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Thermal degradation of photo-polymerized BisGMA/TEGDMA-based dental resins

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Abstract

The thermal behavior of BisGMA/TEGDMA-based dental resins of various degrees of conversion was examined using differential scanning calorimetry (DSC), thermogravimetric-gas chromatography mass spectrometry (TG-GC/MS), and thermogravimetric-mass spectrometry (TG-MS). This study identified pyrolysates of BisGMA/TEGDMA copolymers from mass spectra. Three phases (initial, second, and final phases) of thermal degradation appeared in the TGA and derivative TGA (dTGA) curves. The thermal degradation mechanism in each phase was explained by the thermal behavior of four pyrolysates: methacrylic acid, 2-hydroxyethel methacrylate, propionic acid, and phenol. The thermal characteristics of copolymers of various degrees of conversion were determined from the temperatures at the intersections of the curves of the second and final phase separated from dTGA curves. Regression analysis revealed a very strong correlation ($R^2 = 0.942$) between the degree of copolymer conversion and the temperature at the intersection.

Keywords: BisGMA/TEGDMA; Copolymers; Degree of conversion; TG-GC/MS; TG-MS

1. Introduction

BisGMA (2,2-bis[4-(2-hydroxy-3-methacryloyloxy-prop-1-oxy)-phenyl]propane, bisphenol-A glycidyl ether dimethacrylate) and TEGDMA (triethylenglycol dimethacrylate) monomers are widely used matrixes in dental restorative materials, teeth bonding agents, and fissure sealing agents [1]. Polymerized light-cured composite dental resins require highly cross-linked three-dimensional network structures. Previous reports have shown that the physical and mechanical properties of BisGMA/TEGDMA copolymers are connected to the degree of conversion (degree of cure, degree of polymerization, or the rate at which methacrylate C=C bonds are converted to aliphatic C–C bonds) determined using hardness tests [2–4], FT-IR [4,5], FT-Raman [6], HPLC [7], ESR [8], or NMR [9] techniques. Thermal analysis techniques, using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), or dynamic mechanical analysis (DMA), are suitable for examining the characteristics of polymers [10–14]. The study of thermal degradation processes provide us with more specific information of internal structures of dental resins. However, the thermal behavior of BisGMA/TEGDMA-based dental resins has been described in only a few reports owing to the complexity of the thermal degradation process [15,16]. Many factors affect the thermal degradation of polymers, including the molecular weight distribution, branching chains, cross-linked density, and end-groups [17]. Copolymers exhibit more intricate thermal behavior than homo-polymers, because they are readily affected by the ratio of monomers or degree of conversion [18,19]. However, the correlation between the degree of conversion and the thermal degradation of copolymers is still unknown. Copolymers, such as styrene-divinylbenzene copolymers, show a disproportionally greater thermal stability

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with increasing degree of conversion, while methyl methacrylate-dimethacrylate cross-linked polymers do not show an increased thermal stability, although they have a high density of cross-links [20,21].

Recently, thermal analysis coupled with other techniques, such as thermogravimetric-gas chromatography-mass spectrometry (TG-GC/MS) [22], thermogravimetric-differential thermal analysis-gas chromatography-mass spectrometry (TG/DTA-GC/MS) [23], and TGA/FTIR [24], has contributed greatly to the analysis of polymer degradation. These coupled techniques provide structural information and help to elucidate the paralytic processes. The TG-MS coupled-system technique also allows direct measurements of the weight loss of polymers and the quantity of gas evolved. However, mixture mass spectra of multiple evolved gases generally need separating and identifying characteristic masses using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) or TG-GC/MS [25] in advance.

This work examined the thermal behavior and degradation of BisGMA/TEGDMA-based dental resins of various degrees of conversion using TG-GC/MS and TG-MS. We revealed the relationship between the degree of conversion and the thermal degradation processes of BisGMA/TEGDMA copolymers.

2. Experimental

2.1. Materials

The base monomer was a 60:40 mixture by weight of purified 2,2-bis[4-(2-hydroxy-3-methacryloxy-prop-l-oxy)-phenyl]propane (BisGMA, Kuraray Co., Okayama, Japan) and triethylenglycol dimethacrylate (TEGDMA, Tokyo Kasei Co., Tokyo). Bis(2,4,6-trimethylbenzoil)-phenylphosphine oxide (Aldrich, Milwaukee, WI) was added to the base monomer at 0.25, 0.5, 1.0, or 1.5 mol% as a photoinitiator. The blended BisGMA/TEGDMA comonomers were mixed with the photoinitiator and stirred in a dark room until they dissolved.

2.2. Apparatus and procedure

2.2.1. Sample preparation using DSC

DSC measurements were performed on a DSC-50 (Shimadzu Co., Kyoto, Japan) operating in isothermal mode at 25 °C in air. The BisGMA/TEGDMA-based monomers with the photoinitiator (2.0±0.1 mg) were weighed in an aluminum sample pan. A reference pan contained 2.0 mg of base monomer with no photoinitiator. Each comonomer sample was polymerized using four violet LEDs with a peak wavelength at 405 nm (Lot 02CM08-11, EPITEX, Kyoto, Japan) as the light source. The electric current to the LEDs was varied from 0.38 to 23.0 mA, and produced BisGMA/TEGDMA copolymers of various degrees of conversion. Fig. 1 shows a typical DSC curve measured in this study. Immediately after the LEDs were switched on, exothermic radical polymerization was observed until the DSC curve returned to the base line; then, the light was turned off. Samples with a lower degree of conversion (Po2, Po3, and Po4) were produced by turning off the LED before reaching the peaks in the DSC curves. The equation for the degree of conversion (degree of cure, degree of polymerization, or the rate at which methacrylate C = C bonds are converted to aliphatic C-C bonds) of a polymer is as follows:

$$\text{Degree of conversion (DC)} = \frac{\Delta H}{2Hm},$$

where ΔH (kJ/mol) is the heat of polymerization obtained from the area under the curve of the thermogram using DSC, Hm is the heat of polymerization of methyl methacrylate (54.8 kJ/mol), and the factor 2 arises from the dimethacrylate reaction [26, 27]. Table 1 shows the degree of conversion of the prepared samples. The maximum conversion was 0.901 (Po11) and the minimum was 0 (BisGMA/TEGDMA-based monomer, Po1).

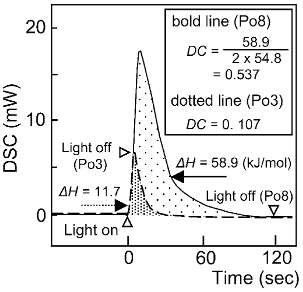


Fig. 1. Bold and dotted lines are DSC curves of sample Po8 and Po3, respectively. ΔH (kJ/mol) is the heat of polymerization obtained from the dotted area. DC (degree of conversion) of sample Po8 and Po3 are 0.537 and 0.107, respectively.

Table 1
Degree of conversion of BisGMA-TEGDMA copolymers obtained by DSC measurements

Code	Photo-initiator	Degree of conversation
Po1	0.00	0.000
Po2	0.25	0.058
Po3	0.25	0.107
Po4	0.25	0.279
Po5	0.25	0.387
Po6	0.50	0.448
Po7	0.50	0.499
Po8	0.50	0.537
Po9	1.00	0.641
Po10	1.00	0.774
Po11	1.50	0.901
Po12	1.00	0.753

2.2.2. TG-GC/MS

TG-GC/MS experiments were performed with a TG-GC/MS system that coupled TGA-50 (Shimadzu Co., Kyoto Japan) with GCMS-QP1100EX (Shimadzu Co., Kyoto Japan) using a transfer tube (0.9 mmΦ 0.35 m) heated at 250 °C. Sample Po12 was pyrolyzed by TGA to give gases, which passed through the transfer tube and were captured by a Tenax mesh trap cooled to the temperature of frozen carbon dioxide. The pyrolysis temperature was programmed to increase from 25 to 550 °C at 10 °C/min under a flow of nitrogen at 35 ml/min. The Tenax trap was flash-heated to 290 °C after pyrolysis and the resulting gaseous products were separated and identified by GC/MS under a nitrogen atmosphere. The chromatography column was an HP-5 capillary (25 m × 0.32 mm i.d., 0.25 μm film thickness) and the other conditions were as follow: carrier gas, nitrogen at 1.9 ml/min; GC oven, starting at 290 °C and heated at 10 °C/min; interface temperature, 300 °C; electric ionization, 70 eV; and mass range, 20–500 amu. The mass spectra obtained were identified from the NIST database.

2.2.3. TG-MS

Thermogravimetric-mass spectrometry experiments were performed with the same TG-GC/MS system. BisGMA/TEGDMA copolymer samples (Po1-11) photo-polymerized in DSC-50 were placed in the TG-GC/MS apparatus within 15 min. The evolved gaseous products were introduced directly into the MS unit without passing through the GC unit. The pyrolysis temperature was programmed to increase from 25 to 550 °C at a rate of 10 °C/min under nitrogen flowing at 35 ml/min. The MS conditions were as follows: interface temperature, 300 °C; electric ionization, 70 eV; mass range, 20–500 amu; and scan rate, 1 scan/s.

3. Results and discussion

3.1. Total ion chromatogram by TG-GC/MS

Fig. 2 shows a total ion chromatogram (TIC) obtained from sample Po12 by TG-GC/MS. TGA and derivative TGA (dTGA) curves are shown in Fig. 3(D)-upper. The compounds recorded in Fig. 2 were identified

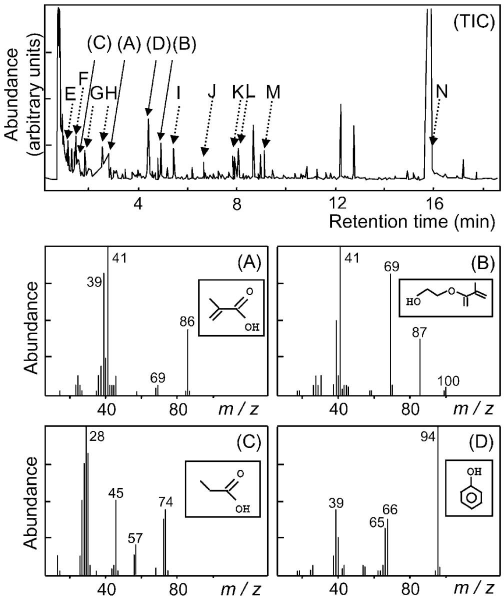


Fig. 2. (TIC) Total ion chromatography of sample Po12 obtained by TG-GC/MS. The volatile gaseous products identified using the NIST database were as follows: (A) methacrylic acid (CAS 79-41-4); (B) 2-hydroxyethyl methacrylate (868-77-9); (C) propionic acid (79-09-4); (D) phenol (108-95-2); (E) acetic acid (64-19-7); (F) 2-methyl-1,3-dioxolane (497-26-7); (G) toluene (108-88-3); (H) cyclohexanone (108-94-1); (I) *o*-cresol (95-48-7); (J) 2-ethyl-phenol (90-006); (K) 2-ethyl-5-methyl-phenol (1687-61-2); (L) 2-methyl-1-hexene (6094-02-6); (M) $C_{10}H_{14}O_4$ (97-90-5); (N) TEGDMA (109-16-0). The mass spectra of (A), (B), (C), and (D) are shown in the lower graphs.

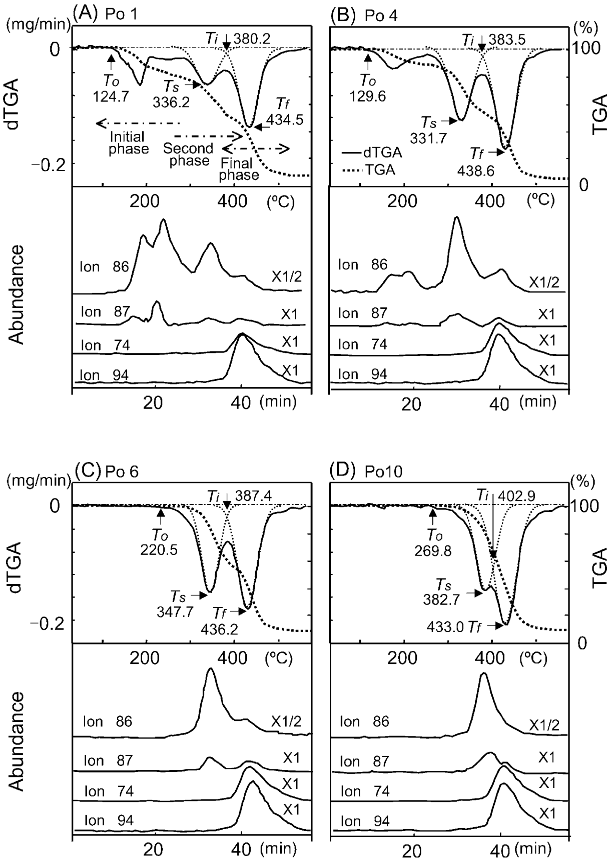


Fig. 3. (A), (B), (C), and (D) are TG-MS data of samples Po1, Po4, Po6, and Po10, respectively. The upper graphs show TGA curves (large dotted line) and dTGA curves (bold line). T_o is the temperature of the onset of weight loss, T_s is the temperature at the maximum degradation rate in the second phase, and T_f is the temperature at the maximum degradation rate in the final phase. T_i is the intersection of the second and final phase curves (small dotted lines) separated from the dTGA curves. The lower graphs show fragment grams of Ion 86 (methyl methacrylate), 87 (2-hydroxyethyl methacrylate), 74 (propionic acid), and 94 (phenol).

as the following products separated at the respective retention times (RT): (A) methacrylic acid (MA) (CAS 79-41-4), RT = 2.85 min; (B) 2-hydroxyethyl methacrylate (HEMA) (CAS 868-77-9) RT = 5.02; (C) propionic acid (PA) (CAS 79-08-4) RT = 1.70 min; and (D) phenol (CAS 108-95-2) RT = 4.53. The major pyrolysate at RT = 15.75 min shown in Fig. 2(TIC)-N was identified as the TEGDMA monomer (CAS 109-13-0).

3.2. TGA curves and ion fragment grams by TG-MS

In Fig. 3, the upper graphs are the TGA and dTGA curves and the lower graphs are the fragment evolution curves of Ions 86 (MA), 87 (HEMA), 74 (PA), and 94 (phenol) obtained by TG-MS of samples Po1, Po4, Po6, and Po10. Three phases (the initial, second, and final phases) of the pyrolysis process for samples Po1-4 were seen in the dTGA curves. The initial values of dTGA decreased as the degree of conversion increased and eventually disappeared, which led to the constitution of two degradation stages with samples Po5-11. Table 2 shows the temperature of onset of thermal degradation (T_o), and the temperature giving the maximum degradation rate in the second (T_s) and final (T_f) phases for each sample. T_f was constant at 436 ± 1.6 °C regardless of the degree of conversion of the copolymers, while T_o and T_s fluctuated irregularly. The solid residual weight remained constant with a char yield of carbonization of about 9 wt.%. MA (Ion 86) and HEMA (Ion 87) were detected in the pyrolyzed products of all the samples in the initial and second phases, and PA (Ion 74) and phenol (Ion 94) were detected in the final phase. These are shown in the fragment evolution curves [Fig. 3(A)–(D)]. The amount of Ion 94 calculated from the area of the fragment evolution curves was constant for all samples. The relationship between the ratio Ion 86 to Ion 94 (MA/phenol) and the degree of conversion is plotted in Fig. 4 (A), and the ratio of Ion 74 to Ion 94 (PA/phenol) and the degree of conversion is plotted in Fig. 4(B). BisGMA/TEGDMA copolymers with a higher degree of conversion had a lower ratio of MA/ phenol (R^2 = 0.874) and a higher ratio of PA/ phenol (R^2 = 0.962).

Table 2
Temperatures at index point

Code	T_o (°C)	T_s (°C)	T_f (°C)	T_i (°C)
Po1	124.7	336.2	434.5	380.2
Po2	129.7	339.3	436.2	382.8
Po3	133.8	337.8	437.7	383.5
Po4	129.6	331.7	438.6	383.5
Po5	132.8	336.0	435.9	384.9
Po6	220.5	347.7	436.2	387.4
Po7	225.4	345.9	436.8	390.0
Po8	220.9	342.5	437.0	390.5
Po9	244.1	366.0	434.4	394.9
Po10	269.8	382.7	433.0	402.9
Po11	271.2	388.2	434.7	405.5

T_o: Temperature onset of weight loss; T_s: Temperature at maximum degradation rate in the second phase; T_f: Temperature at maximum degradation rate in the final phase; T_i: Temperature at intersectional point between the second phase curve and the final phase curve.

3.3. Degradation mechanisms of BisGMA/TEGDMA copolymers

MA is produced by scissoring residual (un-polymerized) BisGMA [Fig. 5 (A)] and TEGDMA [Fig. 5(B)] monomers, and unzipping polymer-chains from BisGMA/TEGDMA copolymers in a similar way to the degradation of poly-methyl methacrylate [24]. HEMA is also produced from TEGDMA monomers [Fig. 5(B)]. The fact that MA and HEMA were observed in the initial pyrolysis phase and their amounts decreased with increasing degree of conversion of the copolymers suggest that MA and HEMA were generated from the residual monomers in BisGMA/TEGDMA copolymers. The two main types of terminated reactions of radical polymerization are known as "coupling " and "disproportionation" [28]. Fig. 5(C) indicates that PA was produced from the ends of new polymer chains generated by the disproportionation-terminated reaction. The fact that the amount of PA increased with the degree of conversion is additional evidence for the production of PA from BisGMA-TEGDMA copolymers. By contrast, phenol was observed at 375–500 °C in the final phase of thermal degradation in our experiments and the amount remained constant regardless of the conversion of copolymers. These results suggest that "specific end scission" occurred in the initial and second phases and "random chain scission" occurred in the final phase. The thermal degradation behavior in the initial and second phases was affected by the degree of conversion of the copolymers, but not that in the final phase. PeakFit (SPSS Science Inc., Chicago, IL, USA) was used to separate the dTGA curves of all the samples and

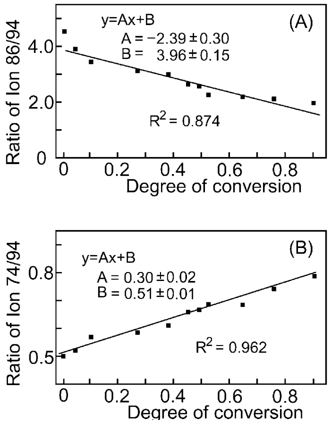
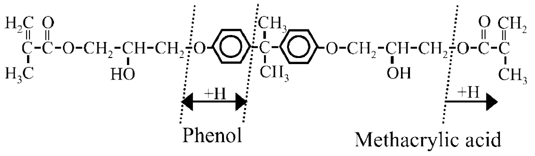
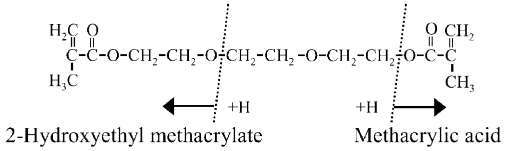


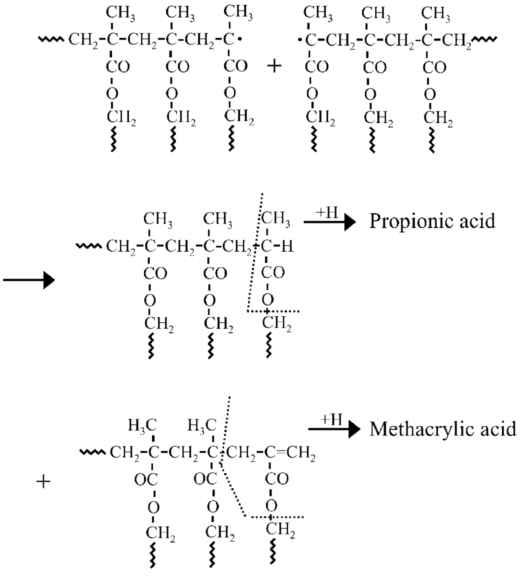
Fig. 4. (A) Relationship between the degree of conversion and the ratio of the amounts of Ion 86 to Ion 94 (methylmethacrylate/phenol). (B) Relationship between the degree of conversion and the ratio of Ion 74 to Ion 94 (propionic acid/phenol).



(A) BisGMA



(B) TEGDMA



(C) BisGMA-TEGDMA copolymer

Fig. 5. (A) BisGMA has two methacrylic groups per molecule. Phenol is produced by chain random scission. (B) TEGDMA has two methacrylic groups per molecule. 2-Hydroxyethyl methacrylate is produced by molecular-end scission. (C) Two growing BisGMA-TEGDMA copolymer chains generate two new types of polymer-chain by the disproportionation-termination process, one of which produces methacrylic acid and the other propionic acid.

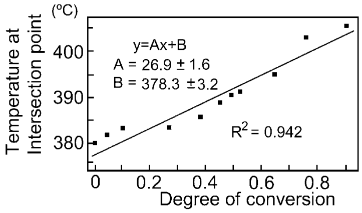


Fig. 6. Relationship between the degree of conversion and the temperature at the intersection points.

define the curves of the second and final phases of thermal degradation to determine the temperatures at the intersection points (T_i), shown in Table 2 and Fig. 3. We found a very strong correlation ($R^2 = 0.942$) between the degree of conversion of BisGMA/TEGDMA copolymers and the temperature at the intersectional points (T_i) using the regression analysis shown in Fig. 6.

4. Conclusion

The TG-GC/MS and TG-MS techniques were very effective for analyzing the degree of conversion of BisGMA/TEGDMA copolymers. Three phases of the pyrolysis processes were seen in the TGA and dTGA curves, and the pyrolysates of the copolymers were separated and identified by TG-GC/MS. The amount and retention time of every pyrolysate (MA, HEMA, PA, and phenol) was examined using TG-MS to elucidate the thermal degradation mechanism of the copolymers at each phase. The amounts of MA and HEMA generated decreased in the initial and second phases, and PA increased in the final phase, with a higher degree of conversion. By contrast, the amount of phenol generated remained constant regardless of the degree of conversion. These results demonstrate that the thermal degradation mechanism of BisGMA/TEGDMA copolymers is dominated by "specific end scission" in the initial and second phases, whereas "main chain random scission" occurs during the final phase. The degree of conversion of the copolymers was strongly correlated ($R^2 = 0.942$) with the temperature at the intersection of the curves for the second and final phases, separated from the dTGA curves.

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