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Synthesis and characterization of photo-curable bis-quaternary ammonium dimethacrylate with antimicrobial activity for dental restoration materials

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ABSTRACT

In this study, new quaternary ammonium bis-phenol A glycerolate dimethacrylate (QABGMA) was synthesized and proposed as a possible antimicrobial dental monomer. Such monomer has the potential to copolymerize with other methacrylate monomers and impart antimicrobial activity in dental resins and other systems. QABGMA monomer was synthesized and incorporated (at 0–15 wt.%) into a 1/1 (wt./wt.) mixture of bisphenol A glycerolate dimethacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA). The mixture was cured by visible light irradiation and degree of conversion (DC) was measured by Fourier Transform Infrared Spectrophotometer (FT-IR). Weight increase and solubility of the cured specimens were measured by immersion in water and ethanol/water solution (75/25, v/v) at 37 ± 1 °C for 30 days. The antimicrobial activity of QABGMA monomer was investigated against Gram-positive bacteria (*Streptococcus mutans*, *Staphylococcus aureus* and *Bacillus subtilis*), Gram-negative bacteria (*Escherichia coli* and *Pseudomonas aeruginosa*) and a fungus *Candida albicans*. Finally, cytotoxicity and viability of resin on L929 fibroblast cells were quantified. The incorporated difunctional QABGMA reduced degree of conversion slightly and increased water absorption of the cured polymer. The dental materials obtained from the QABGMA polymerization system showed good antimicrobial activity against tested microorganisms. Also, resin with ⩾10 wt.% QABGMA showed significantly reduced viability.

1. Introduction

Acrylic based resins, such as bisphenol A glycidyl methacrylate (Bis-GMA) have been used in dentistry for different purposes such as dental restoration materials and bone cements since their introduction about 50 years ago [1–4]. Visible-light cured dental composite resin has been widely accepted as a restorative material due to its ease of handling and its aesthetic merits. Over the past several decades, substantial attempts, including the utilization of photo-curing approach, have been made to obtain more durable crosslinked polymer for dental applications. The mechanical properties of these materials have been enhanced considerably, but their antibacterial properties are still of great interest [5,6]. The resin-based dental composites commonly used in restorations result in more plaque accumulation than other materials. Bacterial biofilm growth

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contributes to secondary caries and failure of resin based dental composites. Methods to inhibit biofilm growth on dental composites have been sought for several years. Therefore, one of the goals should be to introduce the antimicrobial capability in dental materials. Although, there are many methods to create antimicrobial materials [7–11], but two approaches are mostly used. One approach is utilization of filler such as silver compounds in dental applications [12] and in bone cements [7]. Silver element is ionized in the presence of water, tissue exudates or body fluids and can readily interact with amino acid residues, proteins, especially those with thiol groups, free anions and receptors on mammalian and eukaryotic cell membranes [13]. The other high usage approach is the utilization of antimicrobial monomers such as quaternary ammonium compounds. These compounds have been shown to be effective in reducing bacterial growth in a wide range of applications including medical devices [14], textiles [15], dental materials [1,16], and water purification systems [17]. For instance, many monomers such as 2-dimethyl-2-dodecyl-1-methacryloxyethyl ammonium iodine (DDMAI) [18], 2-methacryloxylethyl dodecyl methyl ammonium bromide (MAE-DB) [19], 12-methacryloyloxydodecylpyridinium bromide (MDPB) [20], bis(2-methacryloyloxyethyl)dimethylammonium bromide [IDMA-1] and 2,2-bis(methacryloxyloxyethyl dimethylammonium bromide-1,1-benzyl) (IDMA-2) [1] were synthesized and incorporated in dental resin. Most of them are monomethacrylates, and incorporation of high concentrations of these monomers could considerably affect the overall polymer network structure because of low crosslinking density, and the leaching problems can arise due to release of the inhibitory agent from the composite. Also, low concentrations of monomethacrylate quaternary ammonium lead to low antimicrobial properties. Also, dimethacrylates with quaternary ammonium moieties in the main chain may present degradation problems over time, because the quaternary ammonium moieties are not as a pendant group. Gong et al. [21] showed that the presence of quaternary ammonium in the nanocomposites is responsible for the acceleration of polymer decomposition in the initial stage. Nevertheless, modification of dental materials with a nonleachable antimicrobial agent may be advantageous when preparing materials that undergo continuous physical challenge in the harsh oral environment for many years. Generally, an antimicrobial material is added to the dental resin to obtain antimicrobial activity; but in this work, one of the most used monomer, Bis-GMA, modified to an antimicrobial agent for dental application or other methacrylate systems. Therefore, the main objective of this study is to synthesize a new antimicrobial quaternary ammonium Bis-GMA based dimethacrylate monomer that chemically immobilizes in the backbone of dental resin by free radical photo-polymerization.

2. Experimental

2.1. Material

The epoxy compound used in the study was a bisphenol A diglycidyl ether-based epoxy (DGEBA), Ep. 5: Epoxide equivalent of 196–208, clear yellowish liquid, viscosity of 25,000 mPa s (at 25 °C), provided by Iran Petrochemical Industry (Khuzestan, Iran). Ethanol (EtOH), dimethyl sulfoxide (DMSO), diethylamine (DEA), diethyl ether, bromohexane, camphorquinone (QC), ethyl4-*N*,*N*-dimethylaminobenzoate, Bis-GMA, TEGDMA, and methacryloyl chloride were purchased from Sigma–Aldrich. All materials were used without further purification.

2.2. Synthesis

The target dimethacrylate monomer was synthesized by a simple three steps reactions: (1) reaction between DGEBA and DEA to obtain bis-phenol A glycerolate diethylamine (BGEA), (2) reaction of BGEA with an hexyl bromide to give quaternary ammonium bis-phenol A glycerolate (QABG), and (3) reaction of QABG with methacryloyl chloride to obtain the target

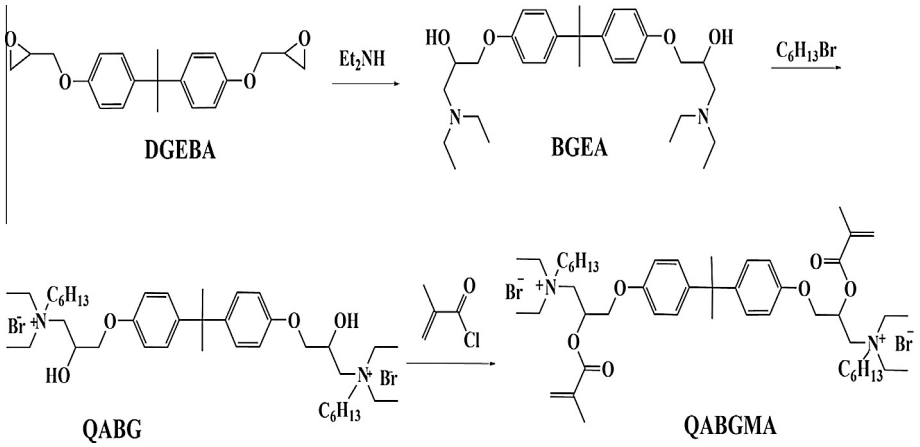

Fig. 1. Reaction scheme for the synthesis of QABGMA monomer.