

# Evaluation of the Light Polymerization Efficiency of Copolymers Used in Dental Formulations by Differential Scanning Calorimetry

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**ABSTRACT:** Different compositions of visible-light-curable triethylene glycol dimethacrylate/bisglycidyl methacrylate copolymers used in dental resin formulations were prepared through copolymerization photoinitiated by a camphorquinone/ethyl 4-dimethylaminobenzoate system irradiated with an Ultrablue IS light-emitting diode. The obtained copolymers were evaluated with differential scanning calorimetry. From the data for the heat of polymerization, before and after light exposure, obtained from exothermic differential scanning calorimetry curves, the light polymerization efficiency or degree of conversion of double bonds was calculated. The glass-transition temperature also was determined before and after photopolymerization. After the photopolymerization, the glass-transi-

tion temperature was not well defined because of the breadth of the transition region associated with the properties of the photocured dimethacrylate. The glass-transition temperature after photopolymerization was determined experimentally and compared with the values determined with the Fox equation. In all mixtures, the experimental value was lower than the calculated value. Scanning electron microscopy was used to analyze the morphological differences in the prepared copolymer structures. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 187–192, 2008

**Key words:** crosslinking; differential scanning calorimetry (DSC); glass transition; photopolymerization

## INTRODUCTION

The most common dimethacrylate monomer used in current commercial dental composites is bisglycidyl methacrylate (Bis-GMA), which is the reaction product of bisphenol A and glycidyl ester methacrylate. The advantages of using Bis-GMA over the first used small dental monomers, such as methyl methacrylate, include less shrinkage, higher modulus, and reduced toxicity due to its lower volatility and diffusivity into tissues.<sup>1–4</sup> These desirable properties of Bis-GMA are partially negated by its relatively high viscosity, which does not permit the use of high amounts of a filler. It is a common practice to use with this material a less viscous monomer as a diluent comonomer, and this is normally triethylene glycol dimethacrylate (TEGDMA). TEGDMA has been shown to adversely affect the properties of the ma-

trix resin by increasing the water sorption and curing shrinkage.<sup>5</sup>

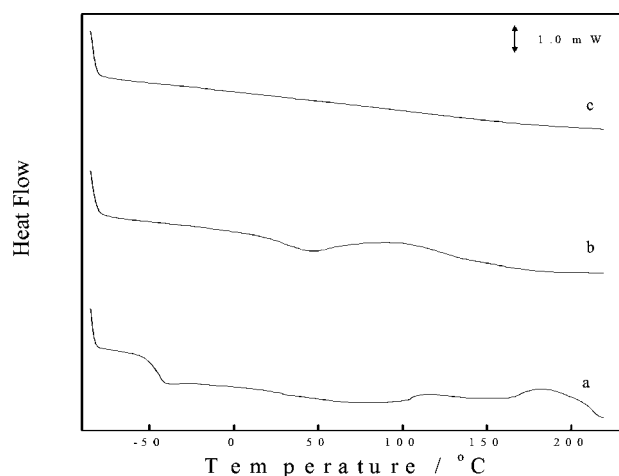
The polymerization of dimethacrylates is chemical or is initiated with visible light, the latter being preferable and allowing finer control of the entire polymerization process.<sup>6</sup> Thus, initiation can be started and stopped almost at will. The room-temperature polymerization of dimethacrylates usually leads to glassy resins in which only some of the available double bonds are reacted. Only very flexible monomers in which the reactive methacrylate groups are relatively far apart can be completely reacted at the ambient temperature. The degree of conversion of resins is a major factor influencing their bulk physical properties.<sup>7,8</sup> In general, the higher the conversion is of the double bonds, the higher the mechanical strength is.<sup>9–11</sup> The unreacted double bonds may be present in either free monomer or pendant groups in the network.<sup>12–15</sup> Thus, it has been shown that trapped radicals are present when the reaction temperature is low. In the case of densely crosslinked dimethacrylates, under an oxygen-free atmosphere and at room temperature, it can be shown that the lifetime of these radicals can reach several days or months.

The radical lifetime depends mainly on the crosslinking density, the storage temperature, and the

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**Figure 1** Heat flow versus the temperature for (a) uncured TB3070, (b) light-cured TB3070, and (c) TB3070 after an isotherm for 20 min at 180°C.

atmosphere. Other studies have shown that this reaction is highly accelerated by moderate heating. Indeed, heating increases the segmental mobility of the network and promotes the reaction between the present radicals and the surrounding unreacted functional groups.<sup>16</sup> Other studies have shown that, according to differential scanning calorimetry (DSC) analysis, a dimethacrylate sample under a nitrogen atmosphere immediately after photopolymerization exhibits an exothermic reaction effect, whereas heating these samples after 1 night under an air-free atmosphere has no detectable exothermic effect.<sup>17,18</sup>

In this study, different compositions of visible-light-curable TEGDMA/Bis-GMA copolymers used in dental resin formulations were prepared and evaluated with DSC. DSC measurements were used to estimate the light polymerization efficiency and the glass transition before and after photopolymerization. The light-induced copolymerization of various compositions was carried out under the same conditions to obtain comparable results. Scanning electron microscopy (SEM) was used to analyze the morphological differences in the structures of the prepared copolymers.

Therefore, the aim of this work was to investigate copolymers with different compositions of dimethacrylate monomers commonly used in dental resin formulations to evaluate the light polymerization efficiency by DSC. The light polymerization efficiency is an important parameter that is directly related to the clinical performance of the material, directly affecting the mechanical and physical properties. A comparison of these results provides valuable information on the relation between the composition of dimethacrylates in the copolymers and the degree of conversion, which can help us in better understanding the behavior of dental resins obtained from these

dimethacrylates and also in improving these materials in the future.

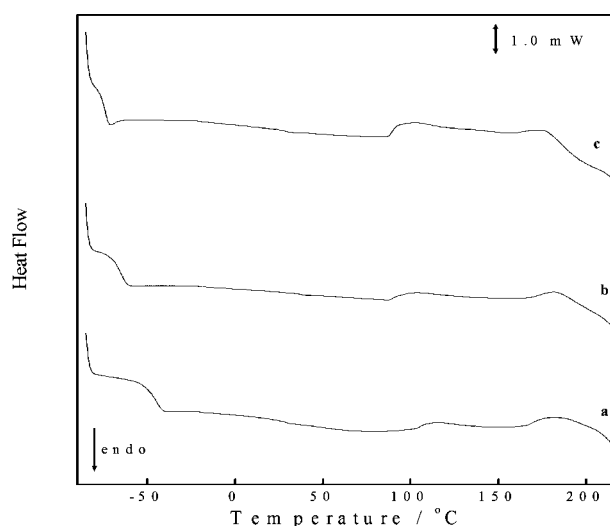
## EXPERIMENTAL

### Materials and methods

The dimethacrylates were TEGDMA (Aldrich Chemical Co., Milwaukee, WI) and Bis-GMA (Aldrich Chemical, Milwaukee, WI). They were used as received and without further purification. Five copolymers of these monomers were prepared from mixtures of TEGDMA and Bis-GMA with the following weight ratios: 30 : 70, 40 : 60, 50 : 50, 60 : 40, and 70 : 30. For light curing, 0.5 wt % camphorquinone (CQ) was used as a photoinitiator, and 0.25 wt % ethyl 4-dimethylaminobenzoate (EDB; 99%) was used as a coinitiator. Because Bis-GMA is a viscous liquid, CQ and EDB were first dissolved in dichloromethane; then, a certain amount of this solution was added to the monomer mixture, and the solvent was subsequently evaporated *in vacuo*. The mixtures were stored in the dark until the photocuring process was initiated.

### Preparation of the copolymers

Discs with a 10-mm diameter and a 1-mm depth were made in a Teflon plate covered with polyethylene film. The desired mixture of the monomers, photoinitiator, and coinitiator was inserted into the groove and irradiated for 60 s. The irradiation was carried out with an Ultrablue IS light-emitting diode with a power of 600 mW (produced by DMC Instruments, São Carlos/SP, Brazil). This irradiation unit emitted radiation predominantly in the  $475 \pm 15$  nm range, where CQ also absorbed (maximum wavelength = 470 nm, and molar absorptivity,  $\epsilon = 3.8 \times 10^4$  cm<sup>2</sup>/mol).<sup>19,20</sup> The light was set at 3 mm from



**Figure 2** Heat flow versus the temperature for uncured mixtures: (a) TB3070, (b) TB5050, and (c) TB7030.

**TABLE I**  
**DSC Data Before the Light Curing of Different Compositions of TEGDMA/Bis-GMA Mixtures**

Mixture	Composition (%) <sup>a</sup>		Temperature (°C)			Heat of polymerization (J/g)	
	W <sub>1</sub>	W <sub>2</sub>	T <sub>g</sub>	Onset polymerization	Peak 1		Peak 2
TB3070	30	70	-45	101	116	183	25
TB4060	40	60	-57	90	104	179	31
TB5050	50	50	-65	89	105	183	34
TB6040	60	40	-69	88	104	177	43
TB7030	70	30	-74	88	102	176	58

<sup>a</sup> W<sub>1</sub> and W<sub>2</sub> are the mass % of TEGDMA/Bis-GMA, respectively.

the sample. The obtained copolymers were named TB3070, TB4060, TB5050, TB6040, and TB7030. TB represents monomers TEGDMA and Bis-GMA, and the numbers represent the different weight ratios of the monomers in the mixture.

### DSC experiments

DSC measurements were performed in a modulated DSC-Q10 (TA Instruments, New Castle, DE). The DSC curves were obtained under a dynamic nitrogen atmosphere (50 mL/min) with about 10 mg of a sample in the temperature range of -90 to 250°C at a heating rate of 10°C/min. Accurately weighed samples ( $\pm 0.1$  mg) were placed in an aluminum open sample holder. The DSC instrument was calibrated for the temperature and enthalpy heat with > 99.99% indium metal.

## RESULTS AND DISCUSSION

### DSC measurements

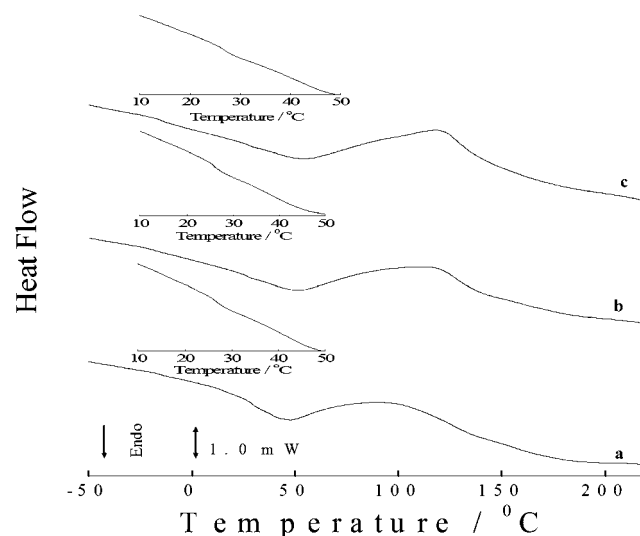
The experimental glass-transition temperature ( $T_g$ ) values of the monomers (TEGDMA and Bis-GMA) and monomer mixtures (TB3070, TB4060, TB5050, TB6040, and TB7030) were determined from the inflection point of the DSC curve. Exothermic peaks in the DSC curves of the mixtures appeared in a range of approximately 100–220°C [Fig. 1(a)]. The DSC curves for the photopolymerized mixtures showed an exothermic peak ranging from 50 to 150°C, but  $T_g$  was not well defined [Fig. 1(b)]. This result can be associated with the particular behavior of the photopolymerization reactions, such as autoacceleration, incomplete functional group conversions, unequal functional group conversions, and free-volume excess. Photopolymerized samples are also characterized by the existence of free radicals trapped within the material. As a result of the rapid gelation and vitrification of the network during photopolymerization, the diffusivity of the reactive species is highly reduced, and a number of radicals cannot react immediately by propagation or termination. Therefore, trapped radicals and an excess of free volume can modify the properties of the material and

represent a problem for its thermal characterization.<sup>21</sup>

The exothermic peak in the DSC curve of the photopolymerized mixtures appeared at a much lower temperature (50–150°C) than that of the uncured mixtures (100–220°C). This result implies the presence of free radicals trapped in the network preformed by light irradiation and therefore having a lower activation energy.

To examine the thermal reaction of the unreacted residual groups, a light-cured sample was subjected to an isotherm treatment for 20 min at 180°C [the region of the exothermic peak in Fig. 1(a)]. After this treatment, there was an absence of the exothermic peak assigned to the unreacted residual groups; therefore, the cure of the material was complete [Fig. 1(c)].

Figure 2 presents the DSC curves for the other compositions of uncured TB copolymers. From these curves, we could estimate the extension of the polymerization, assuming that the heat involved during the measurement was proportional to the fraction of reactive groups/converted double bonds and that it was associated only with the thermal polymerization of the copolymers.



**Figure 3** Heat flow versus the temperature for light-cured copolymers: (a) TB3070, (b) TB5050, and (c) TB7030. Expansions of the DSC curves in the 10–50°C region are shown.

**TABLE II**  
DSC Data After the Light Curing of Different Compositions of TEGDMA/Bis-GMA Mixtures

Mixture	Composition (%) <sup>a</sup>		Temperature (°C)			Heat of polymerization (J/g)
	W <sub>1</sub>	W <sub>2</sub>	T <sub>g</sub>	Onset polymerization	Peak 1	
TB3070	30	70	29	51	98	22
TB4060	40	60	27	52	101	25
TB5050	50	50	26	54	115	27
TB6040	60	40	27	56	119	29
TB7030	70	30	27	57	119	31

<sup>a</sup> W<sub>1</sub> and W<sub>2</sub> are the mass % of TEGDMA/Bis-GMA, respectively.

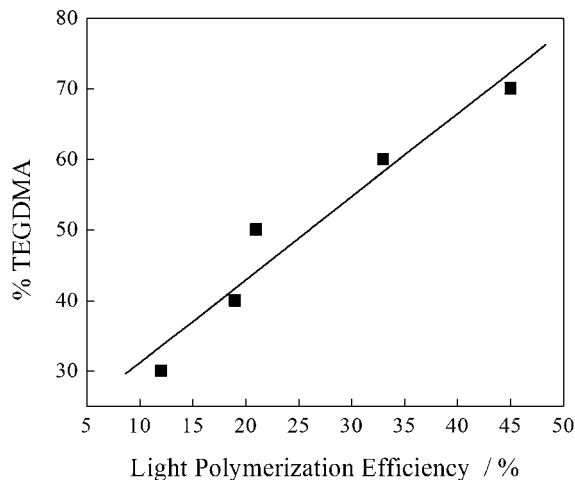
From these data, T<sub>g</sub> at the inflection in the DSC curves, the onset polymerization temperature, and the polymerization heat were determined (Table I).

DSC curves were also obtained for TB mixtures after photopolymerization (Fig. 3). A broad change in the baseline between 0 and 50°C could be attributed to the glass transition. This behavior was due to the breadth of the transition region associated with the properties of the photocured dimethacrylates.<sup>20,22</sup>

The T<sub>g</sub> at the inflection, polymerization peak, and polymerization heat are presented in Table II.

In this case, the evolved heat of polymerization that developed during the measurement (thermal polymerization) was attributed to the conversion of the reactive groups/double bonds or unsaturated pendants groups that did not convert during the photopolymerization.

Therefore, from the data for the polymerization heat, before and after light exposure, obtained from the exothermic DSC curves (Figs. 2 and 3) and presented in Tables I and II, respectively, we could evaluate the light polymerization efficiency. The photopolymerization efficiency is represented as a function of the TEGDMA concentration in Figure 4.



**Figure 4** Variation of the photopolymerization efficiency for all the copolymer compositions.

The photopolymerization efficiency ( $E_p$ ) or degree of conversion also could be evaluated with the following relationship:<sup>23</sup>

$$E_p(\%) = \frac{100\Delta H}{2H_m} \left( \frac{X_1}{M_1} + \frac{X_2}{M_2} \right) \quad (1)$$

where  $\Delta H$  (kcal/mol) is the heat of polymerization of the mixture obtained from the exothermic area under the DSC curve and  $H_m$  is the heat of polymerization of methyl methacrylate (54.8 kJ/mol or 13.1 kcal/mol).<sup>24,25</sup> Factor 2 is attributed to the dimethacrylates (bifunctional monomers).  $X_1$  and  $X_2$  and  $M_1$  and  $M_2$  are the weight fractions and molecular weights of TEGDMA and Bis-GMA, respectively. The photopolymerization efficiency was determined before and after exposure to light, and the light polymerization efficiency or degree of conversion could be evaluated (Table III). The values were in agreement with those determined directly and shown in Figure 4. All the data (the exothermic heat of polymerization as well as the exothermic peak temperatures) before and after light curing indicated that the values increased with the TEGDMA concentration in the copolymers.

A higher conversion was observed for higher concentrations of TEGDMA in the copolymer composition with the most efficient composition (in this study, TB7030).

#### Fox equation

The experimental T<sub>g</sub> values were compared with those calculated with the Fox equation.<sup>26,27</sup>

**TABLE III**  
Light Polymerization Efficiency or Degree of Conversion of the Copolymerization of TEGDMA/Bis-GMA

Copolymer	Light polymerization efficiency or degree of conversion (%)
TB3070	14
TB4060	19
TB5050	21
TB6040	32
TB7030	46

**TABLE IV**  
 $T_g$  Data from the Monomer Mixture Experiments and the Fox Equation

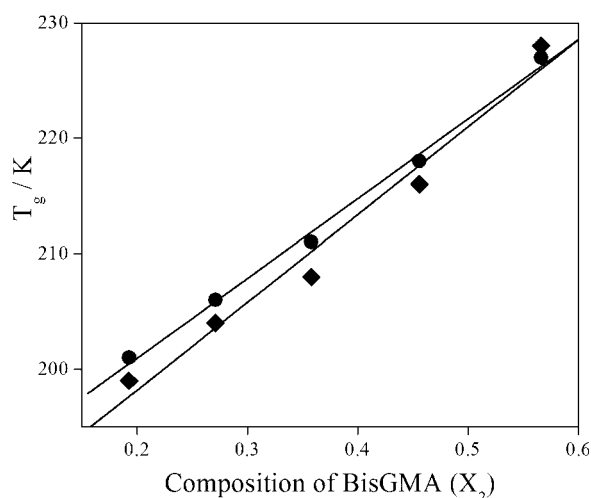
Monomer mixture	$T_g$ of the monomer mixture			
	Experimental (°C)	Experimental (K)	Fox (°C)	Fox (K)
TB3070	-45	228	-44	229
TB4060	-57	216	-55	218
TB5050	-65	208	-62	211
TB6040	-69	204	-67	206
TB7030	-74	199	-72	201

$$\frac{1}{T_g} = \frac{X_1}{T_g(1)} + \frac{X_2}{T_g(2)} \quad (2)$$

where  $T_g$ ,  $T_g(1)$ , and  $T_g(2)$  are the glass-transition temperatures of the copolymer system TEGDMA/Bis-GMA, the homopolymer TEGDMA ( $T_g = -83^\circ\text{C}$ ), and the homopolymer Bis-GMA ( $T_g = -8.0^\circ\text{C}$ ) and  $X_1$  and  $X_2$  are the weight fractions of TEGDMA and Bis-GMA, respectively. The  $T_g$  values of the monomers were experimentally determined and agreed with literature values.<sup>4,22</sup>

The  $T_g$  values of mixtures of the TEGDMA and Bis-GMA monomers with different compositions are shown in Table IV, and the variation of the experimental  $T_g$  values with the composition, along with the  $T_g$  values from eq. (1) (the Fox equation), is shown in Figure 5.

In all the mixtures, the experimental value was lower than the calculated value. The Bis-GMA monomer has the structure of a quasi-network formed by strong hydrogen bonding. In the mixtures, many of these bonds were destroyed, the flexibility of the Bis-GMA molecules increased, and so the  $T_g$  value of Bis-GMA in the mixtures was lower than that of neat Bis-GMA. This effect, which was



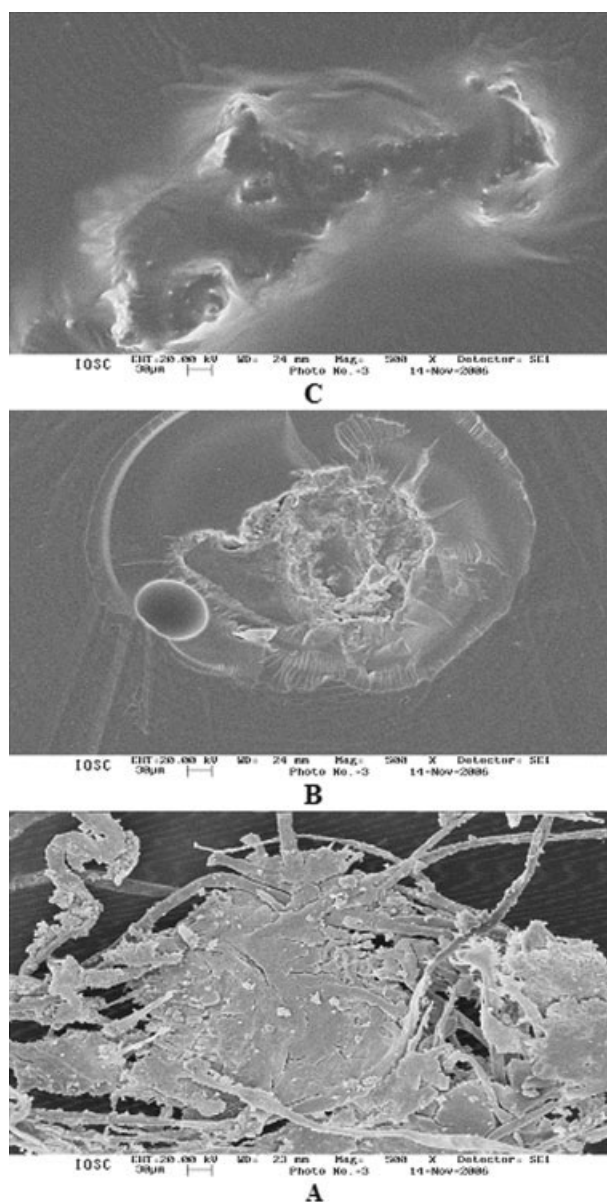
**Figure 5** Variation of  $T_g$  for a mixture with the composition of Bis-GMA ( $X_2$ ): (●) Fox value and (◆) experimental value.

not predicted by the Fox equation, was probably responsible for the lower experimental  $T_g$  values determined in comparison with the calculated values.

At higher concentrations of Bis-GMA ( $X_2$ ), it appears that there was better agreement between the experimental  $T_g$  values and the  $T_g$  values from the Fox equation.

### SEM images

Figure 6 presents typical SEM images of the TB7030, TB5050, and TB3070 copolymers after photopolymerization with an Ultrablue IS light-emitting diode for 60 s with 600 mW of power. We observed significant



**Figure 6** SEM images (500×) for copolymers (A) TB7030, (B) TB5050, and (C) TB3070 cured with an Ultrablue IS light-emitting diode.

changes in the appearance of the images for the different compositions.

SEM photomicrographs of the TB7030 copolymers exhibited the presence of fibers and voids. The voids were also observed in the TB5050 copolymers but were not observed in TB3070. The presence of fibers could be related to the higher conversion of reactive groups determined for copolymer TB7030 (Fig. 4 and Table III).

### CONCLUSIONS

DSC measurements were effective in evaluating the light polymerization efficiency of copolymers used in dental resin formulations. A higher concentration of TEGDMA in the copolymers yielded a higher conversion by light-induced polymerization. The  $T_g$  values of the copolymers could be predicted by the application of the Fox equation and verified by actual DSC measurements. We have concluded that the fibers formed in TB7030 copolymers will impart higher mechanical strength to light-induced-polymerization copolymers.

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