JOURNAL OF MATERIALS SCIENCE 26 (1991) 3185–3190

Cure performance of multifunctional monomers to photo-initiators: a thermoanalytical study on *bis*-GMA-based resins

H. URABE, K. WAKASA, M. YAMAKI
Department of Dental Materials, School of Dentistry, Hiroshima University, 1-2-3 Kasumi, Minami-ku, Hiroshima 734, Japan

In order to assess cure performance in experimental monomer systems containing *bis*-GMA and 3G, differential scanning calorimetry was used to obtain heat for curing, and residual monomers present within the resin systems were measured by high-performance liquid chromatography. Visible light-activated polymerization of these monomer systems was studied using camphorquinone (CQ) and reducing agents of dimethylaminoethyl methacrylate (DMAEMA) and dimethyl-para-toluidine (DMPT). For unfilled *bis*-GMA-based resin (60 wt% *bis*-GMA and 40 wt% 3 G) containing CQ (0.5 wt%) and DMAEMA (0.5 wt%) indicating approximately 100% polymerization, less residual monomer and larger hardness than the other monomer systems were observed.

1. Introduction

In *bis*-GMA-based unfilled resins the degree of polymerization is an important factor in hardness, wear resistance, mechanical strength and colour stability [1–5]. Using various methods, such as transmission Fourier transform–infrared analysis (FT–IR) [3, 6], laser Raman spectroscopy (LRS) [7] and thermoanalytical methods [8–10], polymerization appeared to be due to the monomer composition of the restorative resin and the concentration of polymerization catalyst [1, 6, 11, 12]. These methods were helpful to examine rapidly the extent of polymerization of base monomer systems. The viscosity of monomers and curing temperature were affected by the degree of polymerization in visible light-cured resins [12]. Dental composite resins in which polymerization was initiated by an intense blue light, needed a source of heat in the blue-light range of the spectrum [13, 14]. Differential scanning calorimetry (DSC) was used to analyse the thermal properties of dental composite materials because of difficulties in sample preparation and a strong interference among monomers in infrared spectroscopy [15]. DSC measurement was successfully used to study the polymerization of monomers in dental composites [15–17]. Thus, the present study was performed to assess the heat for curing in experimental dental monomer systems, and the amount of residual monomers in their visible light-cured resins was evaluated by high-performance liquid chromatography (HPLC).

2. Materials and methods

The monomers and photo-initiators used in this study are given in Table I. The materials were used as-received (*bis*-GMA, 2,2-*bis*[*p*-γ-methacryloxy-β-hydroxypropoxy)phenyl]propane; 3G, triethylene glycol dimethacrylate; CQ, camphorquinone; DMAEMA, dimethylaminoethyl methacrylate. Eighteen resin systems were formulated by six comonomers at three different ratios of CQ/DMAEMA (0.5 wt%/0 wt%, 0.5 wt%/0.5 wt% and 0.5 wt%/1.0 wt%) present within the comonomers. In addition, unfilled *bis*-GMA-based resin (60 wt% *bis*-GMA and 40 wt% 3 G) containing dimethyl-para-toluidine (DMPT) was formulated with 0, 0.25, 0.5 and 1.0 wt% DMPT content and 0.5 wt% CQ, and also at the same ratios, as for the resin with DMAEMA. Each *bis*-GMA-based resin was kept in a container at 15 °C for 24 h after adding a photo-initiator to its resin.

2.1. DSC measurement

The visible light-cured specimens were polymerized by illuminating them in a DSC apparatus (DT-30) with radiation from a visible light source (Quick Light) for 40 and 180 s at 37 °C (environmental temperature). Table II indicates the DSC experimental conditions. The distance between a sample and the edge of the light source was 3 mm, according to the instructions.

2.2. High-performance liquid chromatography (HPLC)

Residual monomers from cured resins were determined by HPLC method (Twincle) as indicated in Table III. Figs 1 and 2 show chromatographs indicating *bis*-GMA and 3G monomers and calibration curves of *bis*-GMA ($r = 0.998$) and 3G ($r = 0.997$). Both *bis*-GMA and 3G monomers were eluted in methanol

0022–2461/91 $03.00 + .12

TABLE I Resin formulations used in this study

	Components	Photo-initiator		Code
		CQ (wt %)	DMAEMA (wt %)	
		0.5	0	A-1
A	100% *bis*-GMA	0.5	0.5	A-2
comonomer	0% 3G	0.5	1.0	A-3
		0.5	0	B-1
B	80% *bis*-GMA	0.5	0.5	B-2
comonomer	20% 3G	0.5	1.0	B-3
		0.5	0	C-1
C	60% *bis*-GMA	0.5	0.5	C-2
comonomer	40% 3G	0.5	1.0	C-3
		0.5	0	D-1
D	40% *bis*-GMA	0.5	0.5	D-2
comonomer	60% 3G	0.5	1.0	D-3
		0.5	0	E-1
E	20% *bis*-GMA	0.5	0.5	E-2
comonomer	80% 3G	0.5	1.0	E-3
		0.5	0	F-1
F	0% *bis*-GMA	0.5	0.5	F-2
comonomer	100% 3G	0.5	1.0	F-3

TABLE II DSC measurement

Apparatus	DT-30 (Shimadzu Co.)
Mode	Isothermal DSC
Temperature	37 ± 1 °C
Sample size	3.0 ± 0.1 mg
Environment	Ambient air
Sensitivity	200 mJ s^{-1}
Sampling time	0.5 s

TABLE III HPLC measurement

Apparatus	Twincle (Japan Spectroscopic Co.)
Column	GEL 110 (4.6 mm diameter × 250 mm)
Mobile Phase	90% MeOH–H_2O
Flow rate	2.0 ml min^{-1}
Detector	UVIDEC:100 II
Wavelength	254 nm
Range	0.16 o.d.
Integrator	Chromatopac C-R3A
Temperature	Constant 30 °C

Figure 1 An example (retention time) of HPLC chromatograph containing 0.5 μg μl^{-1} *bis*-GMA and 3G monomers.

and a solution (10 ml) with each concentration was analysed by HPLC. The peak area in the HPLC chromatograph was calibrated (Fig. 2a and b). The specimen (6 mm diameter × 3 mm) was irradiated (40 and 180 s) using plastic strips on the upper surface (no. 687, thickness 0.05 mm). The visible light-cured powder was immersed in methanol (2 ml) for 48 h. After this treatment the sample was centrifuged at 3000 r.p.m. (1158 G) for 15 min, and was taken for HPLC analysis (10 ml).

2.3. Knoop hardness

The visible light-cured specimen (diameter × 3 mm) was used similarly in Section 2.2. Before cutting, the upper surface of the specimen was sealed with masking film. Each specimen for hardness measurement was loaded at 50 g for 30 s (MVK type). Every 0.5 mm distance from the upper surface to deeper surface, the Knoop hardness was measured at three locations at the same depth for three different specimens.

3. Results

Fig. 3 shows typical DSC curves for unfilled *bis*-GMA resins (A-2 to F-2; CQ = 0.5 wt %, DMAEMA = 0.5 wt %) after 40 s irradiation. Table IV indicates peak time, peak height and heat for curing for all visible light-cured resins. The curve had a peak, and the time at the peak is represented by the peak time, which is thus shown by the peak height. The heat for curing is defined as the area to reach the horizontal line of the DSC curve (the value (J g^{-1}) was obtained per gram of a sample, from the DSC curve). The peak time increased with decreasing amount of *bis*-GMA within the resin for the three different ratios of photo-initiators as CQ/DMAEMA. However, the peak height was largest for 20 and 40 wt % *bis*-GMA in the base resin, although the value of the peak height was about 5–7 for CQ/DMAEMA such as 0.5 wt %/ 0 wt %. For all *bis*-GMA-based resins the heat for curing became large when the amount of *bis*-GMA ranged from 0–60 wt %, indicating 200–320 J g^{-1}.

Table V gives the amounts of residual monomers such as *bis*-GMA and 3G. After 40 s irradiation, the unfilled *bis*-GMA resins containing 40 and 60 wt %

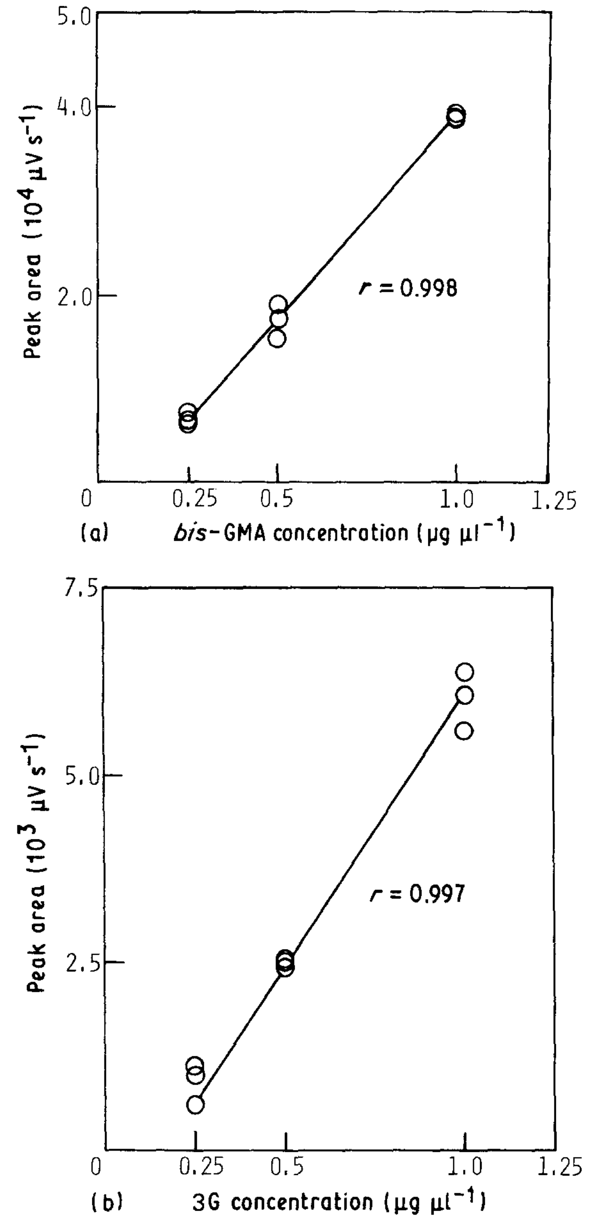


Figure 2 Calibration curves: (a) *bis*-GMA monomer, (b) 3G monomer.

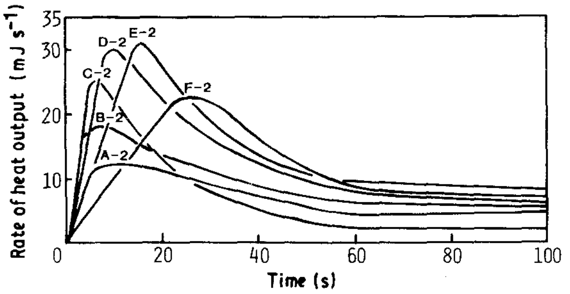


Figure 3 Typical DSC curves obtained for *bis*-GMA-based resins containing CQ/DMAEMA = 0.5 wt %/0.5 wt % (sample temperature 37 °C in the DSC apparatus).

bis-GMA content (0.5 and 1.0 wt % DMAEMA for CQ = 0.5 wt %) and the smallest values, ranging from 3.9–8.0 wt % as total residual monomer. At 180 s irradiation, the amount of residual monomers was very small for the resins (B–F series) except 100% *bis*-GMA-based resin (A series).

TABLE IV Thermal properties of heat for curing, peak time and peak height

Code	Heat of curing (J g^{-1})	Peak time (s)	Peak height (mJ s^{-1})
A-1	149.1 ± 66.0	21.8 ± 4.0	5.1 ± 2.3
A-2	160.9 ± 2.8	13.9 ± 0.5	6.3 ± 0.6
A-3	155.3 ± 58.4	12.8 ± 1.8	7.6 ± 0.2
B-1	193.1 ± 13.3	14.9 ± 0.8	5.7 ± 1.0
B-2	231.9 ± 68.4	8.9 ± 1.1	13.6 ± 1.0
B-3	204.5 ± 13.3	7.5 ± 0.1	16.6 ± 1.5
C-1	198.1 ± 8.9	20.4 ± 1.5	6.5 ± 1.7
C-2	291.3 ± 77.9	9.8 ± 1.0	19.2 ± 1.5
C-3	284.8 ± 79.6	10.0 ± 0.5	20.1 ± 1.7
D-1	273.8 ± 6.6	35.0 ± 2.3	6.2 ± 0.9
D-2	284.8 ± 78.6	12.0 ± 0.4	30.2 ± 2.8
D-3	326.6 ± 39.4	12.1 ± 0.8	29.1 ± 3.4
E-1	208.8 ± 23.2	40.3 ± 6.9	4.5 ± 1.1
E-2	274.7 ± 48.7	18.4 ± 1.0	29.4 ± 2.6
E-3	294.7 ± 29.1	20.3 ± 1.0	23.2 ± 4.2
F-1	216.5 ± 5.6	52.6 ± 2.6	5.3 ± 1.6
F-2	241.4 ± 53.8	40.7 ± 1.0	14.8 ± 2.8
F-3	308.4 ± 28.1	40.4 ± 2.2	13.9 ± 0.8

TABLE V Residual monomers (wt %) of *bis*-GMA and 3G at 40 and 180 s irradiation times

Code	Irradiation time			
	40 s		180 s	
	3G	*bis*-GMA	3G	*bis*-GMA
A-1	n.f.[a]	34.1 ± 4.2	n.f.	28.5 ± 3.0
A-2	n.f.	19.4 ± 0.5	n.f.	8.9 ± 0.5
A-3	n.f.	15.1 ± 0.5	n.f.	7.0 ± 0.9
B-1	3.1 ± 0.7	9.8 ± 2.5	1.7 ± 0.4	5.7 ± 1.2
B-2	3.9 ± 0.2	6.7 ± 1.3	1.7 ± 0.1	4.4 ± 0.1
B-3	2.7 ± 0.5	6.0 ± 0.7	2.2 ± 0.2	3.9 ± 0.1
C-1	3.5 ± 0.6	5.4 ± 1.3	1.5 ± 0.1	1.0 ± 0.2
C-2	4.5 ± 0.2	3.5 ± 0.1	1.6 ± 0.1	1.2 ± 0.0
C-3	3.0 ± 0.7	1.8 ± 0.1	1.9 ± 0.2	1.1 ± 0.1
D-1	20.8 ± 1.3	10.1 ± 1.3	2.6 ± 0.2	0.8 ± 0.1
D-2	3.0 ± 0.1	1.0 ± 0.1	2.1 ± 0.1	0.5 ± 0.1
D-3	3.7 ± 0.4	1.1 ± 0.1	2.2 ± 0.1	0.7 ± 0.1
E-1	34.2 ± 3.6	8.7 ± 1.8	8.1 ± 1.6	1.2 ± 0.6
E-2	7.7 ± 1.7	1.1 ± 0.6	3.8 ± 0.4	0.5 ± 0.2
E-3	4.2 ± 0.7	0.6 ± 0.2	3.5 ± 0.6	0.3 ± 0.1
F-1	45.7 ± 5.2	n.f.	3.3 ± 0.4	n.f.
F-2	18.3 ± 0.2	n.f.	3.2 ± 0.3	n.f.
F-3	12.2 ± 0.6	n.f.	2.5 ± 0.1	n.f.

[a] n.f. = not found

Table VI indicates the values of Knoop hardness of visible light-cured specimens irradiated for 40 and 180 s (the values showed the largest value at 0.5 mm depth from the upper surface). The maximum values were 17.1 ± 1 (40 s) and 20.4 ± 3 (180 s) for unfilled *bis*-GMA resin (C series). When a longer irradiation time was used, a larger hardness was obtained.

The effects of the amount of reducing agent on thermal properties were shown as follows; peak time and peak height (Table IV), heat for curing (Fig. 4),

TABLE VI Knoop hardness at 40 and 180 s irradiation times (depth from the upper surface: 0, 0.5, 1.0, 1.5, 2.0 and 2.5 mm)

Code	Knoop hardness at depths of:											
	0 mm		0.5 mm		1.0 mm		1.5 mm		2.0 mm		2.5 mm	
	40 s	180 s	40 s	180 s	40 s	180 s	40 s	180 s	40 s	180 s	40 s	180 s
A-2	6.7 ± 1.1	11.4 ± 0.5	9.5 ± 1.1	13.2 ± 0.5	5.2 ± 1.0	10.6 ± 0.2	4.5 ± 1.4	9.9 ± 0.7	3.3 ± 0.8	9.6 ± 1.6	2.2 ± 0.4	8.9 ± 1.5
A-3	9.0 ± 2.3	11.1 ± 2.1	9.2 ± 1.2	14.5 ± 0.9	5.1 ± 2.5	9.9 ± 1.8	4.2 ± 2.2	9.0 ± 0.8	4.0 ± 1.9	8.8 ± 1.1	2.7 ± 0.8	6.5 ± 0.4
B-2	13.5 ± 0.7	14.9 ± 1.2	14.5 ± 0.4	15.2 ± 0.5	11.8 ± 0.6	14.0 ± 1.3	11.5 ± 0.3	13.6 ± 1.0	10.3 ± 0.2	13.1 ± 0.9	10.4 ± 0.9	12.0 ± 1.8
B-3	14.8 ± 1.5	15.0 ± 1.2	15.4 ± 0.8	15.6 ± 0.6	12.4 ± 0.5	15.3 ± 1.9	12.3 ± 0.7	14.3 ± 1.6	11.2 ± 0.8	13.5 ± 1.2	10.8 ± 1.7	13.6 ± 1.2
C-2	12.3 ± 0.2	14.1 ± 1.6	17.1 ± 0.9	20.4 ± 3.4	12.8 ± 2.1	18.9 ± 1.6	13.6 ± 1.9	15.4 ± 1.3	12.8 ± 1.6	15.4 ± 1.3	10.7 ± 0.9	15.9 ± 1.6
C-3	13.2 ± 0.4	13.1 ± 1.4	15.8 ± 0.5	17.3 ± 1.5	13.4 ± 0.9	14.8 ± 1.5	13.0 ± 1.0	13.4 ± 0.9	12.7 ± 0.8	12.6 ± 1.3	11.8 ± 1.2	11.9 ± 1.6
D-2	16.4 ± 1.8	16.9 ± 1.1	16.3 ± 1.8	19.0 ± 2.1	14.4 ± 0.6	17.5 ± 0.6	14.4 ± 1.4	16.2 ± 2.0	14.4 ± 0.4	16.4 ± 1.5	12.7 ± 1.0	14.7 ± 1.7
D-3	14.7 ± 1.6	16.4 ± 1.1	15.8 ± 0.4	16.8 ± 0.8	15.0 ± 1.1	15.6 ± 0.7	14.6 ± 2.4	14.7 ± 0.4	14.1 ± 1.7	14.1 ± 0.6	13.7 ± 0.9	13.3 ± 1.3
E-2	13.8 ± 1.1	14.2 ± 1.8	15.0 ± 2.4	17.2 ± 0.3	12.8 ± 0.9	15.1 ± 2.2	12.9 ± 0.2	14.6 ± 1.6	12.6 ± 0.5	13.9 ± 0.2	11.3 ± 0.5	12.1 ± 0.8
E-3	13.7 ± 2.7	14.7 ± 1.1	14.3 ± 3.0	15.6 ± 2.7	12.8 ± 0.8	14.1 ± 0.5	12.3 ± 0.4	13.8 ± 0.2	12.6 ± 1.3	12.5 ± 0.4	12.5 ± 0.5	12.3 ± 0.8
F-2	9.3 ± 3.6	12.5 ± 2.7	11.0 ± 3.4	14.3 ± 1.8	3.8 ± 0.5	8.2 ± 0.9	3.6 ± 0.8	8.2 ± 1.0	3.1 ± 0.4	8.0 ± 0.7	3.2 ± 0.3	7.9 ± 0.8
F-3	8.4 ± 0.7	10.8 ± 0.9	9.6 ± 1.6	11.1 ± 0.5	5.6 ± 0.2	8.6 ± 0.5	4.9 ± 0.5	8.3 ± 0.4	4.5 ± 0.8	8.0 ± 0.6	6.0 ± 0.2	7.7 ± 0.8

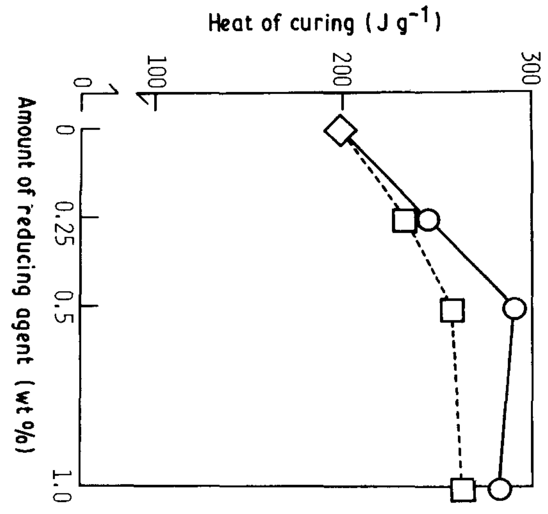


Figure 4 Heat for curing in *bis*-GMA-based resin (60 wt % *bis*-GMA and 40 wt % 3G). (○) DMAEMA, (□) DMPT.

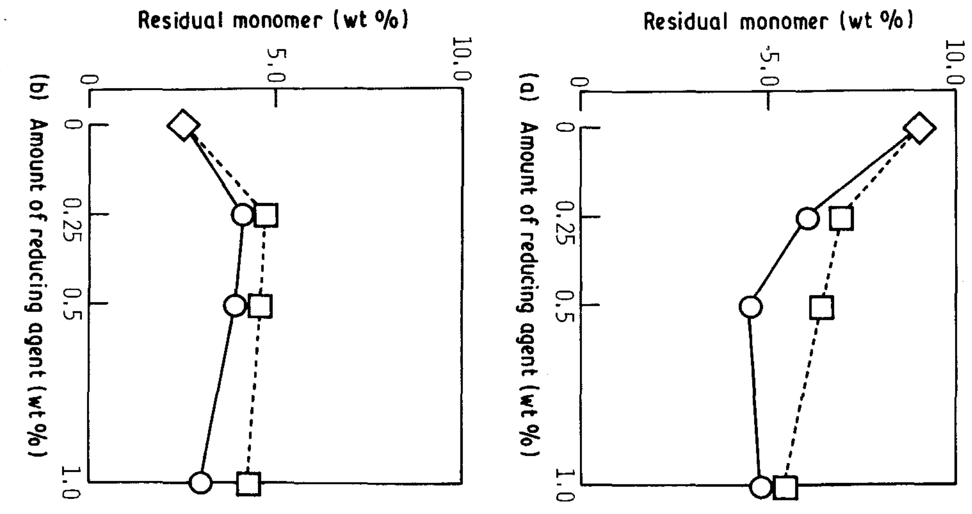
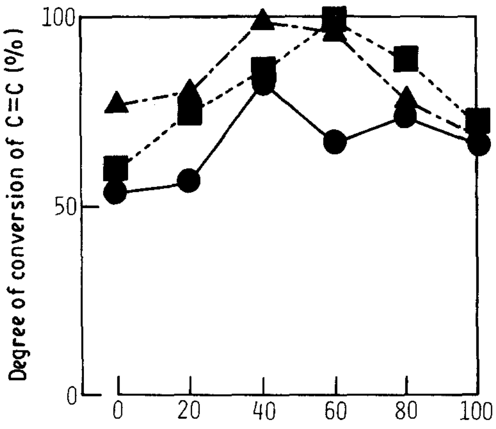
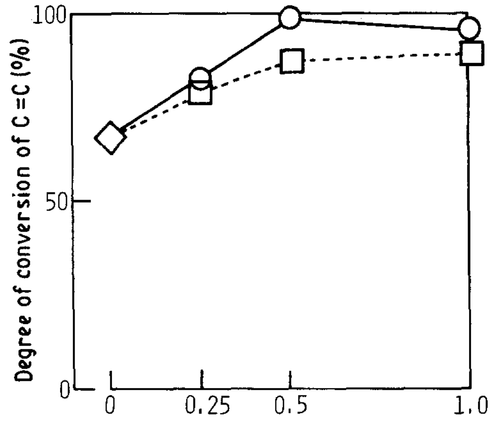


Figure 5 Residual monomers in the unfilled resins shown in Fig. 4 after (a) 40 s irradiation time, (b) 180 s irradiation time.

amount of residual monomer (Fig. 5a and b for 40 and 180 s irradiation times), and the degree of conversion of carbon–carbon double bond (C=C) (Fig. 6a and b for varying amounts of *bis*-GMA and reducing agent content in the base resin). For the visible light-cured *bis*-GMA-based systems containing either three different ratios (CQ/DMAEMA), or two different reducing agents, the appropriate resin formulation was selected.



(a) Amount of *bis*-GMA (wt %)



(b) Amount of reducing agent (wt %)

Figure 6 Degree of conversion of the carbon–carbon double bond. (a) Unfilled *bis*-GMA-based resins (A to F series). For CQ = 0.5 wt % and (▲) DMAEMA = 1.0 wt %, (■) DMAEMA = 0.5 wt %, (●) DMAEMA = 0 wt %. (b) Unfilled resins (60 wt % *bis*-GMA and 40 wt % 3G); for resin base CQ = 0.5 wt %, (○) DMAEMA, or (□) DMPT = 0.25, 0.5 and 1.0 wt %.

4. Discussion

In the polymerization reaction of visible light-cured resins, an exothermic nature was found [16], and a thermoanalytical method has previously been reported for commercial dental composites [10]. An increased curing for unfilled *bis*-GMA-based resin (C series; 60 wt % *bis*-GMA and 40 wt % 3G) was indicated (Table IV), at ratios of CQ/DMAEMA of 0.5/0.5 and 0.5/1.0. This polymerization would be reflected in the degree of conversion of C=C in the chemically cured resin [17]. When the theoretical heat for curing at complete reaction was deduced, the degree of conversion was obtained from the measured heat (Fig. 6a and b). Thus, for a principal monomer (*bis*-GMA, or 3G), the effect of CQ and DMAEMA or DMPT could be evaluated as follows. The maximum value (approximately 100%) was obtained for C-2 unfilled resin (containing 60 wt % *bis*-GMA and 40 wt % 3G) and also for the D-3 unfilled resin (40 wt % *bis*-GMA and 60 wt % 3G). No significant difference in the degree of conversion between 0.5/0.5 and 0.5/1.0 CQ/DMAEMA ratio was found for the *bis*-GMA-based resin (C-2 series). In this *bis*-GMA-based resin, the reducing agent DMAEMA was more activated than DMPT, in amounts more than 0.5 wt % DMAEMA. The effect of 3G monomer present within the resin on the amount of residual monomer was also clarified (Table V). When the amount of 3G monomer increased, the residual monomer of 3G increased, compared to *bis*-GMA monomer, because the reaction rate of 3G monomer would be slower than that of *bis*-GMA monomer at 40 s irradiation. In addition, increasing the amount of reducing agent DMAEMA to 0.5 wt % CQ, decreased the residual monomer for *bis*-GMA-based resin (60 wt % *bis*-GMA and 40 wt % 3G) (Fig. 5a and b).

The difference in Knoop hardness between C-3 and C-2 resins was due to the CQ/DMAEMA ratio. A ratio of 0.5/0.5 CQ/DMAEMA was more useful than 0.5/1.0. The reducing agent and CQ content may act to reactivate groups during the polymerization process. This result agrees with the decrease in residual monomers for the unfilled *bis*-GMA-based resins (Fig. 5a). The amount of residual monomer was improved slightly when using DMAEMA rather than DMPT (Fig. 5b). DMAEMA as reducing agent and *bis*-GMA-based resin containing 60 wt % *bis*-GMA had a greater heat for curing, as shown in Fig. 4, because the polymerization reaction was enhanced by DMAEMA as a reducing agent. The appropriate amount of reducing agent to amount of CQ or CQ content was not evinced. In this study, an appropriate content of *bis*-GMA present within unfilled *bis*-GMA-based resins was determined using our results based on CQ content (0.5 wt %). The degree of conversion of the carbon–carbon double bond was approximately 100% for unfilled *bis*-GMA based resin (60 wt % *bis*-GMA and 40 wt % 3G), and the residual monomer was below 5%. There were significant differences in both heat for curing and Knoop hardness between DMAEMA and DMPT reducing agents ($p < 0.01$). The present results indicate that this experimental multifunctional monomer for dental application has an almost perfect polymerization, showing much lower residual monomers than in other monomer systems tested using thermoanalytical studies in which polymerization is activated by CQ reducing agent on irradiation in the DSC apparatus.

References

1. E. ASMUSSEN, *Scand. J. Dent. Res.* **90** (1982) 484.
2. W. WU, *IADR Progr. Abst.* **62** (192) (1983).
3. J. L. FERRACANE and E. H. GREENER, *J. Dent. Res.* **63** (1984) 1093.
4. J. L. FERRACANE, P. ADAY, H. MATSUMOTO and V. A. MARKER, *Dent. Mater.* **2** (1986) 80.
5. T. W. WILSON and D. T. TURNER, *J. Dent. Res.* **66** (1987) 1032.
6. J. L. FERRACANE, S. NEWMAN and E. H. GREENER, *IADR Progr. Abst.* **61** (832) (1982).
7. H. SHIMOMURA, H. HISAMITSU and S. WAKUMOTO, *Nihon Shika Hozongaku Zassi* **29** (1986) 1252.
8. J. M. ANTONUCCI and E. E. TOTH, *J. Dent. Res.* **62** (1983) 121.
9. J. F. McCABE, *Dent. Mater.* **1** (1985) 231.
10. H. SHINTANI, K. WAKASA and M. YAMAKI, *J. Mater. Sci.* **22** (1987) 1295.
11. I. E. RUYTER and P. P. GYOROSI, *Scan. J. Dent. Res.* **84** (1976) 396.

12. G. C. ELIADES, G. J. VOUGIOUKLAKIS and A. A. GAPUTO, *Dent. Mater.* **3** (1987) 19.
13. W. D. COOK and P. H. STANDISH, *Aust. Dent. J.* **28** (1983) 307.
14. T. HIROSE, K. WAKASA and M. YAMAKI, *J. Mater. Sci.* **25** (1990) 932.
15. J. M. ANTONUCCI and E. E. TOTH, *J. Dent. Res.* **62** (1983) 121.
16. M. A. BASSIOUNY, *IADR Prog. Abst.* **59** (647) (1980).
17. S. BAN and J. HASEGAWA, *Dent. Mater. J.* **3** (1984) 85.

Received 14 August 1989
and accepted 26 October 1990