



# Thiol-ene oligomers as dental restorative materials

Jacquelyn A. Carioscia<sup>a</sup>, Hui Lu<sup>a,b</sup>, Jeffrey W. Stanbury<sup>a,b</sup>,  
Christopher N. Bowman<sup>a,b,\*</sup>

<sup>a</sup>Department of Chemical and Biological Engineering, Engineering Center,  
University of Colorado at Boulder, ECCH 111, Boulder, CO 80309-0424, USA

<sup>b</sup>Biomaterials Research Center, School of Dentistry,  
University of Colorado Health Sciences Center, Aurora, CO 80045-0508, USA

Received 25 November 2004; accepted 7 April 2005

## KEYWORDS

Thiol-ene;  
Photopolymerization;  
Oligomer;  
Polymerization  
shrinkage;  
Shrinkage stress

**Summary Objective.** The aim of this work was to prereact thiol-ene monomers to create reactive thiol or vinyl (ene)-functionalized oligomers, and to investigate the use of these materials as novel dental restorative material. Investigation has focused on the application of oligomeric thiol-ene materials as dental restorative resins with lower polymerization shrinkage and polymerization stress as compared to monomeric thiol-ene systems and particularly with respect to current dimethacrylate-based systems.

**Methods.** Reactive thiol-functionalized oligomers were created via photopolymerization using triallyl-1,3,5-triazine-2,4,6-trione (TATATO), trimethylolpropane tris(3-mercaptopropionate) (trithiol) and pentaerythritol tetramercaptopropionate (tetrathiol). Kinetic and mechanical investigation of Bis-GMA/TEGDMA, and oligomeric and monomeric thiol-ene systems were conducted. More specifically, polymerization shrinkage and stress, polymerization kinetics, glass transition temperature, flexural strength and flexural modulus were evaluated.

**Results.** Upon evaluation, the polymerization stress of oligomeric thiol-ene systems was dramatically reduced by as much as 33% when compared with the stress exhibited by monomeric thiol-ene systems and as much as a 92% reduction in stress relative to the current dimethacrylate-based dental restorative materials. Furthermore, the flexural strength and modulus of the monomeric and oligomeric thiol-ene resins were not significantly different.

**Significance.** Oligomeric thiol-ene systems offer potential as alternative dental restorative resins due to the significant reduction in polymerization shrinkage and stress while retaining the mechanical properties of monomer-based thiol-ene resins.

© 2005 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

\* Corresponding author. Address: Department of Chemical and Biological Engineering, Engineering Center, University of Colorado at Boulder, ECCH 111, Boulder CO 80309-0424, USA. Tel.: +1 303 492 3247; fax: +1 303 492 4341.

E-mail address: christopher.bowman@colorado.edu (C.N. Bowman).

## Introduction

Aesthetic appeal and improved clinical performance have made photopolymerizable dimethacrylate-based composites a leading choice over numerous other materials for use in dental restorations. One of the primary components of polymeric dental materials is 2,2-bis[*p*-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA) owing to its advantageous mechanical strength and low volatility [1]. However, resin composites containing the highly viscous Bis-GMA require lower molecular weight diluents, such as triethylene glycol dimethacrylate (TEGDMA), to improve fluidity, conceding a higher probability of extractable monomer, increased moisture uptake, and greater polymerization shrinkage [2]. Polymerization shrinkage, a consequence of replacing van der Waal distances in the uncured resin with covalent bonds in the polymer, begets polymerization stress, potentially leading to premature failure of the restoration [3].

Reducing or eliminating polymerization shrinkage and the associated stress has been a thrust in dental material research for decades. One of the first attempts, conducted by Bailey and co-workers [4], investigated bicyclic compounds, such as spiro orthocarbonates (SOCs), which undergo a free radical ring opening polymerization, to be used as an expanding comonomer in composite formulations. However, SOC's exhibit incomplete ring-opening as well as limited solubility and minimal copolymerization in dimethacrylate resins, resulting in minimal shrinkage reduction [5,6]. Numerous other investigations of ring-opening systems such as oxiranes and epoxies, which polymerize with lower shrinkage than methacrylates, have improved on these limitations but have not as yet led to a practical system [7-12]. Additional experimentation in low shrinkage dental materials has included multifunctional Bis-GMA derivatives, substitution of pendant hydroxyl groups located on Bis-GMA with alkyl isocyanates, copolymerization with monovinyls, and cyclopolymerization reactions using oxybismethacrylates, all of which have limited success in reducing shrinkage and/or shrinkage stress [13-15].

Recently, a novel approach to low shrinkage polymeric dental resins using thiol-ene photopolymerizable monomers was proposed by Bowman et al. [16]. Thiol-ene resins polymerize via a step-growth mechanism, rather than the chain-growth mechanism characteristic of dimethacrylate resins, resulting in a delayed gel point and enhanced control of the polymerization [17]. Furthermore,

monomeric thiol-ene resins exhibit 12-15 ml shrinkage/mol C=C polymerized, which represents a notable reduction in polymerization shrinkage when compared with the 22.5-ml shrinkage/mol C=C polymerized for methacrylate systems [16,18].

Polymerization via a step-growth mechanism offers the advantages of molecular weight control, delayed gelation, and terminal functionality tunability. Here, utilizing these properties, highly functional, oligomeric thiol and vinyl materials are created by prereacting the starting monomers, *ex situ*, with the desired terminal functionality in excess. The hypothesis is that stoichiometric mixtures of the preformed reactive oligomers, upon final polymerization, will yield polymer with mechanical performance equivalent to polymer formed from bulk, monomeric thiol-ene resins, yet will further reduce polymerization shrinkage and polymerization stress by decreasing the vinyl functional group concentration in the oligomer-based resins.

The objective of this study was to prepare reactive thiol-ene oligomers using a photopolymerization technique and to evaluate the oligomeric thiol-ene resins as viable, low shrinkage and low stress dental restorative materials. More specifically, polymerization shrinkage and stress, polymerization kinetics, glass transition temperature, flexural strength and flexural modulus were evaluated.

## Materials and methods

### Materials

The ene and thiol starting monomers were triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (TATATO), pentaerythritol tetra(3-mercaptopropionate) (tetrathiol) and trimethylolpropane tris(3-mercaptopropionate) (trithiol) (all obtained from Aldrich, Milwaukee, WI). The dimethacrylate monomers evaluated were 2,2-bis[*p*-(3-methacryloxy-2-hydroxypropoxy)phenyl]propane (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) (Esstech, Essington, PA). The visible light photoinitiators used were camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (EDAB) (Aldrich) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Ciba-Geigy, Hawthorn, NY) was used as the UV photoinitiator. All monomers and photoinitiators were used without additional purification. The thiol-ene resins used in this study were prepared as stoichiometric mixtures based on equivalent functional group concentrations, whereas

Download English Version:

<https://daneshyari.com/en/article/10612514>

Download Persian Version:

<https://daneshyari.com/article/10612514>

[Daneshyari.com](https://daneshyari.com)