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Novel aromatic dimethacrylate esters as dental resins

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The preparation of a novel class of dimethacrylate esters, by the reaction of glycidyl methacrylate with various phthalic acid isomers and their halogen substituted derivatives is described. These monomers exhibited low viscosity, possessed similar physical and mechanical properties to bis GMA, and the presence of halogen introduced X-ray opacity into the polymer giving opacity similar to tooth enamel.

1. Introduction

Many composite materials used in conservative dentistry still utilize the Bowen monomer (2,2-bis-[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane), bis-GMA, as the polymerizable monomer phase [1]. The high viscosity of the monomer phase necessitates dilution with low viscosity dimethacrylate esters such as tri- or tetra-ethyleglycol dimethacrylate to achieve high filler loading for a successful composite. Recently less viscous monomers such as urethane dimethacrylates or ethoxylated bis-GMA (2,2-bis-[4-(2-methacryloyloxyethoxy)phenyl]propane) have been successfully utilized as the base monomers for composite restorative materials. Other dimethacrylates that have been reported in this context include the reaction product of 2-hydroxyethyl methacrylate and the isomeric phthalic acids. These esters were found to be solids although a mixture of all three gave a liquid monomer [2].

Here a novel class of low viscosity dimethacrylate esters based upon the reaction of glycidyl methacrylate (GMA) with the isomeric benzene dicarboxylic acids and some of their halogen derivatives is described. Halogen was introduced into the aromatic ring to confer X-ray opacity upon the resin in order to improve this property, which has been shown to be less than satisfactory in the majority of commercial dental composites [3]. These rely solely upon the presence of heavy metal glasses to confer X-ray opacity which can undergo some degree of hydrolysis in the oral environment [4].

2. Experimental procedures

The dicarboxylic acids as shown in Table I were used in this study.

Diacids in column I were commercially available, those in column II were synthesized by standard techniques [5, 6]. Reaction of the diacids with GMA was carried out as follows:

The diacid was stirred at 60 °C with two mol equivalents of glycidyl methacrylate in the presence of hydroquinone inhibitor and 1–2% of a tert-aromatic amine catalyst. The more insoluble acids required the addition of a few millilitres of methanol to increase solubility. The suspension was stirred overnight at 60 °C, by which time all the solid had dissolved. The resulting oil was dissolved in ether, extracted with dilute HCl, then with saturated sodium bicarbonate solution. Finally, the ether solution was dried ($MgSO_4$) and the ether removed under reduced pressure. The liquid product was filtered through a short column of activated charcoal/silica gel which removed virtually all discoloration.

An assessment of the relative viscosities of the various dimethacrylate monomers was obtained by measuring the time taken for the monomer to flow a measured distance at 25 °C through a vertical glass tube of 3 mm internal diameter with unrestricted exit. Results were recorded relative to Bis-GMA and are qualitative as quantitative measurement of viscosity by vertical flow through a capillary requires a more sophisticated design [7].

Polymer samples for testing were prepared by heat curing monomers in the presence of 2% lucidol (1/1 benzoyl peroxide/dicyclohexyl phthalate) at 80 °C overnight. The methods for determination of water uptake and thermal expansion have been described previously [8, 9]. Polymerization shrinkage was ob-

TABLE I

I	II		
		Mpt	Lit
Phthalic acid			
Iso-phthalic acid	4-Br-phthalic acid	169 °C	173 °C [5]
Terephthalic acid	3-I-phthalic acid	162 °C	161 °C [5]
5-Bro-iso-phthalic acid	5-I-iso-phthalic acid	289 °C	289 °C [6]
2-Br-terephthalic acid			

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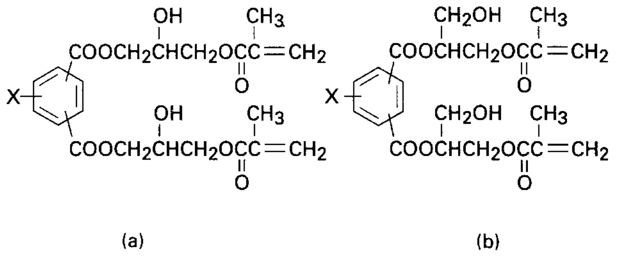
tained from the differential densities of polymer and monomer, glass transition temperatures were determined by differential scanning calorimetry (Perkin Elmer Delta Series DSC7), and diametrial tensile strength by measuring the force required to break 1 cm diameter discs of polymer (3 to 4 mm thick) in compression when applied perpendicular to the face of the disc with a crosshead speed of 1 mm min^{-1}.



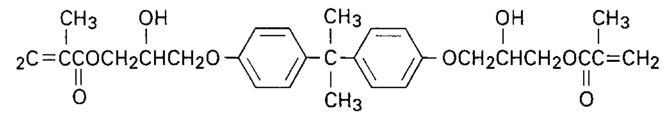
(a) (b)

Figure 1.

TABLE II

Dimethacrylate derived from	Viscosity relative to bis-GMA
Phthalic acid	0.002
Iso-phthalic acid	0.010
4-Bromo-phthalic acid	0.006
4-Bromo-iso-phthalic acid	0.006
3-iodo-phthalic acid	0.015
5-iodo-iso-phthalic acid	0.018
bis-GMA	1.000
Ethoxylated bis-GMA	0.001
Propoxylated bis-GMA	0.002
Urethane dimethacrylate	0.05
bis-GMA/TEGDM (60/40)	0.02

TEGDM: triethyleneglycol dimethacrylate.



bis-GMA

Figure 2.

3. Results and discussion

Ring opening of the epoxy group occurs predominantly at the least substituted carbon atom and nuclear magnetic resonance (NMR) spectroscopy confirmed the main reaction product to have the general structure (Fig. 1a), while the isomeric product possessing primary-OH groups (Fig. 1b) occurred to an extent of ~ 20%.

All the dimethacrylate esters prepared were liquids with the exception of that derived from terephthalic acid (m.p. 109 °C). These liquid monomers were one to two orders of magnitude less viscous than bis-GMA (Table II) even though hydroxy groups were present in the molecule.

In the bis-GMA (Fig. 2) the side chains bearing the polar groups are diametrically opposed across a relatively inflexible central ring system which precludes rotation of the –OH groups to lower energy hydrogen bonded configurations and intermolecular hydrogen bonding occurs.

In these phthalic acid derivatives, not only do the side chains possess much greater freedom of rotation they are also adjacent (Fig. 1a,b) and close approach of the participating polar groups can occur to favour intramolecular hydrogen bonding and thus produce a relatively low viscosity monomer.

Polymerization could be effected by heating the monomer at 80 °C in the presence of benzoyl peroxide, by chemical cold cure utilizing benzoyl peroxide and dimethyl-p-toluidine or by a visible light cure system with camphoroquinone and 3,5,N,N-tetramethyl aniline as radical sources. The representative physical and mechanical properties reported in Table III are for heat cured polymer samples.

The mechanical properties of all the polymers are not significantly different from those exhibited by undiluted bis-GMA and somewhat better than the commercial bis-GMA analogues. This is encouraging when halogen containing polymers are considered;

TABLE III

Dimethacrylate derived from	Shrinkage (%)	Diametral tensile strength (MPa)	T_g (DSC) (°C)	Coefficient of thermal expansion (K × 10^{-5})	Equilibrium water uptake (%)
Phthalic acid	8.70	38.3	109	8.16	4.70
Iso-phthalic acid	6.40	36.9	115	8.64	5.10
4-Br-phthalic acid	8.00	41.1	114	7.34	4.60
4-Br-iso-phthalic acid	8.20	39.8	118	5.76	4.80
3-iodo-phthalic acid	6.40	38.7	105	7.65	4.72
Bis-GMA	5.10	38.9	115	8.29	3.10
Bis-GMA/TEGDM (60/40)	9.80	40.9	122	8.25	4.41
Ethoxylated bis-GMA	7.06	32.4	125	6.38	0.62
Propoxylated bis-GMA	7.15	31.1	115	6.74	0.50
Urethane dimethacrylate	6.88	cold flow	142	8.92	2.70

TEGDM: triethyleneglycol dimethacrylate.

these were prepared to confer X-ray opacity upon the resin itself thereby reducing the necessity of relying upon barium and zirconium glasses. Preliminary investigations have shown that the iodine-containing polymers possess an X-ray opacity approximately three times that of a similar thickness of aluminium over the dental diagnostic region of the X-ray spectrum (electron beam energies 55–90 kVp), giving this polymer an X-ray opacity greater than dental enamel (the opacity of enamel is considered to be twice that of aluminium [3]).

The low viscosity of these dimethacrylate monomers, together with X-ray opacity and comparable mechanical properties suggests two potential applications:

1. As a diluent monomer for bis-GMA to enhance X-ray opacity of existing composite formulations.
2. Undiluted, as an alternative monomer to bis-GMA, where a proportion of the X-ray opacity is derived from the resin itself reducing the need to rely solely upon heavy metal glasses for X-ray contrast. Di-iodo- or tetra-bromo- derivatives would be even more successful in this context and work is continuing to prepare these monomers.

4. Conclusions

A novel class of low viscosity dimethacrylate esters is described with similar mechanical properties to undiluted bis-GMA. The halogen-substituted esters are X-ray opaque and could be used in dental composite resins either to enhance their X-ray opacity, or to reduce the need for heavy metal glass fillers.

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