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Synthesis of BISGMA derivatives, properties of their polymers and composites

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2,2-Bis[4-(2 hydroxy-3-methacryloyloxy propoxy) phenyl] propane (BisGMA) is commonly the main component of the organic matrix of dental filling materials. Derivatives of BisGMA were synthesized from the diglycidyl ether of Bisphenol A (DGEBA) by the parallel reaction with methacrylic acid (MAA) and isophthalic acid as well as mixtures of methacrylic anhydride with palmitic acid and acetic anhydride, respectively, whereby MAA was partially substituted by the latter components. By this technique the structure of BisGMA monomer could be varied with regard to weight content of C=C double bonds, the hydrophilicity of the molecule as well as its flexibility or stiffness. Free-radical initiated homopolymerization of the monomers was carried out at 80 °C. Composites, prepared from mixtures of monomers with triethylene glycol dimethacrylate (TEGDMA) filled with 76% silica were room temperature polymerized using both redox and photoinitiated techniques. The polymerization shrinkage, diffusion coefficients of water in the crosslinked polymer, and some thermal properties of the homopolymers were determined. Mechanical properties of the resulting polymers and composites are compared to those of BisGMA itself.

1. Introduction

Current composite dental filling materials derive directly from the now classical work of R. Bowen [1] in 1962. In particular, it was the development of the monomer 2,2-Bis[4-(2 hydroxy-3-methacryloyloxy propoxy) phenyl] propane, usually termed BisGMA, which seemed to be crucial. Related lower viscosity aromatic dimethacrylates have been developed [2, 3], furthermore, urethane dimethacrylates, which possess lower viscosities, replace BisGMA in some commercial dental composites.

A disadvantage of BisGMA is its high viscosity caused by hydrogen bonding between hydroxyl groups in the alkyl chain (Fig. 1), necessitating a diluent monomer.

The diluent monomer is usually triethylene glycol dimethacrylate (TEGDMA), but both BisGMA and TEGDMA increase the hydrophilicity of the composite leading to the deterioration of mechanical properties in an aqueous environment [4].

Another important aspect of the monomer phase is that it undergoes polymerization shrinkage. Since it has been shown that methacrylates shrink about 22.4 cm^3 per mole polymerized C=C double bond [5], it is clear that polymerization shrinkage can be reduced by utilizing monomers of large molar volume, such as BisGMA and of course, by the inclusion of an inorganic filler. The diluent monomer will increase shrinkage if its molar volume is lower than that of BisGMA, which is the case in the usual dimethacrylate monomers such as TEGDMA; therefore, the viscosity of the organic phase should be as low as possible to enable the preparation of composite pastes with a maximum content of inorganic filler and a minimum of diluent monomer.

In the current work, chemical derivatives of BisGMA have been synthesized by esterification of hydroxyl groups [6] and the mechanical properties evaluated. They possess increased molar volumes compared to BisGMA and consequently exhibit a lower polymerization shrinkage.

2. Materials

Methacrylic acid (MAA) (99.5 wt % acid, stabilized with 200 ppm hydroquinone monomethyl ether (HQME)), methacrylic anhydride (>90 wt %, stabilize with 2000 ppm Topanol A), triethylene glycol dimethacrylate (TEGDMA) (>92 wt %, stabilized with 200 ppm HQME), all kindly donated by Röhm Chemische Fabrik GmbH, diglycidyl ether of Bisphenol-A (DGEBA) (EPILOX 17.01 from Leuna-Werke AG, epoxy value (groups) = 5.81 eq·kg^{-1}), palmitic acid and isophthalic acid (Laborchemie Apolda), 2,6-di-tert-butyl-p-cresol (Ionol) (Merck–Schuchardt), Lucidol CH50, (Bonar Polymers Ltd) a 1:1 wt/wt master batch of benzoyl peroxide ((BPO) with dicyclohexyl phthalate) and dimethyl-p-toluidine were all used as received.

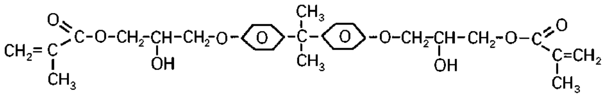

Figure 1 Chemical structure of BisGMA.

Acetic anhydride was purified by distillation and 2,3-dimethylpyridine (DMP) (Laborchemie Apolda) was purified as described in [7].

BisGMA was synthesized by the reaction of DGEBA with MAA (1:2 mol/mol) in the presence of 0.8 mol % of DMP as a catalyst and 0.03 wt % Ionol at 90–100 °C [8].

Quartz powder (Keradenta-Werk Radebeul, average diameter $d = 20$ μm) was silanized with 0.5 wt % 3-trimethylsilylpropyl methacrylate (Fluka AG) before use. The silanized quartz powder was mixed with fumed silica (Wacker HDK) to give a mixture containing 2.63 wt % of fumed silica.

2.1. Synthesis of BisGMA derivatives

Three derivatives of BisGMA were prepared by the competitive reaction of DGEBA with (i) MAA, palmitic acid and methacrylic anhydride (molar ratios = 0.5:0.4:0.3:0.3) (derivative D1); (ii) with MAA and isophthalic acid (molar ratios = 0.5:0.95:0.05) (D2); and (iii) with MAA, methacrylic as well as acetic anhydride (molar ratios = 0.5:0.1:0.45:0.45) (D3), respectively. The parallel reactions were catalyzed in a similar manner to the synthesis of BisGMA (for D1 and D3) but in the case of D2, only 0.5 mol % DMP was used as catalyst. The amounts of Ionol were somewhat increased (D1:0.04 wt %, D2:0.075 wt %, D3 0.05 wt %) to avoid any spontaneous thermal polymerization that might occur during synthesis. The reactions were carried out at 90–100 °C (for D1 and D3) and at 110 °C for D2, until a conversion of $\geqslant 95\%$ of epoxy and carboxylic acid groups was attained (5–8 h). The functional groups were determined during the reaction as described in [8]. The formation of the expected mixed esters D1, D2 and D3 was shown qualitatively by high-pressure liquid chromatography (HPLC) [8]. Chromatograms were recorded on a Knauer Wissenschaftliche Geräte KG apparatus equipped with a LiChrosorb RP-18 column. The gradient elution technique with acetonitrile/water (30:70 to 100:v/v) as eluent was used at a flow rate of 1.5 ml min^{-1} with UV detection at $\lambda = 275$ mm.

3. Methods

3.1. Curing

Each monomer (BisGMA, D1–D3) was mixed with 2 wt % Lucidol (1 wt % BPO) and then polymerized in moulds at 80 °C for 12 h. Composites for chemical cold curing were prepared by compounding monomer mixtures of either BisGMA, D1, D2 or D3 containing 30% w/w TEGDMA with 76% silica. BPO was added to one half of the monomer mixture (1 wt % to that with BisGMA, 1.3 wt % with D1, 0.9 wt % with D2 and 1.8 wt % with D3), while an equimolar amount of activator NN-dimethyl-p-toluidine (DMpT) relative to BPO, was added to the other half. Both monomer mixtures were thoroughly mixed with the filler. Equal weights of these two pastes were mixed for 20 s and cured in TEFLON moulds at room temperature.

Photocured specimens were prepared from similar monomer mixtures, both unfilled as well as filled (76 wt % silica) monomer mixes were prepared containing 0.2 wt % camphoroquinone and 0.3 wt % N,N-3,5-tetramethyl aniline, and curing was achieved by irradiation with visible light (λ_{max} 460 nm).

3.2. Polymerization shrinkage

The polymerization shrinkage was determined by measuring the densities of the monomers (ρ_m) BisGMA, D1, D2 and D3 and those of their heat cured polymers (ρ_p). The densities of the monomers were measured at 20 °C using a 25 ml pycnometer; the densities of the polymers were determined by the hydrostatic weighing technique.

3.3. Glass transition temperature

The glass transition temperature was determined by differential scanning calorimetry using a Perkin-Elmer DSC 7 at temperatures over the range 20° to 350 °C and with scan rates of 5, 10, 15, 20, 25, 30, 35 and 40 °C per minute. The apparent T_g were plotted against the scan rate and the actual T_g were obtained by extrapolating to zero rate.

3.4. Linear thermal expansion

Filled and unfilled samples of about 50 mm length and 5 mm diameter were prepared by curing in cylindrical moulds and thermal expansion was determined using a technique described elsewhere [11, 12].

3.5. Water sorption of composites and water diffusion in heat cured polymers

Chemically cured samples of (the ratio of BisGMA and derivatives to TEGDMA was in this case 8:2 wt/wt) 1 mm thickness and 15 mm diameter, were postcured at 37 °C for 24 h and then stored in distilled water at 37 °C for 7 days. After removal of any residual water from the surface, the samples were weighed and dried in vacuum at room temperature to constant weight and the results expressed as μg/mm^3.

Heat cured rectangular specimens (1 mm × 30 mm × 60 mm) were prepared from BisGMA and its derivatives, and used to determine their water diffusion coefficients as described elsewhere [11].

3.6. Mechanical properties

3.6.1. Diametral tensile strength

Heat cured and chemically cold cured rods of polymers and composites were prepared in teflon moulds (10 mm × 70 mm). These were cut to 10 mm lengths and broken in diametral tension using a Hounsfield Tensometer.

3.6.2. Young's modulus and flexural strength

Testing was carried out by three-point loading using a M30K J.J. Lloyd Instrument. Five rectangular specimens 10 × 60 × 2 mm were prepared by heat curing in Teflon moulds. The test was run three times for every specimen. Their effective length was 30 mm. A 500 N load cell and crosshead speed of 5 mm/min were selected to determine the Young's modulus E; the flexural strength σ_F was obtained by measuring the load applied at break.

4. Results and discussion

4.1. Synthesis of BisGMA derivatives

The derivatives D1, D2 and D3 of BisGMA are mixed esters which can be characterized by the average structural formulae and compositions shown in Figs 2–4 and Table I.

The distribution of the chemical composition of the derivative follows statistical rules and depends only on the ratio of reacting reagents. In the HPLC chromatogram of D2 (Fig. 5) peak 3 represents a very small content of an oligomer consisting of two isophthalic acid groups connecting three DGEBA groups end-capped with two methacrylic groups. However, the main components of D2 are BisGMA (peak 1) and the derivative with one isophthalic acid group (peak 2).

The chromatogram of D1 looks very similar to that of D2, with BisGMA and the palmitic mixed ester as the main components together with a very minor amount of oligomer. However, the HPLC chromatogram of D3 is more complex, with about 14 peaks. Separation of the components on a preparative scale was not carried out. Therefore, quantitative details cannot be given.

4.2. Shrinkage

The densities of monomers and polymers as well as the volume shrinkage (ΔV) and conversion of C=C double bonds, calculated using a molar shrinkage (ΔV_m) of 22.4 $cm^3 mol^{-1}$ [5] are listed in Table II.

A value of 44.4% conversion of olefinic bonds after polymerization of BisGMA compares to the value of 47% which was reported by Patel *et al.* [9] under similar conditions. The conversions are low because attainment of network structure occurs at an early stage, with immobilization of polymerizable sites due to the rigidity of the bisphenol-A units itself and hydrogen bonding between the hydroxyl groups, effectively prohibiting further polymerization. The shrinkage and the conversion of C=C double bonds of the derivatives D1–D3 correlate neither with the molecular weights of D1–D3 nor with their weight content of C=C double bonds. It is apparent that the

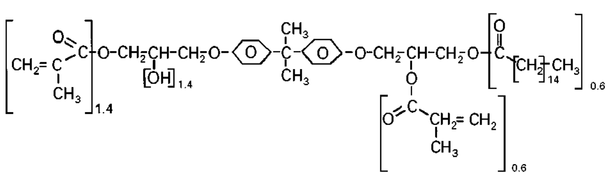

Figure 2 Average structural formula of derivative D1 with 30 mol % palmitic ester groups.

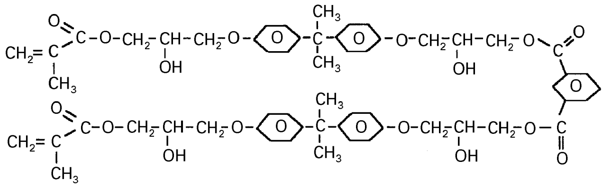

Figure 3 Structural formula of the derivative D2 which is present (10 mol %) in BisGMA.

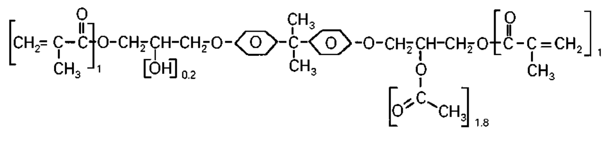

Figure 4 Average structural formula of derivative D3 with 90 mol % acetylated hydroxyl groups.

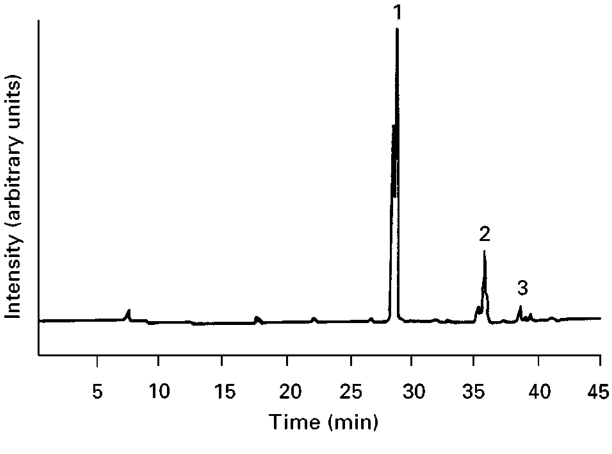

Figure 5 HPLC chromatogram of BisGMA derivative D2 synthesized from DGEBA, methacrylic acid and isophthalic acid (0.5:0.95:0.05 mol/mol) with 0.5 mol % DMP as a catalyst at 90 °C for 4 h.

TABLE I Average structure and molecular weights (MW) of BisGMA and synthesized monomeric derivatives

Monomer	MW ($g mol^{-1}$)	Functional groups per molecule Methacryloyl	 Hydroxy	 Others	 Mol C=C ($g \times 10^{-3}$)
BisGMA	512.60	2	2	–	3.90
D1	655.65	2	1.4	0.6 palmitoyl	3.05
D2	520.60	2	2.2	–	3.65
D3	588.27	2	0.2	1.8 acetoyl	3.40

TABLE II Shrinkage and conversion of C=C double bonds after polymerization with 1 wt % BPO at 80 °C for 12 h

Sample	Density ($g\,cm^{-3}$) Monomer	Polymer	Shrinkage (vol %)	Conversion of C=C double bonds (%)
BisGMA	1.1781	1.2347	4.58	44.4
D1	1.0831	1.1529	6.05	81.7
D2	1.1994	1.2266	2.22	22.6
D3	1.1553	1.2239	5.61	63.8

conversion of the double bonds depends only on the flexibility of the developing network.

The introduction of 10 mol % isophthalic acid units in D2 increases the rigidity of the network and causes polymerization to cease much earlier than in the case of BisGMA itself, while polymerization of the derivative D1 with the lowest weight content of C=C double bonds (Table I) resulted in nearly twice the conversion of BisGMA double bonds and therefore also in greater polymerization shrinkage. The plasticizing effect of 30 mol % palmitic ester groups in D1 (Fig. 2) brings about very late vitrification of the polymer network. The polymer of derivative D3 contains only 10% of the hydroxyl group content of BisGMA and here the overall hydrogen bonding is greatly reduced and the glassy state is attained at higher conversions than with BisGMA. Consequently, greater polymerization shrinkage was observed in spite of a lower molar content of C=C double bonds per gram monomer than in BisGMA (Table I).

4.3. Glass transition

DSC measurements showed that the unfilled polymers themselves are characterized by two and in the case of D2 by three transition temperatures (Table III).

Similar effects were observed by Clarke [10] and Labella *et al.* [11]. The low temperature transitions between 54° and 64 °C may be attributed to a β-transition caused by movements of the pendant branches at the network. These branches are present in a relatively high concentration in the polymers from BisGMA and D2 due to the low conversion of C=C double bonds (Table II). While the flexible palmitic ester groups of the polymer from D1 act as pendant branches, again giving rise to a β-transition even though high conversion to polymer (81.71%, Table II) occurs. The low temperature transition could not be clearly observed for the polymer of D3. Here, the higher conversion of C=C double bonds (63.8%) compared to that of BisGMA or D2 polymerization, decreases the mobility of the residual branches to such an extent that their movements are only possible within those of the chain segments between the crosslinks and are of insufficient magnitude to be detected.

The transition temperatures of the polymers between 110° and 141 °C are attributed to α-transitions. The plasticizing effect of the palmitic ester groups in the polymer of D1 is again clearly visible with $T_g = 111\,°C$. The T_g of the polymers from BisGMA, D2 and D3 were similar, in the range 133–141 °C.

TABLE III DSC transition temperatures of homopolymers from Bis-GMA and derivatives D1–D3

	Transition temperature (°C) of polymers from		
BisGMA	D1	D2	D3
64	54	63	
133	111	137	141
		211	285

Slight indications of a further thermal transition at > 200 °C were observed for all four polymers, but the evaluation was only possible in the case of poly-D2 and poly-D3. The transition temperature of poly-D2 and 211 °C may reflect post-polymerization effects with formation of a more rigid network, while the beginning of the thermal decomposition of poly-D3 is probably indicated by the transition at 285 °C.

4.4. Coefficients of linear thermal expansion of homopolymers and composites

With the exception of the unfilled polymer (D1), none of the polymers or their filled composites showed a linear change of length with temperature over the range − 20 °C to + 44 °C. Similar parabolic curves of ΔL plotted against temperature were reported in [11] for poly(BisGMA-co-tetrahydrofurfuryl methacrylate). The linear coefficient of thermal expansion (β) of poly(BisGMA) given in [12] corresponds to the lower temperature range coefficient measured here, albeit at a lower value than in [12].

The values of β for the homopolymers and their composites given in Table IV were obtained by dividing up the curves into two to three approximately linear segments.

The polymers from D1, with their flexible palmitic ester branches, have clearly the greatest β coefficients. There are no obvious differences between the β coefficients of poly(BisGMA) and poly-D2, whereas poly-D3, where hydrogen bonds are minimized, exhibits greater thermal expansion.

Qualitatively, the expected decrease in the value of β for the composites due to the addition of 76 wt % silica filler was found. For our purposes only the upper range of temperatures is clinically relevant and the changes in the value of β when filler is present are tabulated for this range only (Table IV). The filler influence is most marked for poly-D1 with 57% decrease in the value of β. The latter amounts to only 44–48% for the composites with BisGMA, D2 and D3, respectively. The linear expansion coefficient of tooth enamel $\beta = 1.14 \times 10^{-5}\,°C^{-1}$ [13] is clearly lower. It is only attainable for composites by increasing the filler content, i.e. use of BisGMA with low viscosity, and/or by use of amorphous silica with low or negative thermal expansion instead of crystalline quartz.

4.5. Water sorption and diffusion

The samples of chemically cured composites were prepared from monomer mixtures with a ratio of

TABLE IV Linear thermal expansion coefficients (β) of the homopolymers of BisGMA and derivatives D1–D3, and their composites over various temperature ranges

		BisGMA Temperature range (°C)	$\beta/10^{-5}$ (K^{-1})	D1 Temperature range (°C)	$\beta/10^{-5}$ (K^{-1})	D2 Temperature range (°C)	$\beta/10^{-5}$ (K^{-1})	D3 Temperature range (°C)	$\beta/10^{-5}$ (K^{-1})
Homopolymers	Lower temperature range	− 20–9	4.38	− 20–44	11.18	− 20–12	4.59	− 20–4 4–24	4.43 6.12
	Upper temperature range	9–44	5.42			12–44	5.31	24–44	8.43
Composites	Lower temperature range	− 20–3	2.01	− 2–12	3.38	− 20–6	1.75	− 20–0 0–8	1.99 3.14
	Upper temperature range	3–44	3.04	12–44	4.76	6–44	2.92	8–44	4.38
Percentage of β exhibited by composites over upper T_p range compared to homopolymers		56		43		55		52	

BisGMA or derivatives to TEGDMA of 8:2 wt/wt for determination of their water sorption. With this ratio the differences between BisGMA and its derivatives were expected to be observed more clearly than with the usual ratio of 7:3 wt/wt. However, different behaviour in water sorption is shown only with the composite based on D2 (Table V).

The expected hydrophobic effect due to the presence of additional aromatic units of isophthalic acid in D2 was observed. However, the hydrophobic hydrocarbon unit of the palmitic ester groups of D1 did not result in any decrease of water uptake, nor was it evident in the results obtained for water uptake of composites with D3, where 90% of the hydroxyl groups of BisGMA are substituted by hydrophobic ester groups. No decrease in water uptake was observed.

The diffusion coefficients (*D*) of water of the heat-cured polymers from BisGMA and its derivatives exhibit a difference in rate of more than an order of magnitude (Table V). The high value of $D = 20.10 \times 10^{-9}\,\mathrm{cm^2\,s^{-1}}$ of the polymer from D1 is especially remarkable. It is apparent that the flexibilizing effect of the palmitic ester groups results in regions within the material where water can diffuse very quickly and possibly form droplets according to the theory of Thomas and Muniandy [14]. The same has to be considered for D3, but to a smaller extent. Notwithstanding this, the values for water uptake of the composites themselves are similar and there appears to be no relationship between diffusion coefficient of unfilled polymer and water uptake of its filled analogue.

4.6. Mechanical properties of homopolymers and composites

The diametral tensile strength, the flexural strength and the Young's modulus of heat-polymerized homopolymers and redox polymerized composites were determined. Additionally, the diametral tensile strength was measured for photopolymerized copolymers as well as composites (Table VI).

Again, the presence of the palmitic ester groups has a drastic effect, substantially reducing modulus and strength. Otherwise, the polymers and composites from D2 and D3 compare reasonably well with those from BisGMA in terms of modulus and strength. Only, the polymers from D3 have a somewhat lower diametral tensile strength than those from BisGMA. In this context, the lower values of the diametral

TABLE V Diffusion coefficients *D* of water in heat-cured polymer mixtures containing 20 wt % TEGDMA compared to water uptake of their chemically cured composites

Polymer	D($10^{-9}\,\mathrm{cm^2\,s^{-1}}$)	Water uptake for derived composites (μg/$\mathrm{mm^3}$)
BisGMA	1.90	24.3
D1	20.10	23.7
D2	1.80	14.8
D3	6.13	28.7

TABLE VI Mechanical properties of the homopolymers of BisGMA, derivatives D1–D3 and their composites

Sample	Diametral tensile strength (MPa)	Flexural strength (MPa)	Young's modulus (GPa)
BisGMA, heat cured	44.2	82.5	4.05
BisGMA-co-TEGDMA photocured	30.3		
Composite, chem, cured	33.4	66.1	11.75
Composite, photocured	34.2		
D1, heat cured	18.7		
D1-co-TEGDMA, photocured	23.1	35.2	1.83
Composite, chem. cured	23.8	62.1	7.39
Composite, photocured	28.2		
D2, heat cured	47.1	78.6	3.68
D2-co-TEGDMA photocured	18.4		
Composite, chem. cured	38.8	76.2	11.62
Composite, photocured	34.0		
D3, heat cured	30.6	63.7	3.99
D3-co-TEGDMA, photocured	27.4		
Composite, chem. cured	27.6	84.1	12.01
Composite, photocured	32.2		

tensile strength of the chemically cured composites compared with those of the photopolymerized composites should be noted and attributed to the lower homogeneity of the former two-paste systems compared to that of the photocuring one-paste systems. The strength and modulus of these chemically cured composites correspond to those found by Labella *et al.* [15] for composites from BisGMA with 30 wt % of tetrahydrofurfuryl methacrylate as a diluent monomer and hydroxyapatite as a filler.

5. Conclusions

A simple method for the modification of the structure of BisGMA during synthesis has been developed by (i) introduction of long chain fatty acid with esterification of the hydroxyl groups (D1), (ii) partial extension of the molecule with an aromatic dicarboxylic acid (D2) and (iii) esterification of the hydroxyl groups with acetyl and methacryl functions (D3).

The viscosity of BisGMA can be decreased by use of the modification methods (i) and (iii), whereas it is increased by method (ii).

Polymerization shrinkage of the BisGMA derivatives depends only on the flexibility of the network polymers formed and does not correlate with the weight content of C=C double bonds of the derivatives. The effect of 10 mol % isophthalic ester groups (method (ii)) present in derivative D2 decreases polymerization shrinkage of BisGMA by about 50%; it also exhibits positive effects as regards the thermal expansion coefficient, some mechanical properties as well as the water uptake of the polymer and the composite material.

Hydrophobizing modifications of BisGMA by methods (i) and (iii) do not result in any decrease in water uptake of composites prepared with the derivatives (D1 and D3), and the diffusion coefficients of water absorption are actually increased. The strong flexibilizing effect of palmitic ester groups (method (i)) within the polymer network has a deliterious effect; mechanical strength as well as Young's modulus are reduced, while polymerization shrinkage and linear coefficient of thermal expansion are increased.

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