

Degree of Conversion of a Copolymer of an Experimental Monomer and Methyl Methacrylate for Dental Applications

Eeva K. Viljanen,¹ Mikael Skrifvars,² Pekka K. Vallittu¹

¹University of Turku, Institute of Dentistry, Department of Prosthetic Dentistry and Biomaterials Research, Lemminkäisenkatu 2, FI-20520 Turku, Finland

²University College of Borås, School of Engineering, S-50190 Borås, Sweden

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ABSTRACT: The aim of this study was to determine the degree of double bond conversion of the copolymer of an experimental monomer and methyl methacrylate after photopolymerization. A mixture of an experimental monomer with four methacrylate groups and methyl methacrylate monomer (mass ratio 70 : 30) was polymerized by using various concentrations of light initiator system. The degree of conversion was determined with FTIR spectrometry. A photopolymerized 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane/triethylene glycol dimethacrylate (mass ratio 40 : 60) copolymer was used as a control material for degree of

conversion. The maximum degree of conversion for the experimental monomer/methyl methacrylate copolymer was 62% and was obtained with 2 wt % initiator concentration. It was comparable to that of the control polymer (64%). The results of this study suggest that the experimental monomer/methyl methacrylate system can be polymerized by light initiator system. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1908–1912, 2004

Key words: dendrimers; dental polymers; biomaterials; methacrylates

INTRODUCTION

Even though the properties of dental polymers and composites have been improved since their invention, there are still shortcomings that restrict their use. Usually, the organic matrix of these products is based on methacrylates, the simplest monomer being methyl methacrylate (MMA), but crosslinking dimethacrylates, such as 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane (Bis-GMA), 1,6-bis(2-methacryloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA), and triethyleneglycol dimethacrylate (TEGDMA), are more commonly used nowadays (Fig. 1). The properties of the material formed by free-radical polymerization are strongly influenced by the selection of the monomers. The main shortcomings of currently used materials are polymerization shrinkage, insufficient mechanical properties, and elution of components from the polymer network.^{1–5}

Several approaches were studied to improve the properties of dental composites. Ring-opening polymerization (ROP) was investigated in the attempt to reduce polymerization shrinkage.^{5–8} These polymers

have the disadvantages of high water sorption and low reactivity, and they are not always compatible with the currently used methacrylate systems. The use of reactive molecules bigger than the commonly used dimethacrylates, such as multifunctional methacrylates derived from Bis-GMA,^{9,10} was widely investigated. This kind of material is assumed to give lower polymerization shrinkage because of larger monomer size and better mechanical properties due to more extensive crosslinking. One attempt to enlarge the molecular size of reactive molecules is based on using siloxane molecules with reactive groups of methacrylates (known as Ormocers).¹¹ In commercially available products of this kind, a relatively large percentage of the monomer system is bifunctional methacrylates, which results in properties similar to those of conventional monomer systems.^{5,12}

There is also a growing interest in using hyperbranched polymers such as dendrimers in dental and medical applications.^{5,13,14} Dendrimers are defined to contain symmetrically arranged branches emanating from a core molecule and have a well-defined number of end groups corresponding to each generation.¹⁵ To the authors' knowledge, the performance of light initiated polymerization of dendrimer molecules has not been able to correspond to the properties of dimethacrylate systems.⁵

The subject of interest in this work was the visible light polymerization of an experimental monomer.

Correspondence to: E. Viljanen (eeva.viljanen@utu.fi).

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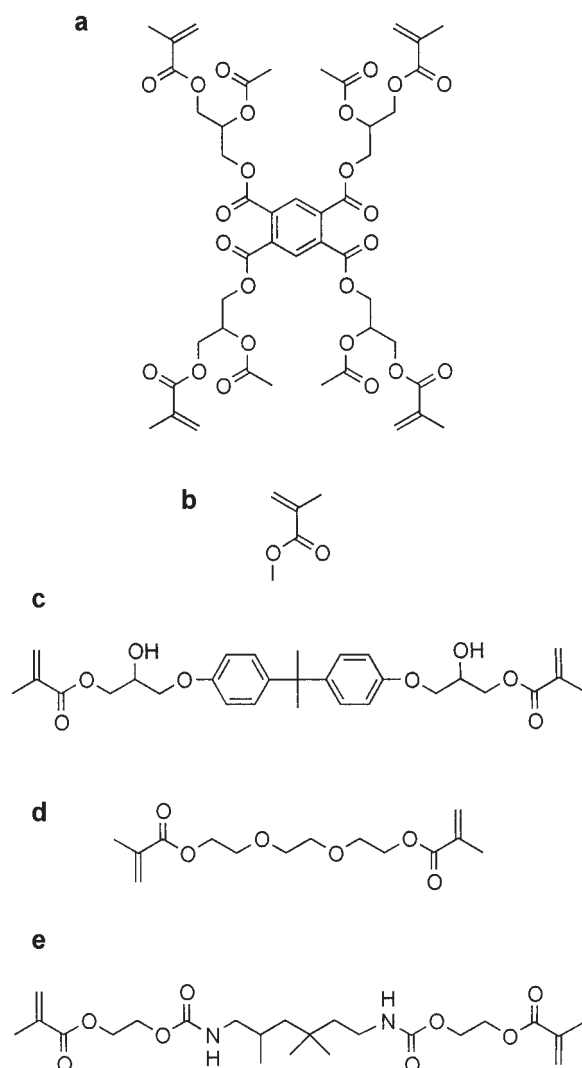


Figure 1 The structural formulas of the experimental monomer D4 (a), MMA (b), Bis-GMA (c), TEGDMA (d), and UDMA (e).

Because a sufficiently high degree of conversion is essential for dental polymers and has to be achieved also with new polymers, the influence of light initiator and activator concentration on the degree of double bond conversion of the experimental monomer D4

was studied. D4 is a branched oligoester with four methacrylate end groups [Fig. 1(a)]. The structure of D4 resembles dendrimers, as it has a core unit and four branches, which are further branched. Due to the high viscosity of D4, a diluting solvent was needed. Optimally, the diluent is a polymerizable monomer. Methyl methacrylate (MMA) was selected as the comonomer because of its advantageous properties during synthesis of the dendrimer D4 molecule.²⁰ MMA has low reactivity in light polymerization, but of the commonly used low-viscosity methacrylates, it is well known for its biological effects and has lower cytotoxicity than TEGDMA, for example.^{16,17}

EXPERIMENTAL

Materials

The materials used in this study are presented in Table I. The structural formulas of D4, MMA, Bis-GMA, and TEGDMA are presented in Figure 1. The monomer D4 was synthesized according to the method by Rånby and Shi.¹⁸ Glycidyl methacrylate (135 mL) was dissolved in 120 mL of *N,N*-dimethylformamide inhibited with benzoquinone. The mixture was heated to 65°C, and 50 g of pyromellitic anhydride was added in portions. The temperature was kept under 75°C. The reaction was left to proceed for 10 h, after which 65 mL of acetic anhydride was added slowly and the mixture was stirred for 3 h. The product was dissolved in a large amount of toluene inhibited with benzoquinone and washed with 10% Na₂CO₃ and water at 55°C and isolated by vacuum distillation at 30 mbar and 75°C to remove the toluene and water.

The experimental monomer system consisted of D4 and MMA in a mass ratio of 70 : 30. The control monomer system contained Bis-GMA and TEGDMA in a mass ratio of 40 : 60. The molar methacrylate C=C bond content was the same in both monomer systems. Camphorquinone (CQ) was used as the light-activated initiator and 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) was used as the activator. They were used in a mass ratio of 1 : 1 and the mass fraction of each was 0.1, 0.25, 0.5, 1.0, 2.0, or 5.0 wt % of the total mixture.

TABLE I
Materials Used in This Study

Code	Material	Description	Manufacturer
D4	Monomer	Experimental monomer with four methacrylate groups (see Fig. 1)	Neste Chemicals, Porvoo, Finland
MMA	Monomer	Methyl methacrylate	Fluka, Buchs, Switzerland
Bis-GMA	Monomer	2,2-Bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane	Chemotechnique Diagnostics, Tygelsjö, Sweden
TEGDMA	Monomer	Triethylene glycol dimethacrylate	Aldrich, Milwaukee, WI
CQ	Initiator	Camphorquinone	Fluka
DMAEMA	Activator	2-(<i>N,N</i> -dimethylamino)ethyl methacrylate	Fluka

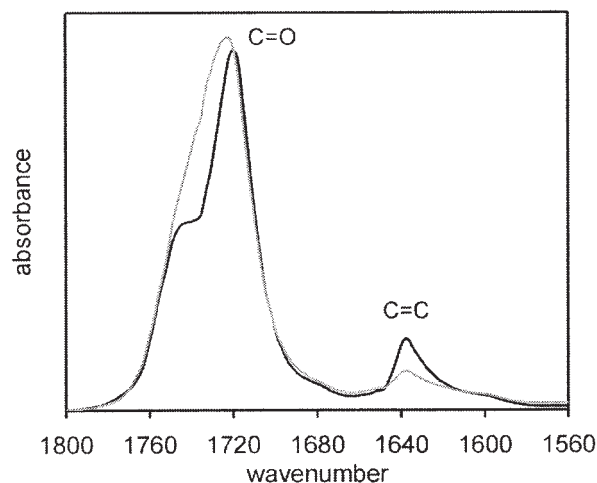


Figure 2 An example of FTIR spectra of D4/MMA mixture (black = unpolymerized, gray = polymerized).

To prepare the sample mixtures, predetermined amounts of D4 were weighed on an analytical balance. Then, the amounts of MMA, CQ, and DMAEMA needed were calculated, weighed on an analytical balance, and mixed with D4. The sample mixtures were stored at $(13 \pm 1)^\circ\text{C}$ in light-protected containers for 20 h to dissolve CQ. The control samples of the Bis-GMA/TEGDMA system were prepared in the same manner.

Methods

The degree of double bond conversion (DC) was determined by using an FTIR spectrometer (Spectrum One, Perkin-Elmer) with an attenuated total reflectance (ATR) accessory. The FTIR spectra were recorded with eight scans at a resolution of 4 cm^{-1} . The experimental and control samples were analyzed in a mold that was 1.0 mm thick and 5.5 mm in diameter. First, the spectrum of the unpolymerized sample was measured. Then, the sample was irradiated for 40 s on the ATR sample tray with a visible light-curing unit (3M Curing Light 2500, $\lambda = 400\text{--}520\text{ nm}$, $I \approx 550\text{ mW cm}^{-2}$). The sample was scanned for its FTIR spectrum 40 s, 2 min, 5 min, 10 min, and 15 min after the beginning of irradiation.

To determine the percentage of remaining unreacted double bonds, the absorbance intensities of the methacrylate $\text{C}=\text{C}$ absorbance peak at 1637 cm^{-1} and an internal $\text{C}=\text{O}$ standard peak at 1720 cm^{-1} were calculated by using a baseline method. The ratios of absorbance intensities were calculated and compared before and after polymerization. The DC was calculated by using the equation

$$\text{DC} = 1 - \frac{[A(\text{C}=\text{C})/A(\text{C}=\text{O})]_{\text{polymer}}}{[A(\text{C}=\text{C})/A(\text{C}=\text{O})]_{\text{monomers}}}$$

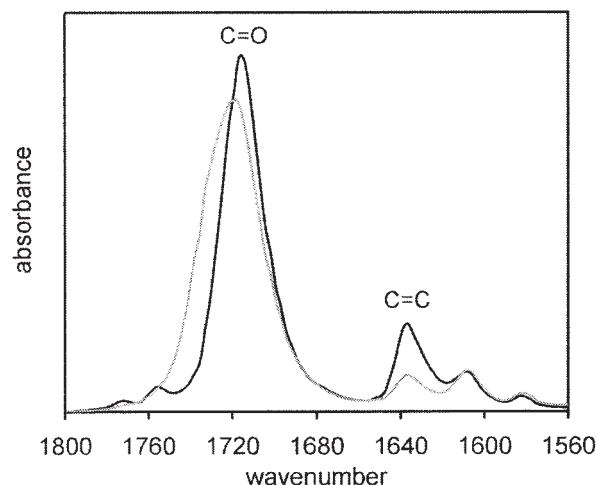


Figure 3 An example of FTIR spectra of Bis-GMA/TEGDMA mixture (black = unpolymerized, gray = polymerized).

where $A(\text{C}=\text{C})$ is the absorbance intensity of the methacrylate peak and $A(\text{C}=\text{O})$ is the absorbance intensity of the internal standard peak. All measurements were carried out in triplicate and the mean value of the three results was recorded. Figures 2 and 3 show typical FTIR spectra for unpolymerized and polymerized samples in the $1550\text{--}1800\text{ cm}^{-1}$ region.

RESULTS AND DISCUSSION

The highest degree of conversion (63.9%) for the control copolymer was obtained with 2.0 wt % initiator and activator concentration (Table II). The experimental copolymer also reached the highest DC (62.1%) with 2.0 wt % initiator and activator concentration (Table II). All the tested mixtures reached their highest degree of conversion in 15 min (Figs. 4 and 5).

This study demonstrated that the experimental copolymer could reach a degree of conversion comparable to that of the control dimethacrylate copolymer.

TABLE II
The Degree of Conversion (DC) of D4/MMA (70 : 30) and Bis-GMA/TEGDMA (40 : 60) Copolymers with 0.1–5.0 wt % of CQ and DMAEMA 15 min After the Beginning of Irradiation (standard deviation is in parentheses).

CQ/wt%	DC (D4/MMA)/%	DC(Bis-GMA/TEGDMA)/%
0.1	40 (3)	51.6 (0.4)
0.25	44.8 (0.5)	56.1 (0.4)
0.5	49 (2)	59.1 (0.2)
1.0	57 (2)	61.4 (0.4)
2.0	62.1 (0.4)	63.9 (0.4)
5.0	60 (8)	52 (6)

However, the measured DC is an overall value of the copolymer and the relative amounts of D4 and MMA reacted in polymerization cannot be determined on the basis of this study alone. Therefore, high-performance liquid chromatographic (HPLC) measurements of remaining unreacted MMA, for example, are necessary.

The maximum DC for both the experimental and the control system were achieved with 2 wt % of CQ and DMAEMA, which is higher than that usually used in commercial dental polymers.¹⁹ It is known that photopolymerization of MMA might not be effective. Therefore, the use of higher quantities of initiator and activator was tested. It is obvious that possible adverse effects from the biological perspective have to be investigated. Whatever the case, CQ was found to be less cytotoxic than, for example, Bis-GMA, and the widely used monomer MMA was also found to be quite safe in this respect.¹⁷

DC was higher for the Bis-GMA/TEGDMA copolymer than for the D4/MMA copolymer when lower concentrations of initiator and activator were used. To achieve a sufficiently high degree of conversion for the D4/MMA copolymer, higher concentrations were tested. As the concentrations were increased, DC increased in both systems until a notable decrease at highest concentrations. At high concentrations of CQ, nearly all of the active wavelength regions of the light are absorbed at the specimen surface (the inner filter effect). The wavelengths transmitted to the depths of the sample are inefficient for photopolymerization. When specimens are irradiated for limited intervals, the conversion achieved is not homogeneous.

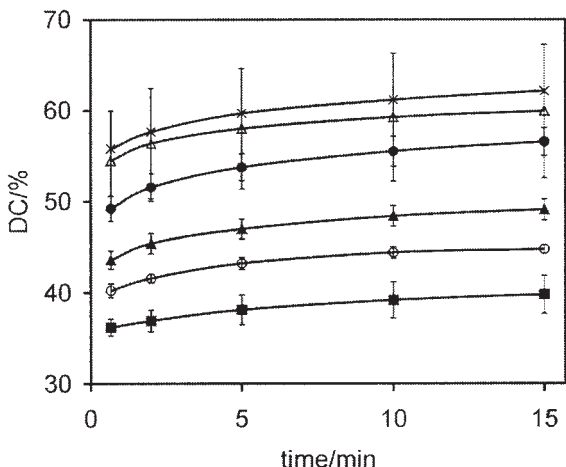


Figure 4 The degree of conversion (DC) of D4/MMA copolymers with 0.1 wt % (■), 0.25 wt % (○), 0.5 wt % (▲), 1.0 wt % (●), 2.0 wt % (×), or 5.0 wt % (△) of CQ and DMAEMA at different time points. Vertical lines represent standard deviation (not visible when smaller than the marker).

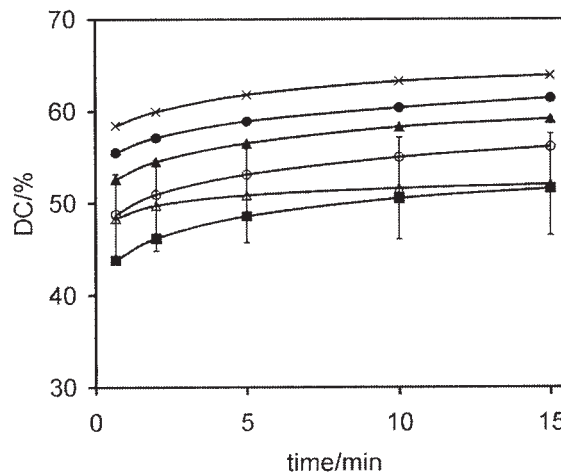


Figure 5 The degree of conversion (DC) of Bis-GMA/TEGDMA copolymers with 0.1 wt % (■), 0.25 wt % (○), 0.5 wt % (▲), 1.0 wt % (●), 2.0 wt % (×), or 5.0 wt % (△) of CQ and DMAEMA at different time points. Vertical lines represent standard deviation (not visible when smaller than the marker).

A high concentration of initiator, which causes inhomogeneous conversion and local microgel formation, may also result in decreased mechanical properties. More studies that focus on this and other properties of these systems are needed. In addition, other monomers similar to D4 with more functional groups and dendrimers are within the interest of our research.

CONCLUSION

A degree of conversion comparable to dimethacrylate polymers can be achieved with a copolymer containing experimental dendrimer-like monomer by light initiator system. Therefore, this kind of large monomers can be considered possible candidates for new dental polymer materials.

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