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## Thiol-ene-methacrylate composites as dental restorative materials

Jordan E. Boulden<sup>1</sup>, Neil B. Cramer<sup>2</sup>, Kathleen M. Schreck<sup>2</sup>, Charles L. Couch<sup>2</sup>, Cora Bracho-Troconis<sup>1</sup>, Jeffrey W. Stansbury<sup>2,3</sup>, and Christopher N. Bowman<sup>2,3,\*</sup>

<sup>1</sup> Septodont, Confi-Dental Division, Louisville CO, 80027

<sup>2</sup> Department of Chemical & Biological Engineering, University of Colorado, CB 424, Boulder, CO 80309

<sup>3</sup> Biomaterials Research Center, School of Dental Medicine, University of Colorado Denver, Aurora, CO 80045

### Abstract

**Objectives**—The objective of this study was to evaluate composite methacrylate-thiol-ene formulations with varying thiol:ene stoichiometry relative to composite dimethacrylate control formulations. It was hypothesized that the methacrylate-thiol-ene systems would exhibit superior properties relative to the dimethacrylate control resins and that excess thiol relative to ene would further enhance shrinkage and conversion associated properties.

**Methods**—Polymerization kinetics and functional group conversions were determined by Fourier transform infrared spectroscopy (FTIR). Volume shrinkage was measured with a linometer and shrinkage stress was measured with a tensometer. Flexural modulus and strength, depth of cure, water sorption and solubility tests were all performed according to ISO 4049.

**Results**—All of the methacrylate-thiol-ene systems exhibited improvements in methacrylate conversion, flexural strength, shrinkage stress, depth of cure, and water solubility, while maintaining equivalent flexural modulus and water sorption relative to the dimethacrylate control systems. Increasing the thiol to ene stoichiometry resulted in further increased methacrylate functional group conversion and decreased volume shrinkage. Flexural modulus and strength, shrinkage stress, depth of cure, water sorption and solubility did not exhibit statistically significant changes with excess thiol.

**Significance**—Due to their improved overall functional group conversion and reduced water sorption, the methacrylate-thiol-ene formulations are expected to exhibit improved biocompatibility relative to the dimethacrylate control systems. Improvements in flexural strength and reduced shrinkage stress may be expected to result in composite restorations with superior longevity and performance.

\*Corresponding author: Christopher N. Bowman, University of Colorado, Dept. of Chemical & Biological Engineering, 1111 Engineering Dr., CB424, Boulder, CO 80309, phone 303-492-3247, fax 303-492-4341, christopher.bowman@colorado.edu.

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## Introduction

Presently, composite restoratives suffer from several significant drawbacks associated with the chain growth nature of the methacrylate-based free radical polymerization process. These problems include the significant shrinkage [1] that occurs during the polymerization process and the corresponding stress [2–4] that arises due to early gelation, thermal expansion mismatch [5], moisture uptake by the sample following polymerization [6], the presence of extractable, unreacted monomer following cure [7,8], and inhibition of the polymerization by oxygen [9,10].

Recently, we have considered the implementation of dental restorative materials based on resins comprised of either binary thiol-ene [9,11–14] or ternary methacrylate-thiol-ene [14,15] compositions. Thiol-ene-based resins exhibit a step growth radical polymerization mechanism in contrast to the chain growth polymerization mechanism of (meth)acrylate systems. The thiol-ene polymerization mechanism comprises the addition of a thiyl radical to an ene functional group, followed by chain transfer to a thiol, thus regenerating the thiyl radical [16–18]. Traditional ene monomers utilized in thiol-ene systems (allyl ether, vinyl ether, norbornene, etc.) are not homopolymerizable, resulting in a true step growth radical polymerization mechanism [19,20]. As a result of the step growth polymerization mechanism, thiol-ene photopolymerizations have numerous kinetic advantages relative to the more common dimethacrylate-based materials. Thiol-ene polymerizations uniquely result in reduced volume shrinkage per double bond and a significantly delayed gel point conversion. The combination of reduced shrinkage and delayed gelation promotes significant reductions in shrinkage stress [9,14]. Additionally, the unique polymerization mechanism also delays the vitrification process, resulting in delayed autodeceleration and ultimately leading to higher functional group conversions as compared to analogous chain growth systems. When oxygen interacts with either carbon or thiyl radicals to form a peroxy radical, chain transfer to thiol functional groups minimizes the effects of oxygen inhibition [16,21]. Since thiol-ene systems exhibit reduced inhibition, initiation in these systems is more effective. This phenomenon is often evidenced by a lack of an inhibition period before the polymerization begins and can also be observed by achieving increased cure depths with minimal tacky layer formation on any air-exposed surface.

Concomitant with the reduction in volume shrinkage in thiol-ene systems is a reduction in crosslink density and therefore one of the drawbacks of thiol-ene systems is that they generally exhibit reduced mechanical properties relative to dimethacrylate-based systems [9,14]. However, the use of thiol-enes as reactive diluents in ternary formulations (e.g. as a replacement for triethylene glycol dimethacrylate) uniquely results in a synergistic combination of both thiol-ene polymerization kinetics and shrinkage dynamics with dimethacrylate mechanical properties [14,15]. Additionally, the methacrylate-thiol-ene systems often exhibit a pseudohybrid polymerization whereby the first stage is dominated by methacrylate homopolymerization and chain transfer to thiol and the second stage is dominated by thiol-ene polymerization [14,15,22]. The hybrid nature of the methacrylate-thiol-ene polymerization results in even greater reductions in shrinkage stress without compromising mechanical properties. When compared to BisGMA/TEGDMA formulations, methacrylate-thiol-ene resins were demonstrated to exhibit increased methacrylate conversion, equivalent cure speed and flexural modulus, and decreased polymerization shrinkage stress [14,15].

In methacrylate-thiol-ene systems, the thiol functional groups are consumed by chain transfer from both the ene-centered radicals (allyl ether or norbornene) and methacrylate-centered radicals). However, the ene functional groups are consumed only by thiyl radical propagation as they do not react with either of the vinyl-centered radicals in the

polymerization. Therefore, the traditional 1:1 stoichiometry that is optimal for thiol-ene polymerizations [16,20] results in low ene conversion and is suboptimal in regards to conversion and mechanism for ternary methacrylate-thiol-ene formulations. By increasing the thiol to ene ratio, the ene conversion and ultimately crosslinking are increased. Additionally, since volume shrinkage is proportional only to the amount of double bonds that react and is not dependent at all on the thiol reaction extent, as the thiol concentration is increased, there are fewer double bonds available to cause volume shrinkage [9]. Thus, with increased thiol content, further reductions in shrinkage stress were obtained while maintaining mechanical properties and increasing overall functional group conversion [15].

For resin systems to achieve the desired property requirements and function as a dental restoration, they must be utilized as composites [23]. Most dental restorative materials are comprised of 60–87 wt% glass filler [24] to improve mechanical properties and reduce volume shrinkage [25,26]. Typically, the larger filler particles provide primary reinforcement as well as radioopacity to the composite while the smaller fumed silica nanoparticles enable increased overall filler loading along with an improved surface finish.

In this study, methacrylate-thiol-ene systems are evaluated as composite systems with glass fillers relative to composite dimethacrylate control resins where each of these resin formulations was filled to the same consistency with inorganic glass fillers. The composites were then initiated with visible light and evaluated for polymerization kinetics, volume shrinkage, depth of cure, water absorption and solubility, flexural modulus, flexural strength, and polymerization shrinkage stress. We hypothesize that the ternary methacrylate-thiol-ene composite systems will exhibit equivalent or improved performance relative to the dimethacrylate controls and that off-stoichiometric thiol to ene ratios would further enhance properties.

## Materials and Methods

### Materials

The monomers 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BisGMA), ethoxylated bisphenol-A dimethacrylate (EBPADMA) and triethylene glycol dimethacrylate (TEGDMA) were donated by Esstech (Essington, PA). Pentaerythritol tetra(3-mercaptopropionate) (PETMP) was donated by Evans Chemetics (Waterloo, NY) and triallyl-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (TATATO) was purchased from Aldrich (Milwaukee, WI). The stabilizer, aluminum N-nitrosophenylhydroxylamine (Q1301), was donated by Wako Pure Chemical (Osaka, Japan) and the initiator, bis acyl phosphine oxide (BAPO/Irgacure 819) was donated by Ciba Specialty Chemicals (Tarrytown, NY). Chemical structures of the monomers used are shown in figure 1.

### Methods

The methacrylate-thiol-ene systems contained 70 wt% dimethacrylate (EBPADMA) and 30 wt% thiol-ene. The thiol-ene portion was comprised of a tetrafunctional thiol and a trifunctional allyl ether at 1:1, 2:1, or 3:1 stoichiometric ratios of thiol to allyl ether functional groups in otherwise equivalent composites. Each resin included 0.035 wt% Q1301 as an inhibitor and 0.3 wt% BAPO as an initiator. BAPO is a commonly available visible light photoinitiator that initiates by a cleavage mechanism. This initiator was used rather than the more traditional camphorquinone/amine system due to the fact that it is a cleavage initiator and the initiation rate is less likely to be affected by the changing chemistry of the various resin systems. In this manner, the initiation rate remained nearly constant across the different systems being evaluated, enabling improved interpretation of

the resulting polymerization kinetics as being dependent on the monomer formulation rather than the initiation rate.

All resins systems were filled to the same consistency with inorganic glass filler comprised of 90 wt% 0.4  $\mu\text{m}$  glass from Schott (Elmsford, NY) and 10 wt% aerosil OX-50 donated from Septodont, Confi-Dental Division (Louisville, CO). The consistency was determined by placing 3.5 kg of weight on a sample of consistent size ( $1.0 \pm 0.2 \text{ cm}^3$ ) for 3 minutes to produce a flattened sample with a diameter of 31 mm. To maintain uniform consistency, the filler loading was slightly different for the different resin systems due to differences in resin viscosity as well as the interaction between the resin and filler. The methacrylate-thiol-ene resins contained approximately 72.5 wt% inorganic glass filler. The control resins were filled with 73.5 wt% glass filler for BisGMA/TEGDMA and 76.0 wt% glass filler for EBPADMA/TEGDMA. The composites were mixed with a Flacktek Speedmixer (DAC 150 FVZ, Flacktek Inc, Landrum SC) at 2000 RPM for 120 seconds. Photocuring was performed with a Maxima Pure Power dental lamp with irradiation intensity of  $500 \text{ mW/cm}^2$ .

### Depth of Cure

A cylindrical mold 6 mm long and 4 mm in diameter was filled with the composite resin and cured for 20 seconds from one end. The uncured material was then removed with a razor blade and the cured specimen is measured in five locations with a micrometer accurate to 0.01 mm. The averaged value was divided by two to obtain the depth of cure. The procedure was performed according to ISO 4049–7.10.

### Flexural Strength and Modulus

Six molds were prepared in dimensions of  $2 \times 2 \times 25 \text{ mm}$ . Samples were irradiated for 120 seconds on each side and then stored in  $37 \pm 1^\circ\text{C}$  distilled water for  $24 \pm 2$  hours. Polymer flexural strength and modulus were calculated using data obtained from a 3-point flexural test, carried out with a hydraulic universal test system (858 Mini Bionix, MTS Systems Corporation, Eden Prairie, MN, USA) using a span width of 20 mm and a crosshead speed of 1 mm/min. The procedure was performed according to ISO 4049–7.11.

### Fourier Transform Infrared Spectroscopy (FTIR)

Functional group conversion was determined by FTIR in the near infrared ( $7000\text{--}4000 \text{ cm}^{-1}$ ) using a Nicolet 750 Magna FTIR spectrometer (Madison, WI) with a KBr beam splitter and a MCT/A detector. Samples were placed between two thin plastic films and two glass slides with a sample thickness of 2 mm. Functional group conversions were monitored utilizing the characteristic  $\text{=C-H}$  methacrylate absorption peak at  $6164 \text{ cm}^{-1}$  and the allyl ether absorption peak at  $6132 \text{ cm}^{-1}$ . A Gaussian fitting peak deconvolution method was utilized to determine the individual functional group conversions. For each system, six trials were performed.

### Volumetric Shrinkage

A small sample of material was placed on the detector of a linometer (ACTA, Amsterdam) and cured for 40 seconds. The linear shrinkage was recorded for an additional ten minutes and the linear shrinkage value at the end of testing was multiplied by three to approximate volumetric shrinkage of the composite. A minimum of three trials were conducted for each material.

### Polymerization Shrinkage Stress

A tensometer (American Dental Association Health Foundation) was used to measure stress development during the photopolymerization reaction [2,3]. Specimens  $\sim 1.5 \text{ mm}$  thick were

placed between 6 mm diameter glass rods with silane treated ends. The curing light was transmitted through the lower glass rod. Samples were irradiated for 40 seconds and the stress profile was monitored for an additional 20 minutes. A minimum of three trials were conducted.

### Water Sorption and Solubility

Cylindrical molds were prepared 15 mm in diameter and 1 mm thick, and cured specimens were maintained in a dessicator at  $37 \pm 1$  °C until a constant weight is recorded (m1). The physical dimensions were recorded and the specimens were then immersed in distilled water maintained at  $37 \pm 1$  °C for seven days. The molds were then blotted dry and air dried for 15 seconds before being weighed (m2). The specimens were then returned to the dessicator at  $37 \pm 1$  °C until a constant weight was achieved (m3). Water sorption ( $W_{sp}$ ) and water solubility ( $W_{sl}$ ) were then calculated according to equations 1 and 2.

$$W_{sp} = \frac{m2 - m3}{V} \quad \text{Equation 1}$$

$$W_{sl} = \frac{m1 - m3}{V} \quad \text{Equation 2}$$

V is equal to the volume of each specimen, calculated from the dimensions recorded. For each composition, 5 replicate experiments were performed. The procedure was performed according to ISO 4049–7.12.

### Statistical Analysis

The experimental results were analyzed using one-way analysis of variance (ANOVA). Multiple pair-wise comparisons were further conducted using Tukey's test with a significance level of 0.05.

### Results

Flexural strength, flexural modulus, and methacrylate and allyl ether functional group conversions were evaluated for each of the composite formulations, and the results are presented in Table 1. The ternary methacrylate-thiol-ene composites exhibited flexural strengths of  $145 \pm 11$ ,  $146 \pm 8$ , and  $150 \pm 9$  MPa for the 1:1, 2:1, and 3:1 systems, respectively. All of the methacrylate-thiol-ene systems exhibited significantly improved flexural strength relative to both the BisGMA/TEGDMA and EBPADMA/TEGDMA ( $87 \pm 8$  and  $101 \pm 10$  MPa, respectively) control composites. The flexural modulus for the methacrylate-thiol-ene systems was the highest for the 1:1 system ( $9.2 \pm 0.9$  GPa) and decreased for the 2:1 and 3:1 systems ( $8.8 \pm 0.8$  and  $8.2 \pm 1.0$  GPa, respectively); however, the differences are not statistically significant. The flexural modulus of the methacrylate-thiol-ene composites was higher than BisGMA/TEGDMA ( $7.2 \pm 0.8$  GPa) and equivalent to EBPADMA/TEGDMA ( $8.9 \pm 0.8$  GPa). Functional group conversions were measured for each of the samples tested for flexural modulus. As the ratio of thiol-to-ene was increased from 1:1 to 3:1, the methacrylate functional group conversion increased from  $69 \pm 1$  % to  $74 \pm 1$  % and the allyl ether functional group conversion increased from  $17 \pm 2$  % to  $35 \pm 3$  %. Methacrylate functional group conversion for all of the methacrylate-thiol-ene systems was increased relative to that for the BisGMA/TEGDMA ( $54 \pm 1$  %) and EBPADMA/TEGDMA ( $59 \pm 1$  %) controls.

The polymerization volume shrinkage measured for the 1:1 methacrylate-thiol-ene system ( $2.3 \pm 0.1$  %) was not statistically different from the BisGMA/TEGDMA and EBPADMA/TEGDMA ( $2.4 \pm 0.1$  and  $2.5 \pm 0.1$  %, respectively) controls (Table 2). Increasing the thiol-to-ene ratio to 2:1 and 3:1 results in the volume shrinkage decreasing to  $2.0 \pm 0.1$  % and  $1.8 \pm 0.2$  %, respectively. Despite the decreased volume shrinkage, the methacrylate-thiol-ene systems did not exhibit any statistically significant differences in shrinkage stress for the 1:1, 2:1, or 3:1 systems (Table 2). The 3:1 system exhibited the least amount of shrinkage stress at  $1.5 \pm 0.3$  MPa versus  $1.7 \pm 0.1$  and  $1.8 \pm 0.2$  MPa for the 1:1 and 2:1 systems. Shrinkage stress was decreased between 20–35 % relative to the BisGMA/TEGDMA and EBPADMA/TEGDMA controls.

The calculated depth of cure, water sorption, and water solubility for each material are shown in Table 3. The methacrylate-thiol-ene systems all exhibited greater depths of cure than the controls which achieved  $2.15 \pm 0.04$  mm for BisGMA/TEGDMA and  $2.26 \pm 0.03$  mm for EBPADMA/TEGDMA. The 2:1 and 3:1 methacrylate-thiol-ene systems exhibited the greatest depths of cure at  $2.62 \pm 0.03$  and  $2.63 \pm 0.06$  mm, respectively. Water sorption for the methacrylate-thiol-ene systems was  $14 \pm 1$ ,  $12 \pm 1$ , and  $13 \pm 1$   $\mu\text{g}/\text{mm}^3$  for the 1:1, 2:1, and 3:1 systems, respectively. There is a significant decrease in water sorption for the methacrylate-thiol-ene systems as compared to the BisGMA/TEGDMA ( $30 \pm 1$   $\mu\text{g}/\text{mm}^3$ ) control and a slight decrease relative to the EBPADMA/TEGDMA ( $15 \pm 1$   $\mu\text{g}/\text{mm}^3$ ) control, though not statistically significant. No significant water solubility was measured for any of the methacrylate-thiol-ene systems as compared to  $5 \pm 1$  and  $3 \pm 1$   $\mu\text{g}/\text{mm}^3$  for the BisGMA/TEGDMA and EBPADMA/TEGDMA controls.

## Discussion

The ternary methacrylate-thiol-ene formulations exhibited increased methacrylate conversion relative to the dimethacrylate controls. At 74% conversion of methacrylate functional groups in the 3:1 methacrylate-thiol-ene system, less than 7% of the methacrylate monomer remains with neither methacrylate reacted and therefore extractable. This behavior is in contrast to the BisGMA/TEGDMA system, where at 54% conversion, 21% of the monomers are theoretically extractable. In the methacrylate-thiol-ene system the ene functional groups exhibited only 35% conversion (3:1 system). However, due to the ene monomer having three functional groups, only 27% of the ene monomer will be completely unreacted and theoretically extractable. Further, the ene monomer comprises only a small fraction (5.5 wt%) of the total resin composition. The methacrylate-thiol-ene systems therefore exhibited an overall reduced amount of theoretically unreacted and extractable monomer. Further evidence for reduced extractables is provided by the water solubility tests, which indicated a significant reduction in extractables for the methacrylate-thiol-ene systems.

The methacrylate-thiol-ene systems also exhibited increased flexural strength relative to the control dimethacrylate systems. We hypothesize that increased methacrylate functional group conversion in these systems results in better integration of the methacrylate functionalized filler particles into the polymer matrix and hence improved properties. The increased conversion values and decreased water solubility not only strengthen important mechanical and wear resistance properties but should also improve the long-term biocompatibility of these systems.

As the ratio of thiol-to-ene is increased, the methacrylate-thiol-ene materials maintained equivalent properties in regards to flexural strength, flexural modulus, shrinkage stress, depth of cure, water sorption, and water solubility properties while experiencing improvements in functional group conversion and decreased volume shrinkage. Relative to



the dimethacrylate controls, all of the methacrylate-thiol-ene systems exhibited improvements in conversion, flexural strength, shrinkage stress, depth of cure and water solubility, while maintaining equivalent properties in regards to flexural modulus and water sorption. The improvements in properties likely will result in superior longevity and performance relative to bulk dimethacrylate composite systems.

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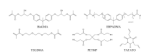
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**Figure 1.**  
Chemical structures of the monomers used in this study with their abbreviations.

**Table 1**

Flexural strength, flexural modulus, and functional group conversions for dimethacrylate controls and methacrylate-thiol-ene composite systems. All samples contained 0.3 wt % BAPO, 0.035 wt% Q1301, and were irradiated for 120 seconds. Within each column, the letters indicate statistically significant differences ( $P < 0.05$ ) as determined by a one-way ANOVA and a Tukey post-hoc pair-wise comparison test.

Formulation	Thiol:Ene Ratio	Methacrylate Conversion (%)	Ene Conversion (%)	Flexural Strength (MPa)	Flexural Modulus (GPa)
BisGMA/ TEGDMA	--	54 (1) <sup>a</sup>	--	87 (8) <sup>a</sup>	7.2 (0.8) <sup>a</sup>
EBPADMA/ TEGDMA	--	59 (1) <sup>b</sup>	--	101 (10) <sup>a</sup>	8.9 (0.8) <sup>b</sup>
EBPADMA/PETMP:TATATO	1:1	69 (1) <sup>c</sup>	17 (2) <sup>a</sup>	145 (11) <sup>b</sup>	9.2 (0.9) <sup>b</sup>
EBPADMA/PETMP:TATATO	2:1	72 (2) <sup>d</sup>	29 (2) <sup>b</sup>	146 (8) <sup>b</sup>	8.8 (0.8) <sup>b</sup>
EBPADMA/PETMP:TATATO	3:1	74 (1) <sup>d</sup>	35 (3) <sup>c</sup>	150 (9) <sup>b</sup>	8.2 (1.0) <sup>ab</sup>

**Table 2**

Volumetric shrinkage and shrinkage stress for the methacrylate controls and methacrylate-thiol-ene composite formulations. Samples contained 0.3 wt% BAPO and 0.035 wt% Q1301 and were irradiated for 40 seconds. Shrinkage stress was monitored for an additional 20 minutes. Within each column, the letters indicate statistically significant differences ( $P < 0.05$ ) as determined by a one-way ANOVA and a Tukey post-hoc pairwise comparison test.

Formulation	Thiol:Ene Ratio	Volumetric Shrinkage (%)	Shrinkage Stress (MPa)
BisGMA/ TEGDMA	NA	2.4 (0.1) <sup>a</sup>	2.2 (0.1) <sup>a,b</sup>
EBPADMA/ TEGDMA	NA	2.5 (0.1) <sup>a</sup>	2.3 (0.1) <sup>a</sup>
EBPADMA/PETMP:TATATO	1:1	2.3 (0.1) <sup>a,b</sup>	1.7 (0.1) <sup>c</sup>
EBPADMA/PETMP:TATATO	2:1	2.0 (0.1) <sup>b,c</sup>	1.8 (0.2) <sup>b,c</sup>
EBPADMA/PETMP:TATATO	3:1	1.8 (0.2) <sup>c</sup>	1.5 (0.3) <sup>c</sup>

**Table 3**

Depth of cure, water sorption and solubility for the methacrylate controls and methacrylate-thiol-ene composite systems. Samples contained 0.3 wt% BAPO, 0.035 wt% Q1301. The letters indicate statistically significant differences ( $P < 0.05$ ) as determined by a one-way ANOVA and a Tukey post-hoc pair-wise comparison test.

Formulation	Thiol:Ene Ratio	Depth of Cure (mm)	Water Sorption ( $\mu\text{g}/\text{mm}^3$ )	Water Solubility ( $\mu\text{g}/\text{mm}^3$ )
BisGMA/ TEGDMA	NA	2.15 (0.04) <sup>a</sup>	30 (1) <sup>a</sup>	5 (1) <sup>a</sup>
EBPADMA/ TEGDMA	NA	2.26 (0.03) <sup>b</sup>	15 (1) <sup>b</sup>	3 (1) <sup>b</sup>
EBPADMA/PETMP:TATATO	1:1	2.53 (0.04) <sup>c</sup>	14 (2) <sup>b,c</sup>	0 (1) <sup>c</sup>
EBPADMA/PETMP:TATATO	2:1	2.62 (0.03) <sup>d</sup>	12 (1) <sup>c</sup>	0 (1) <sup>c</sup>
EBPADMA/PETMP:TATATO	3:1	2.63 (0.06) <sup>d</sup>	13 (1) <sup>b,c</sup>	0 (1) <sup>c</sup>