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Influence of hydrogen bonding on properties of BIS-GMA analogues

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The influence of chemical structure on the important properties of composite matrix resins is being systematically investigated. This study addresses the relationships between pendent side chain structures, viscosity and curing shrinkage. In particular, viscosity is known to be greatly influenced by intermolecular interactions, such as hydrogen bonding, and free volume effects. In order to establish the relative importance of these factors, analogues of BIS-GMA were synthesized in which the pendent hydroxyl groups were replaced by trimethyl siloxyl, and by dimethyl, isopropyl siloxyl groups. The viscosities were determined with a cone and plate viscometer and curing shrinkages were determined gravimetrically. They were compared to previously determined values for BIS-GMA and its methyl and hydrogen substituted analogues. The high viscosity of BIS-GMA is drastically reduced by replacement of the hydroxyl group, or its substitution by silylation. The relatively smaller effects produced by varying the bulk of the substituted side chains indicates that the main effect on viscosity is due to the presence or absence of hydrogen bonding. Conversely, increasing the bulk of the side chain substituent has less effect on viscosity, but significantly reduces the curing shrinkage. Changes in curing shrinkages were explained in terms of effects of free volumes associated with the monomers.

1. Introduction

Many composite materials used in conservative dentistry still utilize the Bowen monomer (2,2-bis-[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane), BIS-GMA, as the main component of the polymerizable monomer phase [1–5]. The high viscosity of this monomer necessitates dilution with low viscosity dimethacrylate esters (such as di- or tri-ethyleneglycol dimethacrylate) to achieve high filler loading for a successful composite. However, increased amounts of diluent such as triethylene glycol dimethacrylate (TEGDMA) will have adverse effects on properties such as water uptake and curing shrinkage [2–4]. In order to avoid the use of increased amounts of the diluents that might produce adverse effects on the properties of the resin matrix, investigations were carried out to determine the major cause of the high viscosity associated with these resin matrices, particularly BIS-GMA. In a study of water sorption of BIS-GMA and ethoxylated bisphenol A dimethacrylate (BIS-H) based on the weight percentage oxygen content (WPO), it was revealed that BIS-GMA monomer with higher WPO (25%) than E-BIS-GMA (21.2%) sorbed relatively less water (2.35%) than E-BIS-GMA (2.6%) (Table 2, [6]). Since WPO is considered predictive of hydrophilic interactions, we expected that BIS-GMA with higher WPO would sorb more water than BIS-H. However, it took up less water than expected on the basis of WPO. This anomaly was explained as being due to the existence of intramolecular hydrogen bonds between hydroxyl and carbonyl groups [6] thus eliminating water binding sites. It has therefore been concluded that intermolecular hydrogen bonding in BIS-GMA not only reduces the water uptake but also induces high viscosity.

The present paper deals with the influence of hydrogen bonding on the properties of BIS-GMA analogues. These analogues were synthesized such that the pendent hydroxyl groups were replaced by –H, –CH_3, trimethyl siloxyl and dimethyl isopropyl siloxyl groups. The objective of the present study was to investigate the influence of hydrogen bonding on the properties, particularly bulk viscosities and curing shrinkage, of monomers.

Our working hypotheses are that:

(1) the absence of hydrogen bonding will reduce viscosity;
(2) reduced free volume in the monomer will lower the shrinkage during polymerization;
(3) substituents close to the vinyl groups will reduce the curing shrinkage.

2. Experimental procedures

2.1. Materials

The following four experimental monomers (A&B structures) were synthesized in the laboratory:

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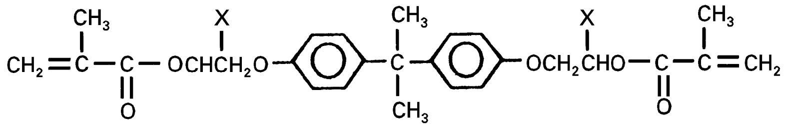
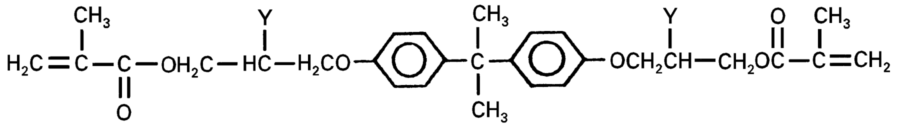
(A)



where X = H; BIS (H); {ethoxy analogue of BIS-GMA}
and X = CH_3; BIS (CH_3); {propoxy analogue of BIS-GMA}

(B)



where
Y = O Si(CH_3)trimethyl siloxy BIS-GMA
Y = O Si$(CH_3)_2CH(CH_3)_2$
dimethyl isopropyl siloxy BIS-GMA

BIS-GMA was obtained from Polysciences, Inc., Warrington, PA, and used as received. It was used as a comparison standard for the experimental monomers: the structure of BIS-GMA is structure B where Y = –OH.

2.2. Methods

The four monomers were synthesized as follows.

2.2.1. *Ethoxy analogue of BIS-GMA*

This was synthesized by the ethoxylation of bis-phenol using ethylene carbonate and tetra ethyl ammonium iodide, and subsequent methacrylation of this product using methacryloyl chloride (3.5 mole for 1 mole of ethoxylated bisphenol A) in the presence of triethylamine as acid scavenger and tetrahydrofuran (THF) as solvent.

2.2.2. *Propoxy analogue of BIS-GMA*

Bisphenol A was treated with propyleneoxide in the presence of NaOH/THF and the reaction product was isolated. It was treated subsequently with 3 moles of methacryloyl chloride per mole of product, together with triethyl amine in tetrahydrofuran (THF) solvent to obtain BIS-GMA (CH_3).

2.2.3. *Trimethyl siloxy analogue of BIS-GMA*

BIS-GMA was refluxed in benzene for 5 h together with 2 moles of trimethyl silane amine and di t-butyl p-cresol (inhibitor). After 5 h refluxing, the reaction mixture was subsequently washed with dilute HCl and saturated sodium chloride solution. After the removal of solvent under vacuum at room temperature, the final product was purified by column chromatography (silica gel 90/10 v/v hexane/ethyl acetate).

2.2.4. *Dimethyl isopropyl siloxy analogue of BIS-GMA*

Bis-phenol A (1 mole) was refluxed in benzene overnight in the presence of 3 moles of dimethyl isopropyl silyl chloride per mole, triethylamine, N,N^1-dimethyl amino pyridine and di t-butyl p-cresol. The amine hydrochloride salt was filtered and the final purified product was obtained by a similar procedure to that used for the preparation of trimethyl siloxy analogue. Final product was identified by spectral analysis, as dimethyl isopropyl siloxy BIS-GMA.

2.2.5. *Characterization*

Fourier transform infrared spectroscopy (FTIR) (Nicolet 2000) and proton nuclear magnetic resonance (NMR) (varian 400 MHz) were used to characterize the reaction products.

Viscosities of the experimental monomers were determined by cone and plate viscometer. Curing shrinkages were calculated by density measurements.

Contact angle measurements were made using a contact angle goniometer (Model 100–00, Rome-Hart, Mountain Lakes, NJ) [6–8].

3. Results

Table I summarizes the data on bulk viscosities and curing shrinkages for all the experimental monomers.

Table II presents the data for all the experimental monomers with reference to their contact angles on glass, PMMA, enamel and dentin surfaces.

Fig. 1 shows a transmission FTIR spectrum of BIS-GMA. At 3458 cm^{-1}, the broad absorption band corresponds to –OH of the BIS-GMA. Disappearance of this signal, as shown in Fig. 2, indicated the completion of the silylation process with replacement of the –H in the –OH group either by $Si(CH_3)_3$ or $-Si(CH_3)_2CH(CH_3)_2$. Spectral analysis also revealed the presence of carbonyl and vinyl groups, as shown by absorption bands at stretching frequencies of 1728 cm^{-1} and 1638 cm^{-1}, respectively.

TABLE I Viscosity and curing shrinkage of nonsilylated and silylated BIS-GMA

Monomer	Viscosity (Pa s)	Cure shrinkage %
BIS-GMA	1200	6.4
BIS GMA-H	3.0	8.0
BIS GMA CH_3	0.32	7.5
Trimethyl silylated BIS-GMA	6.5	5.6
Dimethyl isopropyl silylated BIS-GMA	2.7	4.2

TABLE II Contact angles of pure monomer (in degrees)

Monomer	Contact angle on: Glass	PMMA	Enamel	Dentin
BIS-GMA	26	17	26	16
BIS GMA (H)	34	31	38	34
BISGMA (CH$_3$)	19	14	16	11
Trimethyl silylated BIS-GMA	20	18	19	17

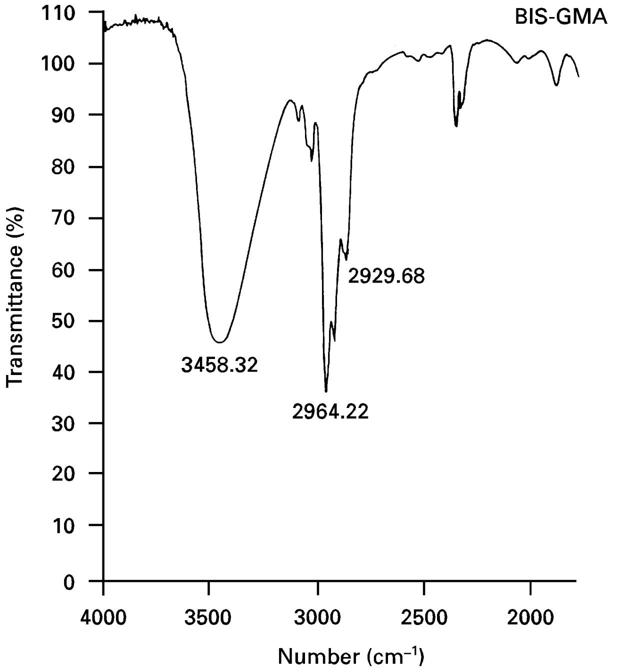


Figure 1 FTIR spectrum showing the presence of the hydroxyl group in BIS-GMA at a stretching frequency of 3458.32 cm^{-1} before silylation.

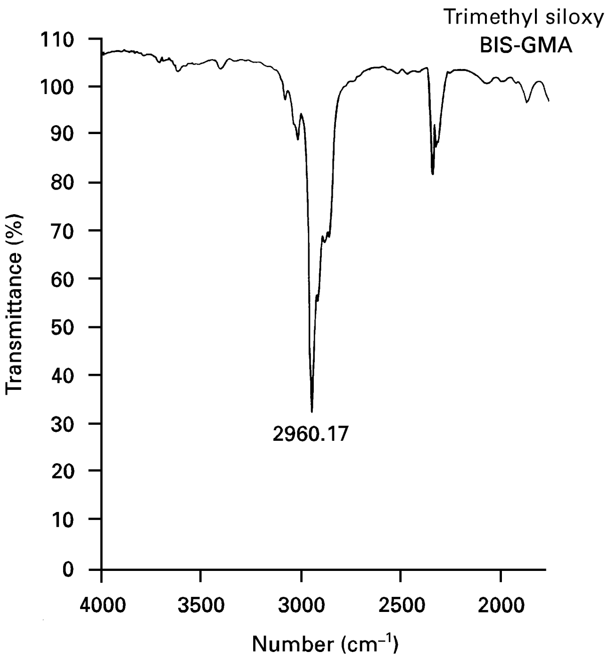


Figure 2 FTIR spectrum showing the disappearance of the hydroxyl group (in BIS-GMA) after the completion of silylation reaction involving replacement of H in –OH by a trimethyl siloxyl group.

Proton NMR analysis produced spectra consistent with the structures of the final products, namely silanated and non-silanated analogues of BIS-GMA.

4. Discussion

FTIR spectral analysis established the complete silylation of the hydroxyl groups in BIS-GMA (Figs 1 and 2).

From the analysis of the data in Table I, it was seen that BIS-GMA has the highest viscosity among all the monomers studied. The observed high viscosity (1200 Pa s) has been explained as due to the existence of intramolecular hydrogen bonds between hydroxyl and carbonyl groups [6]. Replacement of the hydroxyl group in BIS-GMA by –H and –CH$_3$ results in a significant reduction in the values of viscosities, i.e., from 1200 to 3.0 Pa s and 1200 to 0.32 Pa s. This may be attributed to the suppression of intramolecular hydrogen bonding. Replacement of –OH in BIS-GMA by silylation, also drastically reduced the viscosities from 1200 to 6.5 Pa s and from 1200 to 2.7 Pa s, as seen in the case of trimethyl siloxyl BIS-GMA and dimethyl isopropyl siloxyl BIS-GMA, respectively. These effects may also be attributed to suppression of intramolecular hydrogen bonding.

It is of interest to note that the decreases in curing shrinkage in silylated BIS-GMA analogues (trimethyl silylated BIS-GMA = 5.6%; dimethyl isopropyl silylated BIS-GMA = 4.2%) relative to BIS-GMA (6.4%) may be interpreted as due to the presence of bulkier units such as trimethyl siloxyl or dimethyl isopropyl siloxyl units close to the vinyl group (Table I). The silylated BIS-GMA analogues appear to have relatively lower free volume. These bulkier groups presumably allow polymerization to occur only in an extended or linear fashion. As a result, polymerization shrinkage has been found to be relatively lower than for BIS-GMA.

It was seen that silylated monomers exhibited reductions in both viscosity and shrinkage relative to BIS-GMA, while non-silylated monomers displayed a decrease in viscosity with an increase in curing shrinkage (Table I). The former finding may be explained as being due to differences in free volume.

5. Conclusions

1. FTIR spectral analysis established the complete silylation of hydroxyl groups in BIS-GMA.
2. Replacement of –OH group in BIS-GMA with silyl groups drastically reduces viscosity from 1200 Pa s to 2.7 Pa s.
3. Bulkier groups such as dimethyl isopropyl silane further reduced the viscosity to 2.7 Pa s from 6.5 pa s.
4. Ethoxylated (BIS-(H)) and propoxylated (BIS (CH$_3$)) bisphenols exhibited low viscosities (3.0 and 0.32 Pa s).
5. Non-silylated monomers displayed a drastic reduction in viscosity (from 1200 Pa s to 3.08 and 0.32 Pa s) with an increase in cure shrinkage (from 6.4% to 8.0% and 7.5%) relative to BIS-GMA.

6. Silylated monomers exhibited reduction in both bulk viscosity and curing shrinkage (6.5 to 2.7 Pa s and 5.6% to 4.2) when changed to bulkier groups such as dimethyl isopropyl silane.

Acknowledgement

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