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# The Influence of Comonomer Composition on Dimethacrylate Resin Properties for Dental Composites

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**Abstract.** During the polymerization of multifunctional monomers for dental restorations, typical final double-bond conversions range from 55 to 75%. The low conversion results in a large amount of extractable monomer, reduced adhesion to the filler, and the potential for increased swelling. In this work, the ability to increase the maximum conversion by optimizing the copolymer composition is explored. A series of multi-ethylene glycol dimethacrylate monomers of various lengths was used as a model system to determine how the copolymer composition affects the final conversion, the mechanical properties, and the predicted shrinkage. It was found that the ultimate conversion can be significantly increased, shrinkage decreased, and mechanical properties maintained. It was found that up to 30 wt% of poly(ethylene glycol) 600 dimethacrylate could be added to diethylene glycol dimethacrylate without reducing the strength and increasing the conversion. Results for other comonomer combinations were similar.

**Key words:** double-bond conversion, copolymer composition, polymerization conditions, and polymerization shrinkage.

## Introduction

Homopolymerizations of multifunctional monomers (*i.e.*, molecules with more than one double bond) produce highly crosslinked polymer networks with many desirable properties. For example, the high crosslinking density of the polymer provides a very dimensionally stable material which resists absorption of most solvents, and it also enhances the mechanical properties of the polymer. While the applications for these highly crosslinked polymer networks have been extensive, this work focuses on their use in composite dental restorative materials (Ruyter and Øysaet, 1988). All of the studies in this work have been performed with neat monomer resins and examine the influence of resin composition on the polymerization behavior, maximum attainable conversion, and mechanical properties of the cured polymer network.

An ideal polymer matrix would be extremely strong and wear-resistant, unswellable in saliva, well-adhered to the tooth structure and filler particles, and biocompatible. Current failures in composite restoration can be linked to each of these areas, particularly to problems associated with durability and wear. While the mechanism of degradation is not completely understood, several factors have been identified as contributing to wear. One of these factors is induced stresses within the restoration. These stresses arise from differences in thermal expansion between the restoration and tooth structure (Watts *et al.*, 1987; Kandil *et al.*, 1988), swelling from moisture uptake (Pearson, 1979; Swartz *et al.*, 1982; Venz and Dickens, 1991), and volume shrinkage during polymerization (Smith *et al.*, 1992; de Gee *et al.*, 1993; Lai and Johnson, 1993). In particular, swelling behavior and shrinkage during polymerization are further linked to the reaction conditions and the presence of unreacted monomer upon completion of the cure. Perhaps the most adverse effects are related to the potential for residual monomer to be leached from the composite and into the body, where it may cause sensitization and allergic reactions in certain patients (Spahl *et al.*, 1994).

During the polymerization of multifunctional monomers

for dental restorations, typical final double-bond conversions range from 55 to 75% (Kalipcilar *et al.*, 1991; Barron *et al.*, 1992; Vaidyanathan and Vaidyanathan, 1992). These low final conversions are a result of the high crosslinking density in the system which limits the mobility of reacting species. Thus, despite the presence of initiating species and unreacted double bonds in the system, the diffusion control of the propagation reaction limits any additional conversion. If equal reactivity of the double bonds is assumed, this implies that a minimum of 6.25% of the monomer is left completely unreacted and thus may still be extracted. This calculation is based on 75% conversion of double bonds. The probability that a monomer molecule is unreacted is equal to the probability that both double bonds in the monomer remain unreacted, *i.e.*, the probability of finding completely unreacted monomer is equal to (25%)(25%) or 6.25%. In addition to the previously discussed biocompatibility-related issues, all unreacted functional groups in the system will act as plasticizers, diminishing the strength of the polymer and increasing the swelling. Finally, the adhesion to the filler particles will be reduced, since only 55 to 75% of the double bonds have reacted that could contribute to binding the filler phase to the polymer phase.

Therefore, increasing the double-bond conversion in the polymer resin is highly advantageous, since it would decrease the extent of unreacted monomer in the system, increase the strength of the polymer (through decreased plasticization and increased crosslinking density at higher conversions), and reduce swelling. In particular, this work attempted to identify methods to increase conversion significantly and reduce the amount of residual monomer in dental restorations by examining the composition of the resin. Because a well-characterized series of homologous monomers is available, multi-ethylene glycol dimethacrylate monomers of various molecular weights were investigated and copolymerized as a model system. These monomers were chosen so that a wide range of copolymer compositions and monomer molecular weights could be examined. They do not directly correspond to the composition of current dental restorations and would not be homopolymerized in restorations, since they promote water sorption; however, valuable insight can be gained by a study of the model system, especially with respect to the influence of double-bond concentration on the final conversion and resin properties.

While it was anticipated that increasing the molecular weight of the monomer would lead to higher double-bond conversions, higher-molecular-weight monomers also reduce the concentration of double bonds in the system, which may lower the crosslinking density and adversely affect the mechanical properties. However, as an additional benefit, a lower concentration of double bonds in the system also reduces volume shrinkage during polymerization. Thus, to examine these potential advantages (and disadvantages), we studied several comonomer resin compositions with the goal of increasing the double-bond conversion and reducing the polymerization shrinkage while maintaining the mechanical strength of the network.

## Materials and methods

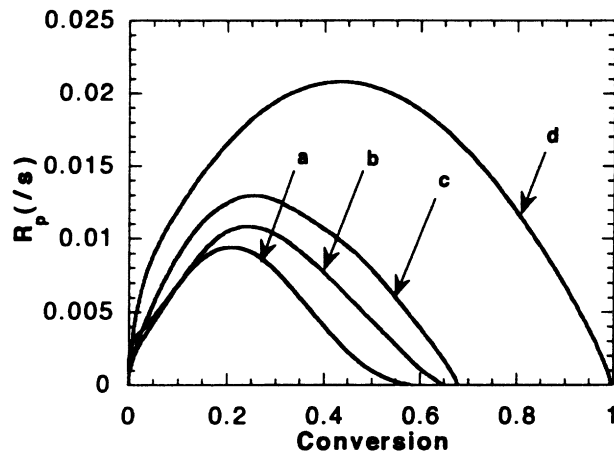
A series of commercially available, multi-ethylene glycol dimethacrylate monomers was used. This series included diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), poly(ethylene glycol 200) dimethacrylate (PEG200DMA), and poly(ethylene glycol 600) dimethacrylate (PEG600DMA) (Polysciences Inc., Warrington, PA). All monomers were used as received. These materials were chosen as a model system for the examination of the influence of comonomer composition and molecular weight between double bonds on the maximum attainable double-bond conversion and the mechanical properties of the polymer. TrEGDMA is a common component in many dental resin compositions (the other monomer is typically a bisphenol-based dimethacrylate such as 2,2 bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl] propane) (Urabe *et al.*, 1990; Smith and Powers, 1991). The conclusions drawn from the influence of molecular weight and concentration of double bonds in the multi-ethylene glycol dimethacrylate series should provide a basis to provide direction to investigators choosing more desirable comonomer resins in developing improved dental restorations.

The monomers were photopolymerized with 2 mW/cm<sup>2</sup> of 365 nm ultraviolet light and 0.1 wt% of the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorn, NY). The cure profiles were monitored with a differential scanning calorimeter adapted with a photocalorimetric accessory capable of producing either monochromatic or full-beam ultraviolet light (Perkin Elmer, DSC-DPA 7, Norwalk, CT). The light intensity was controlled by neutral density filters (Melles Griot, Irvine, CA), and the DSC was cooled with a refrigerated recirculating chiller to facilitate isothermal reaction studies near room temperature (NESLAB, CFT-25, Newington, NH). Small sample sizes and low initiator concentrations were chosen to ensure the applicability of the thin film approximation for uniform light intensity across the sample. In addition, the DSC cell was flushed with nitrogen 10 min prior to and continuously during the polymerization, since oxygen is a well-known inhibitor of these reactions. The DSC monitors heat flux as a function of reaction time, and this heat flux is related to the rate of polymerization. Using the heat of reaction *per* double bond [13.1 kcal/mol for a methacrylate double bond (Moore, 1977; Miyazaki and Horibe, 1988)], we determined the conversion as a function of time.

The mechanical properties of the cured resins were measured by means of a dynamic mechanical analyzer (Perkin Elmer, DMA 7, Norwalk, CT) in the extension mode. We prepared samples by photopolymerizing the desired monomer resin in a mold of dimensions 1 mm x 3 mm x 20 mm. Polymerization conditions matched those of the DSC studies (2 mW/cm<sup>2</sup> of 365 nm ultraviolet light and 0.1 wt% DMPA). The modulus of the cured polymer film was monitored as a function of temperature at a frequency of 1 Hz.

## Results and discussion

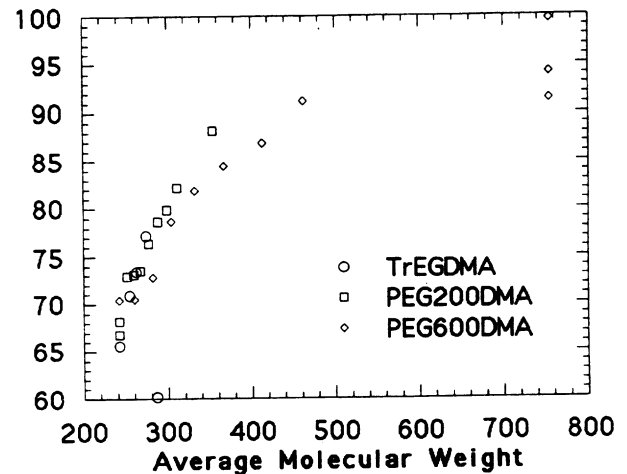
For each of the monomers studied, the homopolymerization behavior is shown in Fig. 1, where the rate of polymerization is plotted as a function of double-bond conversion. The polymerization rate was normalized by the



**Figure 1.** Rate of polymerization vs. double-bond conversion for homopolymerizations of (a) DEGDMA, (b) TrEGDMA, (c) PEG200DMA, and (d) PEG600DMA.

initial concentration of double bonds in each monomer, ranging from  $\sim 8.7$  mol/L in DEGDMA to  $\sim 2.9$  mol/L in PEG600DMA. The reaction profiles are shown for the homopolymerization of these dimethacrylate monomers, and several features of the polymerization are quite evident. For example, distinct regions of auto-acceleration and auto-deceleration in the polymerization rate result from diffusion control of the termination and propagation reaction, respectively. Because these monomers polymerize to form highly crosslinked polymer networks and the system gels at very low double-bond conversions, mobility of the reacting species is severely reduced, even at low conversions. Ultimately, the system reaches a maximum attainable double-bond conversion resulting from mobility restrictions, and this maximum conversion is strongly dependent on the molecular weight of the monomer (*i.e.*, it is greatly influenced by the initial concentration of double bonds in the system). The maximum conversions range from 0.58 (in DEGDMA) to 0.65 (in TrEGDMA) to 0.68 (in PEG200DMA) to 1.00 (in PEG600DMA). These values are comparable with other results for photopolymerized highly crosslinked polymers (Anseth *et al.*, 1995), but are slightly higher since the polymerization was conducted at 37°C.

For dental restorative materials, desirable resins should approach 100% conversion of double bonds upon completion of the cure (as in PEG600DMA), to reduce residual monomer concentrations in the crosslinked resin. Hence, monomers of higher molecular weight and lower double-bond concentrations are potential candidates. However, the disadvantage to these higher-molecular-weight monomers is the reduced crosslinking density of the final polymer network. To overcome this obvious disadvantage, we copolymerized several higher-molecular-weight monomers with lower-molecular-weight monomers. The objective was to optimize the double-bond conversion in the system without altering the crosslinking density of the final polymer network to the extent that the mechanical properties of the network were diminished.

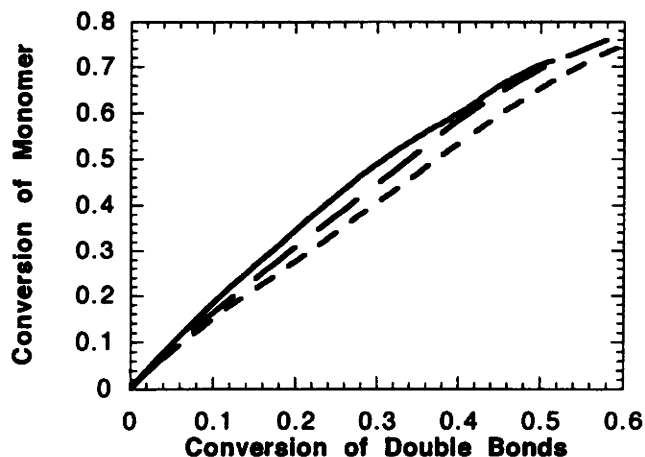


**Figure 2.** Maximum attainable double-bond conversion vs. average molecular weight of monomer resin for copolymerizations of DEGDMA with (o) TrEGDMA, (□) PEG200DMA, and (◇) PEG600DMA.

Fig. 2 plots the maximum attainable double-bond conversion as a function of the average molecular weight of the monomer resin for several copolymerizations of DEGDMA with TrEGDMA, PEG200DMA, and PEG600DMA. Interestingly, the maximum double-bond conversion increases monotonically with increasing molecular weight of the monomer resin. As discussed previously, this increase in the maximum conversion results from a decrease in the initial concentration of double bonds. Since fewer double bonds are initially present (and nearly the same number of double bonds react in each system), the final conversion in the system increases. This increased maximum conversion translates into a lower amount of residual monomer in the final polymer matrix, which is desirable to improve biocompatibility and reduce swelling.

From Fig. 2, it is also evident that different higher-molecular-weight monomers affect the maximum double-bond conversion differently. For example, when TrEGDMA or PEG600DMA is copolymerized with DEGDMA, the maximum double-bond conversion is enhanced to a similar extent in both systems. In contrast, the addition of PEG200DMA to the polymerization mixture increases the maximum double-bond conversion to a greater extent than that of either TrEGDMA or PEG600DMA at similar average molecular weights in the monomer resin. For example, at an average resin molecular weight of 300 g/mol, the maximum double-bond conversion in poly(PEG200DMA-co-DEGDMA) is close to 85%, while those of poly(TrEGDMA-co-DEGDMA) and poly(PEG600DMA-co-DEGDMA) are closer to 80%.

In addition to examining the total double-bond conversion in the system, it is also advantageous to determine the fraction of unreacted double bonds that are monomeric (*i.e.*, unattached to the network) vs. pendant (*i.e.*, attached to the network). In terms of biocompatibility of the polymer matrix, reducing the amount of unreacted monomeric double bonds is critical to limit the risks associated with leaching of these small molecules.

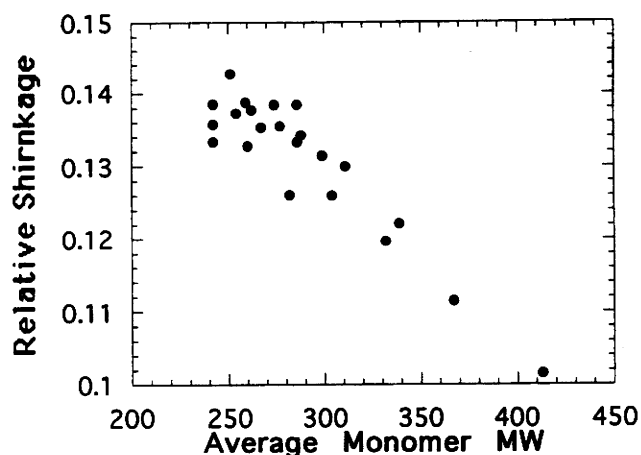


**Figure 3.** Kinetic gelation simulation results for the influence of monomer size on the conversion of monomer as a function of the conversion of double bonds. Results are shown for (---) three-site, (-·-) five-site, and (—) 10-site monomers.

Unfortunately, experimental determination of the fraction of unreacted monomer in densely crosslinked polymer networks is extremely difficult and often impossible. Therefore, to gain a better understanding and to establish further the importance of increased double-bond conversion on the monomeric double-bond conversion, we performed kinetic gelation simulations were performed (Bowman and Peppas, 1992; Anseth and Bowman, 1994). Kinetic gelation simulations are percolation-type simulations for studying the free radical copolymerization of mono- and multifunctional monomers in any relative proportions.

The primary advantage of kinetic gelation simulations for highly crosslinked systems (homopolymerizations of multifunctional monomers) is the ability to predict heterogeneity that is so prominent in these reactions. Heterogeneity in these polymerizations leads to unequal reactivity of the monomeric and pendant double bonds. In the initial phase of the polymerization, all of the pendant double bonds are close to active centers, *i.e.*, radicals, which makes the pendant double bonds highly reactive. This effect increases the amount of unreacted monomer present at a given conversion.

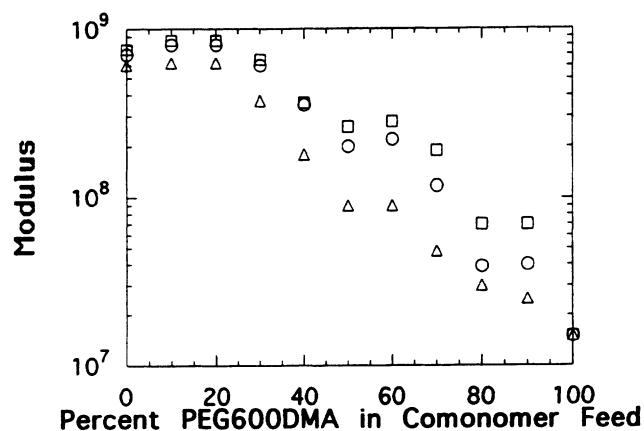
Fig. 3 presents kinetic gelation simulation results for the influence of the monomer size (*i.e.*, molecular weight) on the conversion of monomer as a function of the conversion of double bonds. Specifically, the fraction of monomer which has at least one double bond reacted is plotted as a function of double-bond conversion for a three-, five-, and ten-site monomer molecule (representing an increase one might associate with the increase in size from DEGDMA to TrEGDMA to PEG600DMA). From these results, two observations are clear. First, as the monomer size is increased (*e.g.*, from three sites to ten sites) at a given conversion, the amount of residual monomer is dramatically decreased. This decrease in residual monomer is the result of a reduced relative reactivity of the pendant double bonds relative to the monomeric double bonds as the size of the monomer



**Figure 4.** Predicted relative volume shrinkage upon full cure as a function of average molecular weight of monomer resin for copolymerizations of DEGDMA with TrEGDMA, PEG200DMA, and PEG600DMA.

molecule is increased. As the monomeric double bonds become more reactive, the fraction of monomer that remains unreacted decreases. Second, as the double-bond conversion increases, the residual monomer fraction also decreases markedly. Consider the three-site monomer molecule. As the double-bond conversion increases from 50 to 60%, the amount of monomer that has at least one double bond reacted increases from 63% to 75%. This increase reduces the residual monomer by nearly one-third. Thus, when lower- and higher-molecular-weight monomer molecules are copolymerized, the double-bond conversion and the monomer conversion are both significantly increased.

In addition to the influence of monomer molecular weight on conversion being determined, the volume shrinkage during polymerization was also characterized. During polymerization, a certain amount of volume (22.5 cm<sup>3</sup>/mol) is consumed for each methacrylate double bond that reacts (Patel *et al.*, 1987). Because of this relationship between double-bond conversion and polymerization shrinkage, minimizing the total number of double bonds that react will minimize volume shrinkage during curing of the monomer resin. Hence, the comonomer resin compositions with higher average molecular weights will also have a lower concentration of double bonds, which reduces the potential for shrinkage during polymerization. Fig. 4 plots the predicted relative volume shrinkage upon completion of the polymerization as a function of the average molecular weight of the monomer resin. The resin compositions studied were DEGDMA copolymerized with various weight percents of TrEGDMA, PEG200DMA, and PEG600DMA. In general, the volume shrinkage decreases with increasing average molecular weight of the monomer resin. While this reduction in polymerization shrinkage should help reduce stresses that can cause adhesive failure (marginal leakage) and/or cohesive failure (microcracking of the composite), the crosslinking density of the polymer matrix has been changed. So, while increasing the molecular weight of the

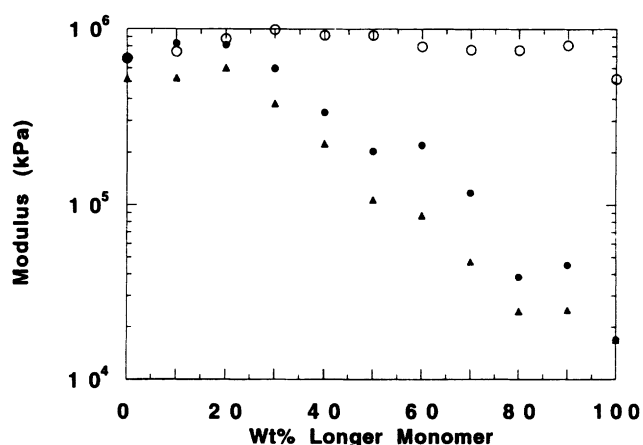


**Figure 5.** Tensile modulus vs. weight percent PEG600DMA in poly(DEGDMA-co-PEG600DMA) at (□) 25°C, (○) 40°C, and (△) 80°C.

monomer resin enhances the double-bond conversion and reduces the polymerization shrinkage, it decreases the crosslinking density of the polymer, which may be detrimental to the mechanical properties of the network.

The influence of monomer resin composition and molecular weight on the mechanical properties of the final polymer matrix were also examined, and the results are presented in Fig. 5, which plots the tensile modulus as a function of wt% PEG600DMA in poly(DEGDMA-co-PEG600DMA) at three different temperatures ranging from 25°C to 80°C. Several trends are apparent. First, as the temperature is increased, the modulus of the polymer is decreased. This decrease results from higher thermal energy, which increases the chain mobility and decreases the modulus of the polymer. Second, over the entire composition range, the modulus of the network decreases nearly two orders of magnitude, from  $\sim 10^9$  Pa for poly(DEGDMA) to  $\sim 10^7$  Pa for poly(PEG600DMA). Clearly, the lower concentration of double bonds in PEG600DMA significantly reduces the crosslinking density and subsequently the modulus. As a further illustration of this point, macroscopic observations show poly(DEGDMA) as a glassy network at room temperature, whereas poly(PEG600DMA) is rubbery.

Finally, perhaps the most surprising and interesting conclusion from Fig. 5 results from examination of the modulus between 0 and 30 wt% of PEG600DMA in DEGDMA. When anywhere from 0 to 20 wt% PEG600DMA is added to the monomer resin, the modulus of the final polymer network remains unchanged. Extending the region even further to 30 wt% of PEG600DMA, the modulus changes by less than 10%. The average molecular weight of a monomer resin with 30 wt% PEG600DMA and 70 wt% DEGDMA is 395 g/mol. So, within certain limits, increasing the molecular weight of the monomer resin and decreasing the concentration of double bonds in the system are an effective approach to increasing the conversion and reducing the polymerization shrinkage, while maintaining the mechanical strength of the polymer. This conclusion is further supported with the results



**Figure 6.** Modulus at 40°C vs. weight percent of longer monomer for (●) poly(PEG600DMA-co-DEGDMA), (○) poly(PEG200DMA-co-DEGDMA), and (▲) poly(PEG600DMA-co-PEG200DMA).

shown in Fig. 6, where the modulus is plotted as a function of wt% of the highest-molecular-weight monomer for several monomer resin compositions. The copolymers studied were poly(PEG600DMA-co-DEGDMA), poly(PEG200DMA-co-DEGDMA), and poly(PEG600DMA-co-PEG200DMA), and the modulus was measured at 40°C. Again, the results reinforce that up to 30 wt% of a higher-molecular-weight monomer can be added to the monomer resin without detrimentally altering the modulus of the final polymer network.

To summarize, this research has shown, with the model multi-ethylene glycol dimethacrylate monomer series, that optimization of copolymer composition can lead to significant increases in the maximum attainable conversion. Additionally, this increase in conversion may be accompanied with a slight decrease in polymerization shrinkage and no significant decrease in the mechanical strength. In spite of the fact that a model system was used in this work, the conclusions regarding the ability to optimize the monomer content can be extended to real systems.

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