigma Aldrich. Nonionic surfactant species Tween 20 and Tween 40 were obtained from Sigma Aldrich, Tween 60 from Acros, and Tween 80 from Amresco. The nonionic surfactants Lutensol XL 70, Lutensol XP 70, Pluronic PE 6400, and Pluronic F108 Pastille were obtained from BASF. Structures of each surfactant can be found in the [Supporting Information](#).

2.2. Thiol-ene suspension photopolymerization

All reactions consisted of 10 ml aqueous solutions with 10 wt. % monomer content relative to water. The concentrations of surfactant were between 0.1 and 5 wt. % (relative to water). The TTT (23.6 wt. %) and PETMP (34.6 wt. %) were combined with the 1-hydroxycyclohexyl phenyl ketone (0.1 wt. % relative to amount of monomers). Toluene (41.7 wt. %) was added in a 1:1 volume ratio relative to the monomers. Reactions were homogenized using magnetic stirring in a glass vial (20 ml, O.D. \times H 25 mm \times 57 mm) and Teflon-coated micro stir bar (12.7 mm \times 3 mm). Upon

combination of the organic phase and aqueous phase, the reaction was allowed to mix for 5 min and then cured under UV light (365 nm, 11 mW/cm²).

2.3. Characterization

Analysis of product particles was performed using an Olympus optical microscope, where samples were prepared by simple air-drying or drying in a vacuum oven. Quantitative analysis of particle size was done via laser diffraction using a Malvern Mastersizer 2000. All product particles were washed with distilled water and ethanol and then dried prior to analysis. Each sample was examined at 50% sonication and 1750 rpm stirring. The zeta potential analyses were conducted using a Brookhaven Instruments Corporation ZetaPALS – Zeta Potential Analyzer. This instrument uses phase analysis light scattering (PALS) in the measurement of electrophoretic mobility (EPM) and the calculation of zeta potential (ζ).

3. Results and discussion

Our approach in developing water-borne thiol-ene polymer particles uses heterogeneous suspension polymerization [33]. This method involves mixing an organic phase, consisting of multifunctional monomers, initiator, and diluent, and an aqueous phase, consisting of surfactant or stabilizing agent dissolved in water [11,40,42–44]. The organic phase is emulsified in the aqueous phase using mechanical agitation, in order to create monomer droplets. Upon exposure to ultra-violet light, polymerization occurs within these droplets to create crosslinked polymer microspheres. A water-immiscible solvent, such as toluene, may be used as the diluent to facilitate emulsification by lowering the viscosity of the dispersed phase. In addition, stabilizing agents can be used to influence average particle size, particle size distribution, and particle stability during particle synthesis. This method of producing water-borne thiol-ene polymer particles [33] is schematically shown in [Fig. 1](#).

Because of the significant role that surfactants play in particle development and stabilization, we investigated their effect on thiol-ene suspension polymerization. Furthermore, changes in surfactant or stabilizing species [24,45–47] can greatly impact the size of polymer particles obtained. Consequently, the selection of surfactant stabilizer plays an imperative role in the overall control and manipulation of final particle size. Thus, in the following discussion we present the effect that various anionic, cationic, and non-ionic surfactant systems have in thiol-ene suspension photopolymerizations.

3.1. Anionic surfactants

Our work has focused on two specific anionic surfactants, the alkyl sulfate SDS and the alkylbenzene sulfonate SDBS. Particle stabilization is achieved through electrostatic interactions due to the charged portion of the surfactant molecule [18,19,48–50]. Our previous work used SDS in the synthesis of thiol-ene polymer particles. However, both SDS and SDBS are widely used in dispersed systems, with SDBS having a lower CMC than SDS (see [Table 1](#)) [18,19,48]. In the present investigation, both anionic species were examined at concentrations of 5, 1, 0.5, and 0.1 wt. %. Images comparing product thiol-ene particles are shown in [Fig. 2](#).

The general trend in particle size that is observed in these reactions with the anionic surfactant SDS is that smaller, spherical particles are formed at higher surfactant concentrations ([Fig. 2A](#)). At lower SDS concentrations ([Fig. 2D](#)), the particles are still spherical but there appears to be a greater variation in particle

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