

# Copolymerization Kinetics of Dental Dimethacrylate Resins Initiated by a Benzoyl Peroxide/Amine Redox System

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**ABSTRACT:** The copolymerization of four dental dimethacrylates initiated by a benzoyl peroxide/4-*N,N*-dimethylamino phenethyl alcohol redox system at 37°C was studied with differential scanning calorimetry. The studied dimethacrylates were viscous bisphenol A glycidyl dimethacrylate (Bis-GMA), bisphenol A ethoxylated dimethacrylate (Bis-EMA), and urethane dimethacrylate (UDMA), which were characterized as base monomers, and low-viscosity triethylene glycol dimethacrylate (TEGDMA), which was characterized as a diluent. Also, three series of dimethacrylate copolymers were prepared by incremental additions (12.5 wt %) of TEGDMA to a base comonomer (Bis-GMA, UDMA or Bis-EMA). The maximum rate of homopolymerization of the dimethacrylates followed the order of Bis-GMA > UDMA > TEGDMA > Bis-EMA, and the final degree of conversion of the corresponding homopolymers

followed the order of TEGDMA > UDMA > Bis-EMA > Bis-GMA. A reaction-diffusion-controlled termination region was clear in all monomers and started earlier in bulky and rigid Bis-GMA and Bis-EMA (followed by the more flexible UDMA and TEGDMA) but lasted longer in the Bis-EMA polymerization. The maximum rate of copolymerization and degree of conversion of copolymers of a base monomer with TEGDMA changed monotonically with an increase in the TEGDMA content in the initial comonomer mixture. A synergistic effect was clear only in the final double-bond conversion of Bis-GMA/TEGDMA. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 515–524, 2008

**Key words:** copolymerization; dental polymers; differential scanning calorimetry (DSC); kinetics (polym.); radical polymerization

## INTRODUCTION

Dental resins, used for nearly 50 years, generally are based on methacrylates and dimethacrylates.<sup>1–3</sup> Today, they are typically composed of two or more monomers, including a relatively viscous dimethacrylate base monomer, such as bisphenol A glycidyl dimethacrylate (Bis-GMA), and a low-viscosity dimethacrylate comonomer, such as triethylene glycol dimethacrylate (TEGDMA), which is used as a reactive diluent. Other commonly used base monomers in commercial dental-resin-based materials are bisphenol A ethoxylated dimethacrylate (Bis-EMA) and urethane dimethacrylate (UDMA).<sup>4</sup> These monomers are copolymerized at the ambient temperature with a photoinitiation or redox initiation system. In the first case, the most common photoinitiation system is a combination of camphorquinone (CQ) and an amine. The generally used redox initiation system is a combination of benzoyl peroxide (BPO) and *p*-substituted *N,N*-dimethylaniline. The photohomopolymerization kinetics of dimethacrylates initiated by

a CQ/amine couple have been extensively studied.<sup>5–9</sup> Some articles on the photocopolymerization of these dimethacrylates have also been published recently.<sup>10–12</sup>

The rapid and efficient polymerization of dental resins with a minimal initiator amount is a critical aspect of the clinical use of dental materials. Moreover, optimized cure is one of the most crucial parameters that govern the long-term performance of the polymeric materials, affecting the mechanical properties, that is, fracture toughness, elastic moduli, flexural strength, and hardness, or the biocompatibility when potentially cytotoxic materials leach from the cured materials.<sup>11</sup>

In a previous work, we examined the homopolymerization of methyl methacrylate initiated by the BPO/*N,N*-dimethyl-*p*-toluidine (DMT) or BPO/4-*N,N*-dimethylamino phenethyl alcohol (DMPOH) redox system at 37°C.<sup>13</sup> It was found that the polymerization rate ( $R_p$ ) and molecular weight of the prepared polymer depended on both the BPO and amine concentrations. When the product of these concentrations was kept constant, the maximum rate and lowest molecular weight were obtained with a slight molar excess of BPO (BPO/amine = 1.6). In a later work, the homopolymerization kinetics and modeling of Bis-EMA and TEGDMA initiated by

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BPO/DMPOH were studied.<sup>14</sup> Also, in another article, the homopolymerization of Bis-GMA, UDMA, and TEGDMA initiated by BPO/DMT, BPO/DMPOH, BPO/4-*N,N*-dimethylamino phenyl acetic acid (DMPAA), and BPO/ethyl 4-dimethylamino benzoate (EDMAB) systems was investigated in an effort to estimate the effect of the amine and monomer chemical structure on the polymerization kinetics.<sup>15</sup> Only the first three amines (DMT, DMPOH, and DMPAA) with electron-donating *p* substituents were able to initiate polymerization at 37°C; DMPOH and DMPAA were slightly more efficient coinitiators with BPO than DMT. EDMAB with an electron-withdrawing *p* substituent could act as a coinitorator with BPO not at 37°C but only at higher temperatures. Polymerizations kinetics are strongly affected by the monomer structure. Bis-GMA and UDMA are more reactive than Bis-EMA and TEGDMA.

The aim of this work was the study of the copolymerization kinetics of dental dimethacrylates initiated by the BPO/DMPOH system. Three separate series of monomer mixtures were formulated by incremental additions of the low-viscosity diluent comonomer TEGDMA to the high-viscosity base monomers Bis-GMA, Bis-EMA, and UDMA. Compositions usually used in dental resin applications were included. The copolymerization kinetics under a fixed initial initiator concentration and identical experimental conditions were studied with differential scanning calorimetry (DSC). A comparison of these results provides valuable information on the effect of the initial composition of the monomer mixture on the maximum polymerization rate ( $R_p^{\max}$ ) and the degree of double-bond conversion, which can help us in better understanding the behavior of dental resins obtained from these dimethacrylates under the specific reaction conditions.

## EXPERIMENTAL

### Materials

The dimethacrylate monomers, Bis-GMA (Polysciences Europe; lot no. 495282; fp > 240°F; Polysciences Europe GmbH, Eppelheim, Germany), Bis-EMA (Aldrich Chemical Co.; lot no. 03514HF; fp = 235°F; inhibited with 500 ppm monomethyl ether hydroquinone; (Sigma-Aldrich Chemie GmbH, Seelze, Germany)), TEGDMA (Aldrich Chemical; lot no. 17529EA-503; inhibited), and UDMA (Ivoclar AG; lot no. 300357; Ivoclar Vivadent AG, Scaan, Liechtenstein), were used as received without further purification. Generally, the monomers for dental restorative resins are not purified and are used as delivered. They contain inhibitors to prevent premature polymerization during storage and working time. Nevertheless, it has been suggested that chromatographic column purification does not affect the poly-

merization kinetics of TEGDMA.<sup>16,17</sup> The initiators were DMPOH (mp = 59–61°C; Aldrich Chemical; lot no. 22032-109), which was used without further purification, and BPO (Sigma-Aldrich), which was purified by fractional recrystallization from a chloroform–methanol mixture (mp = 104°C). All other chemicals used were reagent-grade.

### Procedure

In three different series of experiments, nine resins were formulated by the addition of the diluent monomer TEGDMA to either Bis-GMA, UDMA, or Bis-EMA in weight fractions of 0, 12.5, 25, 37.5, 50, 62.5, 75, 87.5, and 100%, with the final mixture weight always kept at 4 g. Two initial solutions of each individual formulation were prepared, one containing the peroxide initiator BPO (0.01 mol/1000 g of monomer mixture) and the other the amine DMPOH (0.01 mol/1000 g of monomer mixture). To enhance the dissolution of the initiators, an ultrasonic bath was used. Dichloromethane was used for the preparation of solutions of BPO or DMPOH in Bis-GMA because this monomer was too viscous. The solvent was removed *in vacuo*.

The polymerization kinetics of the various formulations were studied with a Pyris 1 differential scanning calorimeter (PerkinElmer, Waltham, MA) equipped with Pyris software for Windows. Indium was used for the enthalpy and temperature calibration of the instrument. In each experiment, equal amounts (~ 0.4 g) of the two solutions, BPO in the monomer(s) and amine in the monomer(s), were mixed in an air atmosphere; from this new solution, a standard mass (15–20 mg) was placed in a PerkinElmer aluminum sample pan, accurately weighed, and then placed into the appropriate position of the instrument. To avoid reaction inhibition due to oxygen entrapped in the sample pans during sealing, open pans were used in all experiments. Isothermal runs were performed at 37°C, with oxygen-free nitrogen circulated in the DSC cell outside the pans, to avoid an atmospheric oxygen supply in the sample. The time that passed from the beginning of the mixing of the two solutions up to the introduction of the pan into the nitrogen environment of the differential scanning calorimeter was always 2 min. Also, the time that passed for the instrument equilibration to the desired temperature was 0.5 min. Thus, the DSC recording was started exactly 2.5 min after the initial mixing of the two solutions. The inhibition time reported in the following section was obtained directly from the DSC recording. Thus, it corresponded to the time that passed after this initial dead time until the observation of an increase in the heat flow produced during the reaction. The reaction temperature was continuously recorded and kept constant (within ±0.01°C) during the whole conversion range.

The reaction exotherm [in normalized values (W/g)] at a constant temperature was recorded as a function of time. All polymerizations showed the presence of an inhibition time during which no reaction was observed. This was due to the inhibitor contained in the commercial monomers used and the oxygen dissolved in the monomer during the mixing performed in an air atmosphere, as in all dental and orthopedic applications. The presence of an inhibition time was, however, beneficial for our study because it enabled us to stabilize the sample temperature in DSC and obtain a good baseline before the beginning of polymerization.

The rate of heat release [ $d(\Delta H)/dt$  (W/g)] measured by DSC was directly converted into the overall reaction rate [ $dX/dt$  ( $s^{-1}$ )] with the following formula:

$$\frac{dX}{dt} = \frac{1}{\Delta H_T} \frac{d(\Delta H)}{dt} \quad (1)$$

where  $\Delta H_T$  (J/g) denotes the total reaction enthalpy calculated from the product of the number of double bonds per monomer molecule ( $n = 2$ ) times the standard heat of polymerization of a methacrylate double bond ( $\Delta H_0 = 54.9$  kJ/mol)<sup>14</sup> over the monomer mixture molecular weight ( $MW_m$ ), that is,  $\Delta H_T = n\Delta H_0/MW_m$ .  $MW_m$  varied, depending on the initial composition of the monomer mixture, and is given as a function of the weight fraction ( $w_i$ ;  $i = 1,2$ ) of each monomer:

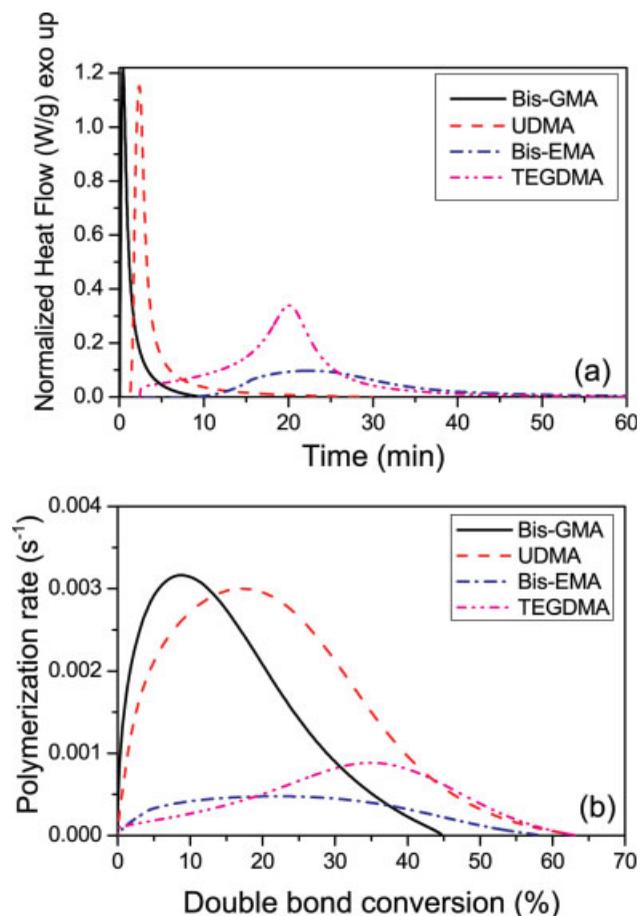
$$MW_m = \left( \frac{w_1}{MW_1} + \frac{w_2}{MW_2} \right)^{-1} \quad (2)$$

The degree of conversion was calculated by integration of the area between the DSC thermograms and the baseline established by extrapolation from the trace produced after complete polymerization (no change in the heat produced during the reaction). All the experimental results reported in the Results and Discussion section were taken from an average of at least two experiments.

## RESULTS AND DISCUSSION

### Homopolymerization kinetics

The DSC thermograms of the homopolymerization of the four dimethacrylates studied are shown in Figure 1(a). There is a considerable variation in the shapes of the curves. The curves of viscous monomers Bis-GMA and UDMA show a sharp peak, whereas the curves of nonviscous monomers Bis-EMA and TEGDMA show a broad peak. Analogous behavior has also been observed in the photopolymerization of these monomers and explained on the



**Figure 1** (a) Thermograms of DSC and (b) rate/conversion profiles for the homopolymerization of the four dimethacrylates initiated by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

basis of their chemical structure.<sup>4</sup> Bis-GMA and UDMA show an immediate dramatic increase in the rate, which is attributed to diffusion limitations of termination dominating from the beginning of polymerization and is termed autoacceleration. The effect of diffusion-controlled phenomena on the termination reaction causes a decrease in the termination rate constant ( $k_t$ ) and an increase in  $R_p$ . The termination reaction becomes increasingly slower, and the propagation rate becomes higher. As the conversion and consequently the viscosity of the system increase, the autoacceleration stops at a point near  $R_p^{\max}$ , at which the network that is formed is too stiff and dense to allow termination via diffusion. At this point, an alternative termination mechanism, so-called reaction-diffusion, is dominant. According to this mechanism, an immobile radical may diffuse in space through the propagation reaction. These events, that is, the onset of diffusion-controlled termination and the change to reaction-diffusion-controlled termination, move closer and closer and eventually merge in the more viscous resin systems

TABLE I  
 $X_{\max}$ ,  $R_p^{\max}$ ,  $X$  at  $R_p^{\max}$ ,  $t_{\text{ind}}$ , and  $t_{\text{peak}}$  for Bis-GMA, UDMA, Bis-EMA, and TEGDMA  
 Homopolymerizations Initiated by BPO/DMPOH at 37°C

| Monomer | $X_{\max}$ | $R_p^{\max}$<br>( $\times 10^3 \text{ s}^{-1}$ ) | $X$ at $R_p^{\max}$<br>(%) | $t_{\text{ind}}$<br>(min) | $t_{\text{peak}}$<br>(min) |
|---------|------------|--|----------------------------|---------------------------|----------------------------|
| Bis-GMA | 0.45       | 3.17   | 8.9                        | 0.05                      | 0.5                        |
| UDMA    | 0.62       | 3.00   | 17.2                       | 1.3                       | 2.5                        |
| Bis-EMA | 0.57       | 0.48   | 21.9                       | 6.9                       | 20.8                       |
| TEGDMA  | 0.63       | 0.86   | 35.0                       | 2.3                       | 20.0                       |

$t_{\text{ind}}$  = induction time;  $t_{\text{peak}}$  = time at the peak;  $X$  at  $R_p^{\max}$  = conversion at the maximum rate;  $X_{\max}$  = maximum double-bond conversion.

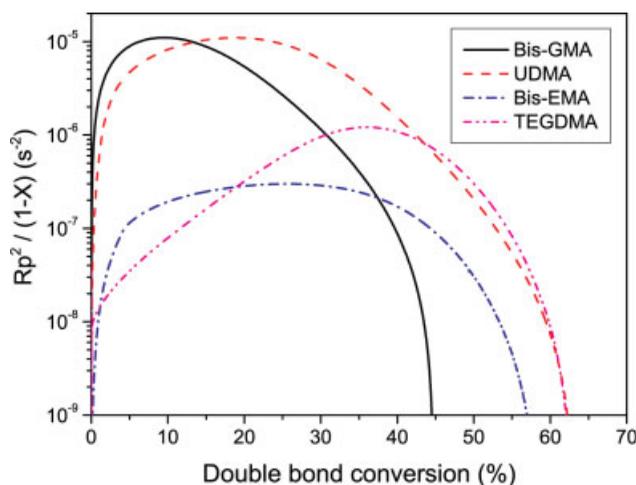
(Bis-GMA and UDMA). Furthermore, as the reaction progresses and the system become more viscous and crosslinked, the mobility of the radicals continues to decrease, whereas the movement of small molecules (i.e., monomers) turn out to be also restricted. Thus, the propagation step becomes diffusion-controlled, and this leads to a decline in  $R_p$ , which is termed autodeceleration. Finally, because of vitrification of the system, the radicals become quite immobile, and the rate eventually drops to zero, leaving residual, unreacted monomer and double bonds. Diffusion-controlled propagation is usually responsible for the apparent end of polymerization before the complete reaction of double bonds. Approximately the same behavior has also been observed in Bis-EMA polymerization, although at a much lower rate.

In TEGDMA polymerization, the sharp initial increase in the reaction rate has not been observed. Instead a shoulder appears, which can be attributed to a delayed onset of diffusion limitations in the termination reaction. This behavior has also been reported in the literature for the photopolymerization of TEGDMA initiated by the system CQ/*N,N*,3,5-tetramethyl aniline<sup>16</sup> or CQ/EDMAB.<sup>11</sup> In the case of TEGDMA, which has a particularly flexible aliphatic ether spacer group in comparison with the connecting groups present in Bis-GMA and UDMA, the propagation reaction initially occurs more extensively by intramolecular attack of the radical site on the pendant double bond (primary cyclization) rather than by intermolecular attack, which leads to network formation (crosslinking). The latter has been demonstrated by the modeling of Bis-GMA/TEGDMA curing kinetics, with which it has been confirmed that TEGDMA forms approximately 3 times more primary cycles than Bis-GMA.<sup>18</sup>

The curves of  $R_p$  versus the double-bond conversion [Fig. 1(b)] show that  $R_p^{\max}$  for Bis-GMA, which has the highest viscosity, is observed at the lowest conversion (8.9%) and  $R_p^{\max}$  for TEGDMA, which has the lowest viscosity, is observed at the highest conversion (35.0%), whereas for UDMA and Bis-EMA,  $R_p^{\max}$  is observed at intermediate values (17 and 22%, correspondingly).

Table I shows the key kinetic results obtained for homopolymerizations of the studied dimethacrylates. The rigid aromatic Bis-GMA with the highest viscosity and hydrogen-bonding ability shows the highest  $R_p^{\max}$  value at the lowest conversion of double bonds and lowest time, together with the lowest final double-bond conversion (45%). Comparing the value of  $R_p^{\max} = 0.00317 \text{ s}^{-1}$  with that reported by other researchers, we have found it to be slightly lower than that reported by Lovell et al.<sup>12</sup> ( $R_p^{\max} = 0.005 \text{ s}^{-1}$ ). Also, the value of the final double-bond conversion is close to that reported in our previous work<sup>4</sup> (39%) and that reported by Lovell et al. (32%). However, this is much higher than that reported by Dickens et al.<sup>11</sup> (7%).  $R_p^{\max}$  for TEGDMA homopolymerization ( $0.00086 \text{ s}^{-1}$ ) is much lower than that reported in ref. 12 ( $0.011 \text{ s}^{-1}$ ). Also, the obtained final conversion of TEGDMA (63%) is close to that reported in ref. 12 (60%) and ref. 4 (76%) and much higher than the value of 34% reported in ref. 11 or 41% in ref. 19. Differences in the reported values could be attributed to different experimental conditions and initiation systems used by the researchers during polymerization. Finally, the induction time is negligible in Bis-GMA polymerization, whereas it is long enough for the less reactive monomer, Bis-EMA (almost 7 min). UDMA and TEGDMA present intermediate values of 1 and 2 min, respectively.

To get valuable information about the effect of the composition on  $R_p^{\max}$ , reaction rate/conversion curves were further studied to provide insight into the phenomenon known as reaction-diffusion-controlled termination. In crosslinked dimethacrylate systems, this type of termination typically becomes the dominant termination mechanism as the polymerization progresses.<sup>12,16</sup> At this stage of conversion, free radicals can no longer diffuse by translational diffusion toward each other to terminate. Instead, termination eventually occurs via the propagation of radicals through unreacted monomer and pendant double bonds. Therefore,  $k_t$  within this regime should be proportional to the propagation rate constant ( $k_p$ ) times the concentration of double bonds ( $[M]$ ):



**Figure 2**  $R_p^2/(1-X)$  versus the double-bond conversion for the homopolymerizations initiated by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$$k_t = Rk_p[M] \quad (3)$$

The proportionality constant ( $R$ ) is termed the reaction diffusion parameter, and a lot of articles have been published on its determination.<sup>10,12,19,20</sup> The typical equation for  $R_p$  ( $s^{-1}$ ), assuming the quasi-steady-state approximation for the free radicals, is given by

$$R_p = k_p(1-X) \left( \frac{R_i}{2k_t} \right)^{1/2} \quad (4)$$

where  $R_i$  is the rate of initiation and  $X$  is the conversion.

In the reaction-diffusion-controlled regime, eq. (4) can be rearranged with eq. (3) into the following:

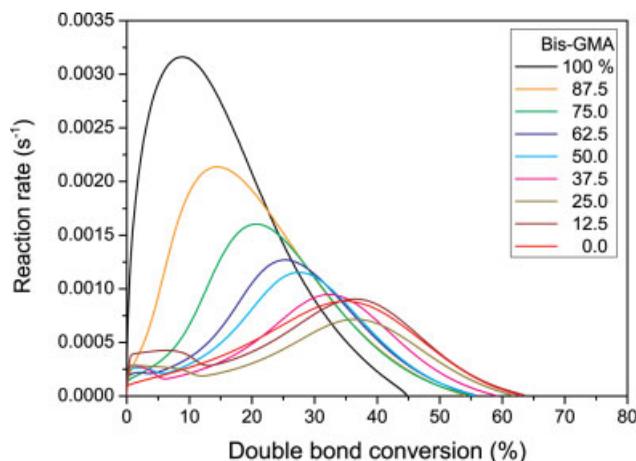
$$R_p = \left( \frac{k_p}{R} \right)^{1/2} (1-X)^{1/2} \left( \frac{R_i}{2} \right)^{1/2} \\ \Rightarrow \frac{R_p^2}{(1-X)} = \left( \frac{k_p}{R} \right) \left( \frac{R_i}{2} \right) \quad (5)$$

In eq. (4), if  $R_i$  is assumed to be constant (at least for the short time of polymerization), then a plot of  $R_p^2/(1-X)$  will plateau in this regime and be proportional to  $k_p$  over  $R$ . Such plots of  $R_p^2/(1-X)$  versus the double-bond conversion for the various resins studied are illustrated in Figure 2. When this plot begins to flatten at its maximum value, this behavior indicates that termination is reaction-diffusion-controlled. The curve then decreases or remains flat, depending on the behavior of propagation.<sup>19</sup> If propagation is reaction-controlled, the plateau in  $R_p^2/[1-X]$  is extended over a larger conversion range until propagation becomes diffusion-controlled. Such a plateau has been observed for all three base monomers almost from the beginning of polymerization (Fig. 2). The conversion range in which reaction-diffusion-controlled termination is the dominant mechanism is rather small in Bis-GMA polymerization (ca. 10%), whereas it is much larger in Bis-EMA (ca. 35%). The region of diffusion-controlled propagation can be identified by the conversion at which  $R_p^2/[1-X]$  begins to decrease. When Bis-GMA is homopolymerized, the propagation reaction appears to be diffusion-controlled at about 12% conversion; for UDMA and Bis-EMA, this occurs at about 20 and 35%, respectively, whereas for TEGDMA, this occurs at about 40%. These differences in the kinetic behavior can be attributed to the mobility of the reacting system.<sup>12,19</sup> TEGDMA is a nonviscous monomer with no hydrogen-bonding ability that forms polymer chains with the highest mobility in comparison with the other monomers.

**TABLE II**  
 $X_{\max}$ ,  $R_p^{\max}$ ,  $X$  at  $R_p^{\max}$ ,  $t_{\text{ind}}$ , and  $t_{\text{peak}}$  as Functions of the Bis-GMA Weight or Fraction for the Copolymerization of Bis-GMA and TEGDMA Initiated by BPO/DMPOH at 37°C

| Bis-GMA (wt %) | $X_{\max}$ | $R_p^{\max}$<br>( $\times 10^3 s^{-1}$ ) | $X$ at $R_p^{\max}$<br>(%) | $t_{\text{ind}}$<br>(min) | $t_{\text{peak}}$<br>(min) |
|----------------|------------|--|----------------------------|---------------------------|----------------------------|
| 100            | 0.45       | 3.17                                     | 8.9                        | 0.05                      | 0.5                        |
| 87.5           | 0.54       | 2.13                                     | 14.5                       | 0.4                       | 2.3                        |
| 75.0           | 0.55       | 1.60                                     | 20.8                       | 0.6                       | 6.1                        |
| 62.5           | 0.56       | 1.26                                     | 25.4                       | 0.7                       | 8.2                        |
| 50.0           | 0.57       | 1.15                                     | 28.6                       | 0.8                       | 9.4                        |
| 37.5           | 0.59       | 0.95                                     | 32.3                       | 1.2                       | 10.7                       |
| 25.0           | 0.62       | 0.72                                     | 36.5                       | 1.4                       | 16.2                       |
| 12.5           | 0.64       | 0.90                                     | 36.4                       | 1.2                       | 13.4                       |
| 0.0            | 0.63       | 0.86                                     | 35.0                       | 2.3                       | 20.0                       |

$t_{\text{ind}}$  = induction time;  $t_{\text{peak}}$  = time at the peak;  $X$  at  $R_p^{\max}$  = conversion at the maximum rate;  $X_{\max}$  = maximum double-bond conversion.

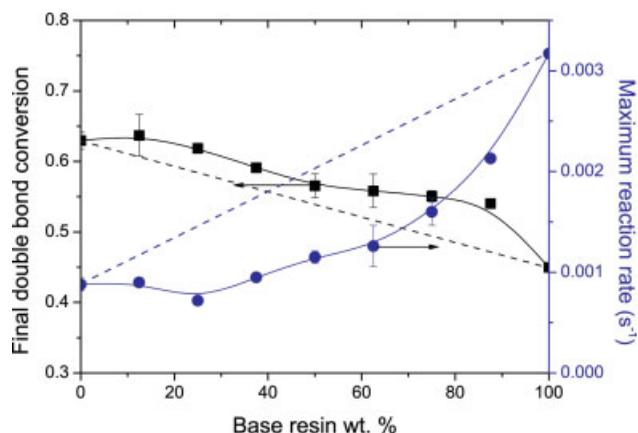


**Figure 3**  $R_p$  as a function of the fractional conversion for Bis-GMA/TEGDMA copolymerizations initiated by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### Copolymerization kinetics

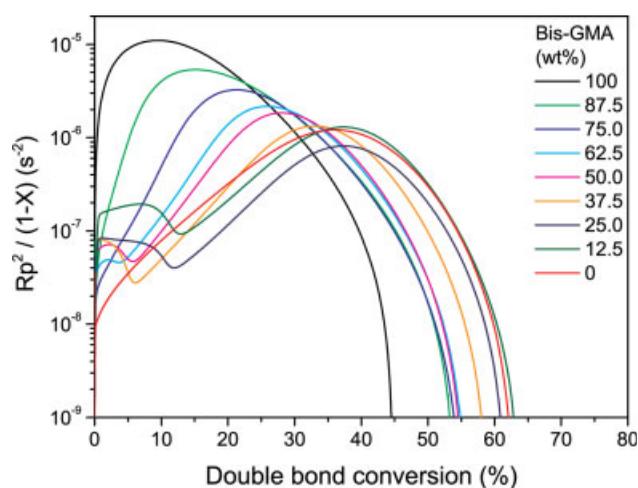
As reported previously, three separate series of monomer mixtures were formulated by incremental additions of the low-viscosity diluent comonomer TEGDMA to the high-viscosity base monomers Bis-GMA, Bis-EMA, and UDMA. To cover a wide range of comonomer compositions between the pure base monomer and pure TEGDMA, an incremental increase of TEGDMA of 12.5 wt % was selected.

The key kinetic results obtained for the copolymerization of Bis-GMA/TEGDMA are shown in Table II. Furthermore, the effect of the composition on the copolymerization rate is graphically illustrated in Figure 3. The incremental increase of TEGDMA in the monomer mixture causes a shift of the reaction rate curves to lower values and longer times. As the amount of Bis-GMA in the samples is increased,  $R_p^{\max}$  increases monotonically (Fig. 4). Furthermore, the final double-bond conversion and the conversion at which  $R_p^{\max}$  occurs decrease with an increasing base resin weight fraction (Fig. 4 and Table II). This behavior is easily explained by the mobility of the system. Because TEGDMA dilutes viscous Bis-GMA, the reaction occurs in a less restricted environment. The decreased viscosity of the system allows the propagation to continue for longer times without being diffusion-controlled.<sup>12</sup> It must be noticed that in the  $R_p^{\max}$  data illustrated in Figure 4, a maximum cannot be observed at a specific composition, as reported in the literature for the photocopolymerization of Bis-GMA/TEGDMA.<sup>11,12,21</sup> In the cited works, the values for the reaction rate and effectively  $R_p^{\max}$  of Bis-GMA homopolymerization were much lower than those of TEGDMA, in contrast to our results. Concerning the possibility of a synergistic effect for the final double-bond conversion and/or



**Figure 4** Rate maxima and final conversions versus the Bis-GMA monomer content in the initial comonomer mixture of Bis-GMA and TEGDMA with the initiator BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

$R_p^{\max}$  (i.e., values following the additive rule of mixing), controversial results have been published in the literature. Thus, Yagci et al.<sup>22</sup> observed a synergistic effect in  $R_p$  but not in the degree of conversion. A synergistic effect for both the final double-bond conversion and  $R_p^{\max}$  was reported by Dickens et al.<sup>11</sup> In a later publication, Floyd and Dickens<sup>23</sup> presented results, from near-infrared measurements, on Bis-GMA/TEGDMA copolymers exhibiting final conversion values always larger than those of the two homopolymers. Using dynamic DSC measurements, Jancar et al.<sup>24</sup> found final conversion values between 45 and 69% for pure Bis-GMA and pure TEGDMA, respectively. All copolymers presented values in this range, with no one exceeding 69%. According to Tar-



**Figure 5**  $R_p^2/(1-X)$  versus the double-bond conversion for various comonomer mixtures of Bis-GMA and TEGDMA copolymerized by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

TABLE III  
 $X_{\max}$ ,  $R_p^{\max}$ ,  $X$  at  $R_p^{\max}$ ,  $t_{\text{ind}}$ , and  $t_{\text{peak}}$  as Functions of the UDMA Weight or Fraction  
 for the UDMA/TEGDMA Copolymerization Initiated  
 by BPO/DMPOH at 37°C

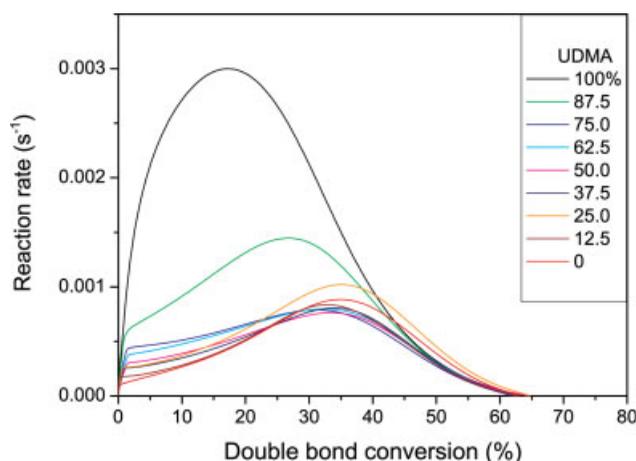
| UDMA (wt %) | $X_{\max}$ | $R_p^{\max}$ ( $\times 10^3$ s $^{-1}$ ) | $X$ at $R_p^{\max}$ (%) | $t_{\text{ind}}$ (min) | $t_{\text{peak}}$ (min) |
|-------------|------------|--|-------------------------|------------------------|-------------------------|
| 100         | 0.62       | 3.01                                     | 17.2                    | 1.3                    | 2.5                     |
| 87.5        | 0.62       | 1.45                                     | 26.7                    | 0.9                    | 4.2                     |
| 75.0        | 0.62       | 0.79                                     | 30.9                    | 1.4                    | 9.2                     |
| 62.5        | 0.64       | 0.80                                     | 32.4                    | 1.2                    | 8.8                     |
| 50.0        | 0.64       | 0.77                                     | 33.5                    | 1.4                    | 12.0                    |
| 37.5        | 0.63       | 0.81                                     | 34.0                    | 1.9                    | 13.5                    |
| 25.0        | 0.65       | 1.00                                     | 35.1                    | 1.9                    | 13.4                    |
| 12.5        | 0.62       | 0.83                                     | 34.8                    | 2.1                    | 16.9                    |
| 0.0         | 0.63       | 0.86                                     | 35.0                    | 2.3                    | 20.0                    |

$t_{\text{ind}}$  = induction time;  $t_{\text{peak}}$  = time at the peak;  $X$  at  $R_p^{\max}$  = conversion at the maximum rate;  $X_{\max}$  = maximum double-bond conversion.

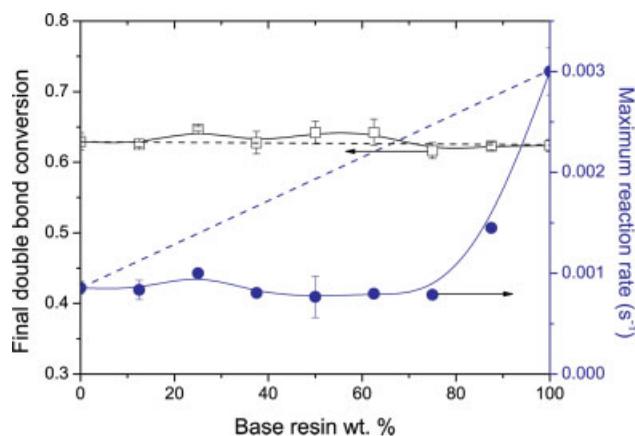
umi et al.,<sup>25</sup> copolymers containing higher amounts of TEGDMA showed higher degrees of final double-bond conversion. The same trend was also observed recently by Rigoli et al.<sup>26</sup> using modulated dynamic DSC measurements and five different copolymer compositions. In addition, in the Bis-GMA/TEGDMA copolymers prepared by the group of Kalachandra<sup>27,28</sup> at 70°C, the final double-bond conversion was always between the values measured for the two homopolymers (26.7 and 78% for pure Bis-GMA and TEGDMA, respectively) and increased with the amount of TEGDMA. In our study, a synergistic effect was observed only in the final double-bond conversion values and not in  $R_p^{\max}$ . Moreover, the trend in the final double-bond conversion and conversion at  $R_p^{\max}$  is the same as that reported in the literature.<sup>11,12,24–28</sup> The differences observed between our data and the corresponding literature data could be attributed to a number of reasons, including the different initiation systems used (redox

in our study vs photopolymerization in some cases<sup>11,12</sup>), a higher reaction temperature (37°C in our study vs 28<sup>11</sup> or 25°C<sup>12</sup>), longer reaction times (until 60 min for TEGDMA in our study vs 10–15 min in the literature<sup>11</sup>), larger sample masses in DSC (15–20 mg in this study vs 1–4 mg<sup>11</sup>), and different monomer suppliers. Thus, it seems that the results presented here could be considered unique for the particular conditions employed. Finally, increased amounts of TEGDMA in Bis-GMA/TEGDMA comonomer mixtures caused an increase also in the time up to the maximum rate and the induction time, which is defined analytically in our previous work<sup>15</sup> (Table II).

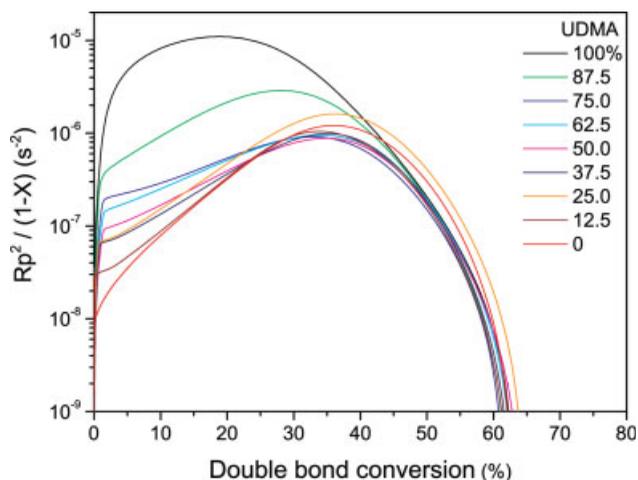
Plots of  $R_p^2/(1 - X)$  versus the double-bond conversion for various comonomer mixtures of Bis-GMA and TEGDMA are illustrated in Figure 5. As the amount of TEGDMA in the initial comonomer mixture increases, the plateau region of the curve shifts to higher conversions. The Bis-GMA polymer-



**Figure 6**  $R_p$  as a function of the fractional conversion for UDMA/TEGDMA copolymerization initiated by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 7** Rate maxima and final conversions versus the UDMA monomer content in the initial comonomer mixture of UDMA and TEGDMA with the initiator BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 8**  $R_p^2/(1-X)$  versus the double-bond conversion for various comonomer mixtures of UDMA and TEGDMA copolymerized by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

ization becomes reaction–diffusion-controlled at very low conversions (ca. 5%), whereas the TEGDMA polymerization does not become reaction–diffusion-controlled until nearly 30% double-bond conversion. Similar results have been also reported in the literature.<sup>12</sup> In almost all formulations, this plateau appears at a rather small interval of approximately 10%. Afterwards, the  $R_p^2/(1-X)$  values drop off as the polymerization proceeds. The decline in the values is attributed to the effect of diffusion-controlled phenomena on the propagation reaction, which results in decreasing  $k_p$  values. These differences in the kinetic behavior are attributed to the mobility and crosslinking density of the reacting media. The increased mobility of the less stiff TEGDMA chains allows the greater segmental diffusion of the molecules. Therefore, as the amount of TEGDMA in the initial comonomer mixture is increased, termination

through segmental diffusion is also increased, and the onset of reaction–diffusion control is delayed.

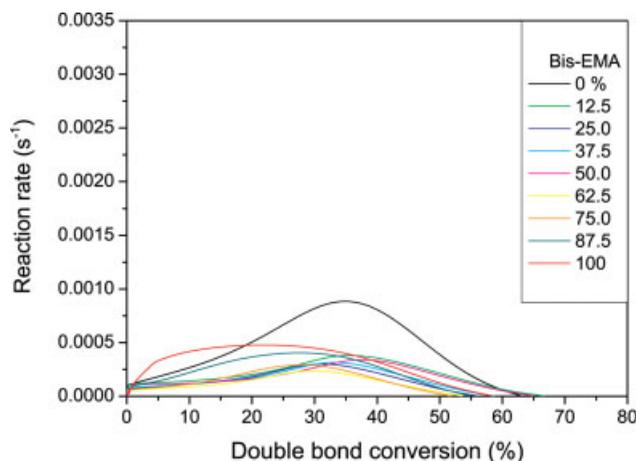
The copolymerization of UDMA and TEGDMA has shown that the presence of a small amount (12.5 or 25 wt %) of TEGDMA in the comonomer mixture results in a significant decrease in the rate, whereas the further addition of TEGDMA has only a small effect on  $R_p$  (Table III and Fig. 6). As a result, the values of  $R_p^{\max}$  are almost the same until 75% UDMA, whereas they are much higher at the 87.5 and 100% UDMA ratios (Fig. 7). As for the final degree of double-bond conversion, it is almost constant for all copolymers because the final degree of conversion for pure UDMA (62%) is similar to that of TEGDMA (63%). No synergistic effect has been observed in either the final double-bond conversion or  $R_p^{\max}$  (Fig. 7). The trend shown for the reaction rate is also clearly shown in the plot of  $R_p^2/[1-X]$  versus the conversion (Fig. 8).

Subsequently, Table IV shows the key kinetic results for the copolymerizations of Bis-EMA and TEGDMA. In contrast to Bis-GMA/TEGDMA and UDMA/TEGDMA copolymerizations, in copolymerizations of Bis-EMA and TEGDMA, a minimum value for  $R_p^{\max}$  of  $0.24 \times 10^{-3} \text{ s}^{-1}$  and a maximum value for the time at the peak of 54.2 min were observed for the initial 62.5/37.5 (w/w) Bis-EMA/TEGDMA comonomer mixture. This is also shown in Figure 9. As shown in Figure 10, the values of  $R_p^{\max}$  of all the copolymers are always lower than those of the two homopolymers. Concerning the ultimate double-bond conversion, low amounts of Bis-EMA (i.e., 12.5 and 25 wt %) lead to values higher than the additive rule values, whereas higher percentages of Bis-EMA produce copolymers with lower values than the additive rule values. From a plot of  $R_p^2/(1-X)$ , it was again verified that except for the 87.5 wt % copolymer, all other formulations are influenced more by the TEGDMA monomer and exhibit similar curves, with the reaction–diffusion con-

**TABLE IV**  
 $X_{\max}$ ,  $R_p^{\max}$ ,  $X$  at  $R_p^{\max}$ ,  $t_{\text{ind}}$ , and  $t_{\text{peak}}$  as Functions of the Bis-EMA Weight or Fraction for the Copolymerization of Bis-EMA and TEGDMA Initiated by BPO/DMPOH at 37°C

| Bis-EMA (wt %) | $X_{\max}$ | $R_p^{\max} (\times 10^3 \text{ s}^{-1})$ | $X$ at $R_p^{\max}$ (%) | $t_{\text{ind}}$ (min) | $t_{\text{peak}}$ (min) |
|----------------|------------|---|-------------------------|------------------------|-------------------------|
| 100            | 0.57       | 0.48                                      | 21.9                    | 6.9                    | 20.8                    |
| 87.5           | 0.55       | 0.40                                      | 27.6                    | 7.6                    | 31.4                    |
| 75.0           | 0.52       | 0.29                                      | 27.9                    | 7.7                    | 44.5                    |
| 62.5           | 0.54       | 0.24                                      | 29.9                    | 6.7                    | 54.2                    |
| 50.0           | 0.56       | 0.34                                      | 31.2                    | 6.7                    | 44.2                    |
| 37.5           | 0.59       | 0.32                                      | 33.2                    | 5.0                    | 44.2                    |
| 25.0           | 0.65       | 0.30                                      | 35.8                    | 4.7                    | 43.4                    |
| 12.5           | 0.67       | 0.39                                      | 35.7                    | 2.0                    | 35.5                    |
| 0.0            | 0.63       | 0.86                                      | 35.0                    | 2.3                    | 20.0                    |

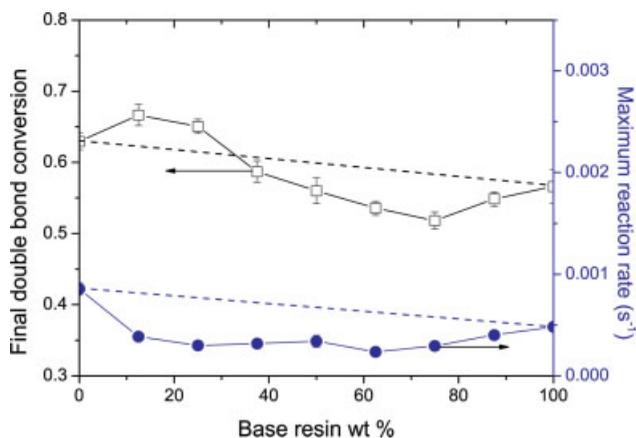
$t_{\text{ind}}$  = induction time;  $t_{\text{peak}}$  = time at the peak;  $X$  at  $R_p^{\max}$  = conversion at the maximum rate;  $X_{\max}$  = maximum double-bond conversion.



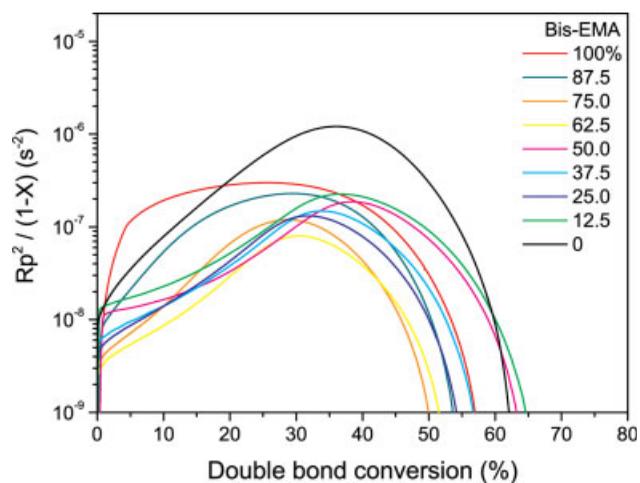
**Figure 9**  $R_p$  as a function of the fractional conversion for Bis-EMA/TEGDMA copolymerization initiated by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

tol starting and ending at approximately the same conversion (Fig. 11).

Finally, it is worth noting that in all copolymerizations studied, the incremental decrease of TEGDMA in the mixture (increase of the base monomer) causes the conversion at the maximum rate to shift to lower conversions (longer times; Fig. 12). This behavior is explained by the mobility of the system. Because TEGDMA dilutes the more viscous base monomer, the reaction occurs in a less restricted environment. The decreased viscosity of the system allows propagation to continue for longer times without being diffusion-controlled. Thus, for Bis-GMA, it increases from 9 to 35% for pure TEGDMA. Similar trends have also been reported in the literature.<sup>12</sup> For pure UDMA, it increases from 17.2 to 26.7% with the addition of 12.5 wt % TEGDMA and to 30.9% with



**Figure 10** Rate maxima and final conversions versus the Bis-EMA monomer content in the initial comonomer mixture of Bis-EMA and TEGDMA with initiator BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

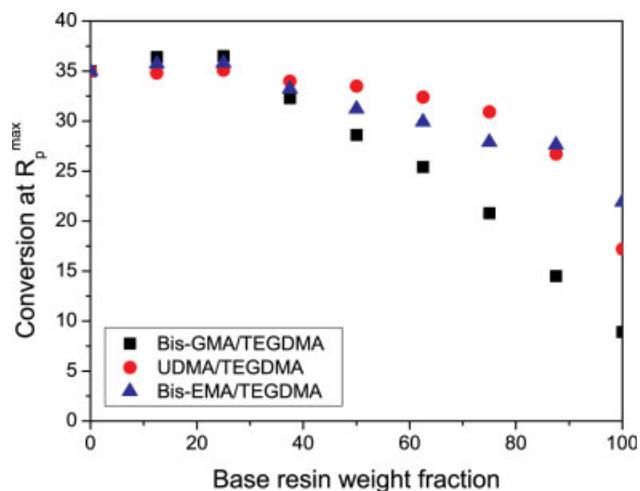


**Figure 11**  $R_p^2/(1-X)$  versus the double-bond conversion for various comonomer mixtures of Bis-EMA and TEGDMA copolymerized by BPO/DMPOH at 37°C. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the addition of 25 wt % TEGDMA and then shows only a small increase up to 35 wt % (pure TEGDMA). After 25 wt % TEGDMA, the values measured for UDMA/TEGDMA copolymers are always higher than the corresponding values for the Bis-GMA/TEGDMA copolymers. Finally, for the three sets of copolymers studied, the conversion at  $R_p^{\max}$  seems to exhibit similar values for low base resin contents (until 25 wt %).

## CONCLUSIONS

In this investigation, the copolymerization of Bis-GMA, Bis-EMA, or UDMA (base monomers) with TEGDMA (diluent) initiated by the BPO/DMPOH



**Figure 12** Dependence of the conversion at  $R_p^{\max}$  on the weight fraction of the base resin in the comonomer mixture. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

redox system at 37°C was experimentally studied with DSC. It was found that, at least under the particular experimental conditions, Bis-GMA and UDMA were more reactive than TEGDMA and Bis-EMA. A reaction–diffusion-controlled termination region was clear in all monomers and started earlier in the bulky rigid Bis-GMA and Bis-EMA (followed by the more flexible UDMA and TEGDMA) but lasted longer in the Bis-EMA polymerization. Furthermore, it was observed that the maximum rate of copolymerization and the degree of final double-bond conversion of all copolymers changed monotonically with the increase in the TEGDMA content in the initial comonomer mixture. A synergistic effect was clear only in the Bis-GMA/TEGDMA final double-bond conversion. The conversion at  $R_p^{\max}$  was almost the same for all three sets of copolymers at low TEGDMA contents (<25 wt %), whereas afterwards the Bis-GMA-based copolymers always exhibited lower values than the others.

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