# NOVEL DENTAL RESINS FROM TRIALKOXYSILANES AND DENTAL MONOMERS BY *IN SITU* FORMATION OF OLIGOMERIC SILYL ETHERS AND SILSESQUIOXANES

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## Inroduction

The vinyl alkyltrialkoxysilane, 3-methacryloxypropyltrimethoxysilane (MPTMS), is currently widely used as a coupling agent in dental and other acrylic polymer-based composites. In this role it is customarily applied to glass fillers either by dry blending or by deposition from a solvent in order to provide a reactive filler that will enhance both the strength and modulus of the dental polymer matrix[1]. These presilanized glass fillers are blended with chemically- or photochemically- activated monomer systems (resins) to form workable composite pastes that, on polymerization, yield strong restoratives that match the appearance of contiguous teeth and that can be bonded relatively easy (in contrast to amalgam fillings) to tooth structure.

An attractive alternative to the above presilanization methods for surface activation of the filler phase of composites is *in situ* silanization of glass fillers.[2,3] This technique is simpler than presilanization and involves adding the silane agent, e.g. MPTMS, as a comonomer to the usual dental monomer systems, and then forming a composite paste by admixture with unsilanized glass filler. While it has been shown (by indirect mechanical tests) that the *in situ* silanization provides effective coupling of the glass and polymer matrix phases, it is not clear that the silanization reaction only occurs between the silanol groups of the glass filler (**Figure 1**) and the -Si$(OCH_3)_3$, –Si$(OH)_3$, etc. groups of MPTMS. It appears plausible that there can also be exchange reactions occurring between MPTMS and the hydroxyl groups of hydroxylated monomers such as 2,2-bis[p-(2'-hydroxy-3'-methacryloxy-propoxy)phenyl]propane (Bis-GMA) (see **Figure 2**, reaction (2)), resulting in the formation of silyl ether derivatives of Bis-GMA. All polar dental monomers such as Bis-GMA, triethylene glycol dimethacrylate (TEGDMA) and 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (UDMA) (an aliphatic diurethane dimethacrylate derived from the reaction of 2-hydroxyethyl methacrylate and trimethyl-1,6-diisocyanatohexane) have hydrophilic functional groups, e.g. hydroxyl, ethylene oxide, and urethane groups, respectively, that can serve as sites for water absorption. Because of the ubiquitous presence water in these polar monomers, it is conceivable that MPTMS also can undergo hydrolysis-condensation reactions to form oligomeric silsesquioxane products. The objectives of this study were to explore not only reaction of MPTMS and similar silane agents with Bis-GMA to form silyl ether derviatives, but also to study their interaction with non-hydroxylated types of dental monomers of varying polarity.

## Experimental*

The dental monomers (Esstech) 2,2-bis[p-(2'-hydroxy-3'-methacryloxy-propoxy)phenyl]propane (Bis-GMA), ethoxylated bisphenol A deimethacrylate (EBPADMA), triethylene glycol dimethacrylate (TEGDMA) and 1,6-bis(methacryloxy-2-ethoxycarbonylamino)-2,4,4-trimethylhexane (urethane dimethacrylate or UDMA) were mixed neat at 22 °C with MPTMS (Aldrich) at a mole ratio of dental monomer/MPTMS of 1.5. After a clear solution was obtained by mechanical stirring (usually within 30 min.), the mixtures were heated at 60 °C in tared opened vials until no further mass loss was observed (usually a period of 31 d). Because the mass loss of TEGDMA/MPTMS was low compared to the other systems heating was continued for an additional 30 d. The viscosities of the final products were visually compared to those of the starting mixtures. Fourier Transform Infrared (FTIR) spectroscopy was used to analyze both the starting monomer/MPTMS mixtures and their final products. Spectra were acquired by coadding 100 scans at 4 wavenumber resolution (wavenumber relative uncertainty of 0.5 $cm^{-1}$). The interactions of n-propyltrimethoxysilane, allyltrimethoxysilane and vinyltrimethoxysilane (all from Aldrich) with these monomers also were studied.

## Results

For Bis-GMA/MPTMS the mass loss after 31 d was 9 %; a significant increase in viscosity occurred compared to that of the starting mixture. FTIR analysis (**Figure** 3) of the colorless, viscous liquid product showed a significant decrease in the broad absorption band of the hydrogen-bonded hydroxyl groups of Bis-GMA in the 3650 $cm^{-1}$ to 3150 $cm^{-1}$ region. In addition, the CH absorption band at 2842 $cm^{-1}$, attributable to –Si $(OCH_3)_3$, no longer was present. New bands appeared in the 1000 $cm^{-1}$ to 1200 $cm^{-1}$ region that are expected to arise from Si-O-Si linkages of the silsesquioxanes products derived from the hydrolysis-condensation reactions of MPTMS[4], and from silyl ether derivatives of Bis-GMA, although no specific C-O-Si bands were identified. Thus, the overall spectral results suggest that significant amounts of the OH groups of Bis-GMA were converted to silyl ether derivatives by a transetherification exchange reaction with MPTMS and that silsesquioxanes products also formed.

In the case of EBPADMA/MPTMS the mass loss was about 8% and a modest increase in viscosity accompanied this loss. Because of the absence of –OH groups and other sources of labile hydrogens in this monomer, silyl ether formation was ruled out. However, FTIR analysis again showed virtually complete loss of the methyl silyl group of MPTMS (2842 $cm^{-1}$) and the appearance of absorption bands attributable to silsesquioxane formation. Apparently, the presence of modest amounts of water in this relatively hydrophobic monomer is still enough to convert MPTMS to silsesquioxane products via the apparently uncatalyzed hydrolysis-condensation reactions of the methyl silyl ether groups.[5]

A similar reaction occurred with TEGDMA/MPTMS. After 31 d the pale yellow liquid had lost only about 1.3 % and had only a slightly higher viscosity than the starting mixture. Continued heating (30 d) resulted in greater mass loss (3.5 %), but during the last days of this extra heating period it polymerized to a hard, pale yellow glassy solid. FTIR analysis of the polymer indicated that only silsesquioxane formation had occurred in the TEGDMA/MPTMS blend.

After 31 d the mass loss of the UDMA/MPTMS product had leveled off at 10 % and a significant increase in viscosity was noted for this blend, greater than that observed with EBPADMA and TEGDMA, but less than that of the BisGMA/MPTMS blend. Although the highly polar structure of UDMA with two potentially labile hydrogens in its urethane group would seem to make this monomer a possible candidate for an exchange reaction with MPTMS, FTIR analysis of the reaction product mixture again showed only loss of the methoxysilyl group (2842 $cm^{-1}$) and the presence of absorption bands attributable to silsesquioxane structure. Results similar to those observed with MPTMS were found to occur with the other trimethoxysilanes and Bis-GMA, EBPADMA or UDMA, respectively.

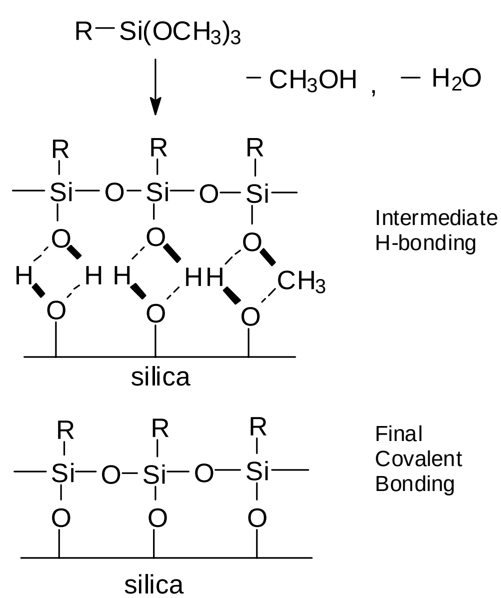


**Figure 1**. Simplified reaction of alkoxysilane with silica surface

**Discussion**

Two mechanistic pathways exist for the reaction of Bis-GMA with MPTMS: (1) silyl ether formation by an exchange or transetherification reaction involving the $–Si\text{-}OCH_3$ groups of MPTMS with the hydroxyl groups of Bis-GMA and, (2) due to the presence of $H_2O$ in this hydroxylated dental monomer (or from the ambient atmosphere), MPTMS also can undergo a series of hydrolysis-condensation reactions via its $–Si(OCH_3)_3$ groups, leading to silsesquioxane formation. **Figure 2** depicts the two possible pathways for these reactions.

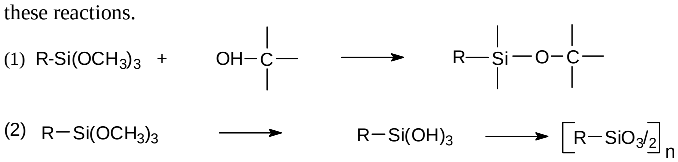


**Figure 2.** Mechanistic pathways in dental monomer/MPTMS reactions

The first and second mechanistic pathway applies to the interaction of these silanes with Bis-GMA only. The second mechanistic pathway prevails with TEGDMA, EBPADMA and even the more highly polar UDMA, (that has potentially polarizable urethane groups) and only silsesquioxane formation was observed. These results are similar to those from a previous study in which it was demonstrated that polymeric silsesquioxanes such as those derived from MPTMS could be obtained by hydrolysis–condensation reactions in aqueous acetone without a catalyst.[5]

The interaction of these dental monomers with other trialkoxysilanes, such as n-propyltrimethoxysilane, vinyltrimethoxysilane and allyltrimethoxysilane, occurs by the same mechanistic pathways. In the reaction of Bis-GMA with the silane, the predominant products were in every case silyl ether derivatives, whereas EBPADMA/TEGDMA and UDMA served only as polymerizable solvents for the *in situ* formation of oligomeric silsesquioxanes. The water content of the monomer also may be a factor in controlling the amount of silsesquioxanes formed from the silane. For example, in contrast to Bis-GMA, a recent study with the more hydrophilic glyceryl methacrylate containing (in a mole ratio of 1.5) MPTMS yielded more oligomeric silsesquioxane products than silyl ether derivatives, presumably because of the greater water content of glyceryl monomer. These reactions of silanes directly with hydroxyl groups of monomers or with water present in non-hydroxylated monomer can provide facile routes to novel types of dental resins that can combine acrylic and silicon chemistries.

**Conclusions**

The exchange reaction of MPTMS, and similar trialkoxysilanes, with dental monomers requires the presence of hydoxyl groups or similar protic functional groups with labile hydrogen. However, polar, but non-hydroxylated monomers can serve as polymerizable solvents for the *in situ* generation of oligomeric silsesquioxanes from MPTMS (and other trialkoxysilanes) by hydrolysis-condensation reactions induced by the presence of water in these monomers.

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***Disclaimer**

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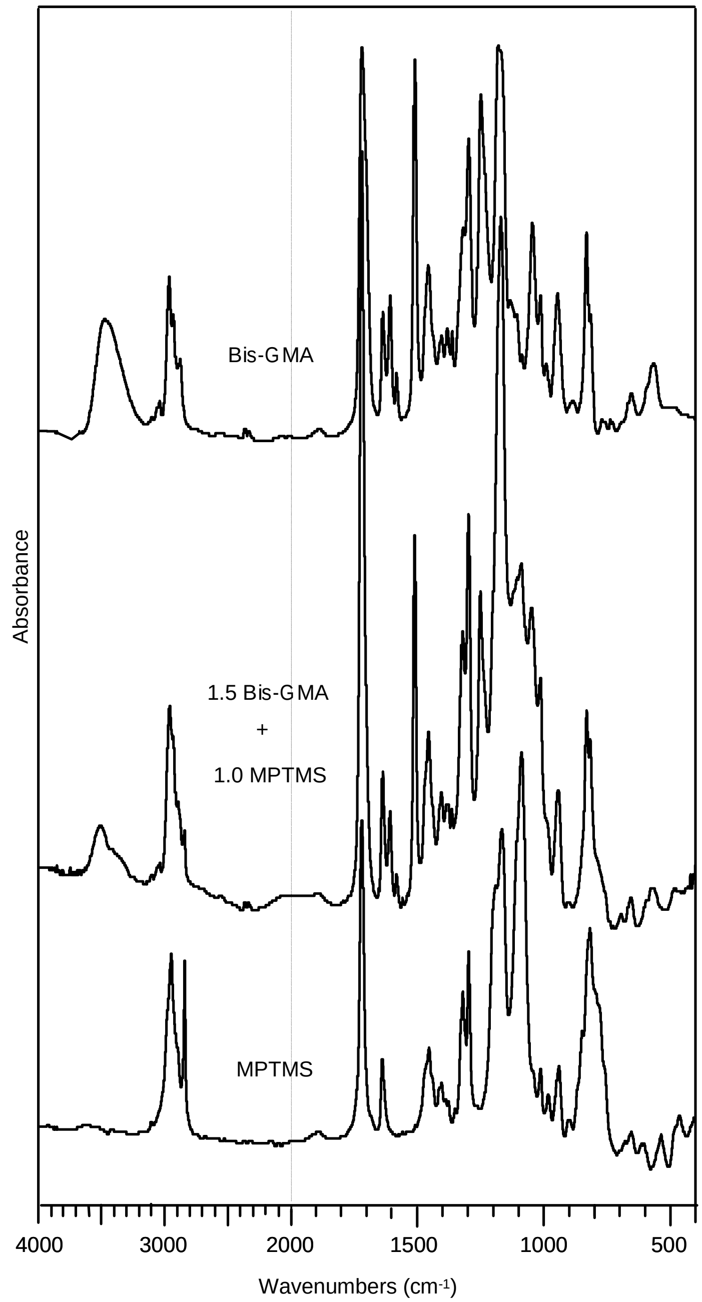


**Figure 3**. FTIR spectra of Bis-GMA, MPTMS and the reaction product of Bis-GMA/MPTMS at a mole ratio of 1.5.