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Thermal degradation and isoconversional kinetic analysis of light-cured dimethacrylate copolymers

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Abstract Thermal degradation kinetics of copolymers based on bis-phenol A ethoxylated dimethacrylate (Bis-EMA) with triethylene glycol dimethacrylate (TEGDMA), and urethane dimethacrylate (UDMA) with TEGDMA in wt/wt ratios 30/70, 50/50, or 70/30 were investigated using thermogravimetric analysis as a means to provide specific information regarding the internal structures of these resins. Thermogravimetric scans were taken at four different heating rates to perform an isoconversional analysis to determine the change of the effective activation energy as a function of conversion. A two-step degradation mechanism was found to occur in almost all copolymer compositions attributed to the existence of inhomogeneities in the macromolecular structure and the formation of weak links inside the polymeric network.

Keywords Activation energy · Dimethacrylate copolymers · Thermal degradation · Thermogravimetric analysis

Introduction

Dimethacrylate-based polymers are materials forming highly crosslinked three-dimensional networks, which find wide applications as biomaterials in dental applications. The monomers typically used combine a relatively viscous dimethacrylate-based monomer, such as 2,2-bis[p-(2′-hydroxy-3′-methacryloxy propoxy) phenylene] propane (Bis-GMA), bis-phenol A ethoxylated dimethacrylate (Bis-EMA), or 1,6-bis-(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethyl hexane (usually referred as urethane dimethacrylate, UDMA) with a low viscosity dimethacrylate comonomer, such as triethylene glycol dimethacrylate (TEGDMA) [1, 2]. These monomers are copolymerized at ambient temperature, using a photoinitiation system. The study of thermal degradation of these polymers is a difficult task and owing to the complexity of the process, very few articles have so far been reported in literature [3–7]. Pielichowski et al. [5] studied the thermal decomposition of copolymers based on long chained diol dimethacrylated and Bis-GMA/TEGDMA. One degradation step was observed using a rather high heating rate (50 °C $\min^{-1}$). The thermal degradation of Bis-GMA/TEGDMA copolymers, prepared by photopolymerizaton, was presented by Teshima et al. [3] and Rigoli et al. [6]. In a previous publication from our group [7], thermal degradation kinetics of polymers produced from these monomers was investigated.

Thermogravimetric analysis (TG) is a common experimental method used to study the overall or macroscopic kinetics of polymer degradation [8–12]. However, apart from a simple TG scan, further computational kinetic analysis is needed to probe the degradation mechanism, as well as to predict the thermal stability of polymers. Among others [8, 9], isoconversional methods have been conceived by many researchers and widely used in thermal degradation kinetic studies [7, 11, 13].

In our recent publications, we have studied the effect of the monomer chemical structure on the degree of conversion, water sorption, modulus of elasticity, and thermal expansion characteristics of dental polymers [14–18]. This study is a continuation of our previous article concerned with the thermal degradation kinetics of

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homo-polymers based on Bis-GMA, Bis-EMA, UDMA, or TEGDMA [7]. Since the copolymers based on Bis-GMA and TEGDMA have already been studied in literature [3, 6], thermal degradation kinetics of Bis-EMA/TEGDMA- or UDMA/TEGDMA-based copolymers was investigated using TG. Copolymers in wt/wt ratios 30/70, 50/50, or 70/30 were prepared by mixing the appropriate monomers and the photoinitiator system. Then, the mixture of monomers was cured using a dental photocuring unit. Thermogravimetric scans were taken at four different heating rates to have adequate data to perform an isoconversional analysis to determine the change of the effective activation energy as a function of conversion [13]. Thus, specific information on the copolymer internal chemical structure was gained. To our knowledge, thermal degradation of copolymers prepared from UDMA/TEGDMA or Bis-EMA/TEGDMA mixtures have not been reported so far in literature.

Experimental

Materials

The dimethacrylate monomers used were UDMA (Ivoclar-Vivadent, Lot No. B00338), TEGDMA (Aldrich Chem. Co., Lot No. 09004BC-275), and Bis-EMA (Aldrich Chem. Co., Lot No. 03514 HF). The photoinitiator system was camphorquinone (CQ) (Lot no: S12442-053) and ethyl-4-dimethylaminobenzoate (4EDMAB) (Lot no: 90909001), and these were purchased from Aldrich. All the materials used in this study were used as received without further purification.

Preparation of specimens

Two sets of copolymers were prepared based on UDMA/TEGDMA or Bis-EMA/TEGDMA. For each copolymer, three different relative mass ratios were employed, namely, 70/30, 50/50, and 30/70 wt/wt. The initial mixture was prepared by mixing the appropriate amount of monomers and the photoinitiator system (CQ 0.2% mass fraction and 4EDMAB 0.8% mass fraction) in an ultrasonic bath, followed by heating in the dark at 40 ± 0.5 °C until the photoinitiator components were dissolved in the mixture of monomers. Then, the mixture of monomers was placed in Teflon molds and light-cured using a XL 3000 dental photocuring unit (3 M Company). This source consisted of a 75-W tungsten halogen lamp, which emits radiation between 420 and 500 nm and has the maximum peak at 470 nm. The samples were irradiated for 200 s on each side, and this time duration has been found to be adequate for the polymerization to reach the limiting degree of conversion [16].

Thermogravimetric analysis (TG)

TG was performed on a Pyris 1 TGA (Perkin Elmer) thermal analyzer equipped with a sample pan made of Pt. Samples of about 8 mg were used. They were heated from ambient temperature to 600 °C under a 20 ml min^{-1} nitrogen flow. TG measurements of each sample were performed at different heating rates of 2.5, 5, 10, and 20 °C min^{-1} to have adequate data to perform an isoconversional analysis to determine the change of the effective activation energy as a function of conversion, and sample mass versus temperature was continuously recorded.

Kinetic analysis of TG data according to isoconversional methods

The kinetics of polymer degradation is usually described by the following single-step kinetic equation [9, 13, 19]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = k(T)f(\alpha) \tag{1}$$

where α represents the extent of reaction, which can be determined from TG runs as a fractional mass loss, t is the time, $k(T)$ a temperature-dependent rate constant, and $f(\alpha)$ denotes the particular reaction model, which describes the dependence of the reaction rate on the extent of reaction. If an Arrhenius-type expression is used to describe the temperature dependence of $k(T)$, then Eq. 1 yields

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{2}$$

with A and E being the pre-exponential factor and the activation energy, respectively.

According to the isoconversional principle, at a constant extent of reaction, the reaction rate is a function only of the temperature. Hence Eq. 2 can be written as

$$\left[\frac{\mathrm{d}\ln(\mathrm{d}\alpha/\mathrm{d}t)}{\mathrm{d}(1/T)}\right]_{\alpha} = -\frac{E_{\alpha}}{R} \tag{3}$$

where the subscript α denotes the value at a specific extent of reaction.

Isoconversional methods employ multiple temperature programs (e.g., different heating rates) to obtain data on varying rates at a constant extent of conversion. Thus, isoconversional methods allow complex (i.e., multi-step) processes to be detected through a variation of E_{α} with α [13].

Simple rearrangement of Eq. 2 leads to Eq. 4, which forms the foundation of the differential isoconversional method of Friedman [20]

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)_{\alpha,i} = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \qquad (4)$$

The subscript i denotes different heating rates.

Application of the Friedman method to the TG data requires numerical differentiation of the experimental α versus T curves. This is typically carried out by the software of the instrument used, and sometimes, it results in quite noisy rate data and thus, unstable activation energy values. This problem of numerical differentiation could be avoided by adopting integral isoconversional methods. For nonisothermal conditions, when the temperature is raised at a constant heating rate β, integration of Eq. 2 involves solving the temperature integral in Eq. 5:

$$g(\alpha) \equiv \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T_\alpha} \exp\left(\frac{-E}{RT}\right)\mathrm{d}T = \frac{A}{\beta}I(E,T) \qquad (5)$$

Since the integral $I(E,T)$ in Eq. 5 does not have an analytical solution, it can be solved by either approximations or numerical integration. One of simplest approximations by Doyle gives rise to the following Eq. 6, which is used in the popular isoconversional methods of Flynn and Wall [21] and Ozawa [22].

$$\ln(\beta_i) = \mathrm{Const.} - \frac{1.05E_\alpha}{RT_{\alpha,i}} \qquad (6)$$

Systematic difference in the activation energies is evaluated by the differential and integral methods The differential method of Friedman employs instantaneous rate values, and, therefore, is sensitive to experimental noise, while in the FWO method, the equation used is derived assuming constant activation energy, introducing thus a systematic error in the estimation of E in the case that E varies with α [9]. Further increase in precision of the integral methods can be accomplished by using numerical integration, a method developed and extensively used by Vyazovkin [23–25]. In this investigation the methods of Flynn, Wall, and Ozawa (FWO) was used.

Results and discussion

Copolymers based on UDMA and TEGDMA

Figure 1a–c shows the TG scans of UDMA/TEGDMA 70/30, 50/50, and 30/70 copolymers, respectively, at different heating rates of 2.5, 5, 10, and 20 °C min^{-1}. In all the cases, it was observed that an increase in the heating rate shifts the TG curves and peak temperatures to higher values as expected, and is common in different types of polymers [6, 26, 27]. Decomposition of cross-linked polymers in an inert atmosphere occurs in such a way that they tend to conserve the structure of their matrix, thus bond breaking inside the polymer matrix requires a large amount of energy [28]. From Fig. 1 and the DTG curves (not shown due to space limitations) it can be observed that a two step degradation mechanism may occur in all copolymer compositions. The two-step degradation mechanism for the homo-polymer UDMA and TEGDMA was explained in our previous publication [7] on the basis of the

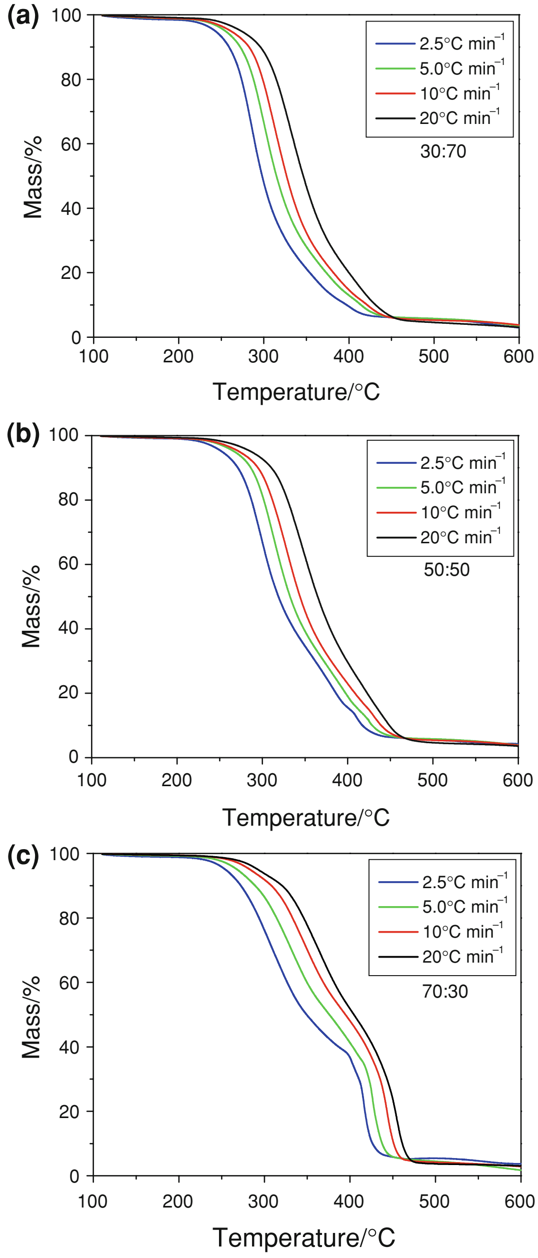

Fig. 1 Effect of heating rate on the TG scans of UDMA/TEGDMA 30/70 (**a**), 50/50 (**b**), and 70/30 (**c**) copolymers

formation of weak links inside the network structure from secondary cyclization reactions taking place during polymer formation. Both TEGDMA and UDMA owing to their non-aromatic nuclei are more flexible monomers and, therefore, the pendant double bonds formed during polymerization can cycle more readily after they are created. The hydrogen-bonding ability of UDMA monomer units makes its copolymers to decompose at higher temperatures.

In 30/70 or 50/50 copolymers, a large initial degradation peak appears followed by a second smaller peak which appears as a shoulder to the first one. In the third copolymer with composition 70/30, these two peaks are rather equal and the second tends to be broader with increasing heating rate. The temperature where degradation starts in addition to that where the maxima appears for all polymers at different heating rates are provided in Table 1. It is noted again that degradation starts at higher values with increasing heating rate. Furthermore, at the same heating rate, an increase in the amount of TEGDMA in the initial mixture meaning a copolymer rich in TEGDMA leads to degradation starting at lower temperatures. As can be seen in Fig. 2, the whole curve is shifted to lower temperature with increasing TEGDMA amount. In this figure, measurements carried out in our laboratory for the two homopolymers and presented in a previous publication [7] also have been included. Going from pure TEGDMA to UDMA, the first peak of the DTG curve tends to be smaller and moves towards higher temperatures, while a second peak at higher temperatures appears which is very pronounced in pure UDMA. It seems that the 30/70 copolymer keeps the same characteristics as those of the TEGDMA, while that of 70/30 is much more close to UDMA as regards characteristics. The 50/50 copolymer lies in between those two. The residual amount at 600 °C lies in between 2 and 4% and does not seem to have a clear dependence either on heating rate or on copolymer composition. The solid residue measured for the two homopolymers was nearly 2% [7].

These results were further investigated using an isoconversional kinetic analysis of data, and the activation energies, E_α, as a function of the extent of degradation, α, were calculated. Analysis of the E_α dependences proves generally to be very helpful in exploring the effect of the structure of the polymeric material on its degradation kinetics. Initially, plots of $\ln(\beta)$ versus $1/T$ according to Eq. 6 of the integral isoconversional method of FWO, were drawn for all the copolymers and at different extents of degradation. Good linearity was observed in almost all sets of experimental data. From the slope of these curves, the effective activation energy is calculated and plotted as a function of the extent of degradation in Fig. 3. For UDMA, activation energy initially starts at nearly a constant value between 100 and 110 kJ mol^{-1} until $\alpha = 0.45$, whereas afterward, a peak appears at $\alpha = 0.55$ and $E_\alpha = 280$ kJ mol^{-1}. Again, these results denote two degradation mechanisms. The first exhibiting the plateau in the E_α values corresponds to the breakage of weak links (such as primary cycles, or hydrogen bonds), while the second with the high enough values of E_α corresponds to degradation of the main network bonds. For TEGDMA, an initial value of about 130 kJ mol^{-1} at $\alpha = 0.05$, slightly decreases up to 120 kJ mol^{-1} at $\alpha = 0.40$. An increase follows, and a peak appears at $\alpha = 0.65$ with a maximum $E_\alpha = 150$ kJ mol^{-1}. Afterward, the E_α values, increase again up to the maximum value of approximately 180 kJ mol^{-1}. The appearance of inhomogeneities in the network of this polymer is probably responsible for the particular shape of the activation energy. As was reported previously, degradation of

Table 1 Temperatures where 1% thermal degradation occurs ($T_{1\%}$) and at the first (T_1) and second (T_2) maximum of thermal decomposition, as well as residual mass at 600 °C for each sample studied at different heating rates

Sample	Heating rate/°C min^{-1}	$T_{1\%}$/°C	T_1/°C	T_2/°C	Residual mass at 600 °C/%
UDMA/TEGDMA 70/30	2.5	190	311	417	3.7
	5.0	221	332	428	1.7
	10	236	347	442	2.9
	20	239	363	442	3.1
UDMA/TEGDMA 50/50	2.5	189	299	411	4.3
	5.0	217	315	424	3.9
	10	218	329	427	3.8
	20	233	351	429	3.6
UDMA/TEGDMA 30/70	2.5	151	286	401	2.9
	5.0	172	301	412	3.5
	10	180	315	415	3.7
	20	210	334	411	3.0
Bis-EMA/TEGDMA 70/30	2.5	180	331	397	4.9
	5.0	199	356	416	3.7
	10	207	368	426	2.6
	20	220	388	441	2.8
Bis-EMA/TEGDMA 50/50	2.5	180	295	370	4.5
	5.0	195	310	401	3.7
	10	235	336	411	3.1
	20	246	360	432	3.4
Bis-EMA/TEGDMA 30/70	2.5	160	270	371	5.0
	5.0	171	302	410	2.9
	10	187	328	416	2.4
	20	180	326	426	1.9

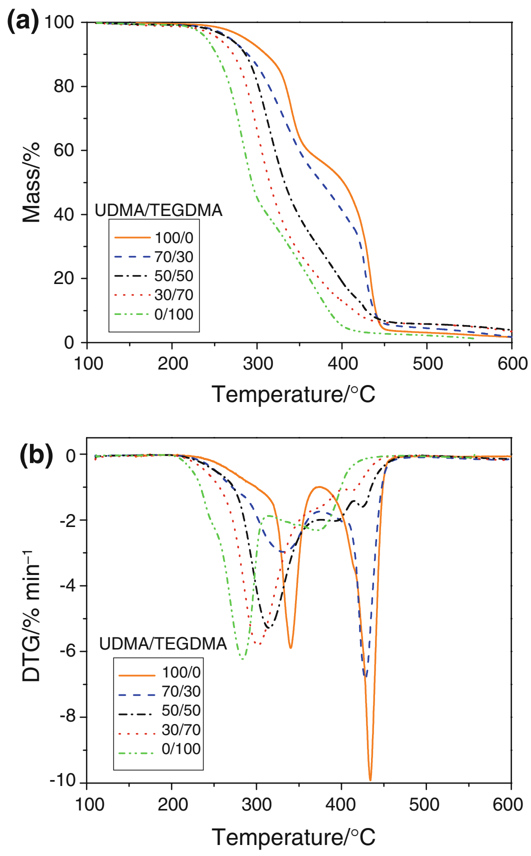

Fig. 2 Effect of the relative amount of monomer on the TG (**a**) and DTG (**b**) curves for UDMA/TEGDMA copolymers at a heating rate of 5 °C min^{-1}

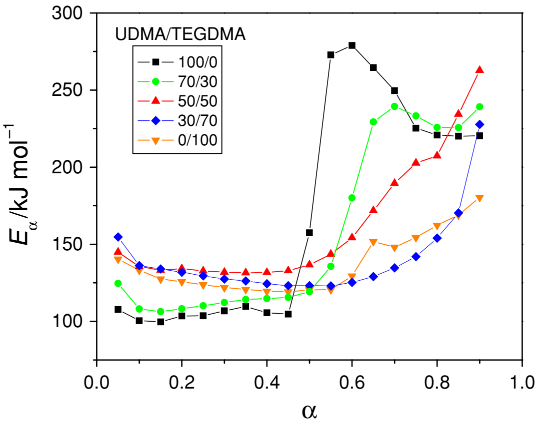

Fig. 3 Effect of the chemical structure of the resin on the activation energy as a function of the extent of degradation estimated using the method of Flynn–Wall–Ozawa

TEGDMA polymers starts at weak links (defects) in the polymer network which have been attributed to cycles incorporated in the network. Therefore, the first initial low E_α values reflect breakage of these parts, and a maximum in DTG appears at $\alpha = 0.40$ where the minimum in E_α has been observed. The end of the first degradation stage is characterized by a decrease in the values of DTG and a peak in the E_α at the same extent of degradation. Therefore, the degradation where the bond breaking changes from one mechanism to the other denotes the local peak in the estimated activation energy values.

As regards the copolymers, the 30/70 exhibits a behavior similar to pure TEGDMA with slightly higher initial activation energy values. A minimum appears at $\alpha = 0.55$, which afterward increases. Therefore, it could be said that the chemical structure of this copolymer is similar to pure TEGDMA. On the contrary, the 70/30 copolymer seems to follow somehow the behavior of pure UDMA with E_α values starting from 110 kJ mol^{-1} increasing slightly up to 120 kJ mol^{-1} at $\alpha = 0.5$. After that point, a rapid increase appears (explained previously) and reaches a value of 240 kJ mol^{-1} at $\alpha = 0.7$, followed by a small decrease. It is, therefore, concluded that this behavior is similar to pure UDMA. However, the 50/50 copolymer exhibits really unique characteristics. It presents the highest initial E_α values of 135 kJ mol^{-1} constant from $\alpha = 0.1$–0.5, meaning the formation of a more strong network. Afterward, a continuous increase appears up to 90% degradation where the highest E_α value was estimated as equal to 263 kJ mol^{-1}. It was thus concluded that in this copolymer, the densest chemical structure is formed.

Copolymers based on Bis-EMA and TEGDMA

Figure 4a–c shows the TG scans of Bis-EMA/TEGDMA 30/70, 50/50, and 70/30 copolymers, respectively, at different heating rates of 2.5, 5, 10, and 20 °C min^{-1}. In all these cases, it was again observed that an increase in the heating rate shifts the TG curves and peak temperatures to higher values, as it was reported previously. From these figures, a two-step degradation mechanism was observed for the 50/50 and 30/70 copolymers, while for the 70/30, a third peak appeared at 258, 275, and 283 °C for heating rates 2.5, 5, and 10 °C min^{-1}, respectively. This peak vanishes at 20 °C min^{-1}. The temperature where degradation starts in addition to that where the maxima appears for all copolymers at different heating rates are provided in Table 1. In the 70/30 copolymer, the larger degradation peak was the second while the smaller first appears as a shoulder to this second one. In the other copolymers (i.e., 30/70 and 50/50), these two peaks were rather equal. It is noted again that degradation starts at higher values with increasing heating rate. Furthermore, at the same heating rate, an increase in the amount of TEGDMA in the initial mixture leads to degradation starting at lower temperatures in most cases. As can be seen in Fig. 5a, b, the initial degradation peak becomes smaller while the second gradually increase as the amount of Bis-EMA in the copolymer

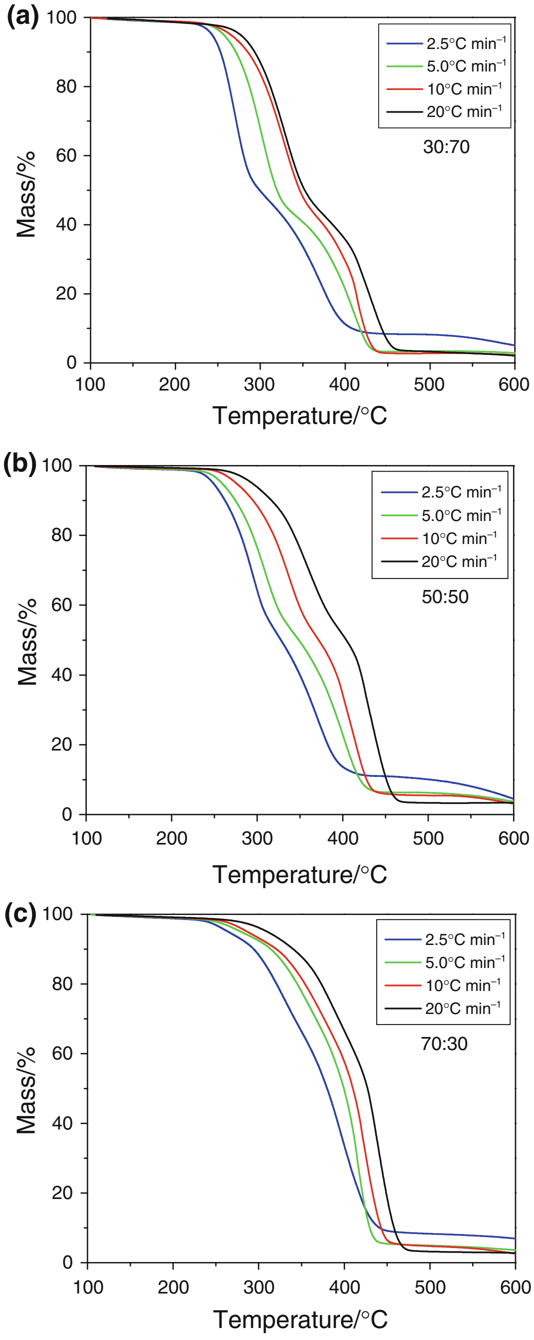

Fig. 4 Effect of heating rate on the TG scans of Bis-EMA/TEGDMA 30/70 (**a**), 50/50 (**b**), and 70/30 (**c**) copolymers

increases. In this figure, results from the two homopolymer carried out in our laboratory and presented previously [7] also have been included. The residual amount at 600 °C lies in between 2 and 5% and does not seem to have a clear dependence either on heating rate or on copolymer composition.

An isoconversional kinetic analysis of data was again performed, and the activation energies, E_α, as a function of the extent of degradation, α, were calculated. The same

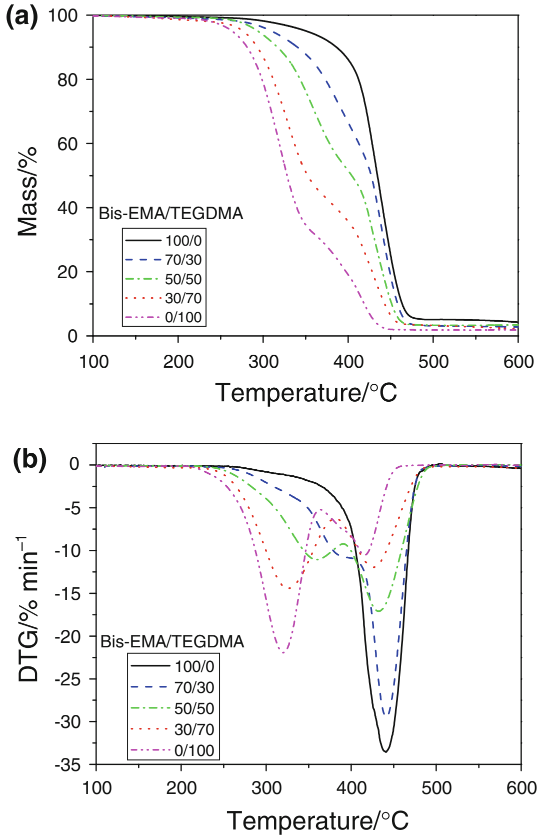

Fig. 5 Effect of the relative amount of monomer on the TG (**a**) and DTG (**b**) curves of Bis-EMA/TEGDMA resins at a heating rate of 20 °C min^{-1}

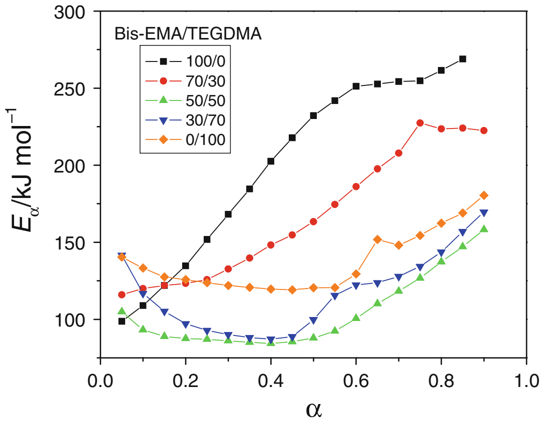

Fig. 6 Effect of the chemical structure of the Bis-EMA/TEGDMA copolymers on the activation energy as a function of the extent of degradation estimated using the method of Flynn–Wall–Ozawa

procedure as the one reported previously was followed. Results on the E_α versus α, dependence for the Bis-EMA resin appear in Fig. 6, where an initial low value estimated for E_α was increasing steadily. These values start at approximately 100 kJ mol^{-1} for $\alpha = 0.05$ and reach a maximum value of 270 kJ mol^{-1} at $\alpha = 0.85$. An interesting observation was that the copolymers 30/70 and 50/50 exhibited always lower E_α compared to both homopolymers. These values started at 140 and 105 kJ mol^{-1}, respectively, at $\alpha = 0.05$ and continuously decreased to 89 and 86 kJ mol^{-1}, respectively, for the above copolymers Afterward, an increase was observed up to 170 and 158 kJ mol^{-1} for the 30/70 and 50/50 copolymers, respectively. This means that the network formed from these polymers could be more easily degraded and, therefore, more weak links were formed. In contrast, the 70/30 copolymer exhibited, a kinetic behavior in between the two homo-polymers with a continuous increase from 116 to 228 kJ mol^{-1} (at $\alpha = 0.75$). Therefore, it seems that this could be the preferred composition for the Bis-EMA/TEGDMA copolymers.

Conclusions

The thermal degradation kinetics of light-cured dimethacrylate copolymers based on Bis-EMA/TEGDMA and UDMA/TEGDMA were investigated using TG. A two-step degradation mechanism was found to occur in almost all the copolymer compositions, which was attributed to the existence of inhomogeneities in the macromolecular structure and the formation of weak links inside the polymeric network. These results were verified by performing an isoconversional kinetic analysis of the experimental data.

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