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Effect of dilution on the kinetics of cross-linking thermal polymerization of dental composite matrix resins

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The effect of dilution of 2,2-bis-(4-(2-hydroxy-3-methacryloxyprop-1oxy) phenyl) propane (*bis*-GMA) with triethylene glycol demethacrylate (TEGDMA) on the extent of polymerization, E_p, has been studied using differential scanning calorimetry. The isothermal and dynamic measurements indicate that the E_p is affected dramatically by dilution. The residual polymerization was also found to be strongly influenced by dilution. However, the apparent activation energy, E_{app}, was found to be independent of dilution.

1. Introduction

Multifunctional methacrylates have been commonly used as the matrix material for dental composite applications [1–5]. Thermal or photochemical polymerization of these systems produces highly cross-linked network systems exhibiting good solvent resistance [1]. The end properties of these systems are strongly influenced by the extent of polymerization, E_p. Unfortunately, the autodeceleration due to vitrification severely affects the E_p during the polymerization of these systems [1, 6–10]. Several techniques have been used to determine the E_p during cure, which include differential scanning calorimetry (DSC) [7–13], Fourier transform–infrared spectroscopy (FT–IR) [13–16] and solid state nuclear magnetic resonance (NMR) [17]. It has been observed that E_p is affected by several parameters, such as the flexibility of the monomer, temperature, intensity of the light, etc. [6, 9–11].

2,2-bis-(4-(2-hydroxy-3-methacryloxyprop-1oxy) phenyl) propane (*bis*-GMA) has been widely used as the matrix resin in the dental composites [1]. However, owing to its high viscosity, it is customarily diluted with Triethylene glycol demethacrylate (TEGDMA), a low-viscosity reactive diluent. Increased amounts of TEGDMA have been found to adversly affect the matrix network by increasing the water sorption and curing shrinkage during polymerization [2–4]. However, the use of TEGDMA as a diluent promotes adhesion to the tooth and increases the extent of polymerization in addition to the processibility [1]. A systematic study has been carried out to determine the effect of dilution of *bis*-GMA with TEGDMA on the extent of polymerization. Isothermal and dynamic DSC measurements were carried out to determine the extent of conversion of olefinic double bonds.

2. Experimental procedure

Bis-GMA and TEGMA were obtained from Polysciences, Inc., and Aldrich Chemical Co., and used as-received. Azobis (isobutyro nitrate) (AIBN) was twice recrystallized from methanol, vacuum dried and used. A series of monomer mixtures were prepared with varied *bis*-GMA, TEGDMA ratios as indicated in Table I. All the polymerizations were carried out using 1 mol % AIBN as initiator. The air trapped during this mixing process was removed under reduced pressure.

The glass transition temperatures of the monomer mixtures were measured using a Du Pont DSC (model 2100). Thermogravimetric analysis was conducted from room temperature to 200 °C under a nitrogen atmosphere. The dynamic and isothermal curing studies were carried out using a Perkin–Elmer DSC (model DSC-7). In all the studies, about 10 mg monomer was weighed into an aluminium sample pan and the curing was performed with open sample pans under a nitrogen atmosphere. The instrument was calibrated with indium for melting point and heat of fusion. The isothermal polymerizations were carried out at 60, 70 and 80 °C for 120 min. They were cooled and subsequently scanned at 10 °C min^{-1} from 30–175 °C. The extent of polymerization, E_p, was

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TABLE I Variation of T_g and viscosity with the composition of the mixtures

Sample code	*bis*-GMA (wt %)	TEGDMA (wt %)	Viscosity (cp)	T_g (°C)
Bis-GMA	100	0	1.2×10^6 (a)	− 6.6
Bis-GMA90	90.0	10.0	–	− 20.7
Bis-GMA76	76.2	23.8	5240	− 39.2
Bis-GMA67	66.5	33.5	1180	− 49.4
Bis-GMA50	50.0	50.0	282	− 61.0
Bis-GMA33	33.3	66.7	245	− 72.1
Bis-GMA15	15.0	85.0	38	− 76.7
TEGMA	0	100	15.0	− 81.7

(a) As cited in [4]

determined by measuring the area of the polymerization exotherm using the following modified relationship developed by Miyazaki and Horibe [11]

$$E_p(\%) = 100\Delta H / 2H_m\left(\frac{x_1}{M_1} + \frac{x_2}{M_2}\right) \quad (1)$$

where ΔH is the heat of polymerization of the mixture (kcal mol^{-1}) and H_m is the heat of polymerization of methyl methacrylate (13.1 kcal mol^{-1}) [11]. The factor 2 represents the dimethacrylate systems. The x_i and M_i are the weight fraction and molecular weights of *bis*-GMA and TEGMA, respectively.

3. Results and discussion

The glass transition temperatures, T_g, and the bulk viscosity values of the mixtures were determined for the mixtures of *bis*-GMA and TEGDMA at different compositions and the values are shown in Table I.

Bis-GMA exhibits very high viscosity, and dilution with TEGMA results in low-viscosity mixtures. The T_g values of the mixtures were calculated from the following Fox equation [18] and variation of both calculated and experimental T_g values with composition for the mixtures are illustrated in Fig. 1

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (2)$$

From Fig. 1 it is evident that the calculated T_g values are higher than the experimental values. Generally, in hydrogen-bonded systems, the T_g of the mixture is higher than the calculated values [19]. This behaviour indicates that the dilution effect is predominant compared to the intermolecular hydrogen bonding in these systems.

Isothermal polymerizations of the mixtures were carried out using DSC. A typical thermogram for the isothermal polymerization of *bis*-GMA50 sample at 70 °C is shown in Fig. 2. From the area under the exotherm peak, the extent of polymerization was calculated using Equation 1. The E_p values determined for different mixtures for the isothermal polymerization at 70 °C are shown in Table II. This table indicates that the extent of polymerization increases with dilution. TEGMA is a very flexible low-viscosity monomer and it exhibits the highest conversion at 70 °C.

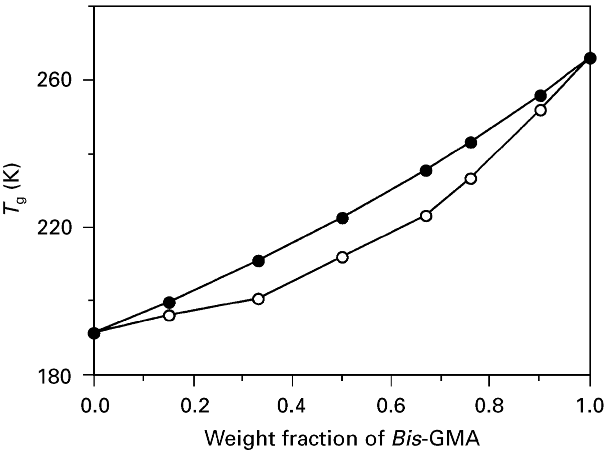

Figure 1 Variation of T_g of the mixtures with the composition: (○) T_g exp, (●) T_g (Fox).

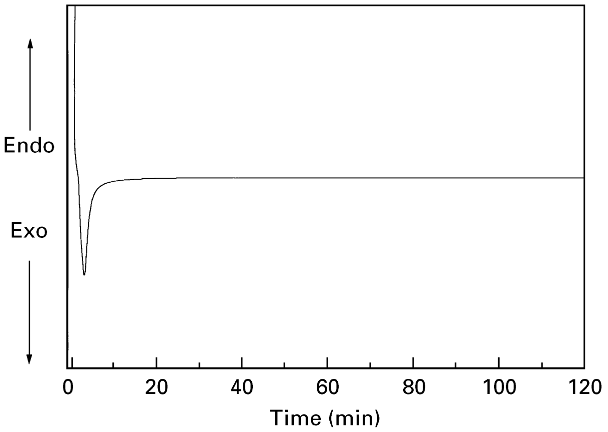

Figure 2 A typical DSC thermogram for the isothermal polymerization of *bis*-GMA50 at 70 °C.

TABLE II Dependence of E_p on the T_g of the monomer mixture

System	T_g (°C)	E_p (%)
Bis-GMA 100	− 6.6	26.7
Bis-GMA90	− 20.7	47.5
Bis-GMA50	− 61.0	67.9
Bis-GMA15	− 76.7	71.5
TEGMA	− 81.7	78.0

The isothermal polymerizations were carried out for the mixtures at different temperatures and the E_p values were determined (Table III). The E_p values were found to increase with temperature and dilution. Under the conditions of high temperatures and low viscosity, the system exhibits more mobility which is responsible for the increased conversions.

The isothermal polymerizations in DSC were followed by dynamic scans in order to determine the extent of residual polymerization in these systems. A typical dynamic scan after the isothermal polymerization of *bis*-GMA50 sample at 70 °C is shown in Fig. 3.

The residual exotherms obtained during this reheating cycle were measured and were related to the residual E_p using Equation 1. The values for *bis*-GMA15 and *bis*-GMA90 are shown in Table IV. The extent of polymerization during the reheating is strongly

TABLE III Variation of E_p on dilution in isothermal polymerization

Temperature (°C)	Extent of polymerization, E_p (%)				
	Bis-GMA	*Bis*-GMA90	*Bis*-GMA50	*Bis*-GMA15	TEGMA
60	21.9	34.5	54.2	60.0	72.0
70	26.7	47.5	67.9	71.5	78.0
80	36.1	60.0	72.0	76.0	87.0

TABLE IV Variation of total extent of polymerization with the isothermal polymerization temperature

Mixture	Isothermal Temperature (°C)	Extent of polymerization, E_p		
		Isothermal E_p (%)	Residual E_p (%)	Total E_p (%)
Bis-GMA15	60	60.0	22.2	82.2
	70	71.5	9.1	80.6
	80	76.0	3.3	79.3
Bis-GMA90	60	34.5	30.2	64.7
	70	47.5	14.3	61.8
	80	60.0	2.6	62.6

influenced by the isothermal temperatures of the first scan (Table IV). For example, the residual E_p values were found to be higher for both *bis*-GMA15 and *bis*-GMA90 when they were polymerized isothermally at 60 °C in the previous scan. As the extent of unreacted double bonds in these systems was relatively higher, they exhibited an increased residual polymerization in the subsequent dynamic scan. It may also be noted that the extent of residual polymerization was found to be very affected by dilution of the mixtures, especially at lower temperatures. For example, *bis*-GMA 90 exhibited higher E_p values during the residual polymerization after 60 and 70 °C isothermal polymerization than the corresponding *bis*-GMA 15 system. It may be explained by the fact that the high-viscosity mixture of *bis*-GMA90 exhibited reduced extent of polymerization at these temperatures and hence they possessed a higher concentration of unreacted double bonds which later cured to larger extents during the second scan.

The total extent of polymerization (which is the sum of the E_p during the first isothermal scan and the E_p during the residual polymerization in the subsequent dynamic scan) were shown in Table IV. Three conclusions may be drawn from the results shown in this Table. (1) The total E_p values were always lower than 100% for the systems studied, indicating that not all of the unreacted double bonds are accessible to the reaction site. (2) The total E_p values were found to be independent of the isothermal temperatures (Table IV). The samples, when polymerized at 60, 70 and 80 °C, isothermally followed by dynamic scanning, exhibited similar values of total E_p (Table IV). (3) However, the total E_p values were found to be strongly influenced by the dilution of the mixtures. For example, *bis*-GMA15 exhibited higher total E_p compared to *bis*-GMA90. In other words, the amount of residual double bonds in *bis*-GMA90 is higher than that of the *bis*-GMA15 system even after the second post-polymerization step. This may be due to the more rigid chains produced in the former systems. Hence the possible difference in mobility of these systems can greatly affect the total curing in the later systems.

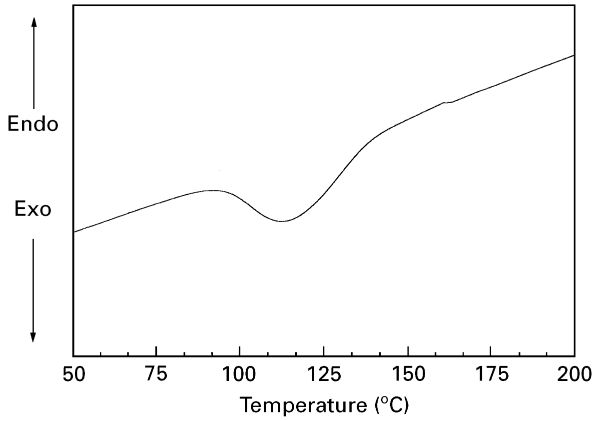

Figure 3 DSC thermogram for the second dynamic run for *bis*-GMA50 after isothermally polymerized at 70 °C for 120 min.

An attempt has been made to determine the effect of viscosities on the apparent activation energy, E_{app}, of the polymerization in these systems. The E_{app} values were determined using Ozawa treatment [10, 20, 21]. The mixtures were scanned at different heating rates and the peak heights were related to the E_{app} using the following relation

$$E_{app} = \frac{-R}{0.4567}\frac{\Delta \log \phi}{\Delta(1/T_p)} \tag{3}$$

where ϕ is the heating rate (°C min^{-1}) and T_p is the peak temperature of the exotherm. A typical plot of log(ϕ) versus inverse of peak temperature is shown for the polymerization of *bis*-GMA50 (Fig. 4). From the slope of the straight line obtained, the activation

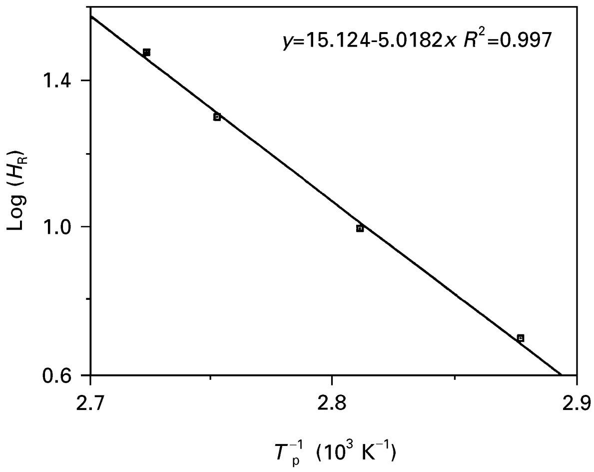

Figure 4 Variation of log heating rate with the inverse of peak temperature for polymerization of *bis*-GMA50.

TABLE V Variation of apparent activation energy, E_{app}, for polymerization with dilution

Monomer	E_{app} (kJ mol^{-1})
Bis-GMA	108
Bis-GMA90	96.0
Bis-GMA50	95.4
Bis-GMA15	95.2

energy was calculated using Equation 2. The values of the activation similarly calculated for several other systems are shown in Table V.

The apparent activation energies for the polymerization of the mixtures were found to be similar (Table V) except for *bis*-GMA. The higher value for *bis*-GMA could be attributed to its very high viscosity which might lead to diffusion problems. However, the values obtained for the other mixtures suggest that the apparent activation energies were very close, indicating that the mechanism of the polymerization is the same.

4. Conclusions

1. The extent of polymerization in the isothermal curing may be correlated to viscosities and the T_g of the mixtures. The systems with low T_g and low viscosities exhibited higher extent of polymerizations.
2. The residual polymerization during the subsequent dynamic scan was found to be higher for high viscosity mixtures.
3. The residual extent of polymerization was found to be affected by the isothermal polymerizations of the previous scans. Higher isothermal temperatures manifested lower residual E_p during the subsequent dynamic scan.
4. The isothermal scanning temperatures did not affect the total E_p of the mixtures.
5. However, the total E_p values were found to be influenced by the viscosity or T_g of the mixtures. Lower viscosities (or lower T_g) of the mixtures exhibited higher total E_p values.
6. The E_{app} values for the polymerization were not influenced by the viscosities of the mixtures.

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