

# Evaluation of Postpolymerization as a Function of the Storage Time of Triethylene Glycol Dimethacrylate/2,2-Bis[4-(2-Hydroxy-3-Methacryloxy-Prop-1-Oxy)-Phenyl]propane Bisphenyl- $\alpha$ -Glycidyl Ether Dimethacrylate Copolymers Used in Dental Resins by Differential Scanning Calorimetry and Dynamic Mechanical Analysis

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**ABSTRACT:** The aim of this work was to evaluate the effect of the storage time on the thermal properties of triethylene glycol dimethacrylate/2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)-phenyl]propane bisphenyl- $\alpha$ -glycidyl ether dimethacrylate (TB) copolymers used in formulations of dental resins after photopolymerization. The TB copolymers were prepared by photopolymerization with an Ultrablue IS light-emitting diode, stored in the dark for 1–60 days at 37°C, and characterized with differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and Fourier transform infrared spectroscopy with attenuated total reflection. DSC curves indicated the presence of an exothermic peak, confirming that the reaction

was not completed during the photopolymerization process. This exothermic peak became smaller as a function of the storage time and was shifted at higher temperatures. In DMA studies, a plot of the loss tangent versus the temperature initially showed the presence of two well-defined peaks. The presence of both peaks confirmed the presence of residual monomers that were not converted during the photopolymerization process. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 679–684, 2009

**Key words:** crosslinking; degree of polymerization (DP); differential scanning calorimetry (DSC); mechanical properties; photopolymerization

## INTRODUCTION

The most common dimethacrylate monomer in current commercial dental composites is 2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)-phenyl]propane bisphenyl- $\alpha$ -glycidyl ether dimethacrylate (BisGMA). Advantages of using BisGMA over other monomers include less shrinkage, higher modulus, and reduced toxicity due to its lower volatility and diffusivity into tissues. These desirable properties of BisGMA are partially cancelled by its relatively high viscosity, which does not allow the use of larger amounts of filler. To overcome the high viscosity problem, a less viscous monomer, usually triethylene glycol dimethacrylate (TEGDMA), is used as a diluting comono-

mer. However, TEGDMA does affect the properties of the matrix resin by increasing the water sorption and the curing shrinkage.<sup>1–9</sup>

During the photopolymerization of dimethacrylate monomers, the propagation and termination rates become diffusion-controlled, so the reaction rate slows down significantly as vitrification decreases the mobility and diffusivity of the reactive species. However, the formation of an insoluble infinitely large network restricts the movements of the macroradicals, so the termination step, which involves the recombination of two macroradicals, becomes diffusion-limited. The decrease in the termination rate leads to a corresponding increase in the polymerization rate; this is known as the autoacceleration or gel effect and is more pronounced in the case of viscous monomers. The functional groups remaining in the system are trapped in the form of residual monomers and unreacted pendent radicals attached to the backbone of the polymer chain.<sup>10–12</sup>

Thus, incomplete conversion during the photopolymerization process results in the presence of radical pendent groups and in the release of unreacted

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monomers as a function of time and, consequently, in changes in the thermal and mechanical properties of the polymers.<sup>13–18</sup> This phenomenon, called postpolymerization or postshrinkage, is characterized by successive steps. As reported in a previous study, the unreacted residual monomers may leach from the photopolymerized materials, irritating the soft tissue and promoting allergic reactions.<sup>19,20</sup> For instance, TEGDMA is suspected of causing bacterial growth around restorations. Furthermore, monomers trapped in restorations may reduce the clinical serviceability of the materials.<sup>21</sup>

Initially, the photopolymerization process is very fast, leading rapidly to vitrification and a severe slowdown of the reaction. This leaves a large amount of free volume trapped in the copolymer network. The relaxation of the network during storage releases the excess of free volume (known as postshrinkage) to a more stable conformation. This free volume change increases the mobility of the trapped radicals, resuming the propagation and termination reactions and leading to a decrease in the overall radical concentration.<sup>22</sup>

In this study, dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to evaluate the effect of storage on the thermal properties and postpolymerization phenomenon of triethylene glycol dimethacrylate/2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)-phenyl]propane bisphenyl- $\alpha$ -glycidyl ether dimethacrylate (TB) copolymers. The storage temperature was 37°C (body temperature). Fourier transform infrared (FTIR) spectroscopy with attenuated total reflection (ATR) was used to confirm the incomplete conversion of the copolymers.

## EXPERIMENTAL

### Preparation of the experimental resins

The dimethacrylates used were TEGDMA (Aldrich Chemical Co., Milwaukee, WI) and BisGMA (Aldrich Chemical). They were used as received and without further purification. Five copolymers of these monomers were prepared from mixtures of TEGDMA and BisGMA with the following weight ratios: 30 : 70, 40 : 60, 50 : 50, 60 : 40, and 70 : 30. The obtained copolymers were labeled TB3070, TB4060, TB5050, TB6040, and TB7030, respectively, the codes referring to the weight ratios of TEGDMA (T) to BisGMA (B).

The photoinitiation system used for light curing consisted of 0.5 wt % camphorquinone (CQ; Fluka Co., Ronkonkoma) and 0.25 wt % ethyl 4-dimethylaminobenzoate (99%; Aldrich Chemical) used as a cointiator. Because BisGMA is a viscous liquid, CQ and ethyl 4-dimethylaminobenzoate 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.

### DSC experiments

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

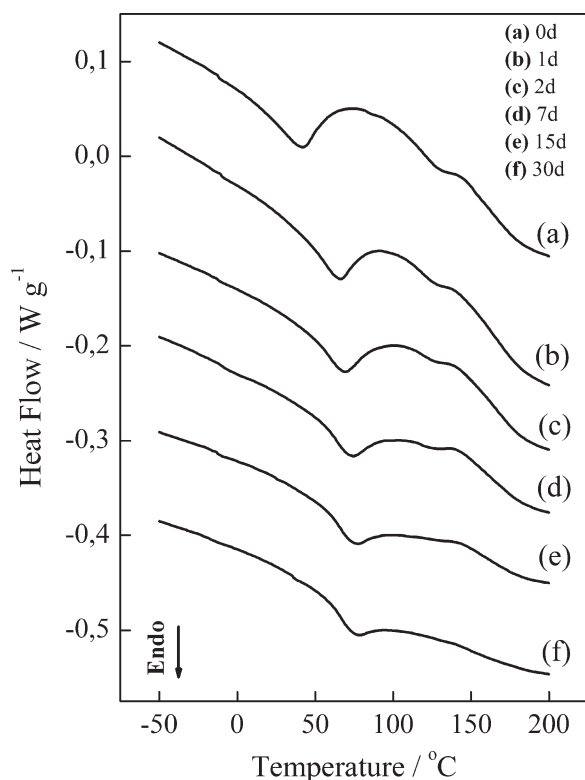
The copolymers were prepared as 10-mm-diameter and 1-mm-deep discs obtained in a Teflon plate covered with polyethylene film. The copolymers were photocured for 60 s with a 350-mW Ultra Blue IS light-emitting diode (DMC Instruments, São Carlos, Brazil) placed 3 mm from the sample. This irradiation unit emitted predominantly in the range of  $475 \pm 15$  nm, where CQ absorbs strongly (maximum wavelength = 470 nm, molar absorptivity ( $\epsilon$ ) =  $3.8 \times 10^4$  cm<sup>2</sup>/mol).<sup>23</sup> The polymerized sample was stored at  $37 \pm 1.0^\circ\text{C}$  for different times (0, 1, 2, 7, 15, and 30 days) before being tested. Small accurately weighed samples were used for DSC analysis after the larger sample was ground.

### DMA

The samples used in DMA analysis were prepared in a Teflon mold [ $10 \times 5.5 \times 1.0$  mm<sup>3</sup>] and photocured in the same way as the samples studied with DSC. A DMA 242C dynamic mechanical analyzer (Netzsch Instruments, Selb, Germany) was used to measure the mechanical properties of samples of the TB3070 copolymer. The polymerized sample was stored in an oven at  $37 \pm 1^\circ\text{C}$  for different times (0, 1, 2, 7, 15, 30, and 60 days) in the dark. DMA was performed in the 150–250°C temperature range at a heating rate of  $2.0^\circ\text{C}/\text{min}$  in the tension mode at the fixed frequency of 1 Hz. Liquid nitrogen was used to cool the sample and to provide an inert atmosphere for the analysis. The loss modulus ( $E''$ ), storage modulus ( $E'$ ), and loss tangent ( $\tan \delta = E''/E'$ ) were recorded as a function of temperature, and the glass-transition temperature ( $T_g$ ) was obtained from the maximum of the curves of  $\tan \delta$  versus the temperature.

### FTIR–ATR spectroscopy

FTIR spectroscopy with ATR is a useful tool for evaluating the degree of conversion of copolymers.<sup>24–27</sup> Infrared spectra were recorded with a Bomem 100 (MB series) spectrometer with a Golden Gate single



**Figure 1** DSC curves of the TB3070 copolymer for different storage times at 37°C: (a) 0, (b) 1, (c) 2, (d) 7, (e) 15, and (f) 30 days.

reflection diamond ATR unit (Specac Co., Woodstock) with a spectral resolution of  $8\text{ cm}^{-1}$ . One drop of the mixture of the monomers was placed on the internal reflectance crystal, where total internal reflection occurred. The reflected radiation penetrated the sample to a depth of only a few micrometers. The degree of conversion (DC) was determined from the ratio of

the absorption peak areas of the aliphatic  $\text{C}=\text{C}$  absorption (ca.  $1635\text{ cm}^{-1}$ ) to the aromatic carbon-carbon absorption (ca.  $1608\text{ cm}^{-1}$ ) between cured ( $A^*$ ) and uncured ( $A$ ) copolymers with the following equation:<sup>28,29</sup>

$$\text{DC}(\%) = 100 - \left\{ \frac{A_{1635}^*}{A_{1635}} \times \frac{A_{1608}}{A_{1608}^*} \right\} \times 100$$

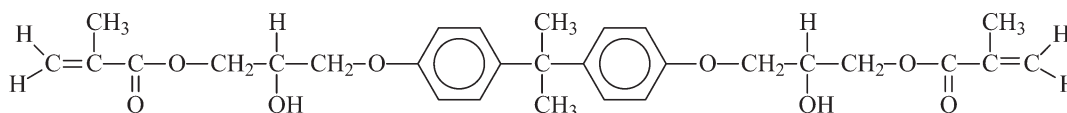
where  $A_{1635}$  and  $A_{1608}$  are the areas of the 1635 and 1608  $\text{cm}^{-1}$  peaks, respectively.

## RESULTS AND DISCUSSION

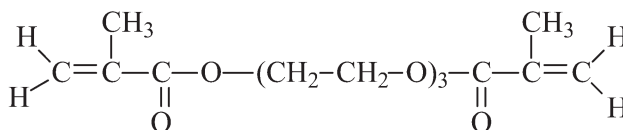
### DSC studies of the TB copolymers

DSC curves were determined for the photopolymerized copolymers TB3070, TB5050, and TB7030 immediately after photopolymerization and after different storage times (1, 2, 7, 15, and 30 days) at 37°C. Figure 1 shows the DSC curves for the TB3070 copolymer. Similar behavior was observed for the other copolymers (TB5050 and TB7030).

The DSC curves of the copolymers obtained immediately after the photopolymerization reaction show an exothermic peak in the 50–150°C interval, which decreases with the storage time (Fig. 1). These peaks indicate the presence of residual monomers and/or unreacted pendent groups that were not converted during the photopolymerization reaction. The reduction of the peaks and their shift to higher temperatures indicate that trapped radicals were converted preferentially during the storage time. Although the formation of new thermally induced radicals requires higher temperatures, trapped radicals may be



**BisGMA** (2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-1-oxy)-phenyl]propane bisphenyl- $\alpha$ -glycidyl ether dimethacrylate)



**TEGDMA** (triethylene glycol dimethacrylate)

**Scheme 1** Molecular structures of the dimethacrylate monomers used and the network formed.

reactivated at relatively low temperatures. Thus, the smaller size of the exothermic peak and its shift to higher temperatures indicate the conversion of free monomers and/or pendent groups trapped in the network by a reaction with the released free radicals.

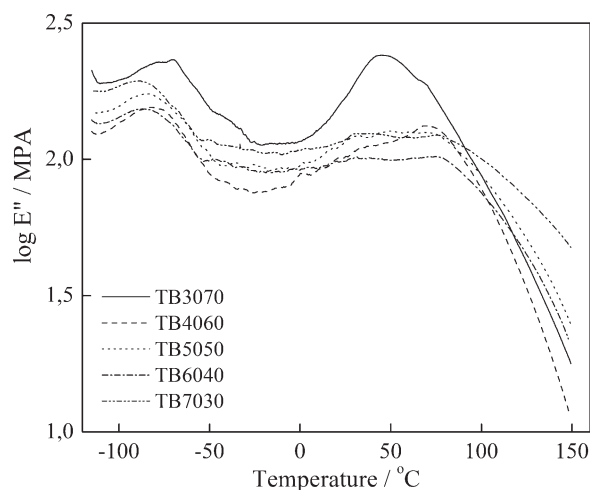
For copolymers involving urethane dimethacrylate (UDMA), such as UDMA/BisGMA, the exothermic peak disappears at shorter times (ca. 120 h).<sup>30</sup> This behavior can be attributed to the lower viscosity of UDMA in comparison with BisGMA;<sup>31</sup> this is due to the strong hydrogen bonding of the latter, which causes a decrease in the mobility of monomer molecules during the photopolymerization reaction and reduces the flexibility of the polymeric network. Therefore, the structure and physical properties (e.g., viscosity) of the dimethacrylate monomers (Scheme 1) affect the degree of conversion of the copolymers.

$T_g$  could not be determined by DSC because the glass-transition peak was overlapped by the peak due to the exothermic conversion of residual monomers and/or pendent groups during heating.

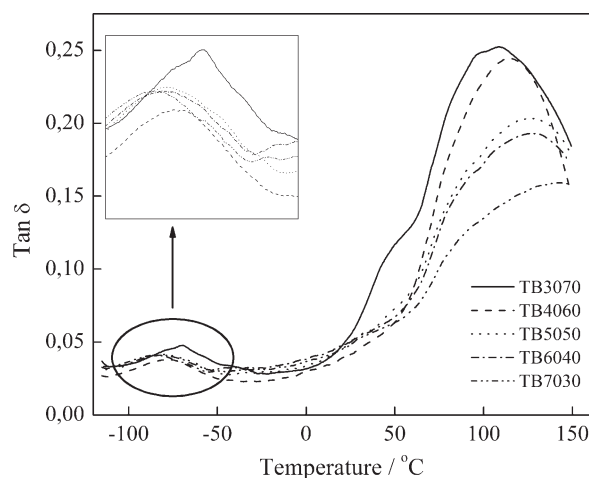
#### DMA of the TB copolymers

DMA is a technique used to acquire useful information about the viscoelastic properties of polymers. The elastic modulus (or  $E'$ ) and the viscous modulus (or  $E''$ ) can be calculated from the in-phase and out-of-phase stress resulting from an applied oscillating strain. The phase angle between the dynamic strain and stress in the oscillating experiment is  $\tan \delta$  (or the mechanical damping obtained from the ratio of  $E''$  to  $E'$ ) and can be associated with  $T_g$ . The position of the loss peaks provides information about internal molecular mobility.<sup>32,33</sup>

Different compositions of TB copolymers were evaluated with DMA (TB3070, TB4060, TB55050, TB6040, and TB7030). Figures 2 and 3 show  $E''$  and  $\tan \delta$ , respectively, for the copolymers.



**Figure 2** Log  $E''$  for different copolymers: TB3070, TB4060, TB5050, TB6040, and TB7030.



**Figure 3**  $\tan \delta$  as a function of temperature for different copolymers: TB3070, TB4060, TB5050, TB6040, and TB7030.

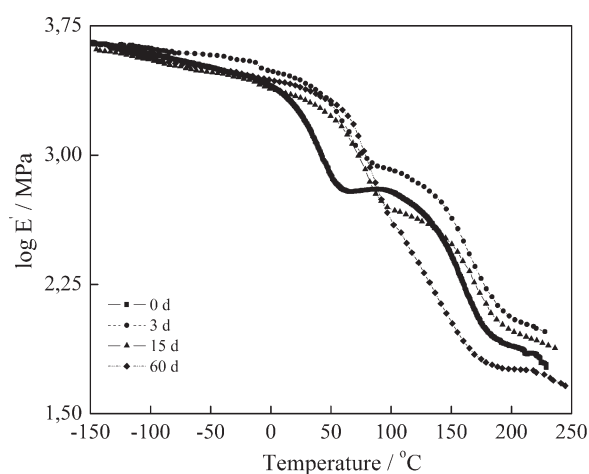
The DMA results for the different copolymers show the presence of two peaks for all compositions, as can be seen in Figure 3. The peak at the low temperature can be associated with residual monomers not converted during the photopolymerization process. It can also be observed that  $\tan \delta$  decreases for the TB copolymers with higher proportions of TEGDMA monomer. These results can be attributed to cyclization of pendant groups with the formation of compact structures that compete with the crosslinking process. The cyclization process of pendant groups leads to an increase in the monomer conversion but does not contribute to network formation.<sup>10,34</sup> The formation of a more compact structure promotes the inhomogeneity of the polymer network, leading to a reduction in the mechanical strength of the copolymers.

The increasing degree of crosslinking in the copolymers makes the changes in their properties less abrupt, so the definition of the glass transitions becomes more difficult. Thus,  $T_g$  values are preferentially determined from the maximum of the  $\tan \delta$  versus temperature curves.<sup>32,33</sup> Another difficulty in the determination of  $T_g$  of uncured composite samples can be traced to the induced postpolymerization during heating, which causes uncertainty in the glass-transition region. Therefore, in this study, the  $T_g$  values were taken from the peak of the  $\tan \delta$  curves.

Table I shows the  $T_g$  values for the different compositions of TB copolymers obtained from the peaks

**TABLE I**  
 $T_g$  and  $\tan \delta$  Values for the TB Copolymers

| Copolymer | $T_g$ (°C) | $\tan \delta$ |
|-----------|------------|---------------|
| TB3070    | 107        | 0.25          |
| TB4060    | 115        | 0.24          |
| TB5050    | 126        | 0.21          |
| TB6040    | 128        | 0.19          |
| TB7030    | 142        | 0.16          |

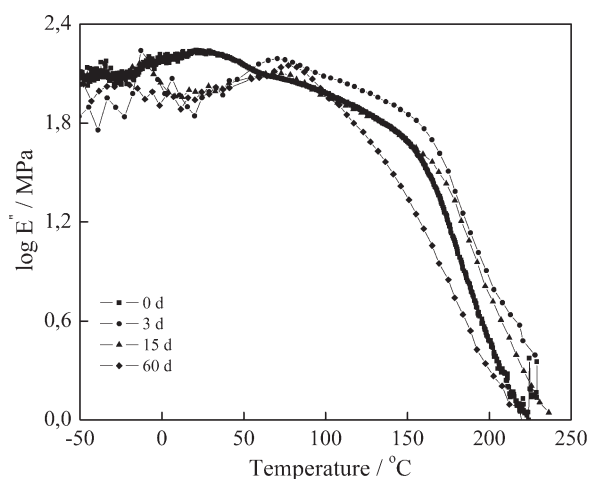


**Figure 4** Log  $E'$  as a function of temperature for the TB3070 copolymer for different storage times at 37°C: (■) 0, (●) 3, (▲) 15, and (◆) 60 days.

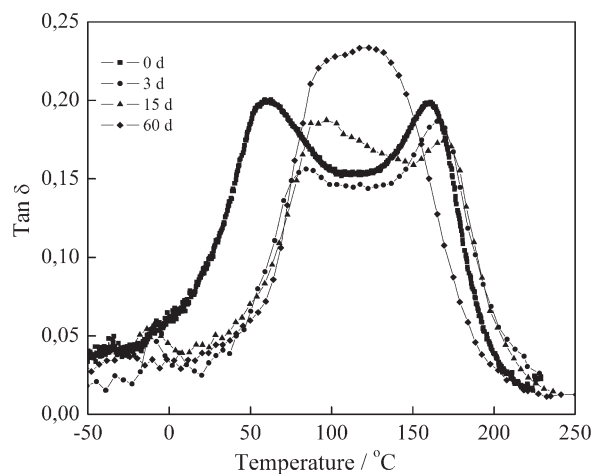
of the  $\tan \delta$  curves. The highest  $T_g$  value was found for the TB7030 copolymer, which contained the largest proportion of TEGDMA. These data can be correlated with the chain flexibility of the network, which depends on its structure. For all TB compositions, the  $\tan \delta$  values ranged from 0.25 to 0.16. Higher values of  $\tan \delta$  indicate higher energy loss and more viscous behavior, whereas lower  $\tan \delta$  values indicate increasingly elastic behavior. Therefore, when the chain flexibility is high, the cyclization reactions of the pendent groups are promoted, conferring larger rigidity to the copolymer.

#### Evaluation of the postpolymerization storage time by DMA

Figures 4, 5, and 6 show  $E'$ ,  $E''$ , and  $\tan \delta$ , respectively, for the TB3070 copolymer immediately after



**Figure 5** Log  $E''$  as a function of temperature for the TB3070 copolymer for different storage times at 37°C: (■) 0, (●) 3, (▲) 15, and (◆) 60 days.



**Figure 6**  $\tan \delta$  as a function of temperature for the TB3070 copolymer for different storage times at 37°C: (■) 0, (●) 3, (▲) 15, and (◆) 60 days.

photopolymerization (0 days) and after storage for 1, 3, 15, and 60 days at 37°C.

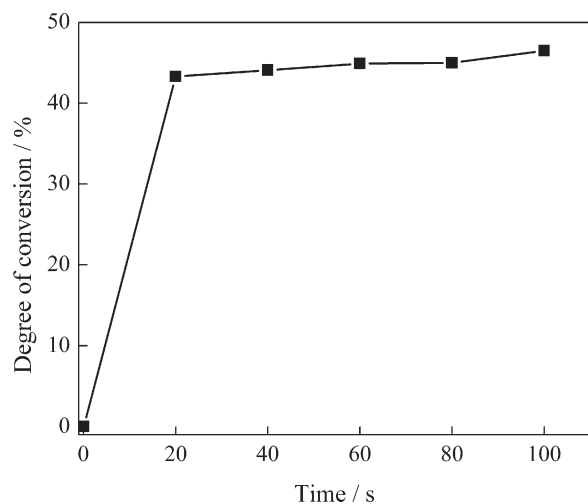
Figure 4 shows that  $E'$  sharply drops when the temperature is raised, and the curves change qualitatively as a function of the storage time. Around 60°C,  $E'$  rises from 2.80 to 3.20 MPa, as expected from the increase in the rigidity of the copolymer during storage.<sup>22</sup>

$E''$  increases up to a maximum in the glass-transition region (ca. 60°C; Fig. 5). Thereafter, this property decreases continuously when the temperature is further raised.

Figure 6 shows  $\tan \delta$  as a function of temperature for the TB3070 copolymer at different storage times.  $\tan \delta$  increases when the temperature is raised, reaching its maximum at the glass-transition region and dropping afterwards. Two well-defined peaks with maxima at 59 ( $T_{g1}$ ) and 160°C ( $T_{g2}$ ) are present immediately after photopolymerization. The intensity of the lower temperature peak is reduced continuously with increasing storage times, and after 60 days, both peaks merge into a single peak with a maximum at about 120°C.  $T_{g1}$  can be associated with the presence of residual monomers, so it cannot be strictly considered a glass-transition process, whereas  $T_{g2}$  corresponds to the glass transition of the cured

**TABLE II**  
 $T_g$  Values of the TB3070 Copolymer for Different Storage Times

| Storage time (days) | $T_{g1}$ (°C) | $T_{g2}$ (°C) |
|---------------------|---------------|---------------|
| 0                   | 60            | 161           |
| 1                   | 75            | 165           |
| 2                   | 85            | 165           |
| 7                   | 95            | 169           |
| 15                  | 96            | 169           |
| 30                  | 122           | 152           |
| 60                  | 120           | 120           |



**Figure 7** Degree of conversion as a function of the irradiation time for the TB3070 copolymer.

material. A shift of the  $\tan \delta$  maxima can also be observed as a function of time, confirming the increasing rigidity of the copolymer as a function of the storage time.

Table II shows the  $T_g$  values as a function of the storage time. Immediately after photopolymerization,  $T_g$  is  $60^\circ\text{C}$ , which is above the working temperature ( $37^\circ\text{C}$ ). This value of  $T_g$  indicates the very low mobility of the polymer chains, which results in rather low conversions at lower temperatures. However, postshrinkage or postpolymerization phenomena can be expected when trapped free radicals acquire a certain mobility due to changes in the free volume associated with the relaxation of the polymer chains.

Therefore, the uncompleted conversion of the monomers during the photopolymerization process affects the mechanical behavior of TB copolymers, and these properties change continuously with the storage time. Figure 7 shows the degree of conversion of the TB3070 copolymer as a function of the irradiation time. The degree of conversion of the polymer confirms that a significant amount (ca. 55%) of free monomers remains after photopolymerization. The same behavior has been observed in other studies.<sup>35</sup> These remaining monomers will continue to be converted during the storage time.<sup>36</sup>

## CONCLUSIONS

The incomplete conversion of the photopolymerized copolymers used in formulations of dental resins was evaluated as a function of the storage time with DSC and DMA techniques. DSC proved the occurrence of postpolymerization, and the DMA studies confirmed changes in the mechanical properties of the copolymers as a result of postpolymerization or postshrink-

age processes during storage. Postpolymerization occurs at relatively low temperatures, and the process can be detected even at temperatures below  $T_g$ .

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