Synthesis and Photopolymerization of Dicarboxylic Acid Dimethacrylates and Their Application as Dental Monomers

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ABSTRACT: New six dicarboxylic acid dimethacrylates (DMAs) were synthesized and studied as photocurable dental monomers. The photopolymerization behavior of the monomers was investigated by FTIR spectroscopy using camphorquinone (CQ) and 2-(dimethylamino)ethyl MA (DMAEMA) as a photoinitiating system. Relatively high conversions (>55%) resulted from photopolymerization of the monomers by visible light. The volume shrinkage of the monomers during photopolymerization was significantly influenced by their molecular weight and degree of conversion. Preliminary tests of the composites formulated with a dicarboxylic acid DMA, a diluent, CQ, DMAEMA, and a glass filler were carried out including a three-point bending test and fluoride release. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1802–1808, 2000

Key words: dicarboxylic acid dimethacrylate; photopolymerization; dental application; volume shrinkage; fluoride release

INTRODUCTION

The two major groups of dental esthetic restorative materials that are now routinely used are the composites and glass ionomers.[1] These materials have significantly different characteristics and properties, and they thus offer different advantages and disadvantages.

A typical polymeric dental composite consists of a dimethacrylate (DMA) monomer, a DMA diluent, a photoinitiator system, and a large quantity of inorganic fillers.[2,3] Difunctional MAs such as 2,2-bis[4-(2′-hydroxy-3′-methacryloyloxypropoxy)phenyl]propane (bis-GMA) and 1,6-bis(2′-methacryloyloxyethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) are used as photocurable monomers in commercial dental composites. The MAs (monomer and diluent) are photopolymerized by visible light to form a crosslinked network. The composite materials have good mechanical properties after photocuring and ease of application. However, they need to be used together with adhesives for adhesion to tooth substrates. Polymerization shrinkage is still a major cause of clinical failure of composite restorations, and its elimination or minimization is therefore one of the most important research tasks in this field.[4]

Conventional glass ionomer systems undergo setting through an acid–base reaction between an aqueous polycarboxylic acid and an ion-leachable glasslike fluoroaluminosilicate.[5] The chief advantages of glass ionomers are the release of fluoride, biocompatibility, and adhesion to tooth substrates. In spite of these advantages, traditional glass ionomers suffer from the disadvantages that they have short working times, rather long set times, and relatively low mechanical properties.

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Recently a new class of dental restorative material, which is a hybrid of composite and glass ionomer, has become the subject of interest because it could have advantageous properties of both materials.[1] The purpose of this study was to develop novel monomers having potential as components of the hybrid system. New photocurable dental monomers were synthesized that simultaneously have two MA and two carboxyl groups in a single molecule. The photopolymerization behavior of the dicarboxylic acid DMAs and properties of the photocured formulations based on the monomers were investigated.

EXPERIMENTAL

Materials and Instruments

Neopentyl glycol diglycidyl ether (NGDE), 1,4-cyclohexanedimethanol DE (CHDE), and methacrylic acid were purchased from Aldrich Chemical Co. and purified by vacuum distillation. Bisphenol A DE (BADE) was purchased from Lancaster Synthesis Ltd. and used as received. Succinic anhydride, phthalic anhydride, 4-(dimethylamino)pyridine, camphorquinone (CQ), 2-(dimethylamino)ethyl MA (DMAEMA), tri(ethylene glycol) DMA (TEGDMA), UDMA, and 4-methoxyphenol were purchased from Aldrich Chemical Co. and used without purification. Tetrahydrofuran (THF) was distilled from sodium. Fluoroaluminosilicate glass was purchased from GC Corp.

^{1}H- and ^{13}C-NMR spectra were taken on a Varian Gemini 300-MHz spectrometer in deuteriochloroform using tetramethylsilane as an internal standard. IR spectra were recorded on a Genisis FTIR spectrophotometer (Mattson Instrument Co.). The viscosities of the monomers were measured with a Rheometrics dynamic spectrometer (Rheometrics). Exposure of the samples was made on a XL100 curing light (3M Dental Products) with a range of 420–500 nm.

Preparation of Dicarboxylic Acid DMAs

A mixture of NGDE (6.49 g, 30 mmol), methacrylic acid (5.17 g, 60 mmol), 4-methoxyphenol (0.037 g), and 4-(dimethylamino)pyridine (0.15 g) was stirred at 90°C for 4 h. Succinic anhydride (6.00 g, 60 mmol) in THF was added to the resulting material, and the mixture was refluxed for 36 h. After cooling to room temperature the THF was removed under reduced pressure, and the residue was dissolved in dichloromethane. The resultant solution was washed with 0.5*M* HCl and brine and dried over anhydrous magnesium sulfate. The solvent was stripped off and **1b** (15.40 g, 87%) was obtained as a pale yellow oil.

The other monomers having 3-carboxypropanoyloxy groups (**2b** and **3b**) were synthesized in a similar fashion starting from CHDE and BADE, respectively. Monomers **1a, 2a,** and **3a** that have 2-carboxybenzoyloxy groups were prepared using phthalic anhydride instead of succinic anhydride.

2,2-bis{[2′-(2-carboxybenzoyloxy)-3′-methacryloyloxypropoxy]methyl}propane (**1a**): yield 80%. IR (neat): ν (cm^{-1}) 3500–2800 (br), 2965, 1729, 1638, 1600, 1581, 1172, 1126. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.83 [s, 6H, $(OCH_2)_2$—C—$(CH_3)_2$], 1.93 [s, 6H, 2 C═C—CH_3], 3.23 [m, 4H, $(OCH_2)_2$—C—$(CH_3)_2$], 3.70 [d, 4H, 2 CH_2O—CH_2—C], 4.45 [d, 4H, 2 COO—CH_2—C], 5.35 [m, 2H, 2 COO—CH—$(CH_2)_2$], 5.58 [s, 2H, 2 H—C═C—COO (*trans*)], 6.12 [s, 2H, 2 H—C═C—COO (*cis*)], 7.47–8.00 [m, 8H, 2 Ar—COO], 9.65–10.20 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.37 [CH_2═C—CH_3], 22.05 [$(OCH_2)_2$—C—$(CH_3)_2$], 36.57 [$(OCH_2)_2$—C—$(CH_3)_2$], 63.37 [OCO—CH_2—C], 69.08 [COO—CH—$(CH_2)_2$], 69.63 [CH_2O—CH_2—CH], 72.19 [C—CH_2O—CH_2], 126.28 [CH_2═C—CH_3], 128.92, 130.04, 131.12, 132.25, 133.20 [Ar], 136.09 [CH_2═C—CH_3], 167.40 [carbonyl of methacrylate], 172.02 [Ar—COO], 172.27 [Ar—COOH].

2,2-bis{[2′-(3-carboxypropanoyloxy)-3′-methacryloyloxypropoxy]methyl}propane (**1b**): yield 87%. IR (neat): ν (cm^{-1}) 3500–2800 (br), 2963, 1722, 1637, 1161. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.85 [s, 6H, $(OCH_2)_2$—C—$(CH_3)_2$], 1.92 [s, 6H, 2 C═C—CH_3], 2.65 [s, 8H, 2 OOC—CH_2CH_2—COO], 3.18 [s, 4H, $(OCH_2)_2$—C—$(CH_3)_2$], 3.57 [d, 4H, 2 CH_2O—CH_2—C], 4.33 [d, 4H, 2 COO—CH_2—C], 5.25 [m, 2H, 2 COO—CH—$(CH_2)_2$], 5.78 [s, 2H, 2 H—C═C—COO (*trans*)], 6.09 (s, 2H, 2 H—C═C—COO (*cis*)], 9.00–9.45 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.31 [CH_2═C—CH_3], 22.00 [$(OCH_2)_2$—C—$(CH_3)_2$], 29.06, 29.11 [HOCO—CH_2 CH_2—COO], 36.53 [$(OCH_2)_2$—C—$(CH_3)_2$], 63.30 [OCO—CH_2—C], 69.67 [COO—CH—$(CH_3)_2$], 70.90 [CH_2O—CH_2—CH], 71.00 [C—CH_2O—CH_2], 126.20 [CH_2═C—CH_3], 136.02 [CH_2═C—CH_3], 167.13 [carbonyl of methacrylate], 171.54 [OOC—CH_2CH_2—COOH], 177.77 [COOH].

1,4-bis{[2′-(2-carboxybenzoyloxy)-3′-methacryloyloxypropoxy]methyl}cyclohexane (**2a**): yield 82%. IR (neat): ν (cm^{-1}) 3500–2700 (br), 2965, 1722, 1637, 1600, 1580, 1170, 1128. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.92 [m, 2H, cyclohexane], 1.32–1.57 [m, 4H, cyclohexane], 1.66–1.87 [m, 4H, cyclohexane], 1.98 [s, 6H, 2 C═C—CH_3], 3.28 [d, 4H, 2 cyclohexane-CH_2O], 3.69 [d, 4H, 2 CH_2O—CH_2—C], 4.45 [d, 4H, 2 COO—CH_2—C],

5.44 [m, 2H, 2 COO—CH—$(CH_2)_2$], 5.58 [s, 2H, 2 H—C=C—COO (*trans*)], 6.13 [s, 2H, 2 H—C=C—COO (*cis*)], 7.47–7.98 [m, 8H, 2 Ar—COOH], 8.95–9.50 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.23 [CH_2=C—CH_3], 35.35, 38.08, 65.88 [cyclohexane], 63.15 [OCO—CH_2—C], 68.94 [COO—CH—$(CH_3)_2$], 70.80 [CH_2O—CH_2—CH], 75.02 [cyclohexane-CH_2O], 126.06 [CH_2=C—CH_3], 128.78, 129.82, 130.42, 130.95, 131.90, 133.11 [Ar], 135.97 [CH_2=C—CH_3], 167.18 [carbonyl of methacrylate], 170.94 [Ar—COO], 171.25 [COOH].

1,4-bis{[2′-(3-carboxypropanoyloxy)-3′-methacryloyloxypropoxy]methyl}-cyclohexane (**2b**): yield 86%. IR (neat): ν (cm^{-1}) 3500–2700 (br), 2925, 1724, 1637, 1201. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 0.92 [m, 2H, cyclohexane], 1.32–1.57 [m, 4H, cyclohexane], 1.66–1.87 [m, 4H, cyclohexane], 1.93 [s, 6H, 2 C=C—CH_3], 2.65 [s, 8H, 2 OOC—CH_2CH_2—COO], 3.27 [d, 4H, 2 cyclohexane-CH_2O], 3.57 [d, 4H, 2 CH_2O—CH_2—C], 4.37 [d, 4H, 2 COO—CH_2—C], 5.28 [m, 2H, 2 COO—CH—$(CH_2)_2$], 5.58 [s, 2H, 2 H—C=C—COO (*trans*)], 6.10 [s, 2H, 2 H—C=C—COO (*cis*)], 8.90–9.55 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.32 [CH_2=C—CH_3], 29.23, 29.30 [HOCO—CH_2CH_2—COO], 35.48, 38.21, 65.95 [cyclohexane], 63.25 [OCO—CH_2—C], 69.29 [COO—CH—$(CH_3)_2$], 70.81 [CH_2O—CH_2—CH], 75.11 [cyclohexane-CH_2O], 126.08 [CH_2=C—CH_3], 136.05 [CH_2=C—CH_3], 167.12 [carbonyl of methacrylate], 171.70 [OOC—CH_2CH_2—COOH], 177.21 [COOH].

2,2-bis{4-[2′-(2-carboxybenzoyloxy)-3′-methacryloyloxypropoxy]phenyl}propane (**3a**): yield 77%. IR (neat): ν (cm^{-1}) 3500–2800 (br), 2967, 1720, 1638, 1602, 1581, 1285, 1247. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.56 [s, 6H, Ar_2—C—$(CH_3)_2$], 1.91 [s, 6H, 2 C=C—CH_3], 4.25 [d, 4H, 2 Ar—O—CH_2], 4.59 [d, 4H, 2 COO—CH_2—C], 5.56 [s, 2H, 2 H—C=C—COO (*trans*)], 5.70 [m, 2H, 2 COO—CH—$(CH_2)_2$], 6.12 [s, 2H, 2 H—C=C—COO (*cis*)], 6.73–7.20 [dd, 8H, 2 C—Ar—O], 7.42–8.10 [m, 8H, 2 Ar—COOH], 8.30–9.15 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.34 [CH_2=C—CH_3], 31.12 [Ar_2—C—$(CH_3)_2$], 41.84 [Ar_2—C—$(CH_3)_2$], 62.92 [OCO—CH_2—C], 65.81 [COO—CH—$(CH_2)_2$], 71.24 [Ar—O—CH_2—CH], 114.24, 127.90, 143.89, 156.27 [C—Ar—O], 126.45 [CH_2=C—CH_3], 128.91, 130.07, 131.12, 132.37, 133.16 [OCO—Ar—COO], 135.95 [CH_2=C—CH_3], 167.18 [carbonyl of methacrylate], 171.65 [Ar—COO], 171.90 [Ar—COOH].

2,2-bis{4-[2′-(3-carboxypropanoyloxy)-3′-methacryloyloxypropoxy]phenyl}propane (**3b**): yield 79%. IR (neat): ν (cm^{-1}) 3500–2800 (br), 2967, 1740, 1638, 1608, 1583, 1237, 1159. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.61 [s, 6H, Ar_2—C—$(CH_3)_2$], 1.92 [s, 6H, 2 C=C—CH_3], 2.63 [s, 8H, 2 OOC—CH_2CH_2—COO], 4.10 [d, 4H, 2 Ar—O—CH_2], 4.45 [d, 4H, 2 COO—CH_2—C], 5.45 [m, 2H, 2 COO—CH—$(CH_2)_2$], 5.58 [s, 2H, 2 H—C=C—COO (*trans*)], 6.10 [s, 2H, 2 H—C=C—COO (*cis*)], 6.65–7.20 [dd, 8H, 2 C—Ar—O], 9.75–10.10 [br, 2H, 2 COOH]. ^{13}C-NMR ($CDCl_3$, 300 MHz): δ 18.30 [CH_2=C—CH_3], 29.02 [HOCO—CH_2CH_2—COO], 31.10 [Ar_2—C—$(CH_3)_2$], 41.85 [Ar_2—C—$(CH_3)_2$], 62.90 [OCO—CH_2—C], 66.22 [COO—CH—$(CH_2)_2$], 70.37 [Ar—O—CH_2—CH], 114.22, 127.90, 143.94, 156.26 [Ar], 126.36 [CH_2=C—CH_3], 135.89 [CH_2=C—CH_3], 167.04 [carbonyl of methacrylate], 171.54 [OOC—CH_2CH_2—COOH], 177.75 [COOH].

Measurement of Polymerization Shrinkage

Photocurable pastes were formulated using a weight ratio of monomer : CQ : DMAEMA of 100 : 1 : 1. The measurements of polymerization shrinkage were conducted according to the previously reported method.[6,7] The test apparatus consists of a dilatometer tube containing a microcapillary graduated in divisions of microliters attached to a 25-mL density bottle by means of a ground glass fit. All the measurements were conducted in a water bath operating at 25 ± 0.1°C, and three or four specimens were measured for each monomer. The shrinkage values obtained are quite reproducible and are in good agreement with the previously reported results. For example, the shrinkages of bis-GMA and TEGDMA were determined to be 5.2% (lit.[8] 5.2%) and 14% (lit.[9] 13.8%), respectively.

Three-Point Bending Test

The ratio of monomer : TEGDMA : filler : CQ : DMAEMA of 28 : 12 : 60 : 0.40 : 0.40 was used for each formulation. The samples were prepared by inserting the mixed paste into Teflon molds, covering the open ends with polyethylene films, and irradiating each side for 80 s. A three-point bending test was carried out to evaluate the flexural strength of the cured specimens with a universal testing machine (Instron 6022) at a crosshead speed of 0.75 mm/min. The sample average dimensions were 25 × 2 × 2 mm, and four or five specimens were measured for each test.

Measurement of Fluoride Release

The compositions and preparation method of the specimens were the same as those for the three-point bending test. The light-cured disk-shaped specimens (20-mm diameter and 1-mm thickness) were placed in a 100% relative humidity chamber for 1 h at 37°C. Then the samples were stored at 37°C in 25 mL of distilled water for 7 days. A fluoride ion selective electrode (Orion 920A,

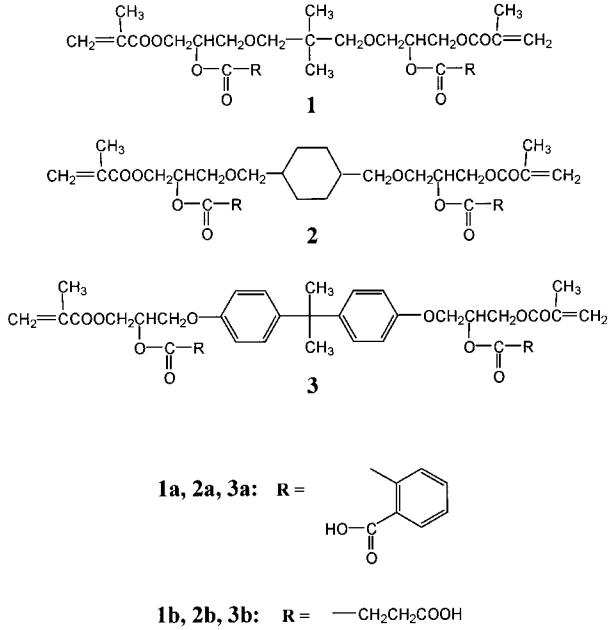

Figure 1 The structures of the dicarboxylic acid dimethacrylates.

model 94-09) was used to quantify the amount of fluoride ions released from each specimen into the distilled water. The electrode was calibrated with a 100-ppm F^- standard fluid. The ionic strength was controlled by TISAB buffer. An experimental curve of relative millivolts versus F^- concentration was generated by the use of various buffered dilutions of the standard solution. The total amount of fluoride released into the distilled water was calculated from the calibration curve. Each datum point was the average of two samples.

RESULTS AND DISCUSSION

Synthesis and Physical Properties of Monomers

New dental monomers simultaneously have two MA and two carboxyl groups in a single molecule (Fig. 1). This type of monomer would be able to not only form a crosslinked network by radical polymerization but also undergo an acid–base neutralization reaction with cations liberated from the glass particles.[10] Incorporation of carboxyl groups into a DMA monomer was expected to provide the advantages of fluoride release and adhesion to tooth substrates.

As exemplified by the preparation of **1a** (Fig. 2), the diepoxy compounds reacted with methacrylic acid to afford the DMA intermediates, which were converted to the dicarboxylic acid DMAs by the reaction with succinic or phthalic anhydride. The monomers were obtained as pale yellow oils except for **3a** and **3b,** which solidify at room temperature, and their structures were fully characterized by ^{1}H- and ^{13}C-NMR and FTIR spectra. The monomers are highly soluble in bis-GMA, UDMA, and TEGDMA.

Table I summarizes the viscosities of the new monomers and three comparison monomers (bis-GMA, UDMA, and TEGDMA). The monomers with higher molecular weights tend to show higher viscosity values. The dicarboxylic acid monomers having 2-carboxybenzoyloxy groups showed higher viscosities than those having 3-carboxypropanoyloxy groups. The viscosities of the monomers were greatly reduced by adding the diluent TEGDMA.

Photopolymerization

Photocurable formulations comprising a DMA monomer with a mixture of CQ and DMAEMA as

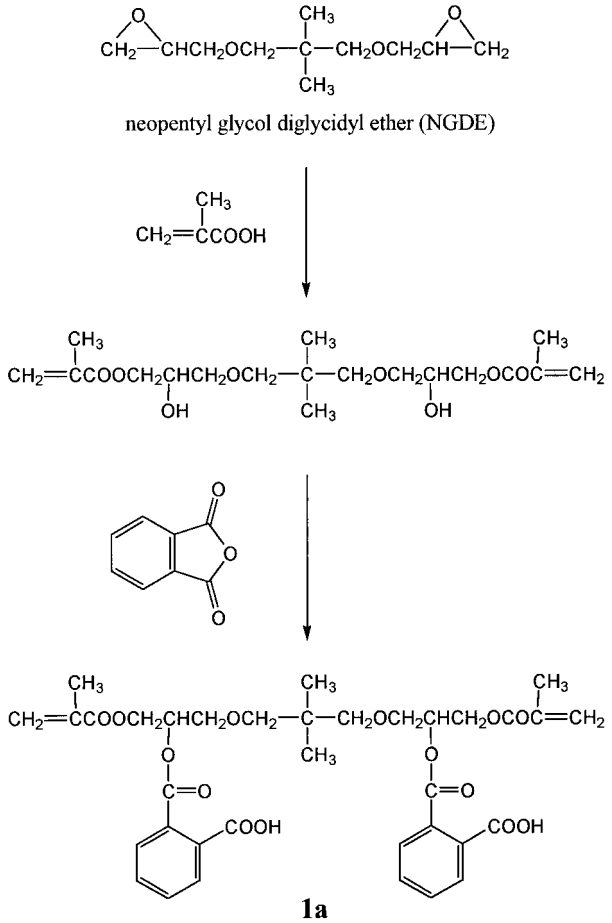

Figure 2 The synthesis of **1a.**

Table I Molecular Weights and Viscosities of Methacrylate Monomers

Monomer	Molecular Weight	TEGDMA (wt %)	Viscosity (Pa s)
1a	685	0	2,100
		20	12
		40	5.2
1b	589	0	48
		20	3.7
		40	1.5
2a	491	0	820
2b	443	0	5.8
3a	809	0	11,000
3b	713	0	3,100
bis-GMA	513	0	2,500
		20	27
		40	3.1
UDMA	471	0	40
		20	5.3
		40	0.92
TEGDMA	286	—	0.0052

All molecular weights and viscosities were measured at 30°C, except for **3a** and **3b,** which were measured at 50°C.

a photoinitiating system[11,12] were irradiated with visible light (420–500 nm), and their photopolymerization behavior was investigated by FTIR spectroscopy. The absorption at 1637 cm^{-1} representing the MA C═C stretching vibration gradually decreased with increasing exposure time, indicating photopolymerization of the monomers (Fig. 3). The ratios of the calculated areas of the two absorption bands (1637 cm^{-1} for C═C and 1722 cm^{-1} for C═O) before and after exposure

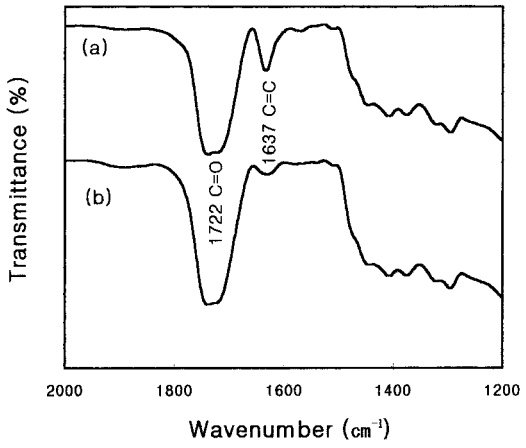

Figure 3 The IR spectral change of **1b** (a) before and (b) after visible light exposure for 60 s.

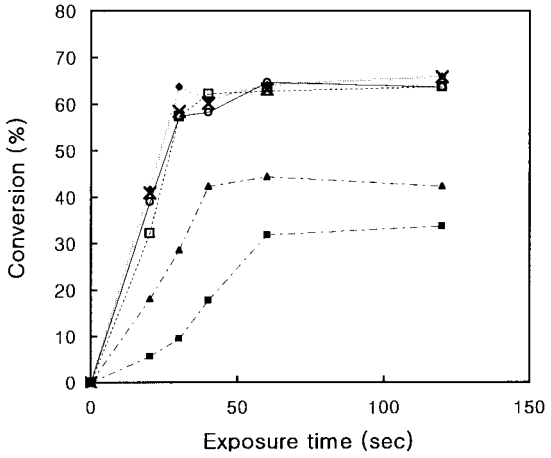

Figure 4 A plot of conversions of **1a** vs. exposure time at various concentrations of the CQ-DMAEMA photoinitiating system: (■) 0.3%, (▲) 0.6%, (□) 1.0%, (○) 1.5%, (×) 2.0%, and (◆) 3.0% for CQ (wt %).

were compared to determine the degree of conversion of the MA C═C bonds.[13] The absorption band at 1722 cm^{-1} was used as an internal standard for the conversion determination. As shown in Figure 4, **1a** revealed saturated conversions when irradiated for 60 s and no appreciable increase in conversion upon prolonged exposure.

The conversions of the monomers are summarized in Table II. UDMA showed the highest conversion of 91%, and **1b** was relatively high at

Table II Polymerization Conversion and Volumetric Polymerization Shrinkage of Monomers and Flexural Strength of Composites

Monomer	Degree of Conversion[a] (%)	Polymerization Shrinkage[a] (%)	Flexural Strength[b] (MPa)
1a	63	3.3 (0.1)	61 (7)
1b	74	6.4 (0.1)	43 (5)
2a	61	5.4 (0.1)	56 (3)
2b	57	5.7 (0.2)	47 (3)
3a	56	2.0 (0.0)	52 (7)
3b	55	2.8 (0.1)	52 (6)
bis-GMA	61	5.2 (0.1)	62 (6)
UDMA	91	8.5 (0.2)	66 (5)
TEGDMA	45	14 (0.2)	—

[a] Photoirradiation was carried out on the monomers containing 1 wt % CQ and 1 wt % DMAEMA. The mean values of shrinkage are listed with standard deviations in parentheses.

[b] The weight ratio of monomer : TEGDMA : filler : CQ : DMAEMA of 28 : 12 : 60 : 0.40 : 0.40 was used for each composite formulation. The mean values of flexural strength are listed with standard deviations in parentheses.

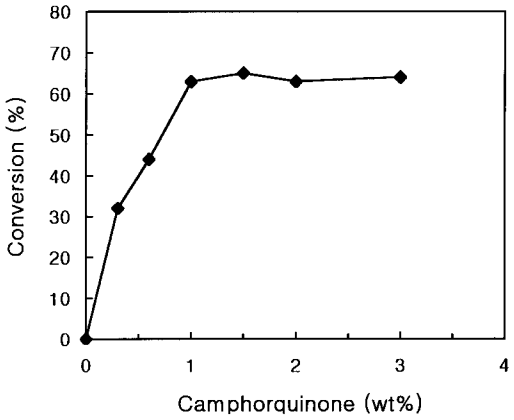

Figure 5 A plot of conversions of **1a** vs. the concentration of CQ after being exposed for 60 s.

74%. The other monomers revealed conversions of about 60% except TEGDMA, which showed the lowest 45% conversion.

The effect of varying the concentration of the CQ-DMAEMA photoinitiating system on the degree of conversion of the MAs was investigated. The weight ratio of CQ and DMAEMA was nearly unity in all the cases. When the sample derived from **1a** was exposed, the degree of conversion increased with increasing amounts of the photoinitiating compounds as shown in Figures 4 and 5. However, a maximum conversion value was reached at the concentration of 1% and a further increase in the amount of CQ-DMAEMA rendered no appreciable change in conversion.

Polymerization Shrinkage

Volumetric polymerization shrinkages of the monomers were measured using a weight ratio of monomer : CQ : DMAEMA of 100 : 1 : 1. A test method was employed that was based on the water level drop in a capillary tube attached to a pycnometer containing a material exhibiting polymerization shrinkage.[6,7] The shrinkage values of the unfilled resins were attained with good reproducibility and are listed in Table II.

The polymerization shrinkage of the MAs decreased with increasing molecular weight except UDMA and **1b** (Fig. 5). It has been reported that the polymerization shrinkage value decreases when the molecular volume is increased.[9] The relatively high shrinkage values of UDMA and **1b** are attributable to their high polymerization conversions (91 and 74%, respectively).[6] TEGDMA showed the highest shrinkage of 14% (lit.[9] 13.80%), despite its relatively low conversion. Compounds **1a, 3a,** and **3b** showed lower shrinkage values than the traditional dental monomers UDMA and bis-GMA. A reduction of polymerization shrinkage results in improvement of the clinical performance of composite restorations.[14]

Flexural Strength and Fluoride-Releasing Property

Three-point bending tests and measurements of fluoride release for nonoptimized composites formulated with the dicarboxylic acid DMAs were performed to evaluate their applicability as dental monomers. The composite specimens were prepared by mixing a DMA monomer, TEGDMA, CQ, DMAEMA, and a fluoroaluminosilicate glass, followed by irradiation with visible light. Of the composites derived from the dicarboxylic acid DMAs, the **1a** sample exhibited the highest flexural strength, which was comparable to those of the composites of bis-GMA and UDMA (Table II).

Disk-shaped specimens prepared by light curing were stored at 37°C in distilled water for 7 days to evaluate the fluoride-releasing property of the composites. The cumulative amount of fluoride ions released from each specimen into the distilled water was measured using a fluoride ion-selective electrode. The composites based on the dicarboxylic acid monomers released higher amounts of fluoride than those of bis-GMA and UDMA (Table III), implying that carboxyl groups promote the fluoride release. The fluoride release from the composites made from the dicarboxylic acid monomers might result from an acid–base reaction between carboxyl groups and fluoroalu-

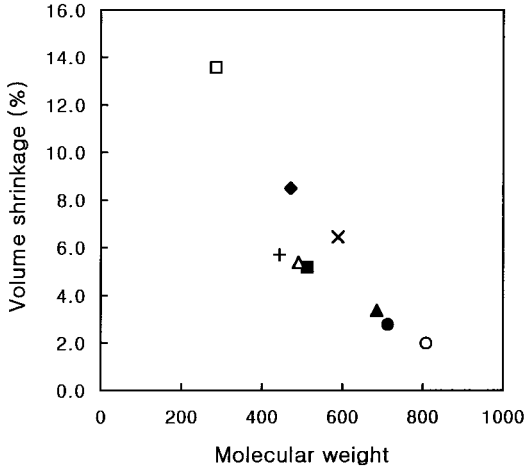

Figure 6 A plot of the volumetric polymerization shrinkage vs. molecular weight for the methacrylate monomers.

Table III Fluoride Release of Composites

Monomer	Fluoride Release[a] ($\mu g/cm^2$)
1a	23.6
2b	34.9
Bis-GMA	12.6
UDMA	13.5

[a] The values are the cumulative amount of fluoride released over 7 days. A ratio of monomer : TEGDMA : filler : CQ : DMAEMA of 28 : 12 : 60 : 0.40 : 0.40 was used for each composite formulation.

minosilicate glass with the aid of water diffused into the cured composites.[10] However, in this work it was difficult to clarify the mechanism of the fluoride release and further research is required.

CONCLUSIONS

Except for **3a** and **3b,** the new dicarboxylic acid DMAs showed lower viscosities than bis-GMA. The photopolymerization conversions of the dicarboxylic acid monomers were comparable to that of bis-GMA. Monomers **1a, 3a,** and **3b** produced lower polymerization shrinkages than the conventional UDMA and bis-GMA. Monomer **1a** is the most promising for dental applications because of its relatively high flexural strength, low shrinkage value, and fluoride release. Further tests are in progress for the dicarboxylic acid DMAs as dental monomers, including bond strength to tooth substrates, and the results will be described elsewhere.

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