

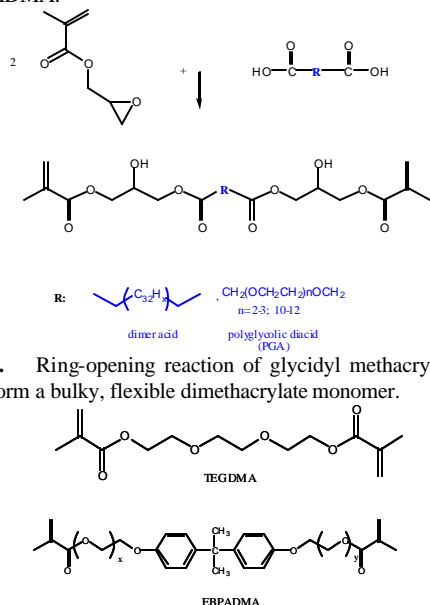
Structural Effects of Experimental Comonomers on Conversion and Polymerization Shrinkage of Dental Composites

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Introduction

Polymer based materials are increasingly being used in dentistry and allied biomedical fields. We have devised a facile synthetic route to crosslinking monomers that are biocompatible, fast curing, and can be tailored to specific applications. This approach is illustrated in Scheme 1, where by reacting glycidyl methacrylate (GMA) with a diacid, hydroxylated dimethacrylates can be formed in high yield. The benefit of this scheme is that by changing the spacer group, R, in the diacid, we can potentially alter the physicochemical and mechanical properties of the crosslinked network. This will allow us to use selected monomers to investigate the influence of specific structural features on polymer properties, such as conversion and polymerization shrinkage, and should have significant impact on the development of improved materials. Maximum conversion is desirable in order to minimize leaching of potentially toxic monomers and reduce shrinkage, which minimizes potentially damaging stress. Our initial study contrasts the behavior of a hydrophilic dimethacrylate (based on poly(glycolic acid), PGA) with that of a hydrophobic dimethacrylate (based on dimer acid, DIM) when used as a diluent comonomer with ethoxylated bisphenol A dimethacrylate (EBPADMA). As a control, the diluent comonomer triethylene glycol dimethacrylate (TEGDMA) (Figure 1) was also used with EBPADMA.



Scheme 1. Ring-opening reaction of glycidyl methacrylate with a diacid to form a bulky, flexible dimethacrylate monomer.

Figure 1. Chemical structure of base monomer (EBPADMA) and control comonomer (TEGDMA) used in this study.

Experimental*

Synthesis of Hydroxylated Dimethacrylates. Combined in a 20 mL vial were 7.03 mmol glycidyl methacrylate (Aldrich), 3.52 mmol of polyglycolic diacid ($M_n \approx 600$, Hoechst Celanese), 15 mg butylated hydroxytoluene (BHT) as an inhibitor and 0.15 g triethylamine (Aldrich) as a catalyst. The vial was heated at 63 °C for 20 h. Additionally, hydrogenated dimer acid ($M_n \approx 570$, Henkel Inc.) was used as the diacid in an identical synthesis. The reaction products obtained were named DIM-GMA and PGA-GMA, based on the reaction of GMA with DIM and PGA respectively, and were characterized using nuclear magnetic resonance, near infrared (NIR) and mid-IR spectroscopies. NIR was used to monitor the progress of the reaction by following the disappearance of the band associated with the oxirane ring at 6165 cm^{-1} . NIR spectra were acquired by collecting 64 scans at 2 wavenumber resolution (wavenumber relative uncertainty of 0.5 cm^{-1}).

Polymerization of Composites. DIM-GMA ($M_w \sim 854$) and PGA-GMA ($M_w \sim 884$) were blended with equal masses of EBPADMA (Esstech), photoactivated for visible light photopolymerization with 0.015 mass fraction of a modified bis-acyl phosphineoxide photoinitiator

(1850, CIBA) and mixed with mass fraction 0.847 of silanized Z100 glass (3M). As a control a similar composite was prepared with an equivalent amount (~ 0.16 mass fraction) of TEGDMA ($M_w = 286$) as the diluent comonomer for EBPADMA ($M_w \sim 540$). The degree of conversion of vinyl bonds was assessed by NIR and polymerization shrinkage by a computer controlled mercury dilatometer.

Results and Discussion

Figure 2a shows a representation of the near-IR spectra of the DIM-GMA/EBPADMA composite prior to polymerization, immediately after irradiation and after 24 h. The decrease in the vinyl band at 6165 cm^{-1} upon irradiation is characteristic for all the composites in this study. Figure 2b summarizes the results from degree of conversion and polymerization shrinkage calculations. The composites containing the high molecular weight diluent monomers PGA-GMA and DIM-GMA, exhibit a higher conversion than either EBPADMA alone or TEGDMA/EBPADMA, which may be related to the higher viscosity of these diluent monomers when compared to TEGDMA or EBPADMA. Both the DIM-GMA and PGA-GMA composites showed lower polymerization shrinkage values when compared to the TEGDMA system. Preliminary evidence also suggests that, along with polymerization shrinkage and conversion, the strength properties of silanized glass composites can be enhanced by the use of DIM-GMA as a comonomer. Additionally, the reaction scheme presented is robust in nature and has been extended to the synthesis of potentially biodegradable monomers for tissue engineering applications.

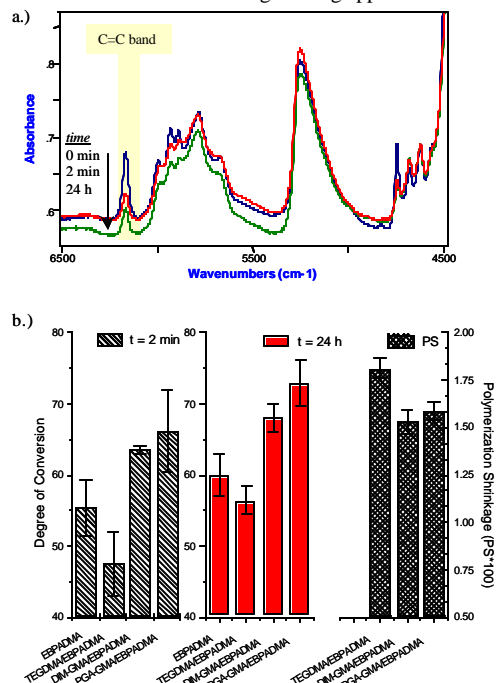


Figure 2. NIR spectra of DIM-GMA/EBPADMA composite at $t = 0$ min, 2 min and 24 h (a); Degree of conversion and polymerization shrinkage of composites (b). Error bars in the graph represent two standard deviations from the mean and is an estimate of the standard uncertainty.

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