Polymerization Behavior of an Organophosphorus Monomer for Use in Dental Restorative Materials

Gabriel Adusei,[1] Sanjukta Deb,[1] John W. Nicholson,[1] Liyuan Mou,[2] Gurdial Singh[2]

[1]Department of Dental Biomaterials Science, Guy's, King's and St Thomas' Dental Institute, King's College, London SE1 9RT, United Kingdom
[2]Department of Chemistry, University of Sunderland, Sunderland, SR1 3SD, United Kingdom

INTRODUCTION

The use of polymerizable materials in esthetic (tooth-colored) restorative dental materials has been well established.[1] The monomers employed in such materials are based on bisGMA (Fig. 1) and also diluents such as triethyelene glycol dimethacrylate. These monomers are blended with inert fillers, typically silica of varying mean particle sizes and size distributions, to create materials known as *resin composites.*[1] These materials are widely used and have good success under clinical conditions, especially where esthetics are important, typically in the anterior teeth.

In the early 1990s, a new class of material was introduced to clinical dentistry, in which the monomer blend was augmented with a monomer containing a few carboxylic acid groups and a fraction of the inert filler was replaced by acid-leachable glass.[2] The effect was to create a material capable of absorbing a small amount of water form the saliva and undergoing a modest acid–base reaction.[3] This conferred the property of fluoride release on these materials[4] and also made them capable of buffering aqueous lactic acid,[5] both potentially important clinical properties that basic resin composites do not possess. These materials are known as *polyacid-modified composites.*[2]

The monomers used for the modification to date have been aliphatic and not structurally analogous with the monomers used for unmodified resin composites. A disadvantage of this has been that the mechanical properties, notably resistance to wear, of the polyacid-modified systems have been inferior to those of the unmodified materials.[6] To address this problem, we set about synthesizing a novel monomer that was formally derived from bisGMA but contained acid functional groups. Also, because phosphonic acid groups are known to assist adhesion of a material to the tooth surface,[7] we chose to incorporate these functional groups rather than carboxylic acid ones.

The synthesis of the monomer has been reported elsewhere.[8] Briefly, it involves the base-catalyzed rearrangement of the corresponding diethyl arylphosphonate in tetrahydrofuran at $-78°C$ and results in the diphosphonated bisGMA monomer illustrated (Fig. 2). This approach has been used previously to prepare aromatic phosphonates[9] but has not, we believe, been used to prepare monomers for use in clinical dentistry.

In this article, we report on the results of our studies on the polymerization of this monomer using initiator systems and conditions appropriate for clinical dentistry. In particular, this involved the use of a camphorquinone–amine initiator system[10] and curing with a halogen lamp that emitted light mainly in the blue region of the electromagnetic spectrum, that is, 470 nm.

EXPERIMENTAL

The pH of the novel monomer and bisGMA were determined with an electrode (type 2000 PHA, Whatman, United Kingdom). The monomer bisGMA was supplied by Esstech (PA) and the novel monomer was prepared by us, as described previously.[8] Both were used without further purification.

To carry out the polymerization, a photo-initiator system consisting of camphorquinone (0.2 wt %) and dimethylaminoethyl methacrylate (0.15 wt %) was added to the neat monomer liquid. Specimens were prepared by curing of the monomer/initiator combi-

Correspondence to: J.W. Nicholson, Floor 17, Guy's Tower, Guy's Hospital, London SE1 9RT, United Kingdom (john.nicholson@kcl.ac.uk).
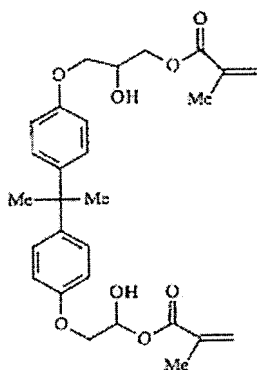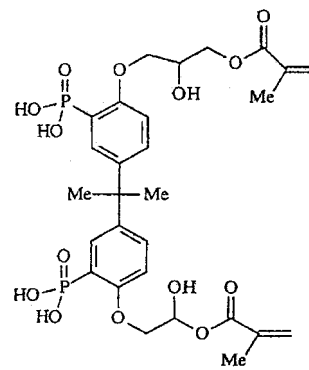
Figure 1 BisGMA monomer.

Figure 2 Phosphonated bisGMA.

nation for 20 s in a metal mold 1.45 mm in height and 6.5 mm in diameter with a standard dental halogen lamp (75 W, 470 nm maximum wavelength, Primetic Lite). Following polymerization, specimens were carefully removed from the mold and subjected to analysis by FT Raman spectroscopy (with an FT-Raman spectrometer, Nicolet 910, 680 DSP with workstation, equipped with an $Nd:YVO_4$ YAg laser at 1024 nm, resolution-4 cm^{-1}).

Water uptake was determined in duplicate on discs of polymerized material as follows. Specimens were stored in deionised water at 37°C and allowed to take up mass until they had equilibrated. They were then dried to a constant mass, after which they were again stored in deionized water at 37°C, and they were weighed at weekly intervals until they had reequili-

brated. This ensured that no water-soluble monomer or oligomers remained in the material to influence the extent of water uptake.

RESULTS

The pH of bisGMA was 6, whereas that of the organophosphorus monomer was 2. Using FT Raman spectroscopy and determining the relative intensity of the aliphatic C=C to aromatic C—C bond stretch, we were able to estimate the degree of polymerization for each monomer, as shown in Table I.

The values for net mass gain at equilibrium after the second stage of storage in water are shown in Table II.
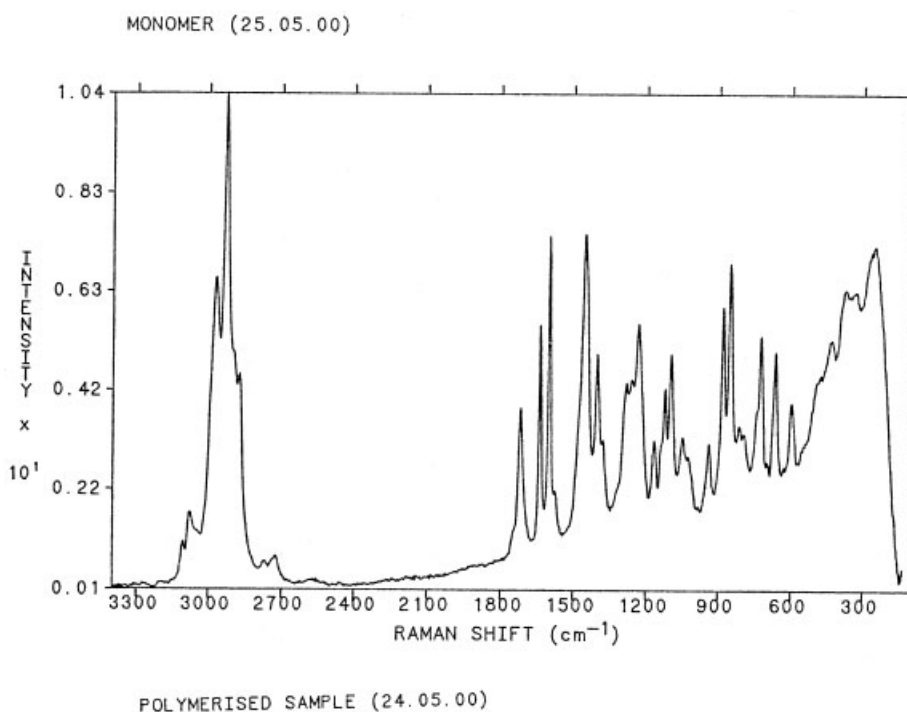

Figure 3 Raman spectrum of the phosphonated bisGMA monomer.
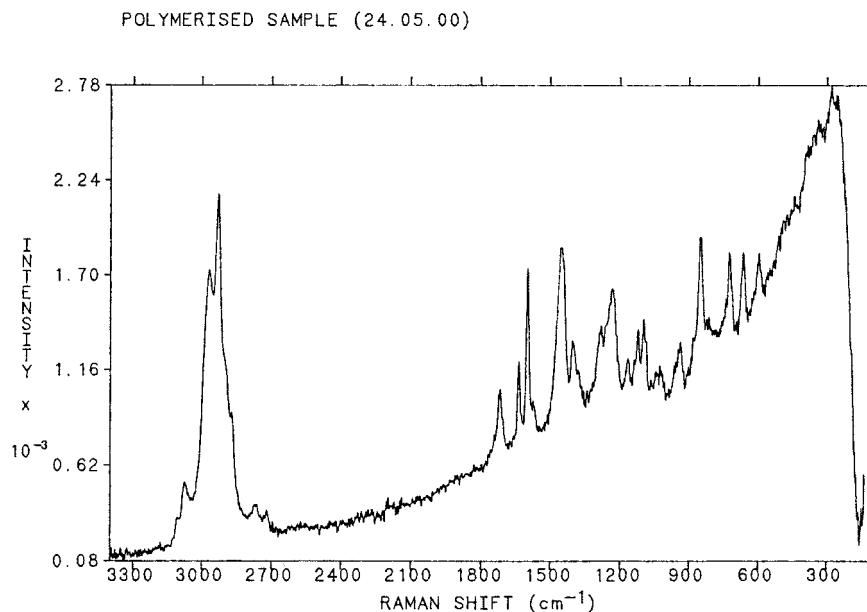
POLYMERISED SAMPLE (24.05.00)

Figure 4 Raman spectrum of the phosphonated bisGMA polymer.

DISCUSSION

The pH of the monomers demonstrated that the novel phosphonated bisGMA was highly acidic, a property that is required for application within polyacid-modified composites. The monomer is clearly capable of undergoing polymerization under conditions relevant to clinical dentistry, that is, with the camphorquinone-amine initiator pair and with the standard blue curing lamp as used in dental surgeries.

The results of the Raman study enabled us to make an estimate of the extent of conversion of monomer to polymer. We did this by comparing a band that was unaffected by polymerization, that is, that due to the aromatic C—C at 1600 cm^{-1} with the aliphatic C=C band at 1637 cm^{-1}. Comparison of the intensities of these two bands in the Raman spectra of the two bisGMA monomers showed that the phosphonated monomer was less readily polymerized than bisGMA
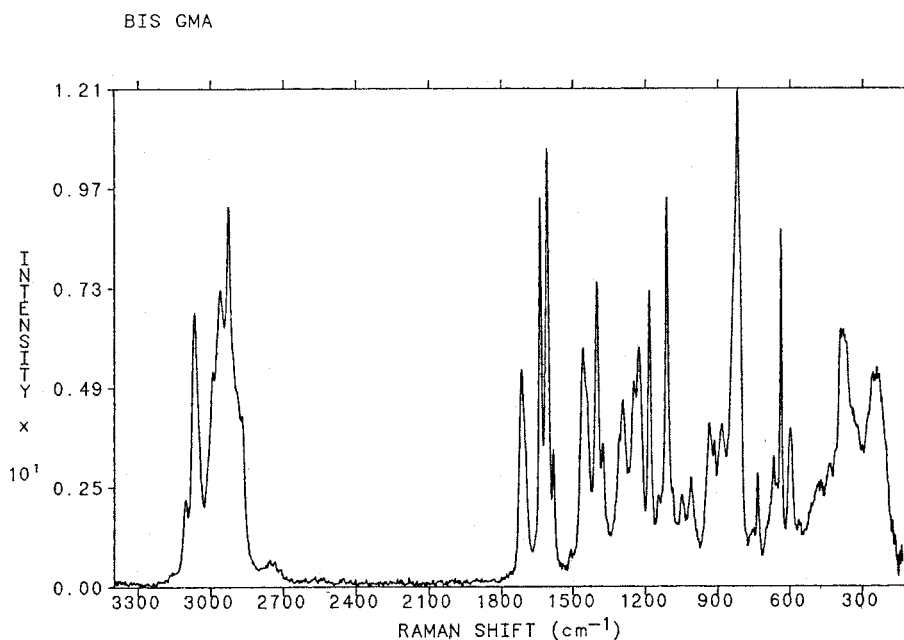
BIS GMA

Figure 5 Raman spectrum of the bisGMA monomer.
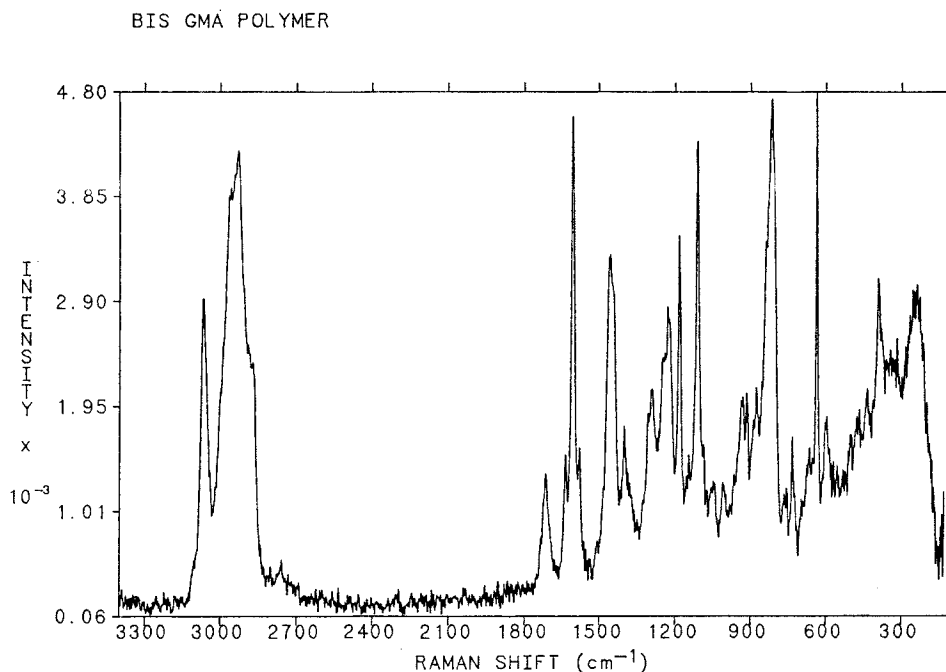
BIS GMA POLYMER

Figure 6 Raman spectrum of the bisGMA polymer.

itself. This is typical of monomers containing phosphonic acid functional groups and arises from the deactivating effect of these groups on free radicals.[11,12] The deactivation may be partly attributed to inductive effects, which arise from the relatively electronegative character of both of the elements in the phosphonic acid functional group, and partly from mesomeric effects, which cause partial spreading of the unpaired electron of the free radical across the functional group. The overall result is that the free radical formed by the phosphonated derivative is more stable and, hence, less reactive than the free radical formed from bisGMA. This, in turn, reduces the readiness with which polymerization will occur.

Water uptake of the resulting polymer was found to be greater in the phosphonated derivative than in poly(bisGMA) in terms of the rate of total net uptake at equilibrium. This could be assumed to be primarily due to the polar nature of the substituent, which increases the hydrophilic nature of the polymer. There may also have been some effect of the reduced readiness of the phosphonated bisGMA monomer to undergo polymerization, which resulted in a lower molar mass and a greater free volume within the sample.

Water may accumulate in such free volume. However, we assumed that the polarity effect had the greater contribution, and this finding showed that the phosphonated bisGMA monomer had the capability of enhancing the water uptake of the polyacid-modified composite formulation into which it was incorporated. This feature is necessary to activate the acid functional groups and promote the secondary acid–base reaction that is characteristic of these dental restoratives.[3]

CONCLUSIONS

Phosphonated bisGMA was shown to be capable of undergoing polymerization in the presence of camphorquinone and amine initiator, following irradiation with blue light from a dental curing lamp. FT Raman spectroscopy indicated that such polymerization gave a lower conversion of monomer to polymer than the unmodified bisGMA. This finding was attributed to the effects of the organophosphorus substituents in increasing the stability of the related free radicals and, hence, inhibiting the polymerization. The water uptake of the phosphonated polymer was greater than that of poly(bisGMA), and this result,

TABLE I
Degree of Polymerization After 20 s of Light Cure

Monomer	Degree of conversion (%)
bisGMA	68
Phosphonated bisGMA	38

TABLE II
Net Mass Gain in Water for Polymers

Monomer	Mass gain (%)
bisGMA	6.3
Phosphonated bisGMA	8.5

coupled with the much lower pH of the monomer, indicates that the phosphonated monomer has both of the necessary properties, that is, acidity and hydrophilic character, to enable it to be employed successfully in polyacid-modified composite dental restoratives.

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